NANO-PRODUCT ENGINEERING, LLC

INTRODUCTION PACKET TO PLASMA ASSISTED PVD TECHNOLOGIES

Lafayette, Colorado, 2017

Nano-Product Engineering, LLC

Nano-Product Engineering, LLC (NPE) is a research, development and technology transfer/commercialization company specializing in advanced surface engineering techniques to enhance material properties for wide variety of applications. These techniques include patented ionized Physical Vapor Deposition (iPVD) and Plasma Assisted Chemical Vapor Deposition (PACVD) processes, which result in high coating deposition rate, eliminated coating defects and imperfections with uniform large-area coverage at industrial production scale. Coatings are specifically developed for applications ranging from wear and corrosion resistance to optics, semiconductors and fuel cell systems. Other plasma technologies developed at NPE include advanced plasma thrusters, plasma actuators and energetic particles generators.

Founded in 2006, NPE is a small, fast-growing start-up company based in Lafayette, CO. NPE inherited research and development of various innovative technologies, processes and applications from its predecessors: Arcomac Plasma processing Lab. of Toronto CA (APPL), UES-Arcomac, Inc. of Dayton OH, and Arcomac Surface Engineering, LLC of Missoula MT (ASE). Proven applications include: superhard and corrosion resistant coatings for medical instruments and implants; low-friction, wear resistance coatings for gears and bearing races; erosion and corrosion resistant coatings for compressor and rotor blades; high temperature oxidation resistant and conductive coatings for fuel cells; diamond and related superhard coating materials for tools, machine parts; synthesis of ceramic ,superhard powders and coating of powders; arcjet and combined thrusters for electric propulsion; plasma actuators for high altitude aircraft and missiles; plasma generators of energetic particles.

During last 20 years Nano-Product Engineering, LLC and its predecessors have developed and built several surface engineering systems. By taking fundamental novel approach in design and development, NPE has successfully developed plasma source which generates and streamline higher volume of ions which can be guided to modify or create surfaces with nanostructured features. These plasma sources have successfully eliminated the constraints that burden conventional plasma sources used in PVD and PACVD technologies. Also these LAFAD™ plasma sources can be placed in series to cover large coating area ranging from 500mm to 1500mm. Thus large area deposition is possible as the LAFAD™ sources have theoretically unlimited scaleup capability and can be used as retrofit sources for conventional planar cathodic arc sources or magnetron sputtering sources. NPE's advanced LAFAD™-500C-2 surface engineering system, utilizes two LAFAD™ -500C unidirectional dual filtered arc sources providing a 300mm tall x 500mm diameter deposition area and more than 3 μm/hr average deposition rate with +/-10% uniformity. The LAFAD™ plasma source utilizes different types of primary cathodic arc sources for deposition of metallic and cermet coatings (nitrides, carbides, oxides), Diamond-Like Carbon (DLC) and related superhard coatings. The LAFAD™ metal vapor plasma sources can be also coupled with conventional magnetron sputtering source for hybrid filtered arc assisted magnetron sputtering (FAAMS™) technologies. All types of primary cathodic arc sources are interchangeable and can be provided by Nano-Product Engineering, LLC.

NPE's commercialization plans for this technology are to secure IP protection (patent), build and install equipment at customer's facilities, and provide surface engineering of customer's specific components on reliable commercial service basis, where volume, security or similar concerns dictate that a customer perform the process in their own manufacturing facility, we are prepared to sell and/or lease the necessary equipment, license the process, and provide any attendant engineering service.

Introduction to Conventional Direct Arc Deposition Technology

For the past 40 years, vacuum arc discharge plasma has been successfully used for depositing hard coating for cutting tools, dies, drive train components, and other tribological applications. But current evaporation, sputter and cathodic arc processes still suffer from specific limitations. New advances in cathodic arc plasma technology used in a physical vapor deposition (PVD) process can eliminate many of these problems, resulting in performance improvements for coated components.

In conventional direct cathodic arc source (DCAS) deposition, a jet of a highly-ionized metal plasma, flowing from a cathodic arc spot 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. There is no simple way to eliminate macro-particles from the depositing plasma flow in the direct arc source configuration, since the operating surface of cathode target lies in a straight line in front of the surface of substrates to be coated. These macro-particles deleteriously influence critical properties of the coatings. A schematic view of cathodic arc deposition process is shown in **Figure 1**.

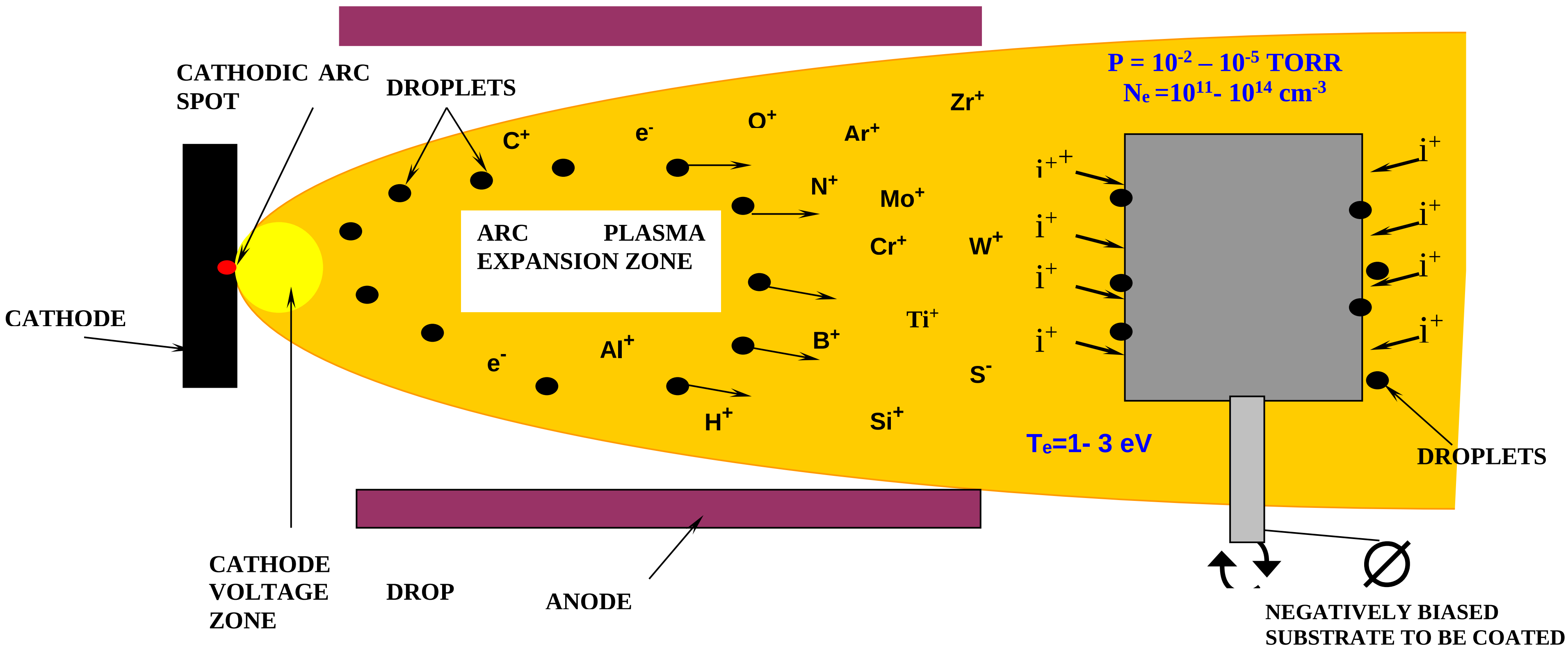


Figure 1: Schematic view of the conventional direct cathodic arc (DCAS) deposition process.

Historical Development of Filtered Cathodic Arc Deposition (FCAS) Technology

The first macro-particle filter, based on the plasma-optical principle, was a quarter-torus cylindrical electromagnetic plasma guide based on the torus-type plasma traps developed for controlled nuclear fusion devices such as the Stellarator in the USA and the Tokamak in the former USSR. The filtered cathodic arc source (FCAS) based on this principle effectively removed macro-particles, but has relatively small deposition rate typically less than 1μm/hr, can operate only with small cathode targets and could not be scaled up due to the difficulty of scaling up cylindrical magnetic coils. This type of FCAS consists of a quarter torus plasma duct geometry, surrounded by a magnetic system that directs the plasma current, while baffles for removing the macroparticles are positioned along the walls of the plasma duct. The plasma duct connects two chambers, one which holds the target and the other, the coating deposition chamber, encloses a substrate holder. Due to the nature of the quarter torus plasma duct, the substrate holder is installed off the optical axis of the plasma source.

Filtered cathodic arc sources allow for deposition of droplet-free coatings by deflecting the plasma flow along the curvilinear magnetic lines of force towards the substrate, while the droplets, having straight trajectories, are captured on the baffles. Thus, only a fully ionized flow of metal vapor plasma is directed to the substrate. The filtered arc plasma also contains a relatively highly dissociated, ionized and activated reactive gas. This leads to a maximum fluency of bombarding ions within a small energy deviation. As a result, it is possible to produce metastable coatings with highly disordered structures, with unique properties. **Figure 2** shows a micro photograph of SS surface with TiN coatings deposited by direct cathodic arc vs. filtered arc technology.

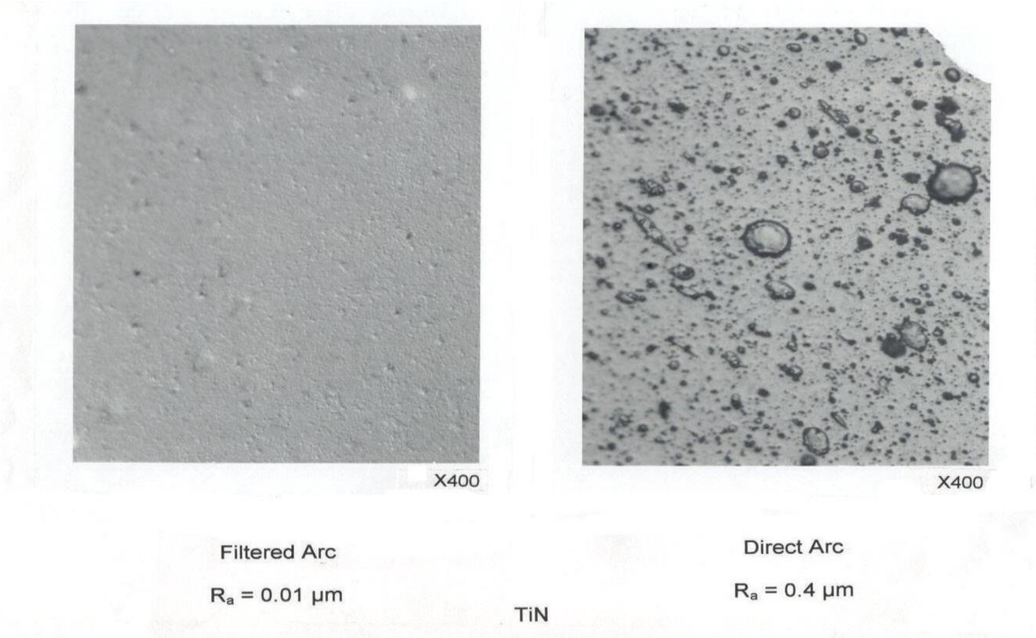


Figure 2: Direct arc TiN coating vs. filtered arc coating.

