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News from Institutes and Research Centers Around the World

This column is a forum to inform the thermal spray community on current activities in institutes and research centers active in the field of the thermal spray. Research efforts carried out in these organizations are oftentimes the starting point of significant developments of the technology that will have an impact on the way coatings are produced and used in industry. New materials, more efficient spray processes, better diagnostic tools, and clearer understanding of the chemical and physical processes involved during spraying are examples of such developments making possible the production of highly consistent performance coatings for use in more and more demanding applications encountered in the industry.

This column includes articles giving an overview of current activities or a focus on a significant breakthrough resulting from research efforts carried out in institutes and research centers around the world. If you want to submit an article for this column, please contact Jan Ilavsky, JTST associate editor, address: Argonne National Laboratory, Advanced Photon Source, 9700 S. Cass Ave., Argonne, IL 60439; e-mail: JTST.Ilavsky@aps.anl.gov.

Recent Research at Plasma Materials Engineering (PME) Laboratory, Department of Materials Engineering, The University of Tokyo, Japan

Introduction to PME

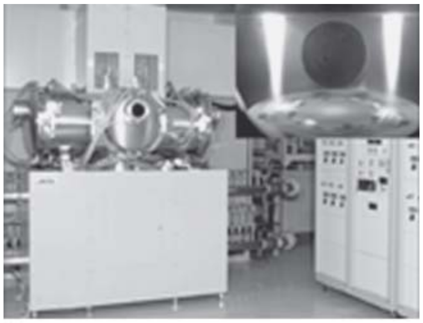
The Department of Materials Engineering at the University of Tokyo, located in the central Tokyo, originated from the Department of Mining and Metallurgy established in 1886 as one of the oldest university departments in Japan. The Plasma Materials Engineering (PME) laboratory, successor of the Electro-metallurgy laboratory, established in 1982, has specialized in research of plasma processing of a wide range of materials. In particular, the invention of hybrid plasma torch in 1983, which integrates dc and rf plasmas, has strengthened the potential of thermal plasma processing to evolve into practical technology for various functional coatings and nanoparticles. Research of low-pressure plasma started with the thin-film processing of diamonds and boron nitrides in the mid 1980s. This was followed by exploitation of the medium-pressure plasma as an evolutional plasma technology for high-rate deposition of device grade thin films in the late 1990s. At this time, the PME lab thus has particular expertise in powder spraying (TP-PS), thermal plasma chemical vapor deposition (TP-CVD), thermal plasma physical vapor deposition (TP-PVD), sputtering, and ICP-CVD for various kinds of materials system, such as solid-oxide fuel cells, solar cells, thermal barrier coatings, high-temperature superconductors, superhard coatings, wide gap semiconductors, and so forth.

The current research activities at the PME lab can be primarily classified by the three principal plasmas they employ:

- **Thermal plasma:** comprehensive plasma spray processing for the next-generation thermal barrier coatings (TBCs), with particular emphasis on the fundamental study on TP-PS, TP-PVD, and TP-CVD
- **Mesoplasma:** a feasibility study of medium-pressure plasma processing as a novel thin-film production route for photovoltaic device applications
- **Low-pressure plasma:** establishment of low-pressure plasma processing of cubic boron nitrides (CBN) thin films for high-temperature electronic devices

Thermal Plasma Processing

Single Molten Droplet Dynamics. The radical improvement and evolution of plasma powder spraying largely rely on the basic research of the individual droplet dynamics on the underlying substrate. In particular, its interaction with textured substrate is a critical step in the actual coating process, and its understanding may open up the option of using this technique to manufacture novel micronano patterned coatings. To cope with this, an in situ measurement system, capable of collecting about 10 single particles in series within 10 s, has been developed. This system enables precise one-to-one correlation between splat morphology and the thermal history of the corresponding droplet during deformation, solidification, and splashing on a substrate. Noteworthy achievement is that some of YSZ droplets were observed supercooled before impingement. In addition, the physical properties at high temperatures, such as viscosity of molten YSZ and the thermal contact resistance between YSZ and quartz substrate, were identified by combination of measurements with physical modeling. In the meantime, unique deformation of alumina droplets was observed on a variety of patterned substrates. Examples are the anisotropic elongation of splat in a direction perpendicular to the L/S pattern, characteristic fingering on the grid patterned substrate, and the off-centered air entrapment in a splat irrespective of the pattern layout. These could be of practical importance to develop an optimal surface design for a better adhesion in grit-blasting treatment.


