JTTEE5 14:162-167
DOI: 10.1361/10599630524105
1059-9630/$19.00

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: Dr. Jan Ilavsky, UNICAT, APS Bldg 438E, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439; tel: 630/252-0866; fax: 630/252-0862; e-mail: ilavsky@aps.anl.gov.

Institute for Manufacturing Technologies of Ceramic Components and Composites (IMTCCC), University of Stuttgart, Germany—Activities in the Field of Surface Technologies and Composites

1. Introduction

Process and product development with advanced surface technologies is a key strategy and core business in the Institute for Manufacturing Technologies of Ceramic Components and Composites (IMTCCC) at the University of Stuttgart, Germany. A special focus is the application of state-of-the-art thermal spray technologies to create performing layer composites with a broad variety of substrate materials, functional coatings, and industrial applications. Furthermore, chemical processing and liquid-phase technologies are applied for coatings based on ceramic precursors, special lacquers, and micro- and nanoscale dispersions in high-end polymer coatings.

In the field of thermal spraying, IMTCCC concentrates on hypersonic flame spraying with gas and kerosene high-velocity oxygen fuel (HVOF) systems, both integrated in advanced steering and control systems according to industrial manufacturing standards of leading OEM. The use of acetylene as a fuel gas enables processing of oxide ceramics to form dense oxide coatings that are of interest for many novel applications. The second center of activities is in atmospheric plasma spraying with a focus on functional ceramic coatings on sensitive substrate materials and components. Electric arc spray deposition using light metal alloy wires and even complex multiphase powder and fiber-filled wires are a further field of research and development.

Beside the research in thermal spray processing and production engineering with integrated systems, IMTCCC deals with composite technologies as a fundamental and as an essential tool to optimize the chemical and mechanical compatibility in various layer composites. Modeling and simulations using finite-element modeling (FEM) tools and coupled stress temperature analysis are performed to manage the impulse, heat, and mass transfer during the coating formation and deposition as well as the occurring residual stresses. Thermally induced stresses in combination with load stresses under operation conditions in thermal engines are limiting factors for any type of advanced coating under severe or extreme operation conditions.

Based on the experience and hardware capacities in chemical and ceramic engineering in IMTCCC, the full manufacturing chain for advanced powders and agglomerates for thermal spraying is available from the preparation of aqueous and nonaqueous slurries, fine milling technologies, spray dry granulation, and finally calcination and HT treatment up to 2000 K.

Industrial manufacturing with advanced coating technologies includes all necessary measures to achieve high process stability, availability of the equipment, reproducibility, and last but not least the reliability of the product. Therefore, modern systems and tools of total quality management (TQM) are a further center of activity.

The following sections present some of the recent research projects and activities of the Institute.

2. Lanthanum Hexaaluminate Thermal Barrier Coatings

Lanthanum hexaaluminate in magnetoplumbite structure is a promising competitor to yttria-partially stabilized zirconia (Y-PSZ) as a thermal barrier coating (TBC), since most zirconia coatings age significantly, including densification at temperatures exceeding 1100 °C.

Coatings consisting of lanthanum hexaaluminate have a platelet-containing microstructure. The magnetoplumbite crystal structure is characterized by a highly charged La^{3+} cation located in an oxygen position in the closest-packed hexagonal structure of oxygen ions. Diffusion is strongly suppressed due to the crystallographic structure, and the material shows nearly no postsintering during operation. Operating temperatures above 1100 °C (up to 1600 °C) are possible because of the thermal stability of lanthanum hexaaluminate.