The Disadvantages of the Quarter Torus FCAS Design

The torus-shaped plasma duct limits the dimensions of the component to be coated to 200 mm, which significantly limits the range of its application. Another disadvantage of cylindrical quarter torus FCAS is non-uniformity of the deposited coating. The variation of coating thickness with this design can be as high as 50-100% over the deposition area of 100-150 mm. Furthermore, there is no provision in the torus-shaped plasma duct for changing the configuration of the magnetic field. One can only change the magnetic field intensity. The maximum value of the ion current at the exit of the plasma duct does not exceed 1% of the arc current. This relates primarily to the turbulence of the plasma current in the torus, which causes a drastic rise in the diffusion losses of ions on the torus walls. Another disadvantage is the relatively low level of ionization of reaction gases such as nitrogen, methane or oxygen. In comparison to nearly 100% ionization of metal plasma, the gaseous plasma ionization is less than 1%. Some improvement of coating properties can be achieved by gaseous ion-assisted filtered arc deposition (FAD), in which the ratio of metal to gaseous ions can be controlled.

NPE's Solution - Large Area Filtered Arc Deposition

The limitations of the quarter torus filter design have been largely overcome by an innovative rectangular electromagnetic filter design, developed at Nano-Product Engineering, LLC (NPE). NPE's unidirectional large-area dual filtered arc deposition (LAFAD™) surface engineering metal vapor plasma sources use a rectangular plasma duct chamber with two rectangular coils installed in opposite sides, as schematically illustrated in **Figure 3a.** Two cathodic arc sources with rectangular or circular (billet) targets are installed in the side walls of the plasma duct chamber, surrounded by rectangular focusing and deflecting coils. A quasi-flat deflecting magnetic field configuration significantly reduces plasma losses in the direction close to the plasma duct walls, allowing for metal vapor plasma propagate freely along the magnetic field lines to reach remote parts of the deposition chamber. This results in a dramatic increase of output arc current, which can exceed more than 10 amperes for an input current of 300 amperes for two incorporated cathodic arc sources. At the same time ionization rate of gaseous plasma components within magnetized arc plasma column can reach more than 30%. As a result, the deposition rate of a LAFAD™ source has been found to be almost the same or even greater than that of direct (not-filtered) cathodic arc source. This advanced filtered design provides practically macro-particle free coatings in large areas, ranging from about 250 mm in width to heights on the order of 300 mm to 3 m or more. Typical target utilization rate for a cylindrical primary cathodic arc sources of the LAFAD™ dual filtered arc source, utilizing round targets is as high as 80-90% for primary cathodic arc sources with cylindrical (billet) targets, and up to 40% in case of using the planar or rotary primary DCAD cathodic arc sources with large planar rectangular or rotary tubular targets. The scale-up capability of LAFAD™ unidirectional dual arc metal vapor plasma sources and complete coating deposition systems utilizing billet targets are illustrated in **Figures 3b, 3c**. The thickness non-uniformity for the coatings deposited by LAFAD™ sources with billet primary cathode targets is typically less than 10%. The LAFAD™ plasma sources utilizing both planar and rotary primary DCAD cathodic arc sources are illustrated in **Figure 3d**. In this case the non-uniformity of coating thickness distribution is reduced to <2%.

In addition, the vacuum arc cathode is also a theoretically unlimited electron emitter, thereby providing an efficient source of high-density electron current. In this mode, it facilitates the generation of a uniform, high-density plasma cloud in the coating deposition chamber. This results in a "plasma-immersion" environment, which provides a uniform condition for plasma ion etching, ion nitriding, low energy ion implantation, plasma-assisted chemical vapor deposition and multilayer filtered arc PVD coatings in a single vacuum cycle.

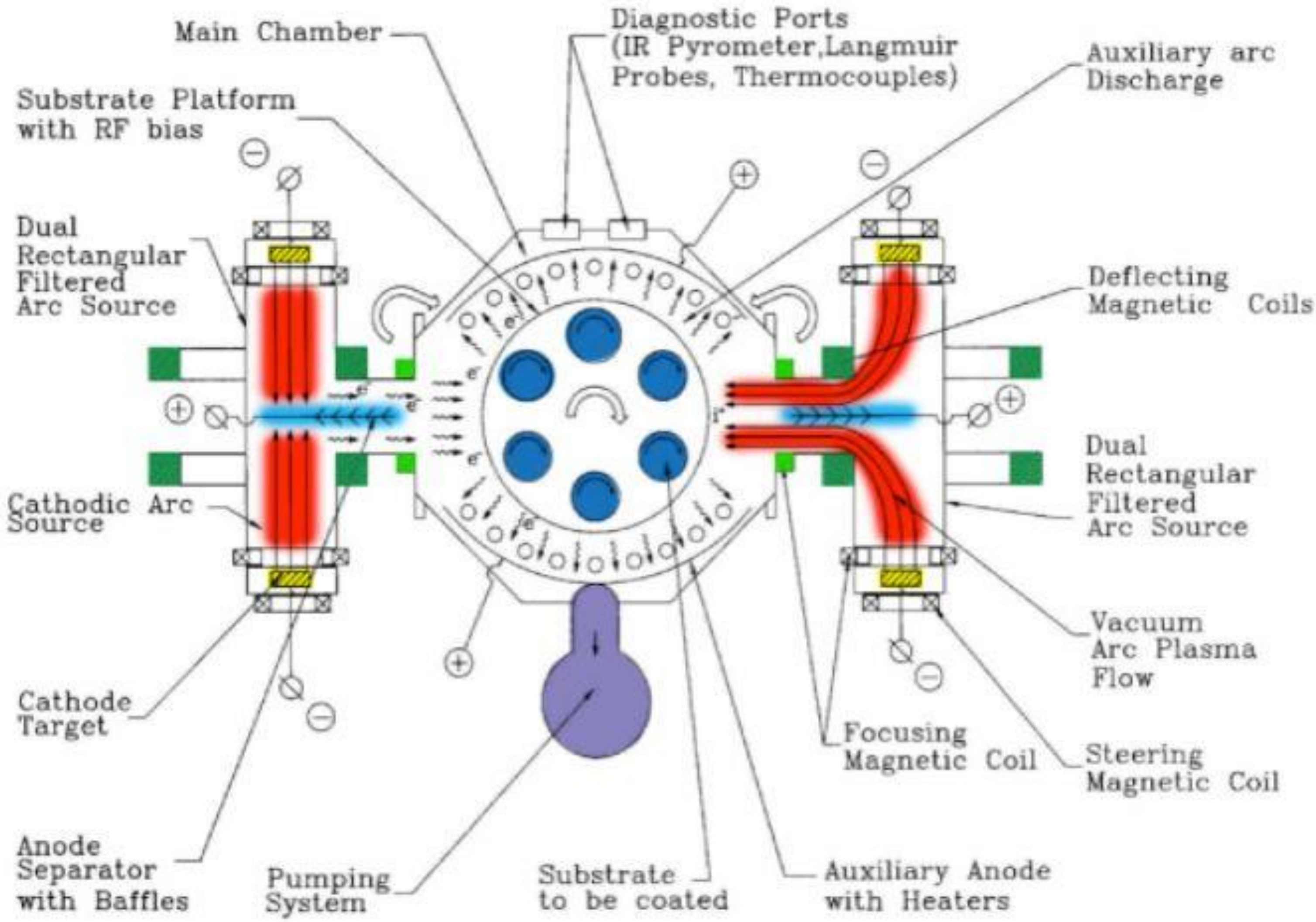


Figure 3a. Schematic view of LAFAD™ plasma immersion surface engineering system.

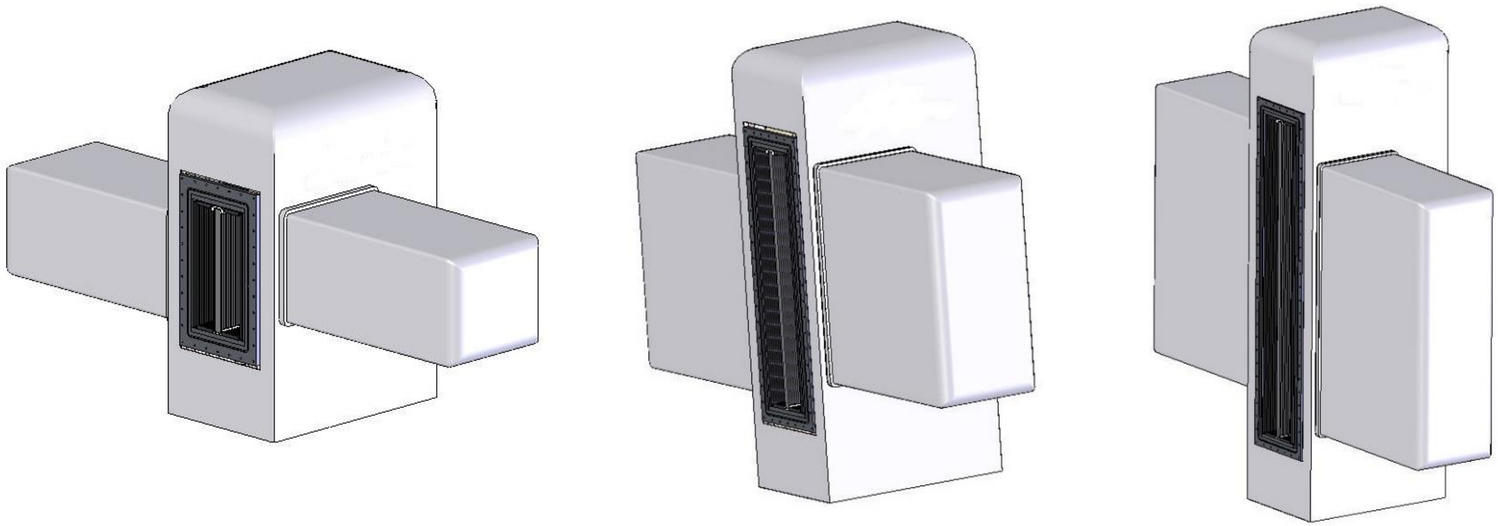


Figure 3b. Schematic view of LAFAD^{TM} unidirectional dual filtered arc plasma sources.