(a)

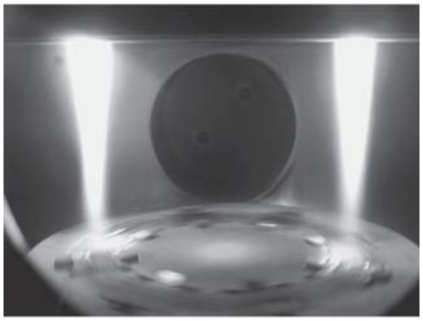

(b)

Fig. 1 (a) High-power twin hybrid plasma spray system. (b) Typical view of the two plasma flames reaching the rotating substrates

Development of Twin High-Power Hybrid Plasma System. Numerical modeling of plasma system has been conducted to complement experimental research. Recent results have proved that the high-power capacity of the hybrid plasma spraying is effective for the full melting and/or evaporation of YSZ. The PME lab has thus developed a novel and unique twin hybrid plasma spraying (THPS) system (Fig. 1). The system is equipped with two sets of 150 kW hybrid plasma torches (Fig. 1b), each of which is capable of various spraying techniques, such as TP-PS, TP-PVD, and TP-CVD. The primary advantages of this system are (a) large throughput, (b) complete melting/evaporation of high-temperature ceramics, and (c) ability to manufacture layered coating systems by combining the aforementioned spraying processes. In fact, in experiments with spraying of large YSZ powders, flattening degree of around 5 was seen with a 100 μm droplet in the 100 kW hybrid plasma. In addition, a new previously not observed layered PVD structure has been produced by the control of plasma power and powder feeding rate. Another interesting feature of this processing is its high deposition efficiency. Such TP-PVD structures are produced at one-fourth of the deposition rate for the TP-PS coatings and at about 10 times faster rates than that achieved by the EB-PVD processing.

Nanocomposites by Comprehensive Plasma Spraying. In the THPS system, the substrates on a rotary holder are exposed by turns to two plasma flames, which are separately assigned a different spray processing. Therefore, alternate layers with designed microstructures and/or different materials can be realized at practically high rates. Composite coatings with the combination of TP-PVD Al$_2$O$_3$, and TP-PS YSZ have been manufactured by the twin torch at the ultrafast rate of 30 to 60 μm/min (10 times faster than that by EB-PVD). Its microstructure exhibits the well-flattened YSZ splats (white) between the vapor deposited Al$_2$O$_3$ layers (black) as shown in Fig. 2(a). In addition, the unusual layered YSZ composite coating structure has been deposited by combination of TP-PS and TP-PVD (Fig. 2b). Such porous YSZ composite was deposited at high rates of >50 μm/min and achieved significantly reduced thermal conductivities of ~0.7 W/m $\cdot$ K. The dense YSZ coatings with interlaced t′ domains, in contrast, were deposited at 150 μm/min and exhibited a high nanohardness of 27.85 GPa and high infrared (IR) light reflectance. These various characteristic coatings allowed the authors to design a novel, advanced multilayered TBC, in which the dense layer with high hardness and high IR reflectance are at the top, the porous layers with low thermal conductivities in the middle, and the high adhesive splat layer at the bottom.

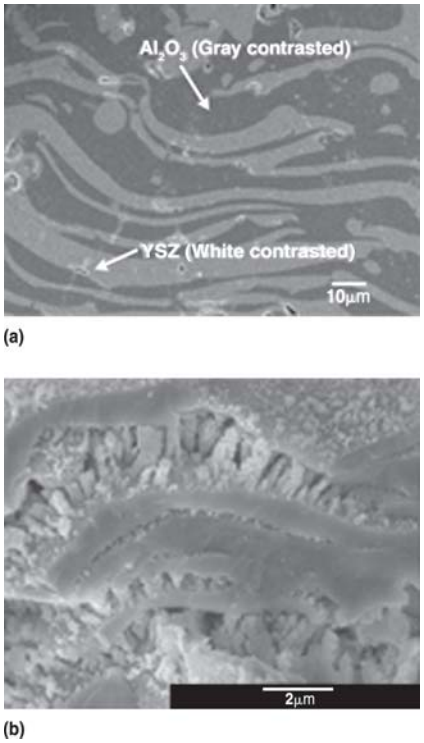


Fig. 2 FE-SEM images of the cross-section of (a) TP-PVD Al$_2$O$_3$ and TP-PS YSZ and (b) YSZ composite coatings