IMTCCC has developed an optimized thermal spray powder by spray drying technique of aqueous slurries. Additionally, the APS deposition process of these granulates has been optimized in order to produce homogeneous crystalline coat-

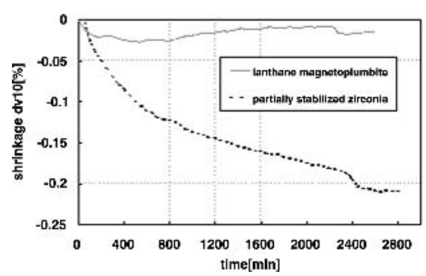


Fig. 1 Comparison of the aging behavior of APS sprayed La-MP and PSZ at a temperature of 1300 °C

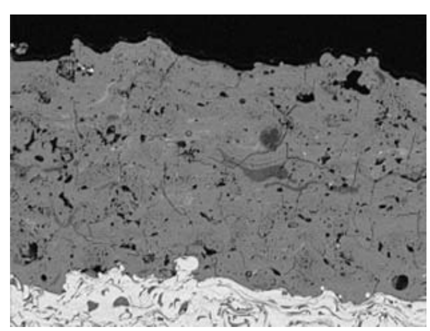


Fig. 2 Cross-section micrograph of thermally sprayed La-MP coating

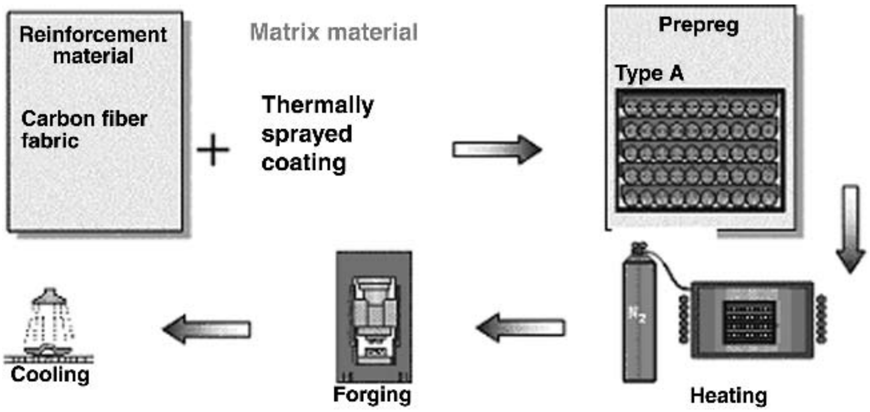


Fig. 3 Production route of MMC using thermally sprayed prepregs

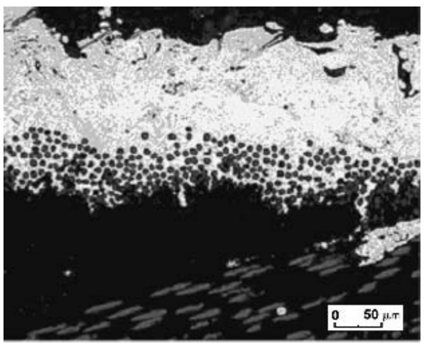


Fig. 4 Cross section of a HT-carbon fiber fabric with a thermally sprayed AlSi 7 coating

ings with controlled microporosity and residual stresses. Due to the superior qualities of this new material, it can replace conventional PSZ-TBCs in the future.

3. Prepreg Fabrication for MMC Production by Thermal Spray Coating of Reinforcement Fiber Fabrics

High mechanical performance in combination with low density is the key feature for lightweight engineering in automotive and aerospace applications. Light metals are promising candidates to realize safe, relevant, lightweight components because of their high specific strength and ductility. However, for many applications their stiffness and temperature stability as well as their fatigue behavior are insufficient. Tailor-made fiber reinforcements in light metal matrices can solve this problem, but the integration of fibers with conventional manufacturing techniques such as squeeze casting, hot pressing, or diffusion bonding leads to restrictions in the component geometry and results in elevated process cost caused mainly by long cycle times, complex investment, and the need for additional fiber coatings.