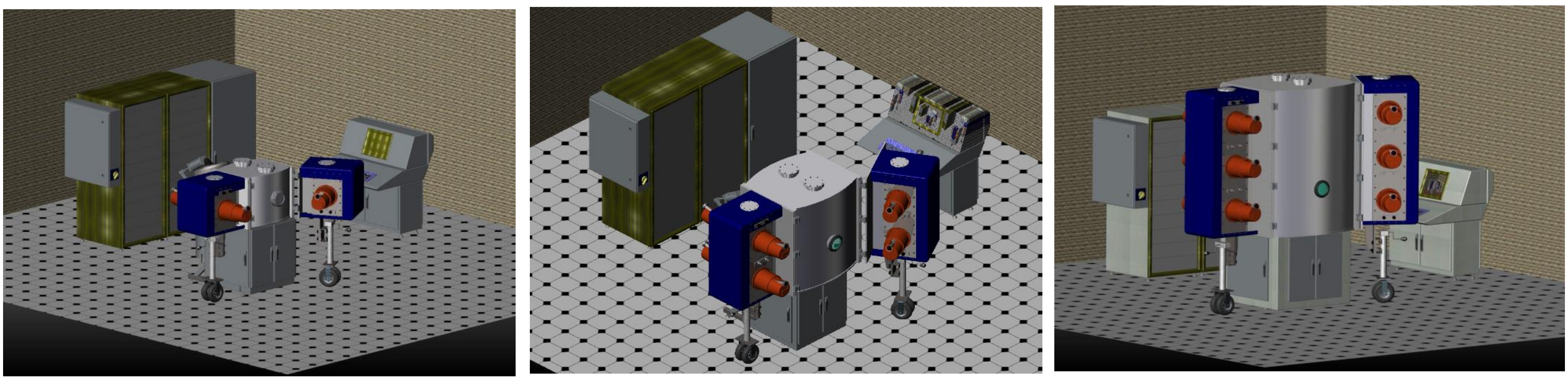


Figure 3c. LAFAD^{TM} series of coating systems accommodating 300 mm, 600 mm and 900 mm tall deposition area with +/- 10% coating thickness non-uniformity.

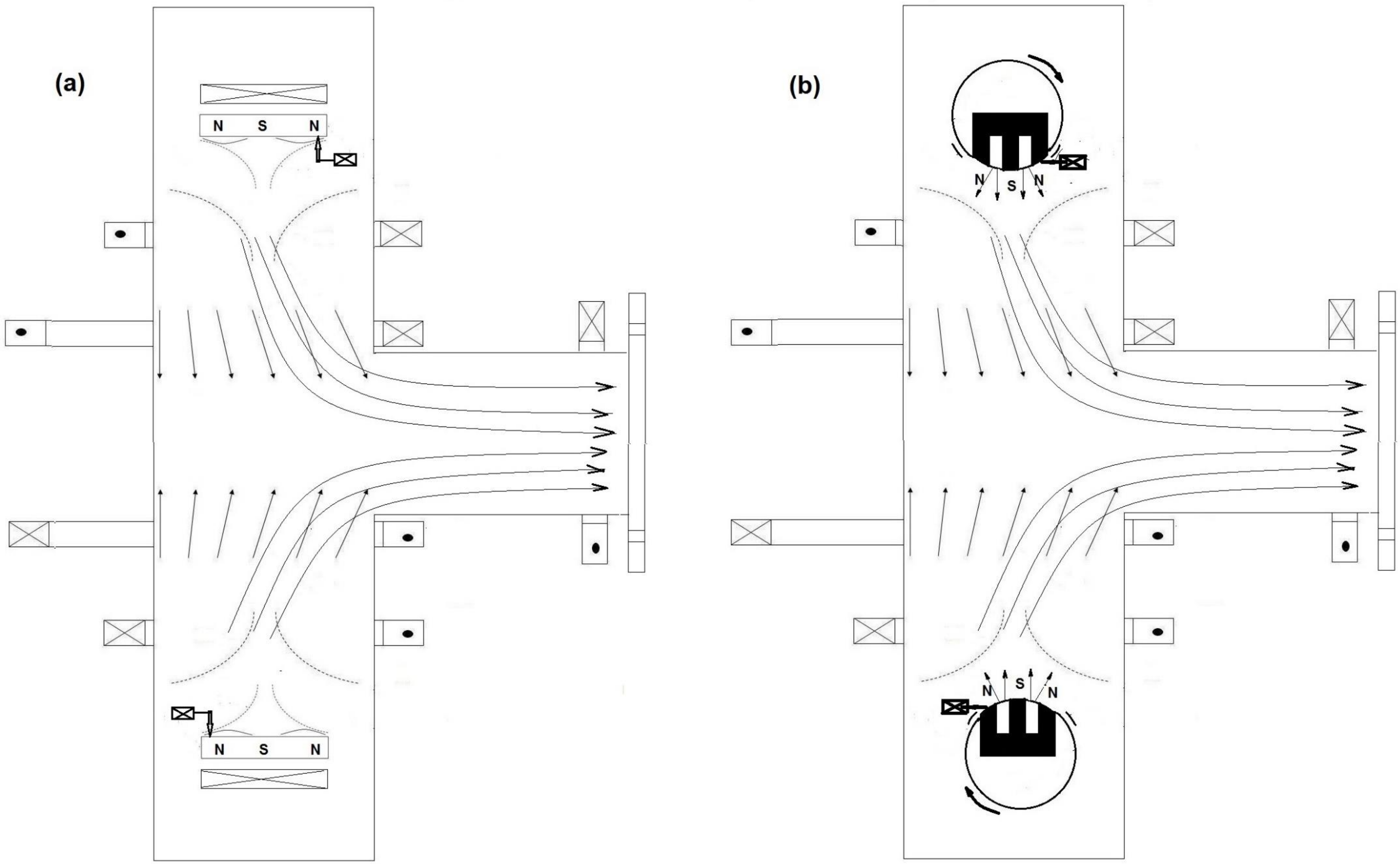


Figure 3d. LAFAD™ unidirectional dual filtered arc metal vapor plasma source with (a) planar primary DCAD and (b) rotary primary DCAD.

NPE State of the Art: Hybrid Filtered Arc Assisted Magnetron Sputtering Technology

NPE's latest advances in PVD technology are hybrid coating processes utilizing the synergetic combination of LAFAD^{TM} sources and magnetrons or electron beam sources in a one universal vacuum chamber layout. This type of hybrid surface engineering systems is capable of deposition of large variety of coating compositions and architectures. The unique *Filtered Arc Assisted Magnetron Sputtering (FAAMS^{TM})* process developed by Nano-Product Engineering, LLC offers the opportunity for significant improvement in performance of surface engineered components by addressing critical issues of coating microstructure and interface integrity. The hybrid FAAMS^{TM} surface engineering system is shown schematically in **Figure 4a**. The design of this modular hybrid PVD surface engineering equipment consists of four powerful LAFAD^{TM} plasma sources in combination with 8 conventional unbalanced magnetrons (UBM), either planar or rotary, all of which are integrated into one universal coating chamber layout, as illustrated schematically in **Figure 4b**. This design layout enables the evaporation of different ceramic and metals in a highly-ionized vapor plasma immersion environment. FAAMS^{TM} technology is capable of depositing nano-structured coatings having functionally graded or multiple-layer architectures. These coatings are characterized by improved adhesion and toughness, and noted for their smoothness and structural integrity. FAAMS^{TM} can also provide plasma immersion thermal-chemical treatment of substrates (ionitriding, carbonitriding, carburizing). Combinations of thermal-chemical treatments (e.g. ionitriding) followed by coating deposition (duplex process) can be accomplished in a single vacuum cycle. FAAMS^{TM} process results in improved adhesive and cohesive toughness, reduced coating residual stresses, and allows deposition of relatively thick and extremely hard cermet coatings such as BCN, TiB_2, and B_4C, which would otherwise be impossible due to high residual stress adhesion failures.

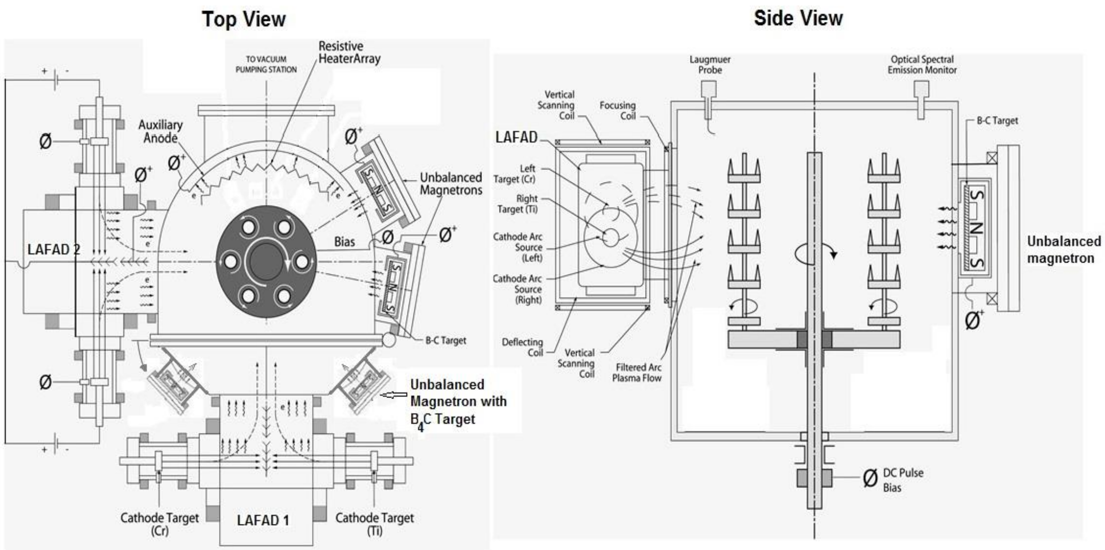


Figure 4a: Schematic illustration of NPE's FAAMS^{TM} surface engineering system. This system utilizes the Large Area Filtered Arc Deposition (LAFAD^{TM}) sources in a universal hybrid layout with conventional magnetron sources.

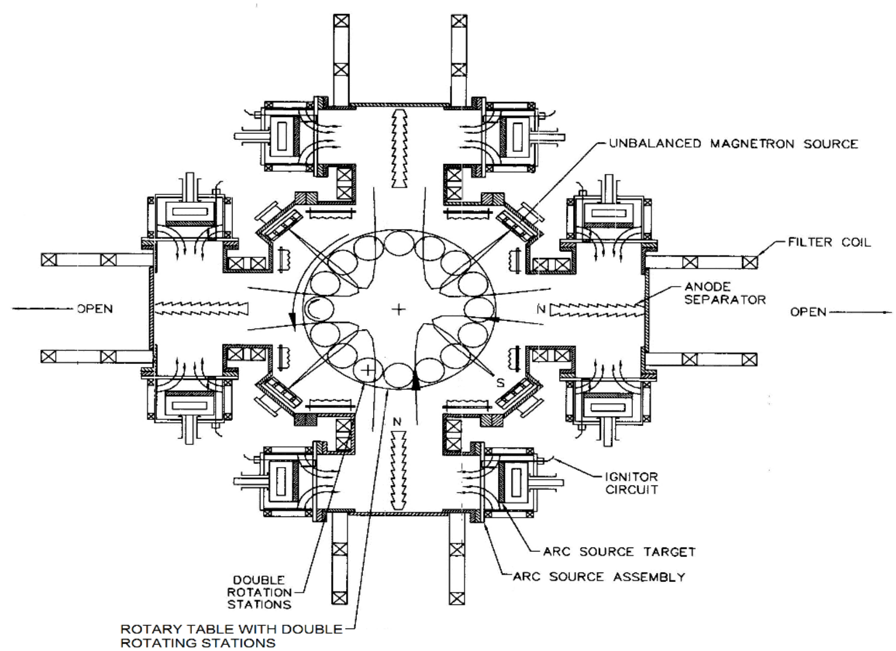


Figure 4b: Schematic illustration of NPE's FAAMS-4-1400C-8MS hybrid filtered arc assisted magnetron sputtering system utilizing 4 LAFAD-1400C unidirectional dual filtered arc sources coupled with 8 magnetron sputtering sources.