Mesoplasma Processing

High-Rate and Low-Temperature Epitaxy. At the medium operating pressure region, the plasma is anticipated to possess advantages of both the low-pressure plasma and the thermal plasma. Thus the processing with this plasma is expected to realize high rate and direct transport of selective species to the substrate due to rather low electron and gas temperatures and high-density plasma flow. In view of these potential characteristics, the group has started a feasibility study of this "mesoplasma" for large-scale thin-film electronics applications that require high rates of materials processing. The primary achievements in this processing are ultrafast deposition of microcrystalline silicon at rates of 1 μm/s and fast rate synthesis (20 nm/s) of amorphous silicon with a photosensitivity of ~10^3. Furthermore, recently, epitaxial growth of silicon has been achieved at rates around 60 nm/s at around 600 °C while maintaining reasonably high electronic properties. These examples clearly demonstrate the high potential of this type of plasma. The current research is directed toward establishment of mesoplasma processing as a versatile, high-rate and low-temperature homo-/hetero-epitaxial technique for various applications.

In situ Cluster Characterization. In this high growth rate film processing, nanosized clusters, created within the plasma, and substrate boundary, are believed to be effective precursors, which enhance the growth rate and also improve the quality of the film produced. Further improvement of the growth rate and quality of the films may be thus realized if such cluster characteristics could be controlled through direct observation during processing. To observe the cluster formation during processing, an in situ x-ray scattering measurement has been attempted (Fig. 3). Preliminary results have indicated that the scattering of the x-ray beam, passing through the plasma/substrate boundary, was enhanced upon SiH$_4$ injection to argon plasma during deposition. The scattered intensity further increased, when the epitaxial film was attained at high rates. This suggests that nanosized silicon clusters are formed in the boundary, serving as scatterers, and contributed to the high-rate epitaxy.

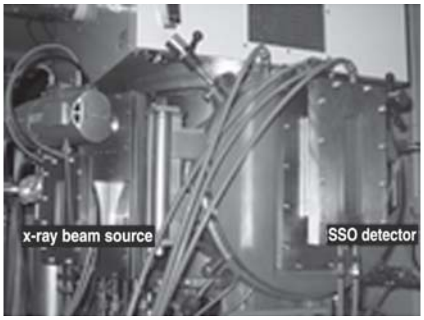


Fig. 3 Mesoplasma CVD reactor, equipped with an in situ x-ray scattering measurement system

Low-Pressure Plasma Processing

High-Temperature CBN Device Fabrications by Sputtering. The low-pressure plasma research at the PME has been primarily focused on the synthesis of cubic boron nitrides (CBN). This material possesses the second highest hardness, high thermodynamic stability, wide band gap, high thermal conductivity, and other interesting properties, which make it a top candidate for the next-generation high-temperature devices outstripping the current silicon technologies. The synthesis of CBN thin film has been conducted by the phase-regulated RF bias sputtering. The effects of ion bombardment, which has an essential role in the CBN growth, are investigated by a real-time monitoring of the distribution and flux of the ion energy on a growing CBN surface. In addition, the group has recently developed a simple, but innovative, doping technique for this material. This method provides control of the dopant concentration in the BN films, which has resulted in an enormous increase in the electronic conductivity by a factor of 10^6. As a result, highly pure CBN thin films have been deposited on silicon substrate, and its layered device structure has exhibited quite high electric rectification at temperatures up to 300 °C. These results are being further studied with intention to realize novel CBN high-temperature devices.