In a collaboration between the Institute for Metal Forming Technology (IFU) and IMTCCC, new manufacturing methods for metal-matrix composites (MMCs) are being developed. Prepregs consisting of laminated fiber woven fabrics with thermally sprayed metal coatings are used as preforms for compaction and forming by an advanced thixoforging process. Therefore, a coating process of even temperature-sensitive and flexible fiber fabrics is developed using the thermal spray process. The semisolid forming and simultaneous infiltration in short cycle times offer the possibility to realize complex near-net-shape geometries and make additional fiber coatings dispensable.

4. High-Velocity Oxygen Fuel (HVOF) Metallurgical Coatings for High-Temperature Erosion Protection of Diesel Engine Pistons

A main task of engine technology is to reduce fuel consumption and pollution emission. One possible approach is a constructive modification of the engine by changing the fuel-injection angle; another one is to increase the fuel-injection pressure, which causes a better fuel atomization and thus leads to improved combustion. In both cases, the engine materials are subjected to higher thermal corrosive and mechanical loads. In order to reduce the fuel consumption and pollution emission, the fuel-injection angle is also modified. After 400 h of operation, erosion can be detected on the top of nonarmed pistons mainly beneath the exhaust valve. Therefore, a reinforcement of the piston surface, for example, by protective coatings, is necessary. HVOF has been successfully used to apply different protective coatings to the piston top.

5. Thermally Sprayed Multilayer Coatings as Electrodes and Dielectrics in High-Efficiency Ozonizer Tubes

The aim of this research and development project is a novel, powerful ozonizer tube that cuts down the production cost and thus causes ozone to be an economically competitive alternative compared to traditionally used chlorine compounds. Standard ozonizer tubes consist of a borosilicate glass tube with a metal coating applied to the inner surface of the tube serving as the HV electrode. In this arrangement, the tube itself serves as a dielectric. In order to increase the ozone production efficiency, one possibility is to increase the capacity of the ozonizer tubes. For this reason, the use of a material with a higher permittivity is needed.

IMTCCC has developed a novel concept of atmospheric plasma sprayed (APS) tubes where a plasma sprayed ceramic layer serves as the dielectric. It is deposited together with the metal electrode on top of the glass tube. The ceramic reaches a layer thickness up to 1000 µm. An increase of up to approximately 30% (for type I) and 60% (for type II) in ozone production efficiency could be achieved.

Fig. 5 As-sprayed HVOF coated steel pistons with various metallurgical protective coatings before use in diesel engines (left). Partially cleaned HVOF chromium-molybdenum-base coated steel piston after the use in a (stationary) ship diesel engine with increased fuel injection angle showing no wear, erosion, or corrosion damage or coating delamination (right)