NPE and its Predecessors Coating Equipment and Processes: Success Stories

- Developed industrial scale Remote Arc Plasma Assisted CVD (RAPCVD™) technology and equipment for polycrystalline diamond coatings (1992-2000)
- Developed Large Area Filtered Arc Deposition (LAFAD™) technology (1997)
- Developed Filtered Arc Assisted Magnetron Sputtering (FAAMS™) technology (1997)
- One FAAMS-1-500C surface engineering system was purchased by UES, Inc. of Dayton, OH, www.ues.com (1998), where it is used for various R&D projects and coating service. This system utilizes LAFAD™ unidirectional dual filtered arc metal vapor plasma source in hybrid combination with two magnetron sputtering sources
- One LAFAD-1-500C surface engineering system was purchased by Exactatherm, Ltd. of Mississauga, Ontario, www.exactatherm.com (2000), where it was used until 2016 for PVD coating service
- One LAFAD-1-500C surface engineering system was purchased by American Eagle Instruments of Missoula, MT, www.am-eagle.com (2001), where it is used in mass production of hard coatings for dental instruments
- Developed and built a hybrid Filtered Arc Assisted PVD/PACVD surface engineering system utilizing LAFAD™ metal vapor source, two unbalanced planar magnetrons, EBPVD, and thermal evaporation, all in one vacuum chamber layout. This hybrid surface engineering system was used for R&D projects and prototype production at ASE facilities in Bozeman, MT
- Four LAFAD™ and FAAMS™ surface engineering systems are currently installed at the surface engineering and coating center of American Eagle Instruments, Inc. of Missoula MT and use in production surface engineered dental and medical instruments
- The photographs of the LAFAD™ and FAAMS™ surface engineering systems having 500 mm rotary table for loading substrates with single or double rotation capability and 12” vertical coating area with +/-10% of coating thickness non-uniformity operating at customer’s locations are shown in Figures 5a-5d

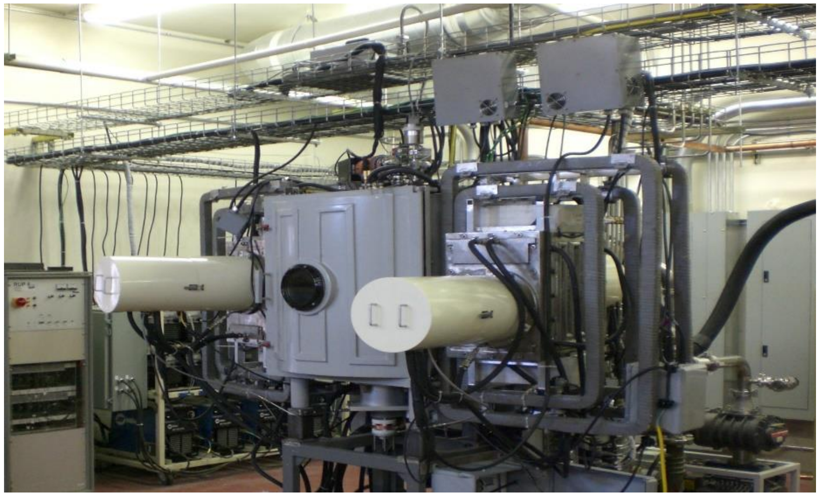


Figure 5a: LAFAD-2-600C dual plasma immersion surface engineering system at American Eagle Instruments, Inc., Missoula MT.

Figure 5b: FAAMS-1-600C-2MS hybrid surface engineering system at UES, Inc., Dayton OH.

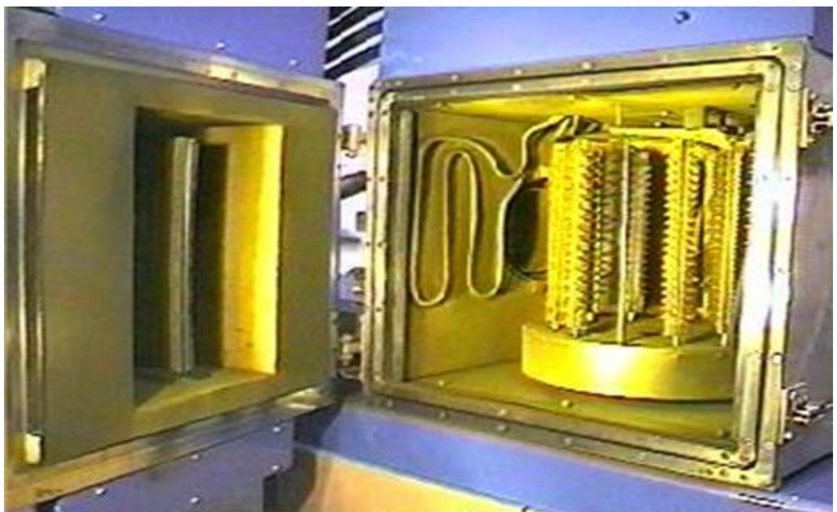


Figure 5c: LAFAD-1-600C coating chamber loaded with compressor blades at Arcomac Plasma Processing Lab., Toronto Canada.

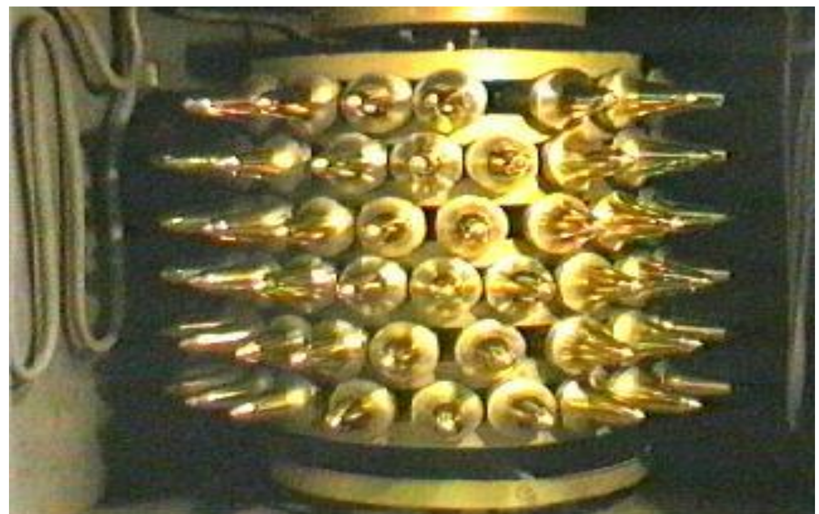
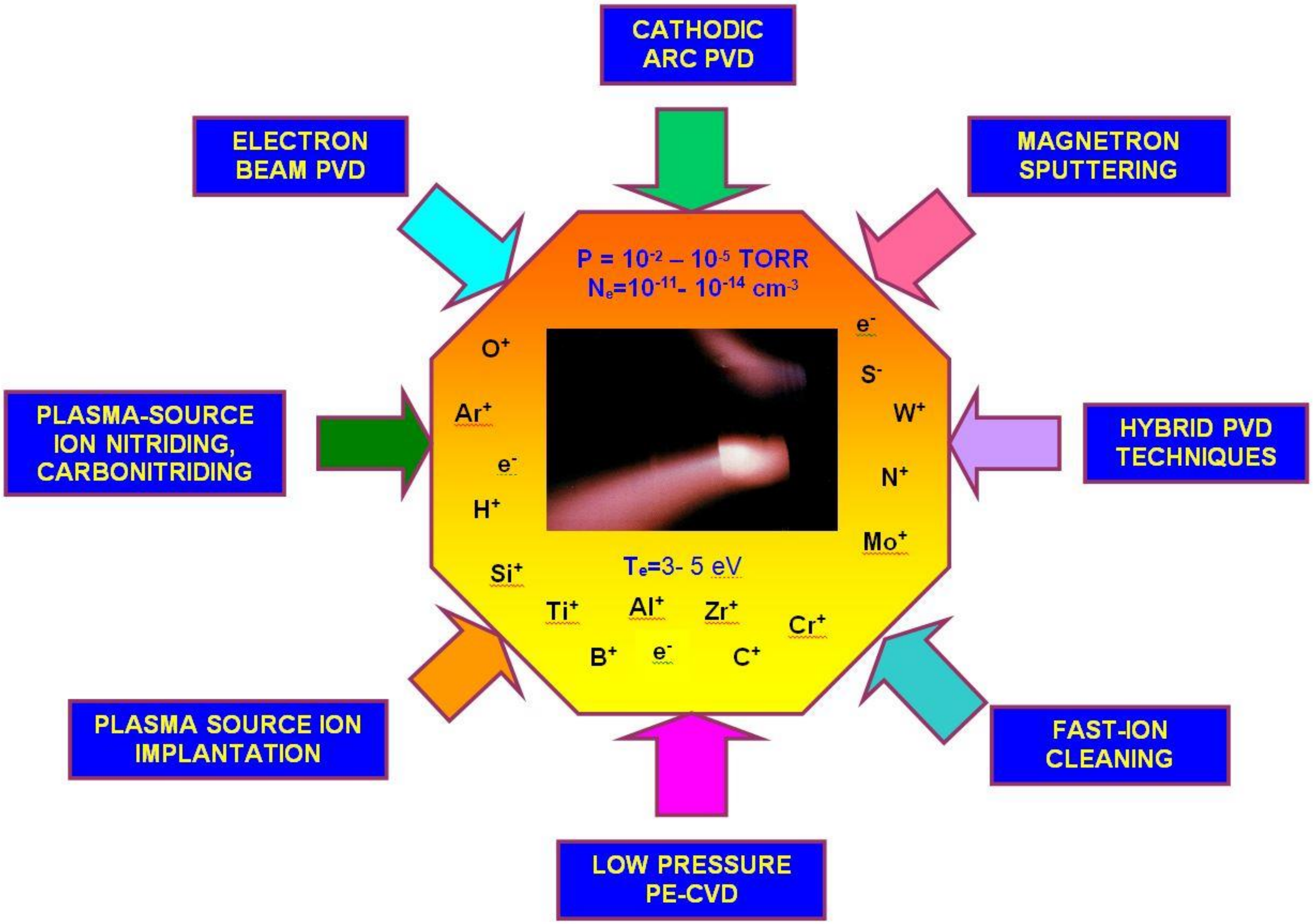


Figure 5d: LAFAD-1-600C coating chamber loaded with mining picks at Arcomac Plasma Processing Lab., Toronto Canada.