Control of the CBN Growth. An ultrahigh vacuum ICP-CVD system has been developed recently to further improve the CBN growth control. With this apparatus, high-density plasma can be generated with an input power of 7 kW, which enhances the CBN phase formation at lower temperatures. In addition, the substrate RF bias is controlled independently of the main plasma source, allowing one to dynamically regulate the ion impact energies on the growth surface. The group has developed the technique, named "time-dependent biasing technique," and succeeded in a reduction of the unwanted initial layer that is inevitably created before CBN growth starts. The current research therefore concentrates on the establishment of an innovative growth control to accomplish CBN heteroepitaxy on silicon substrates. An additional achievement includes the unique viscoelastic behavior with high curvature radius observed for the designed nanosized array of the hexagonal BN wall.

PME Facilities and Funding

Processing Equipment. The PME lab is fully equipped with unique and state-of-the-art plasma and thin-film processing facilities that include: a twin hybrid plasma spraying system (2 × 150 kW), two sets of hybrid plasma spraying system for powder spraying (70 kW), hybrid plasma spraying system (50 kW) for mesoplasma CVD, ICP-CVD (15 kW + 300 W) for CBN synthesis, two sets of RF-bias sputtering system (500 W + 300 W), two sets of electron beam evaporation chamber (2 kW), atmosphere and pressure controllable furnace (~1500 °C). The auxiliary equipment for these plasma facilities are an in situ droplet observation system, an in situ x-ray scattering system, and a quadrupole mass spectrometer. Also available in the department are EB and photolithography systems.

Characterization and Testing Instruments. A variety of characterization facilities are fully accessible, which include atomic force microscope, scanning tunneling microscope, Fourier transformation infrared spectrometer, Raman spectroscopy system, laser microanalyzer, nano indenter, micro Vickers, Hall measurement system, semiconductor parameter analyzer, surface profiler, and solar simulator. Also full access is given to the common facilities, such as field emission scanning electron microscope, 1200 keV high-resolution transmission electron microscope, x-ray photoelectron spectroscope, electron probe microanalyzer, electron backscattering diffraction pattern system, x-ray diffraction, and rocking curve.

Funding. A six-year multidisciplinary "Nanocoating" project, led by Prof. Yoshida, is in progress with support from the New Energy and Industrial Technology Development Organization (NEDO). The objective of this project is to establish the ceramic coating technologies for thermal and environmental barriers, thereby offering massive reduction in device energy consumption and loads to the environment. Four universities and three national laboratories collaborate on the fundamental and scientific aspects, and the exploitation and dissemination is strengthened by the participation of six industrial companies, ranging from materials production to engine manufacturers. In parallel, a three-year project on "mesoplasma processing" and a five-year "CBN high-temperature devices" project are underway, supported by the Japan Society for the Promotion of Science (JSPS). Additional support is given by the "Center of Excellence" program of MEXT for the promotion of international collaborations. The total budget of the PME comes together to approximately $0.7M for the year 2005.

Contact: Prof. Toyonobu Yoshida, Department of Materials Engineering, Graduate School of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan; tel: +81-3-5841-7100; fax: +81-3-5841-8641; e-mail: web@plasma.t.u-tokyo.ac.jp; Web: http://www.plasma.t.u-tokyo.ac.jp/eng/index.htm.

Industrial News

Coatings Release Corrosion Inhibitors on Demand

One method of corrosion protection is the slow, controlled release of corrosion inhibitors when needed. Chromate conversion coatings have this property, releasing chromate ions when corrosion initiates and stopping when no longer required. While such coatings have been the first line of defense for aluminum structures in aircraft since before World War II, they are due to be phased out because chromate ions are carcinogenic and highly toxic.

A team at the University of Virginia have invented a family of amorphous Al-Co-Ce alloys that act as multifunctional corrosion protection coatings (Jakab and Scully, *Nat. Mater.,* Vol 4 (No. 9), 2005, p 667). The alloys provide a tunable supply of environmentally friendly corrosion inhibitors in response to a pH change, as well as serving as a barrier and a sacrificial anode. The researchers coated a structural aluminum alloy with their protective amorphous Al-Co-Ce alloy. A scratch was introduced into the coating and the sample placed in an aqueous solution.

The team showed that corrosion of the underlying aluminum changed the pH of the solution. This prompted dissolution of the amorphous alloy, releasing the corrosion-inhibiting ions. The ions migrate to the damage site and suppress the corrosion damage on reaching a critical concentration. When the corrosion stops, the pH of the solution returns to neutral and the dissolution of the Al-Co-Ce alloy returns to a low level.