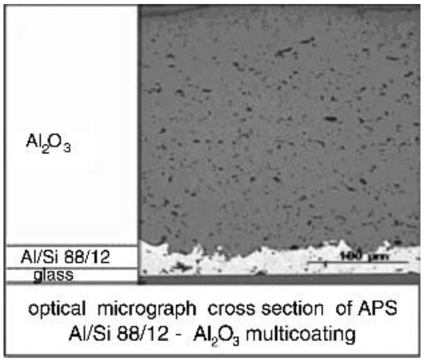


Fig. 6 Metal-ceramic layer composite plasma sprayed on borosilicate glass

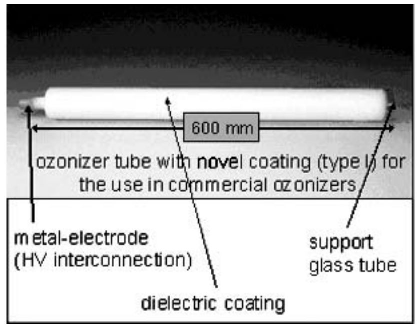


Fig. 7 Glass tube with applied metal ceramic layer composite

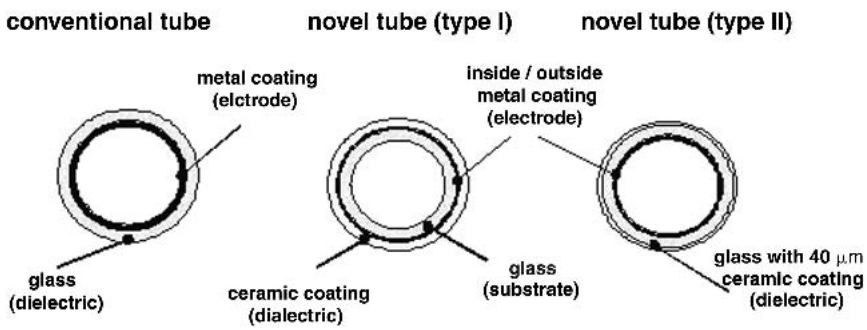


Fig. 8 Different tube types. Left side shows the conventional glass tube with inner electrode. Right side shows the two newly developed tubes, type I and II.

6. Thermally Sprayed Ceramic-Metal Layer Composites on Glass-Ceramic Substrates Used as a Film Heater Device

This work focuses on the investigation and development of plasma sprayed metal-oxide layer composites that serve as combined resistance heating elements and electrical insulating coatings. Oxide ceramics with high chemical purity are chosen as an insulating material between the glass ceramic and the film heater. Metal alloys and cermets are chosen as the film heater material.

Regarding the thermal spray process, glass and glass ceramics substrates behave very differently compared with traditional metal substrates: (a) Adhesion is strongly temperature dependant, of chemical nature, and can be very strong. (b) Glass is very sensitive concerning strong temperature gradients. (c) Especially glass-ceramic substrates feature a very low or even zero coefficient of thermal expansion (CTE) that does not suit the CTE of most coating materials.

Therefore, the coating process has to be optimized to minimize internal stresses. Also of great importance is a high homogeneity of the film heater microstructure, that is, its porosity, film thickness, and oxide content. The determining factor here is the substrate temperature during the coating process.

Any inhomogeneity in the temperature distribution during the coating process operation will cause inhomogeneities of the electrical resistance in the film heater that lead to temperature fluctuations and hot spots during operation that will destroy the metal film.

7. Advanced Coatings for Ultralightweight Engines with Thermally Sprayed Cylinder Liners and Crankcases

The reduction of fuel consumption and pollution emissions and the improvement of the engine efficiency as well as the cost reduction in manufacturing and assembly are in the focus of actual research activities in the automotive industry. Most of these requirements can be fulfilled by a reduction of the total vehicle weight. This results in an increasing utilization of light metals for chassis, body, and engine components. Significant weight savings are obtained by changing the engine block material from cast iron to aluminum. Due to the harsh operation conditions, the aluminum cylinder must be reinforced. Approaches to increase combustion as well as operation efficiency and lifetime of light metal engines are thermally sprayed APS and HVOF coatings on cylinder liners of the aluminum crankcases.

For this purpose, IMTCCC developed an HVOF coating process (with different fuel gases/fluids) together with the complete kinematic control of HVOF torch and engine block. Unlike in other coating techniques where a rotating miniaturized torch is inserted into the cylinder liner, the HVOF torch is operated externally. It follows an elliptically shaped moving path, whereas the cylinder liner is rotating. This enables an improved coating microstructure (less porosity) and superior coating adhesion. The HVOF coatings are homogeneous, with a dense, bulklike microstructure, a low porosity (<<3%) and surface roughness as well as a superior coating adhesion compared with APS coatings.

8. Ceramic Coatings on Fiber-Woven Fabrics

There is an increasing demand for ceramic and cermet coatings on all kinds of fiber fabrics, as they can significantly extend the functionality of these flexible materials in many applications. Based on thermal spray technologies, IMTCCC has developed a coating process for temperature-sensitive fiber substrates that allows the coated fabrics to retain their flexibility. High-speed and high-rate cermet and ceramic coatings are deposited with simultaneous substrate cooling in order to apply thick, hard, and refractory cermet and oxide ceramic coatings. These coatings can be applied, for example, on lightweight aramide fabrics without damaging the fibers. This way a fully flexible, highly tenacious, and lightweight fabric with a hard and refractory top coating has been realized. One key application is stab and ballistic protection. The penetration of bullets, knives, and blades through such hard material coated multilayer fabrics can be effectively prevented. Other applications cover heat- and fire-resistant flexible materials for human protection, for use in biomedical applications, and many more.