VACUUM ARC PLASMA IMMERSED SURFACE ENGINEERING TECHNOLOGIES



LAFAD^{TM} and FAAMS^{TM} Technology Highlights:

- Atomic-level (atom-by-atom) deposition
- Nanostructure size ceramic crystal growth at the nanometer level
- Capability of producing super-lattice and nanocomposite structuring with multi- phase ultra-fine polycrystalline and/or amorphous structures
- Super adhesion properties
- High ionization and activation of metal-gaseous plasma (up to 100% for metal vapor and more than 30% for gaseous plasma)
- Capable of Supporting the duplex and triplex plasma immersion surface engineering processes in one vacuum cycle
- Capable of supporting near all PVD and low pressure CVD Processes in strongly ionized filtered arc plasma immersion environment, which allows for "hybrid" processing and enhancement of conventional PVD and CVD processes
- NPE's modular design approach is commercially scalable and cost effective for individual customer requirements

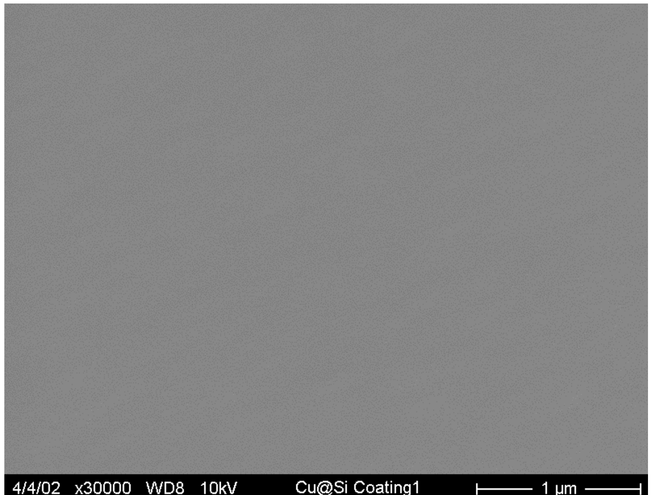
LAFAD^{TM} and FAAMS^{TM} Wide Range of Applications:

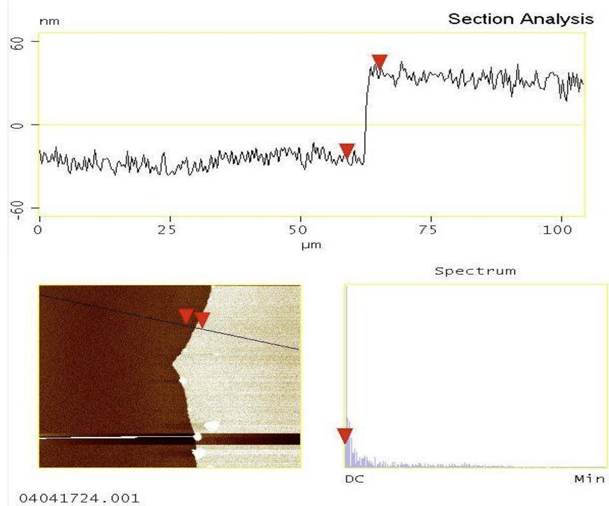
- Cutting and forming tools - printed circuit board drills, round shank tools, die-casting dies, saw blades
- Electronics - photovoltaic coatings, hard disks and thin film heads conductive photolithography coatings, heat sinks, flat panel displays, large IC substrates, sensors
- Automotive - piston rings, engine valves, decorative trim
- Biomedicine - surgical and microsurgical tools, dental and orthopedic implants
- Decorative - glass and ceramic coatings, cutlery, chrome replacement, costume jewelry, hardware
- Aerospace - bearings, turbine blades, compressor blades, mechanical linkages
- Optics - infrared optics, laser mirrors, X-ray windows, fiber optics
- Machine parts - joints and linkages, sliding and rotating parts, bearings, corrosion control coatings
- Power generators – turbine blades, electrical contacts, fuel cell bi-polar plates

Overview of NPE's and its Predecessors Research and Development Contracts

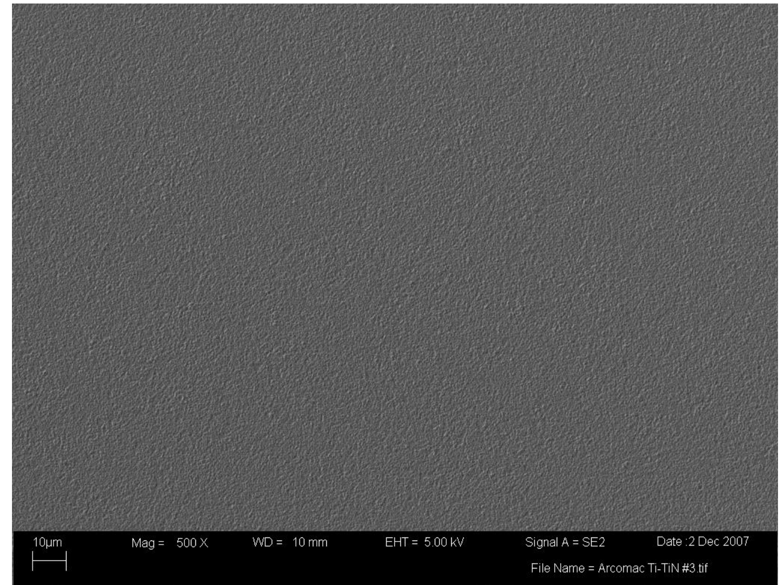
- In 1998 APPL was awarded by Canadian NRC with IRAP project for development of polycrystalline diamond coatings using innovative large area arc plasma reactor. The industrial scale remote arc plasma assisted CVD diamond deposition process developed by APPL has demonstrated high deposition rate over large coating deposition area
- In 2004 ASE successfully completed work on Air Force SBIR Phase I topic AF04-142: *Nanocomposite Tribological Corrosion Resistant Coatings for Robust Bearings and Gears*, and was awarded a $700,000 Phase II follow-on contract (2005-2007). The program involves developing surface engineering technology for gears used in advanced fighter aircraft. During this effort ASE has demonstrated the superior performance of TiCrCN+TiCrBC nanocomposite multilayer coatings deposited by a hybrid filtered arc–magnetron process. Hot perfluoro-polyalkyether (PFPAE) corrosion-resistance in rolling contact fatigue (RCF) tests at 350 °C and 3.2GPa Hertzian contact demonstrated order of magnitude improvements over uncoated gear and bearing materials. Order of magnitude improvements were also achieved in high load reciprocated sliding and lubricated friction tests.
- In 2004 ASE was awarded a contract from the Department of Energy SECA program to develop and demonstrate a cost-effective corrosion-resistant $(Mn,Co)_3O_4$ coatings for solid oxide fuel cell (SOFC) interconnect plates deposited by LAFAD™ process and by the hybrid process combining LAFAD™ with EBPVD sources. During the EBPVD deposition of the $(Mn,Co)_3O_4$ layer, the LAFAD™ source was used as a powerful emitter of electrons, effectively ionizing the $(Mn,Co)_3O_4$ vapor and densifying the resultant coating. Filtered arc deposited nanocomposite $(Cr,Al)_2O_3$ coatings demonstrated excellent long-term stability in 800°C air and outstanding barrier properties, completely protecting ferritic stainless steel against oxidation for over 1,000 hours and blocking Cr volatility.
- In 2005 ASE was awarded Air Force Phase I SBIR topic number AF05-181: *Coatings and Surface Treatment for Bearing Wear and Corrosion Prevention in Advanced Gas Turbine Engines*. The focus of this research was to develop and demonstrate bearing coatings and/or surface treatments for advanced gas turbine engine applications for fighter aircraft and the Versatile Affordable Advanced Turbine Engines (VAATE) programs. ASE's specific approach was to use a triple segment coating to address boundary lubricated sliding wear and "oil-off" operating conditions common in gas turbine engines. Through an advanced simulation testing collaboration with Wedeven Associates, ASE was able to show up to 5 times greater survivability of coated M50 operating in "oil-off" conditions, compared to uncoated contact pairs. Order of magnitude improvements in wear volume were also realized for coated M50 and coated Pyrowear 675. ASE was invited to submit a Phase II proposal for this project, but declined in order to provide more research focus on related projects.
- Since 2005 ASE has received $9,000,000 in funding from a directed sole source US Army contract that was awarded to ASE by the Army Research Laboratory, Aberdeen Proving Grounds, MD. Coatings deposited by ASE's LAFAD™ technology are being developed under this contract for a wide variety of Army applications, including erosion resistant coatings for turbine and compressor blades and coatings for protectors of helicopter rotary blades.
- In 2007 ASE successfully completed work on Air Force SBIR Phase I topic AF06-088: *Protective Coatings for Large Diameter Bearing Races*. The focus of the research effort was to provide a uniform protective coating on the case hardened surfaces of large size bearing races. Coating requirements were to enhance high load wear (3-4GPa contact pressure) and marine environment corrosion resistance; preserve mechanical properties and fatigue life of the core material; be compatible with fluorinated (PFPAE) lubricants at high temperatures (up to 350°C) in hybrid metal-ceramic bearing systems; and avoid geometrical distortions of the bearing during fabrication. A two segment functionally-graded coating architecture was developed under this work to address the multifunctional needs of the application. Data resulting from this research showed a complete elimination of oxidation during high temperature PFPAE testing for coated Pyrowear 675. In comparison: uncoated Pyrowear 675 experienced severe oxidation up to 200µm (~0.008") thick.
- In 2007 ASE was awarded a Navy DARPA Phase-I SBIR contract to develop improved Thermal Barrier Coatings (TBC's) for turbine blades. ASE's approach to this problem will involve the use of our hybrid filtered arc / electron beam (FAD/EBPVD) process to deposit nanostructured bond-coats and very thick, multilayer, nanocomposite top-coats with integral diffusion barriers. The developed high temperature oxidation resistant coatings of (Ti-Al-Cr) oxide system have demonstrated exceptional barrier properties and spallation resistance.
- In 2008 NPE completed the project for modification of the existing vacuum chamber at the GE Global Research Center at Niskayuna, NY, providing it with large area filtered arc coating capability.
- Since 2006 NPE has developed software for thermodynamic calculation of the composition of gaseous plasma systems and solid phase systems. The thermodynamic software packages were distributed to various customers, including Argonne National Laboratory, Write Paterson AFB Material Laboratory, Pacific North National Laboratory, UTC, Montana State University among others.

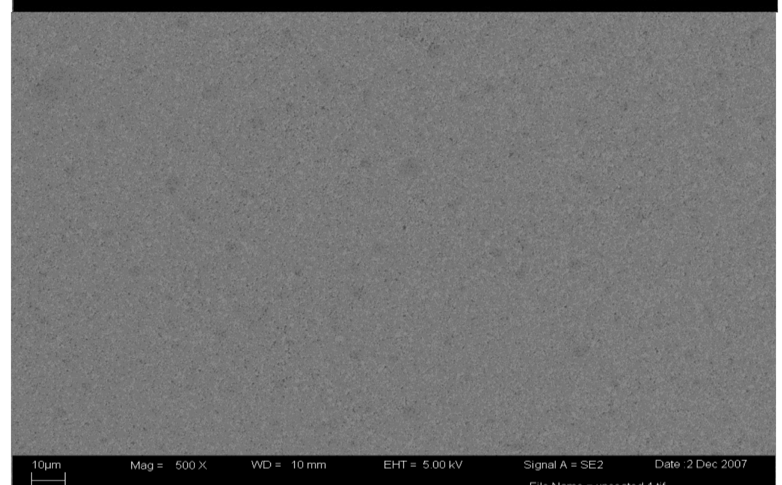
LAFAD^{TM} Coatings Feature Defectless High Density Surface Morphology and Microstructure