The researchers found that the new alloy was able to protect aluminum in the presence of a corrosive, acidic solution. The released inhibitors greatly reduced pitting and decreased pit size. This is very important for prolonging the fatigue life of components. "In theory, this could be a field-replaceable coating for aircraft fuselage and wing skins, as well as a coating for landing gear, etc." said John Scully. The coating could be applied to damaged or repaired areas using thermal spray methods or laser surface glazing, for example. "Our next step is to try some of these application methods on mimics of real parts and see if it protects against corrosion," said Scully. "Lab results so far have been promising."

Adapted from J. Wood, *Materials Today,* Oct 2005.

High-Velocity Oxygen Fuel Coatings for High-Temperature Applications

Air Force Research Laboratories (AFRL) materials engineers recently conducted an evaluation of high-velocity oxygen fuel (HVOF) thermal sprayed coatings as potential alternatives to electrolytic hard chrome (EHC) plating processes for elevated-temperature applications. (See the related article, "Engineers Evaluate Cold Spray Coating Processes," *AFRL Technol. Horizons,* Vol 6 (No. 2), April 2005, p 43-44, or http://www.afrlhorizons.com/Briefs/Apr05/ML0326.html.) Air Force (AF) Air Logistics Center maintainers use EHC plating processes extensively to rebuild, rework, and repair worn components during the overhaul of aircraft turbine engines. Chrome plating provides beneficial metallurgical properties such as hardness, wear and corrosion resistance, and lubricity. However, because the EHC plating process uses hexavalent chromium (a known carcinogen), federal and state regulatory agencies strictly control its use and disposal. Complying with these regulations increases costs, liability, and risk for the AF. Thus, reducing the use of EHC plating during maintenance operations significantly decreases not only expenses but also worker exposure to this hazardous material.

The AF and other Department of Defense organizations selected HVOF coating technology as the primary process to replace hard chrome plating. During this project, engineers evaluated the high-temperature metallurgical properties of several HVOF plasma sprayed coatings—tungsten carbide cobalt, WC-17Co; Tribaloy 400, Co-29Mo-8Cr; and Diamalloy 3007, Cr_3C_2 20(Ni 20Cr)—to determine their suitability as alternatives to EHC for gas turbine engine applications.

The Aeronautical Systems Center's Propulsion Environment Working Group (PEWG) is working with turbine engine manufacturers to transition HVOF coating technology. To complement the PEWG program, AFRL materials engineers established the High-Temperature HVOF Applications project. Funded by Air Force Materiel Command's Weapon System Pollution Prevention program, the AFRL team is providing in-depth metallurgical and materials analysis of the elevated-temperature performance of HVOF-applied coatings and their effect on applicable substrates.

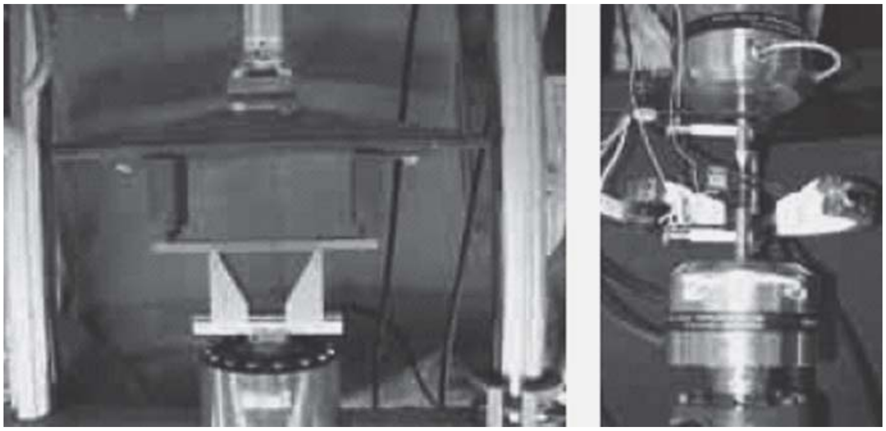


Fig. 1 The test regimen included axial loading (left) and four-point bending (right) tests to evaluate bond strength and delamination.