9. Bioceramic Coatings and Composites for Implants and Prostheses in Modern Surgery

Bioresorbable polymer implants are a promising research field in maxillofacial

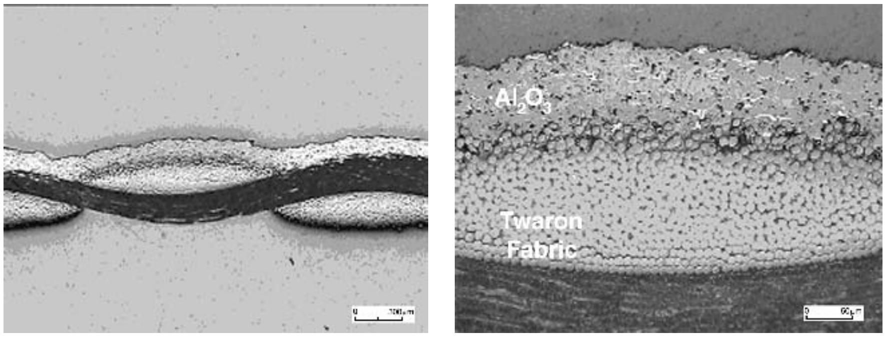


Fig. 9 Cross section of a thermally sprayed Al_2O_3 coating on a Twaron fabric

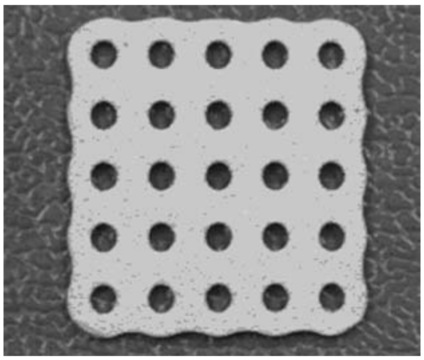


Fig. 10 A poly(D,L) lactide implant plate coated with tricalcium phosphate by APS

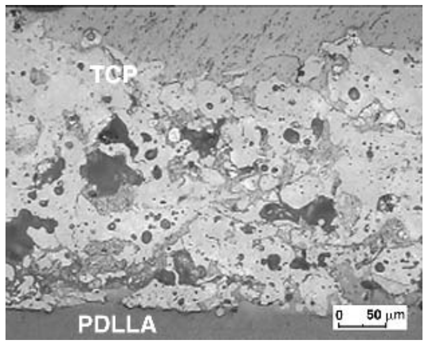


Fig. 11 Light microscope shot of micro and macro pores in the tricalcium phosphate coating

surgery, since their use eliminates the need for a secondary operation to remove metal implants. Mechanical properties and biocompatibility of these implants are nevertheless not completely satisfactory, and new composite devices are demanded. Thermally sprayed tricalcium phosphate (TCP) coatings may significantly increase the biocompatibility of polymer implants and contribute to matching the resorption rate of the implant with the bone-healing rate. IMTCCC has manufactured β-TCP powders suitable for APS via spray drying granulation and the thermal spray coating process on flexible and bioresorbable poly(D,L) lactide implant structures.