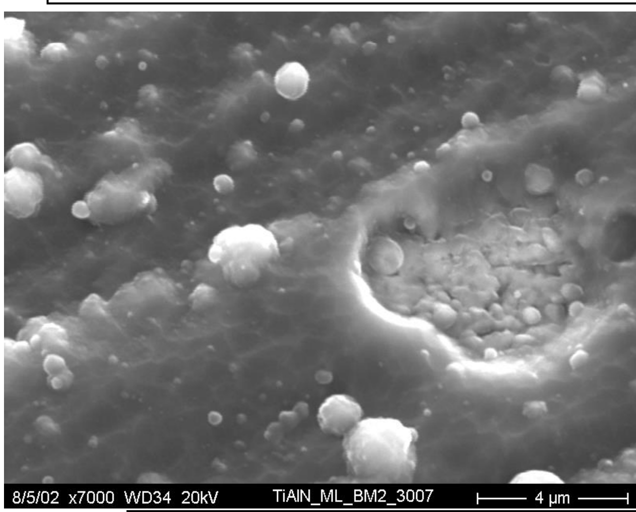


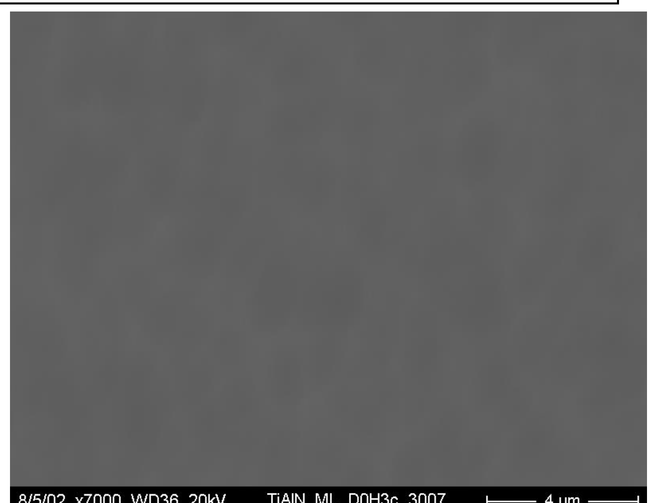
LAFAD^{TM} copper coating over silicon wafer, 100 nm thick, shows highly conformal morphology suitable for copper interconnects applications: SEM microimage (left); AFM analysis (right).





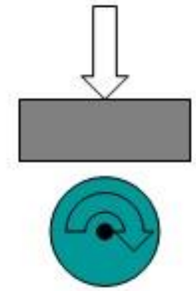
Droplet-free LAFAD^{TM} Ti/TiN nanolaminated coating, 1.5um thick (top), deposited on highly polished carbide substrate (bottom).





TiAlN coating deposited by conventional (not-filtered) cathodic arc deposition (left) vs. LAFAD^{TM} coating (right). Coating thickness 3.5 um.

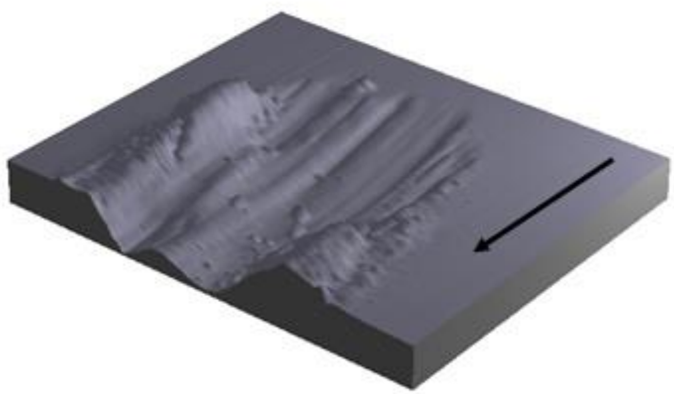
FAAMS™ Coating Performance: Turbine Bearing Applications



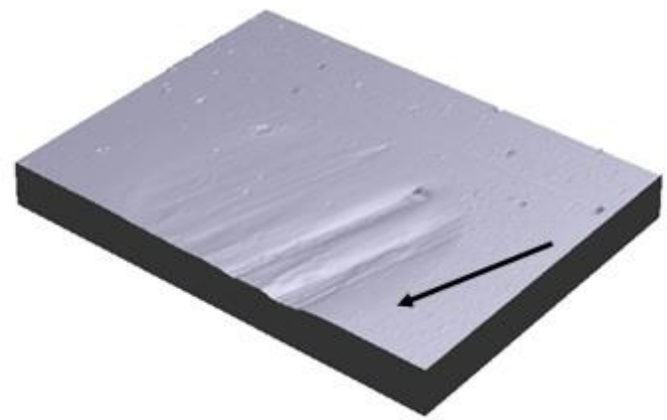
High Contact Stress Boundary Lubricated Sliding Wear

- Ball (rotating) on Disk Test - 3.0GPa contact, 0.36m/sec sliding velocity, Mobil Jet 254 Oil, Boundary Lubrication Regime Ra/h<1, 85m (4min) sliding distance

Ball: M50
Disk: Pyrowear 675
Maximum Wear Depth: 16um



Ball: M50
Disk: Pyrowear 675 + Arcomac Coating
Maximum Wear Depth: 1.5um

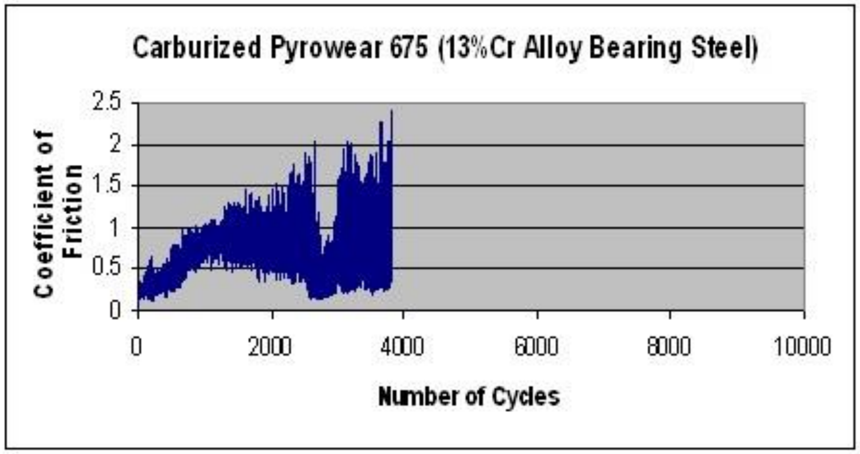


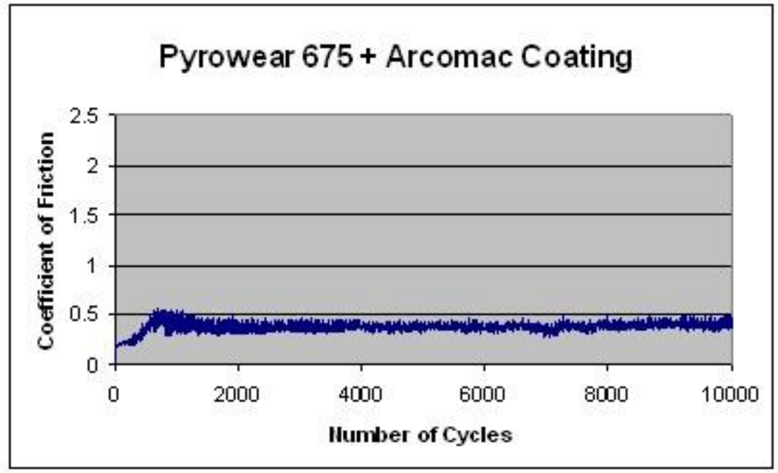
- Uncoated bearing steel experiences severe adhesive wear, damaging both the disk and ball
- Coated bearing steel experience mild abrasive wear, wear to ball only measures 0.05um deep
- Sliding wear resistance is important to address the inherent slip (~3%) that occurs in high speed bearings between balls and raceways, as well as sliding wear between cages and lands, and cages and balls.

FAAMS™ Coating Performance: Hybrid Bearings Applications

Dry Sliding Friction of Si3N4 vs. coated and uncoated bearing steel

Pin-on-disk testing – 200mm/sec, 300MPa, 25°C, 40%RH, 1cycle = 50mm distance





- Uncoated bearing steel rapidly becomes unstable and testing is prematurely halted at ~4,000cycles
- Coated bearing steel has stable friction behavior out to 10,000cycles (test stop)
- Stable friction values indicate steady and predictable wear in regards to component design
- Low friction values are desirable to minimize adverse heating of the bearing-lubricant system, high ΔT values result in loss of bearing tolerances and rapid bearing failure

FAAMS™ Coating Performance: Corrosion Resistant Applications

Atmospheric Corrosion Testing

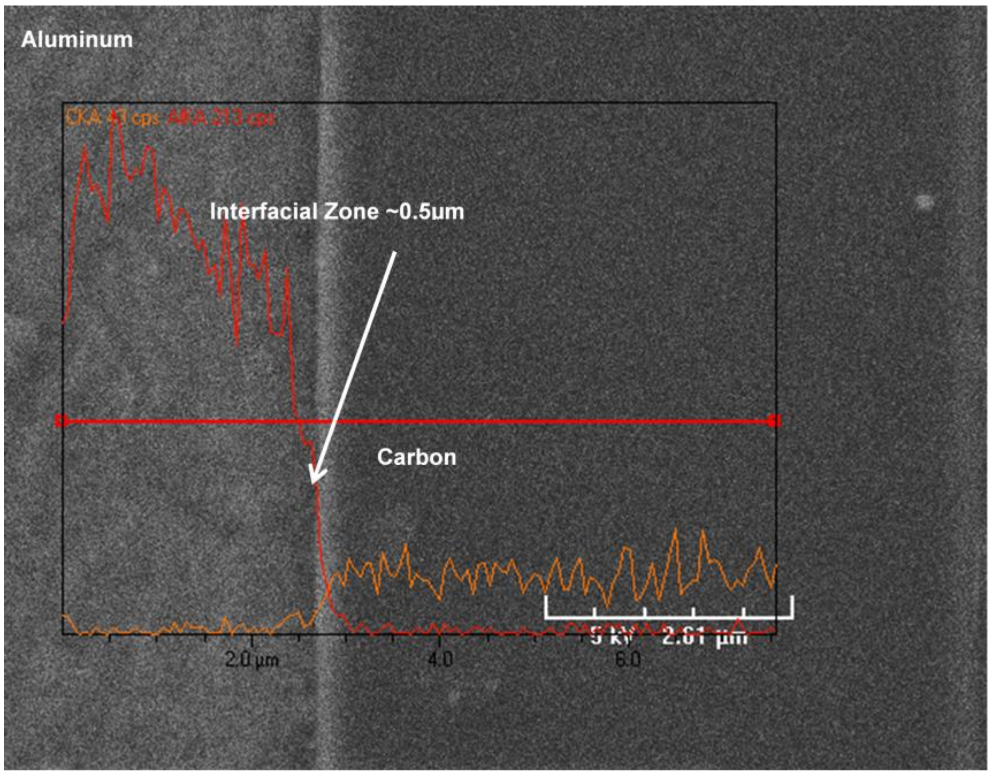
Cyclic Temperature Testing – 8hrs 150°F, 16hrs 37°F, Test duration 14days, samples are suspended above saltwater in a sealed corrosion cell.