Using test specimens prepared from the same high-temperature alloys used in turbine engine applications (Timken 17-22-AS low-alloy steel and nickel-base Inconel 901), AFRL engineers conducted extensive in-house fatigue and tensile strength testing at elevated temperatures (300 and 750 °F, or 150 and 400 °C). To determine the quality of the bond between the coatings and each substrate, they also performed in-depth post-test materials analysis (Fig. 1), including nondestructive inspection evaluations. In addition, the engineers performed acoustical emission analyses at elevated temperatures to accurately establish the relationship between the applied load and the onset of cracking in the coatings.

The results of this investigation demonstrated that the performance of these HVOF-applied coatings (a) is superior to that of the same coatings applied by plasma spraying, and (b) is equal to or better than that of EHC plating on the tested substrates. These data will further justify the transition of HVOF coating technology to AF depot maintenance operations.

Adapted from article by T.A. Naguy, J.R. Kolek (consultant), and T.R. Anderl (Anteon Corp.) of the Air Force Research Laboratory's Materials and Manufacturing Directorate.

Contact: TECH CONNECT at 800/203-6451 or place a request at http://www.afrl.af.mil/techconn/index.htm. Reference document ML-H-04-32.

Improved Small-Particle Powders for Plasma Spraying

Improved small-particle powders and powder processing conditions have been developed for use in plasma spray deposition of thermal barrier and environmental barrier coatings. Heretofore, plasma sprayed coatings have typically ranged in thickness from 125 to 1800 μm. As explained below, the improved powders make it possible to ensure complete coverage of substrates at unprecedentedly small thicknesses—of the order of 25 μm.

Plasma spraying involves feeding a powder into a hot, high-velocity plasma jet. The individual powder particles melt in the plasma jet as they are propelled toward a substrate, upon which they splat to build up a coating. In some cases, multiple coating layers are required. The size range of the powder particles necessarily dictates the minimum thickness of a coating layer needed to obtain uniform or complete coverage. Heretofore, powder particle sizes have typically ranged from 40 to 70 μm; as a result, the minimum thickness of a coating layer for complete coverage has been about 75 μm.

In some applications, thinner coatings or thinner coating layers are desirable. In principle, one can reduce the minimum complete-coverage thickness of a layer by using smaller powder particles. However, until now, when powder particle sizes have been reduced, the powders have exhibited a tendency to cake, clogging powder-feeder mechanisms and feed lines.

Hence, the main problem is one of synthesizing smaller-particle powders having desirable flow properties. The problem is solved by use of a process that begins with a spray-drying subprocess to produce spherical powder particles having diameters of <30 µm. (Spherical-particle powders have the best flow properties.) The powder is then passed several times through a commercial sifter with a mesh to separate particles having diameters <15 µm. The resulting fine, flowable powder is passed through a commercial fluidized-bed powder into a plasma spray jet.

This work was done by Q.N. Nguyen and R.A. Miller of Glenn Research Center and G.W. Leissler of QSS Group, Inc. For further information, access the Technical Support Package (TSP) free on-line at www.techbriefs.com/tsp under the Materials category. Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Commercial Technology Office, Attn: Steve Fedor, Mail Stop 4-8, 21000 Brook Park Rd., Cleveland, OH 44135. Refer to LEW-17433-1.

News from TSS

New TSS Board Members

In accordance with the Rules of Governance, the ASM Thermal Spray Society has completed their election of officers and board members. The TSS Board members represent the industry (suppliers, service organizations, and users), universities (academia), research and development organizations, government agencies, and the non-North American (international) thermal spray community and are responsible to the members of the Thermal Spray Society and the ASM International Board of Trustees. The following two new members were elected in 2005.

Charlie Kay

Charlie Kay, Vice President, Marketing, for ASB Industries, was elected to the TSS Board for a three-year term. Kay has been an active member in the thermal spray community for more than 12 years and is also the Chair of the TSS Membership and Marketing Committee.

Lysa Russo

Lysa Russo, Industrial Liaison Manager at Stony Brook University has also been elected to the TSS Board for a three-year term. Russo has also served on the TSS Safety Committee as both a member and co-chair since 2000.