The successful development of complex coating systems for surface engineering requires a precise knowledge of material properties of the used materials. They are the basis for an optimized layer quality and functionality. The IMTCCC has abilities in sophisticated materials testing and characterization, all important physical investigation methods for the material characterization are available:

- Computer-assisted microhardness measurements
- Zetasizer for determination of surface loads on powders and/or diluted slurries
- Determination of the specific surface on powders with gas adsorption measurement (BET method)
- Optical laser diffraction spectroscopy for determination of powder grain size and distribution
- X-ray diffraction (XRD) for phase determination on powders bulk materials and coatings
- Diffrac+ Software for evaluation of XRD spectra
- High-temperature dilatometry for determination of thermal expansion and/or sinter shrinkage of materials during thermal processing
- Mercury high-pressure porosimetry for determination of the porosity, the pore size, and distribution in materials
- Incident light and transmitted light microscopy with integrated video analysis for qualitative and quantitative texture analysis
- CCD camera based image analysis
- EDX for qualitative and quantitative texture analysis
- Topographic imaging by mechanical and optical methods
- Oscillation tribometry
- High-resolution manufacturing metrology
- High-voltage resistivity and electric breakthrough testing
- Impedance spectroscopy

Selected References

- M. Baccalaro, R. Gadow, A. Killinger, and K. von Niessen, Processing of Thermally Sprayed Tricalcium Phosphate (TCP) Coatings on Bioresorbable Polymer Implants, *Symposium 8: Bioceramics and Biocomposites,* 29th Annual Cocoa Beach Conference & Exposition (Cocoa Beach, FL), Jan 23-28, 2005, The American Ceramic Society

- A. Candel, R. Gadow, D. López, and M. Buchmann, "New Approaches in the Hypersonic Flame Spray Coating for Cylinder Liners in Aluminum Crankcases," SAE/SP 1820, Compression Ignition and Spark Ignition Power Cylinder Systems," Technical paper 2004-01-0601, SAE International, 2004, p 23-28

- A. Friedrich, R. Gadow, and A. Killinger, Thermally Sprayed Multilayer Coatings as Electrodes and Dielectrics in High Efficiency Ozonizer Tubes (Thermisch gespritzte Kombinationsschichten für Elektroden und Dielektrika von Hochleistungsozonisatorröhren), *Conference Proceedings UTSC'99,* United Thermal Spray Conference and Exposition, Beschichten für die Praxis, E. Lugscheider and P.A. Kammer, Ed., DVS-Verlag GmbH, Düsseldorf, 1999, p 676-682

- C.J. Friedrich, R. Gadow, and T. Schirmer, Lanthane Aluminate—A New Material for Atmospheric Plasma Spraying of Advanced Thermal Barrier Coatings, *Thermal Spray Surface Engineering via Applied Research,* Proceedings of the First International Thermal Spray Conference, C.C. Berndt, Ed., ASM International, 2000, p 1219-1226

- R. Gadow, A. Killinger, C. Li., and K. Wermbter, Product Development with Thermally Sprayed Functional Coatings on Glass and Glass Ceramic Substrates (invited paper), NMT New Material Technologies Stuttgart and

Schott Glas Mainz, *Ceram. Eng. Sci. Proc.,* Vol 24 (No. 3), W.M. Kriven and H.-T. Lin, Ed., The American Ceramic Society 2003, p 601-614

- R. Gadow and K. von Niessen, Thermally Sprayed Ceramic Coatings on Flexible Fiber Woven Fabrics, *Proc. International Thermal Spray Conference, ITSC 2002,* C.C. Berndt, K.A. Khor, and E.F. Lugscheider, Ed., ASM International, 2002, p 220-224

Industrial News

Ceramic-Based Coating Seals Thermal Spray Coatings

Ceramacoat 503-VFG-C, a new high-temperature ceramic coating manufactured by Aremco Products, Inc., is now used to seal corrosion protective thermal spray coatings that are used in bag houses, incinerators, and other metal structures found in power plants, chemical processing plants, and foundries.

Ceramacoat 503-VFG-C high-temperature sealant fills microporosity in corrosion protective, thermal spray coatings. It is formulated as single-part, water-dispersible, alumina-filled system. Inert, chemically resistant, inorganic material will not outgas or decompose in high-temperature, corrosive applications up to 1750 °C (3200 °F). Product is applied using sponge brush or pneumatic spray equipment. Full cure is achieved after exposure for 1 to 2 h at 370 °C (700 °F).