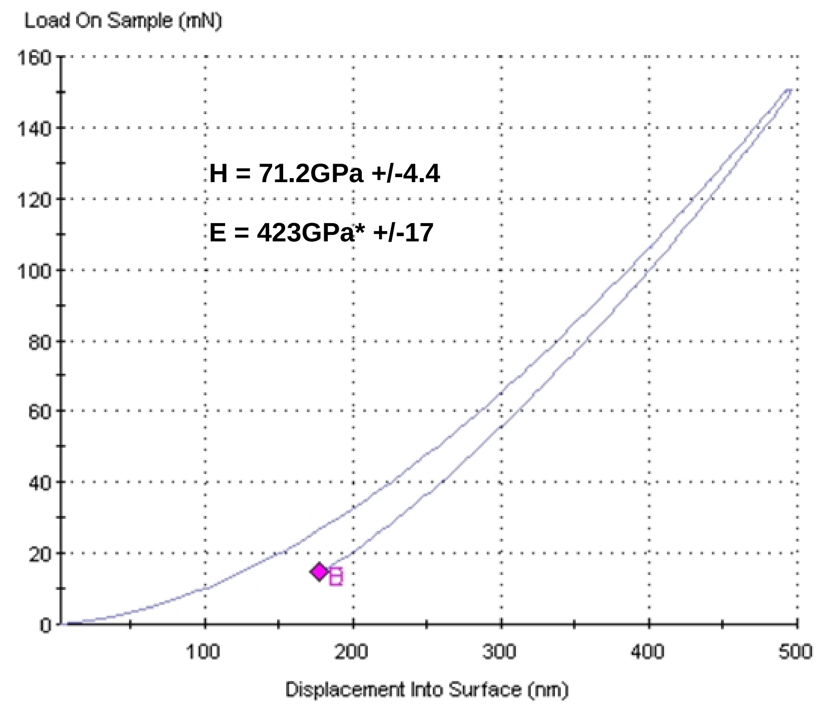
• Uncoated M50 samples experience pitting corrosion to depths of 30um-100um, surface roughness is increased up to 100x in corrosion areas

• Coated M50 samples are fully protected with the exception of mild pitting to depths of 1-5um where coating defects expose the M50 substrate

LAFAD^{TM} Coating Performance: Superhard Diamond-Like Carbon (DLC) Coatings

The filtered cathodic arc deposition technology is used from late 1970s as a source of 100% ionized carbon plasma flow free of any macroparticles non-carbon atomic species. This technology is proved to be able to produce DLC films with properties which closely resemble that of diamonds. In this process, each carbon ion is coming to the condensing surface with the energy defined by applied substrate bias. The conventional filtered arc technology is suffering from the limited scale-up capability, which restricts its use in industrial applications. The large area filtered arc deposition (LAFAD^{TM}) technology is able to override these limitations. The DLC coatings are characterized by its mechanical properties and corrosion resistance. A special attention is paid to interfacial areas between neighbor coating layers and coating–to substrate interface. The thermal management of substrates and substrate bias as well as deposition process parameters are used for optimization of coating performance for industry specific applications.





Elemental distribution by SEM/EDS technique across relatively thick (~6um) DLC film on aluminum. The film was deposited by LAFAD^{TM} source with graphite targets on water-cooled aluminum disk under RF bias with autopolarization potential ~100 volts (estimated C+ ion bombardment energy during coating deposition ~100eV).

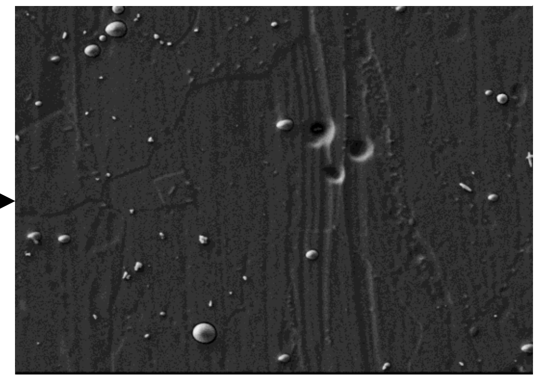
LAFAD™ Coating Performance: High Temperature Oxidation Resistance: Interconnect Plates for Solid Oxide Fuel Cells (SOFC)

NPE has developed advanced physical vapor deposition (PVD) technologies to engineer protective, functional coatings for intermediate temperature (~750ºC) SOFC metallic interconnects. Interconnect alloys (commercially-available ferritic stainless steels) are provided by Alleghany Ludlum, and unique thin-film (<5µm) nanocomposite oxide coatings are deposited using NPE's patented large area filtered arc (LAFAD™) filtered arc assisted magnetron sputtering (FAAMS™) and/or filtered arc-assisted electron beam evaporation (FAAEB™) technologies. In total, over 50 different coating compositions have been explored. Compared with oxide layers forming on uncoated alloys, NPE coatings exhibit significantly enhanced thermal stability, high and stable electronic conductivity, and negligible Cr volatility. Coatings have been successfully engineered to provide favorable and durable SOFC interconnect characteristics at both cathode-contact and non-contact regions.

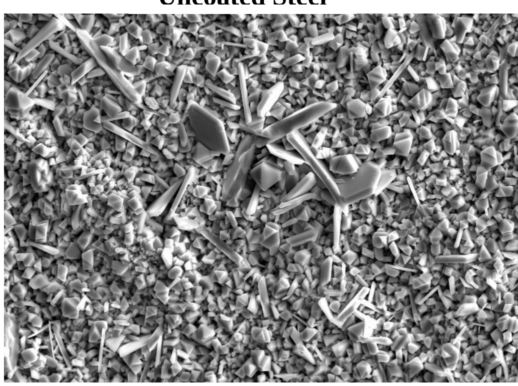
Uncoated Steel

Surface Before Testing

~4um LAFAD Coated Steel

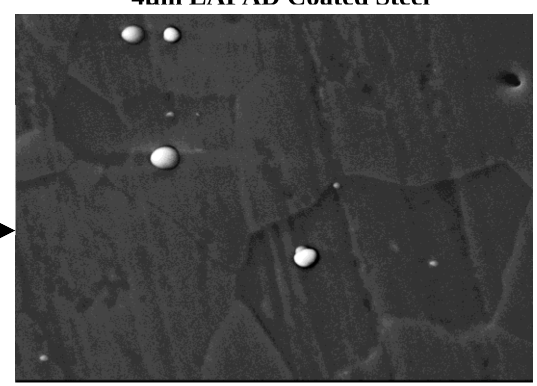


Uncoated Steel



Surface After >1,000 hours in 800°C air

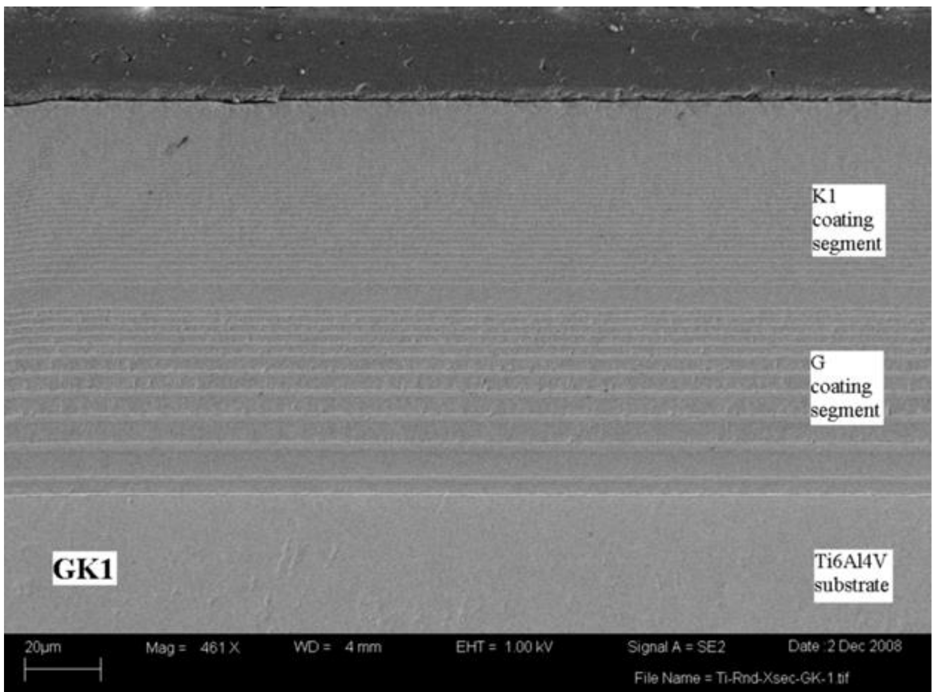
~4um LAFAD Coated Steel



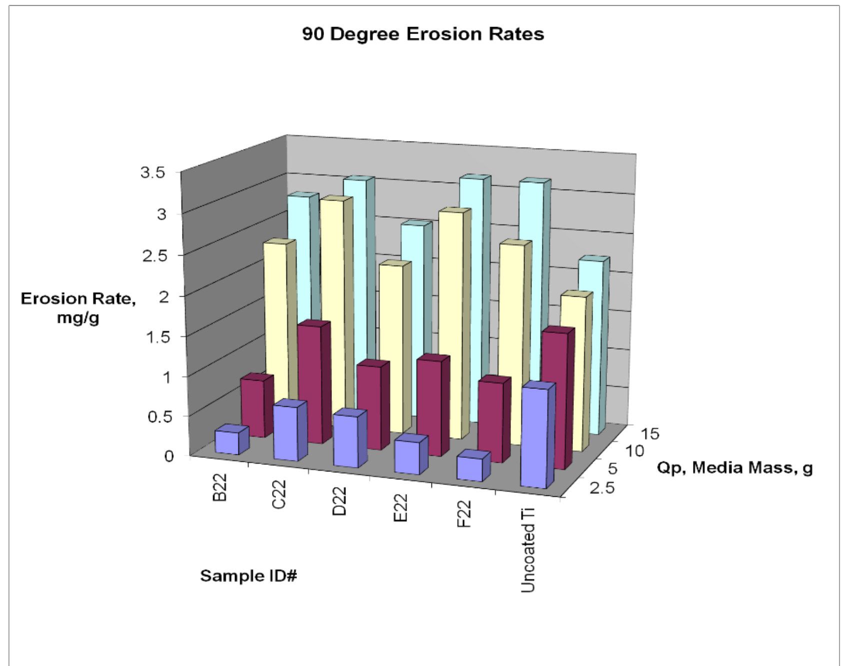
NPE coatings demonstrate protection of ferritic stainless steel for >1,000 hours in 800°C air

NPE coatings for turbomachinery

LAFAD™ technology combines the capability of depositing ultra-thick, but extremely hard, ceramic and cermet coatings having various multilayer architectures with nearly defect-free, atomically smooth. This coating morphology is in sharp contrast with the conventional direct (non-filtered) cathodic arc coatings that has a large density of macroparticles, holes, and growth defects ranging in sizes from submicrons to several tens of microns, which create a large number of ridges and bumps on the surface. Nano-multilayer LAFAD™ coatings, having ductile metallic sublayers followed by superhard ceramic sublayers, provide a desirable combination of soft plastic metal vs. hard and brittle ceramic properties which are optimized to achieve the best erosion resistance in heavy particulate impact conditions. The defect-free LAFAD™ coatings have neither inclusions nor porosity, and have nearly theoretical maximum density, resulting in high resistance against corrosion and chemical attacks both at ambient conditions and at high temperatures. The LAFAD™ process is enable for deposition of hard erosion and corrosion resistive coatings for turbomachinery components such as airfoils and protectors for the helicopter rotorblades with thickness ranging from 10 mm to 500 mm during commercially acceptable processing time. Coatings may have different architectures: monolithic, nano-multilayer or nanocomposite. The cross-section of the typical LAFAD™ TiN nano-multilayer 2-segment coating for turbomachinery applications is shown in Figure below (left). The erosion testing of LAFAD™ Ti/TiN nano-multilayer coating at the University of Cincinnati supersonic wind tunnel facility have demonstrated outstanding erosion resistance performance illustrated in Figure below (right).