Contact: Peter Schwartz, Aremco Products; tel: 845/268-0039; fax: 845/268-0041; Web: http:/www.aremco.com.

High-Pressure Natural Gas Torch Booster for HVOF/Flame Spray

G-TEC Natural Gas Systems introduces a line of torch boosters capable of boosting utility natural gas pressure for high-velocity oxyfuel (HVOF) and flame spray applications, replacing propane, propylene, or acetylene.

G-TEC's TB-500H torch booster can raise gas pressure as high as 150 psi with volume up to 1000 scfh, enough to operate two HVOF spray guns simultaneously. The TB-125H torch booster can boost gas pressure to 80 psi at 200 scfh to operate two wire spray guns simultaneously.

Ceramacoat 503-VFG-C now used to seal thermal spray coatings

Torch boosters are designed to replace cylinder gases and provide a constant supply of natural gas without ever running out. Natural gas prevents reliquification problems, cuts fuel gas costs, and provides a coating quality better than that of propane or propylene.

G-TEC torch boosters compress and supply high-pressure natural gas as it is used; there are no tanks to fill, and the unit is ready for service as soon as it is turned on. They require no special site preparation for installation.

TB-500H torch boosters are designed for HVOF applications, and with a gas supply pressure of 15 psi one TB-500H can operate two HVOF guns simultaneously. With standard ¼ psi gas service, the TB-500H can supply one HVOF gun. TB-125H Torch Boosters are designed for wire spray applications, and with as little as 5 psi supply pressure can operate two wire spray guns simultaneously.

Components for HTE Cells Made by Plasma Deposition

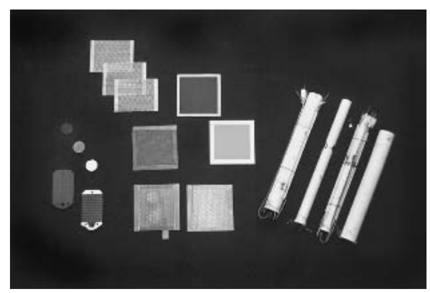
Components of high-temperature electrolysis (HTE) cells for producing hydrogen are made by coating substrates via plasma deposition, reports Idaho National Engineering and Environmental Laboratories, Idaho Falls.

The coinlike items are small (1 in.) diam button cells for testing the plasma deposition process. The six square metallic parts are interconnection plates, which carry the steam to the planar electrodes, carry the hydrogen and oxygen away, and conduct the electricity from one cell to the next. The squares with white rims are planar electrolytes, 0.2 mm thick, with the green and dark gray electrodes on opposite sides.

The four tubes are fixtures for testing button cells in a small furnace.

Contact: Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID 83415; tel: 800/708-2680; Web: www.inel.gov.

Adapted from *Advanced Materials and Processes,* Feb 2005.



From left to right, the two corrugated items are nickel aluminide substrates on which the electrodes and electrolytes are deposited via plasma deposition.

Ceramic Coatings Market

The North American market for high-performance ceramic coatings services, estimated at $1.1 billion in 2004, is expected to reach $1.6 billion by 2009. According to Business Communications Co. Inc. (BCC), Norwalk, CT, the United States has an edge in new coating technologies and is likely to hold onto its lead over the near term.

Thermal spray coatings will continue to dominate the market due to increased demand for commercial and military aircraft in the next five years. Many airlines are acquiring new aircraft, and there is increased demand in Asia as well.

Adapted from *American Ceramic Society Bulletin,* Feb 2005.

Table 1 High-performance ceramic coatings, North America

	2004 (SM)	2009 (SM)	AAGR, %
Thermal spray	690	1040	8.6
PVD	143	190	5.8
CVD	193	246	5.0
Other(a)	82	124	8.6
Total	1108	1600	7.6

(a) Includes spraying, dipping, sol-gel, micro-oxidation, and laser-assisted techniques. Source: BCC

New General Manager at Wall Colmonoy Corporation (WCC) Dayton Facility

Donald C. Hainley

Donald C. Hainley was recently appointed to the position of General Manager for the WCC Dayton Business Unit. Hainley will oversee all operations at the WCC Dayton facility, which specializes in thermal spraying, furnace brazing, and thermal processing of all types of materials. Hainley has 20 years of experience in heat-transfer technology and product development in the aerospace industry. Most recently, he was Technical Director for an aerospace component manufacturer.

Hainley received an MBA from Ohio State University and a Master's Degree in Mechanical Engineering from Pennsylvania State University. He is also a Licensed Professional Engineer in the state of Ohio.

Contact: Wall Colmonoy Corporation, Web: www.wallcolmonoy.com.

Wigren Receives Thulin Silver Medal

Jan Wigren

The Thulin silver medal went this year to **Jan Wigren,** who works with thermal spray at Volvo Aero Corporation. Jan is known in the thermal spray community for his numerous original contributions to the science and technology of thermal barrier coatings. Up until recently, he was member of the Editorial Committee of JTST.

"This is a huge honor for me and Volvo Aero," said Jan Wigren, who received the Thulin silver medal for his achievements in the field of thermal barrier film.

The Thulin medal, in gold or silver, has been given to usually two or three persons every year since 1944. This Swedish Society of Aeronautics and Astronautics award, approved by the Royal Swedish Academy of Engineering Sciences, is considered to be the most distinguished in aerospace technology in Sweden.

Contact: Jan Wigren, tel: 46 520 948 56; e-mail: jan.wigren@volvo.com.

Mark Smith Named Deputy Director of Manufacturing Science & Technology at Sandia

Mark F. Smith

Sandia National Laboratories, a U.S. Department of Energy national security laboratory, has appointed **Dr. Mark F. Smith,** FASM, as the new Deputy Director for its Advanced Manufacturing Science and Technology Center. Dr. Smith, who received his Ph.D. in metallurgy from Iowa State University, has led the thermal spray program at Sandia for nearly 25 years, moving from Distinguished Member of the Technical Staff to Department Manager of the Joining and Coating Department in 1999. Over the years, Sandia's Thermal Spray Research Laboratory (TSRL) has conducted fundamental and applied thermal spray R&D on virtually all of the major thermal spray processes, with a focus on advancing fundamental understanding and pushing the limits of spray technologies. Dr. Smith was among the first to apply modern noninvasive diagnostic and modeling tools to processes such as low-pressure or vacuum plasma spray and high-velocity oxyfuel (HVOF) in the 1980s and, more recently, has spearheaded U.S. efforts to advance the state-of-the-art for cold spray deposition, a process to rapidly deposit metals at or near room temperature.

Dr. Smith has also been very active in the professional thermal spray community, publishing and presenting extensively and serving as organizing committee member or conference chairman for numerous technical conferences. He was one of the co-founders of the original Thermal Spray Technical Division (TSD) of ASM in the mid-1980s, and he served as the founding Chairman of the Editorial Review Committee of the *Journal of Thermal Spray Technology*. During his term as TSD Chairman, Dr. Smith assisted Frank Hermanek in the formation of the Thermal Spray Hall of Fame and supported Dr. Ronald Smith (no relation) in forming the current Thermal Spray Society. Dr. Smith currently serves on the TSS Board.

In his new position, Dr. Smith will have expanded process R&D responsibilities that include a diverse range of technologies, such as thin-film deposition, laser engineered net shaping (LENS), advanced microelectronics packaging, low-temperature cofired ceramics (LTCC), and direct-write 3D electronics. He intends to remain active in the thermal spray community and looks forward to expanding his professional involvement in other selected areas.

Contact: Mark Smith, tel: 505/845-3256; fax: 505/844-6584; e-mail: mfsmith@sandia.gov.