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



Erosion rate of samples made of Ti6Al4V alloy with various LAFAD™, compared to uncoated titanium, as a function of erodent media mass at a 90-degree angle of impact (runway sand, 1200 fps, 500°F).

Literature

- "Superhard i-C Coatings Used in Complex Processes of Surface Strengthening of Tools and Machine Parts," N. Novikov, V. Gorokhovsky, B. Uryukov. Surface and Coatings Technology, Volume 47 (1), August 1991.
- "On the Atomic Nitrogen Role in Titanium Nitride Coatings Synthesis in a Vacuum-Arc Discharge," V. Gorokhovsky, D. Otorbaev. Physics and Chemistry of Materials Treatment, 1989, Number 2 (in Russian).
- "Process in Plasma-Arc Installation for Vacuum Depositions, Part I: Plasma Generation; Part II: Plasma Propagation," V.I. Gorokhovsky, V.P. Polistchook, I.M. Yartsev. Surface and Coatings Technology, Volume 61, December 1993.
- "Distributed Arc Sources," J. Glaser, V. Gorokhovsky, V. Polistchook, I. Yartsev. Invited Section in Monograph "Vacuum Arc Science and Technology", ed. By R.Boxman, P.Martin and D.Sanders, Noyes Publications, 1995.
- "Characterization of Large Area Filtered Arc Deposition Technology: Part I-Plasma Processing Parameters," Vladimir I. Gorokhovsky, Rabi Bhattacharya, Deepak G. Bhat. Surface and Coatings Technology, Volume 140 (2), May 2001.
- "Characterization of Large Area Filtered Arc Deposition Technology: Part II-Coating Properties and Applications," Gorokhovsky, V.I., Bhat, D.G., Bhattacharya, R., A.K. Rai, K. Kulkarni, R. Shivpuri, Surface and Coatings Technology, Volume 140 (3), June 2001.
- "Principles and Applications of Vacuum Arc Plasma-assisted Surface Engineering Technologies ", Gorokhovsky, V.I., Bhat, D.G., In Proceedings of the GOI-UNDP International Workshop on Surface Engineering and Coatings, Bangalore, India, ed. by I. Rajagopal, K.S. Rajam, R.V. Krishnan, Allied Publishers, Ltd., Mumbai, India, 1999.
- "Characterization of Cascade Arc Assisted CVD Diamond Coating Technology, Part I: Plasma Processing Parameters," V. Gorokhovsky. Surface and Coatings Technology, Number 194, May 2005.
- "Characterization of Cascade Arc Assisted CVD Diamond Coating Technology, Part II: Coating Properties and Applications," V. Gorokhovsky. Surface and Coatings Technology, Number 194, May 2005.
- "Using CrAlN multilayer coatings to improve oxidation resistance of steel interconnects for solid oxide fuel cells" R.J. Smith, C. Tripp, A. Knospe, C.V. Ramana, A. Kayani, Vladimir Gorokhovsky, V. Shutthanandan, D.S.Gelles *Journal of Materials Engineering and Performance 13(3) (2004) 295-302.*
- "The Effect of Multilayer Filtered Arc Coatings on Mechanical Properties, Corrosion Resistance, and Performance of Periodontal Dental Instruments," Vladimir Gorokhovsky, Brad Heckerman, Philip Watson, Nicholas Bekesch. Surface and Coatings Technology, Volume 200, Issues 18-19, May 2006.
- "Chromium Volatility of Coated and Uncoated Steel Interconnects for SOFCs," C. Collins, J. Lucas, T.L. Buchanan, M. Kopczyk, A. Kayani, P.E. Gannon, M.C. Deibert, R.J. Smith, D.S. Choi, V.I. Gorokhovsky. Surface and Coatings Technology, Volume 201, Issue 7, December 2006.
- "Oxidation Studies of CrAlON Nanolayered Coatings on Steel Plates," A. Kayani, R.J. Smith, S. Teintze, M. Kopczyk, P.E. Gannon, M.C. Deibert, V.I. Gorokhovsky, V. Shutthanandan. Surface and Coatings Technology, Volume 201, Issues 3-4, October 2006.
- "Tribological Performance of Hybrid Filtered Arc-Magnetron Coatings, Part I," V. Gorokhovsky, C. Bowman, P. Gannon, D. VanVorous, A.A. Voevodin, A. Rutkowski, C. Muratore, R.J. Smith, A. Kayani, D. Gelles, V. Shutthanandan, B.G. Trusov. Surface and Coatings Technology, Volume 201, Issue 6, December 2006.
- "Tribological Performance of Hybrid Filtered Arc-Magnetron Coatings, Part II," Vladimir Gorokhovsky, Chris Bowman, Paul Gannon, Dave VanVorous, Andrey Voevodin, A. Rutkowski. Surface and Coatings Technology, Number 201, 2007.
- "Deposition and Characterization of Hybrid Filtered Arc-Magnetron Multilayer Nanocomposite Cermet Coatings for Advanced Tribological Applications," V. Gorokovsky, C. Bowman, P.E. Gannon, D. VanVorous, J. Hu, C. Muratore, A.A., Voevodin, Y.S. Kang. Wear 265 (2008) 741-755.
- "Deposition and Evaluation of Protective PVD Coatings on Ferritic Stainless Steel SOFC Interconnects," V.I.Gorokhovsky, P.E.Gannon, M.C.Deibert, R.J.Smith, A.Kayani, M.Kopczyk, D.VanVorous, Zhenguo Yang, J.W.Stevenson, S.Visco, C.Jacobson, H.Kurokawa and S.Sofie, Journal of The Electrochemical Society, v. 153 (10) A1886-A1893 (2006).

- “Thermal stability and oxidation resistance of TiCrAlYO coatings on SS430 for solid oxide fuel cell interconnect applications”, H. Chen, J. A. Lucas, W. Priyantha, M. Kopczyk, R. J. Smith, K. Lund, C. Key, M. Finsterbusch, P. E. Gannon, M. Deibert, V. I. Gorokhovsky, V. Shutthanandan, P. Nachimuthu, Surface and Coatings Technology 202, 4820 (2008).
- “Advanced Surface Engineering Technology for Endodontic Instruments and Related Applications,” V. Gorokhovsky, B. Heckerman, T. Brown. ROOTS, Number 2, 2006.
- “Deposition of Various Metal, Ceramic and Cermet Coatings by an Industrial-Scale LAFAD Process”, V. Gorokhovsky, C. Bowman, D. VanVorous, J. Wallace, *JVST A*, **27**, 1080-1095 (2009).
- “Internal stresses in TiN/Ti multilayer coatings deposited by large area filtered arc deposition”, Y. H. Cheng,_ T. Browne, B. Heckerman, J. C. Jiang, E. I. Meletis, C. Bowman, and V. Gorokhovsky, Journal of Applied Physics **104**, 093502 (2008).
- “LAFAD Hard Ceramic and Cermet Coatings for Erosion and Corrosion Protection of Turbomachinery Components,” Vladimir Gorokhovsky, Chris Bowman, John Wallace, Dave VanVorous, John O’Keefe, Victor Champagne, Marc Pepi, Widen Tabakoff, Proceedings of ASME Turbo Expo 2009: Power for Land, Sea and Air, Paper No. GT2009-59391, Orlando, Florida USA (2009).
- “Influence of Si content on the structure and internal stress of the nanocomposite TiSiN coatings deposited by large area filtered arc deposition”, Y. H. Cheng,_ T. Browne, B. Heckerman, J. C. Jiang, E. I. Meletis, C. Bowman, and V. Gorokhovsky, Journal of Applied Physics **104**, 093502 (2008).
- Simulated Solid Oxide Fuel Cell Interconnect Performance of Crofer22 APS with and without Filtered Arc Cr-Al-O-N Coatings P. Gannon, A.Kayani, C.V. Ramana, M.C. Deibert, R.J. Smith, V. Gorokhovsky, *Electrochemical and Solid-State Letters, 11(4), B54-B58 (2008).*
- “Enabling inexpensive metallic alloys as SOFC interconnects: An investigation into hybrid coating technologies to deposit nanocomposite functional coatings on ferritic stainless steels,” P.E. Gannon, V.I. Gorokhovsky, M.C. Deibert, R.J. Smith, A. Kayani, P.T. White, S. Sofie, Zhenguo Yang, D. McCready, S. Visco, C. Jacobson, H. Kurokawa, *International Journal of Hydrogen Energy, 32, 3672 (2007).*
- **“**Thin Film YSZ Coatings on Functionally Graded Freeze Cast Anode Supports,” Gannon, P.E., Sofie, S.W., Deibert, M.C., Smith, R.J., and Gorokhovsky, V.I.,**.** Journal of Applied Electrochemistry, 2009. **39**(4): p. 497-502.
- “Large Area Filtered Arc (Al, Cr, Ti, Co, Mn, Y) Nanocomposite Oxide Coatings on T430 Ferritic Steel: Solid Oxide Fuel Cell Interconnect Performance and Substrate Surface Finish Effects*,”* Gannon, P.E., Gorokhovsky, V.I., Deibert, M.C., Smith, R.J., Chen, H., Priyantha, W., White, P.T., and Musz, E., Surface and Coatings Technology, 2007.
- “Influence of Si Content on the Structure and Internal Stress of the Nanocomposite TiSiN Coatings Deposited by Large Area Filtered Arc Deposition,” Y.H. Cheng, T. Browne, B. Heckerman, J.C. Jiang, E.I. Meletis, C. Bowman, and V.I. Gorokhovsky, *J Phys D: Appl Phys* **42** 125415 (2009).
- “Characterization of Thick Ceramic and Cermet Coatings Deposited by an Industrial-Scale LAFAD Process,” V.I. Gorokhovsky, *Surf Coat Tech*, **204**, 1216-1221 (2010).
- “LAFAD-Assisted Plasma Surface Engineering Processes for Wear and Corrosion Protection: A Review,” V. Gorokhovsky, In Advanced Ceramic Coatings and Interfaces V: Ceramic Engineering and Science Proceedings, Vol. 31, No. 3, Ed. by Dongming Zhu, Hua-Tay Lin, 204 pg.
- “Evaluation of SOFC interconnects made of ferritic steels with nano-structured oxi-ceramic protective coatings deposited by the LAFAD process,” V.I. Gorokhovsky, P.E. Gannon, J.Wallace, D. VanVorous, C.Bowman, M.C. Deibert, R.J. Smith**,** T. Wittberg, Journal of The Electrochemical Society, 158 (5) B526-B535 (2011),
- “Ion treatment by low pressure arc plasma immersion surface engineering processes,” V. Gorokhovsky, P. Del Bel Belluz, Surface and Coatings Technology Volume 215, 25 January 2013, Pages 431–439.

PATENTS: USPat#5435900, USPat#5587207, US#7252745, USPat#7300559, US#pat7939172, USPat#8282794, USPat#8658010, USPat#9257263, USPat#9482105, USPat#9761424, USPat#9765635.