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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.

Laboratory of Diagnostics and Imaging of Industrial Processes, National Engineering School of Saint-Etienne

The Laboratory of Diagnostics and Imaging of Industrial Processes (DIPI) at National Engineering School of Saint-Etienne was established in 2001. In 2003 it was labeled with prestigious title Host Team (EA 3719) by the French Research Ministry.

The staff currently consists of seven full time faculty, eight students of different levels, two engineers, and three technicians. The laboratory has about 700 m^2 of experimental facilities and about 150 m^2 of research and administrative offices. The main experimental equipment consists of different kinds of lasers for 3D cladding and direct manufacturing including TRUMPF DMD 505 and PHENIX PM-100 machines, industrial type spraying booth with cold spray and wire spray systems.

The major research objective of the DIPI is fabrication of graded/nanostructured coatings/tools using laser-assisted deposition and thermal spraying technologies. The main research directions are: (a) process engineering (high-temperature industrial processes employing concentrated energy sources—laser, plasma, flame; manufacture and treatment of high-temperature materials including protective coatings); (b) modeling of industrial process (high-temperature heat and mass transfer in thermal spraying, laser-assisted processes, etc.); (c) Diagnostics by pyrometry, spectroscopy, and CCD camera imaging (laboratory uses a unique set of optical diagnostic tools including 12 wavelengths and 2D pyrometers, several advanced CCD-camera-based image processing systems, etc.). On-site spray setup is available to perform development of innovative coatings (including the nanostructured coatings).

National Engineering School of Saint-Etienne (ENISE) has participated in a number of nationally and internationally funded programs and projects, namely Growth, Craft, Copernicus, Brite/Euram, and INTAS. For example, ENISE was a coordinator of recently completed (2001-2004) Growth project TRIBO "Nanostructured Coating for Engineering Tribological Applications."

Optical Diagnostics

A new diagnostic system was developed for real-time monitoring of in-flight particle diameters, velocities, and temperatures. The system is based on the nonintensified CCD image sensor with high sensitivity in near-infrared spectral region. An original software package developed in-house and used for calibration, treatment of powder jet gray image, and statistical analysis of particle parameters is the essential part of the system.

This diagnostic system was tested under actual industrial conditions of plasma spraying and laser cladding processes for three visualization modes: (a) jet visualization (real image of jet structure and its evolution applying different spatial and temporal scales); (b) particle/substrate interaction (particle sticking, particle splashing), visualization of near substrate zone for powder rebound monitoring; (c) Dynamics of coating growth including quantitative estimations of its thickness in real time. Experiments were performed for a wide range of industrial equipment and for various geometry of spraying parts (cylinder, plate, etc.). Typically, the systems studied are TBC (ZrO_2 and Al_2O_3) and wear-resistant coatings (WC-Co, Mo, CuSn, etc.).

Statistical processing of recorded data on particle size, velocity, and temperature (Fig. 1) was carried out to develop understanding of the influence of process variables (arc current, plasma forming gases flow rates, oxygen and fuel flow rates, powder flow rate, carrier gas flow rate, spraying distance, laser power, clad-

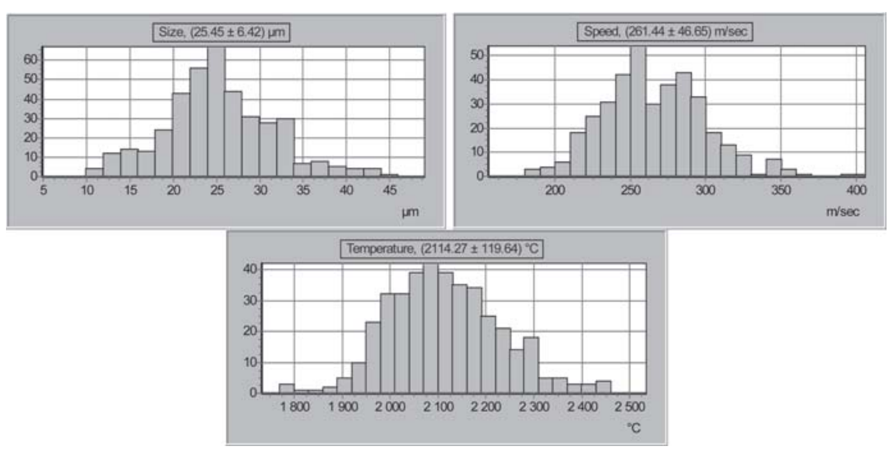


Fig. 1 Histograms of powder diameter, speed, and temperature for nominal spraying conditions. Spraying of Cr_2O_3 powders (grain size–53+5 µm) by Plasma Technik system.

ding velocity, etc.) on powder parameters.

The particle flux can be visualized in real time and therefore can be used for monitoring of its position, direction, density, and homogeneity. When observing the near-substrate region, the camera easily distinguishes the particles that adhered and that rebounded, allowing analysis of the powder loss and improvement of the deposition efficiency. This diagnostic system demonstrated high performance: 10 μm particle size detection limit, detectable temperature range 1200 to 3500 °C, and particle velocity range from 1 m/s up to 900 m/s. The results compared favorably with the results obtained with the DPV 2000 diagnostic system.

This CCD-camera-based diagnostic system can be also applied in industry for both spraying and cladding process optimization (correct spraying distance choice, powder injection optimization, maximum efficiency of powder usage, coating growth control, etc.) and for real-time monitoring of process stability.

Numerical Simulation

A project using simulation of plasma spraying is underway at DIPI. The simulation takes into account nonuniform temperature distributions inside particles in the plasma flow and their melting and evaporation. The spray process is analyzed based on numerical integration of model differential equations. The developed model is especially useful in case of nonuniformly heated and partially melted and evaporated particles. Such situations may arise when extending the range of materials or plasma flow parameters.

The dynamic equation for the particle is

$$\frac{d\vec{V}_p}{dt} = \frac{3}{4} \cdot C_D \cdot \frac{\rho_g(\vec{V}_g - \vec{V}_p) \cdot |\vec{V}_g - \vec{V}_p|}{\rho_p d_p} + \vec{g} \quad \text{(Eq 1)}$$

where $\vec{V}_p$ is the particle velocity, $\vec{g}$ is the gravity acceleration, $\vec{V}_g$ is the gas velocity, ρ_p is the particle mass density, d_p is the particle diameter, C_D is the drag coefficient. The convective thermal flux from the plasma to the particle is:

$$Q = \text{Nu} \cdot \lambda_g \cdot \frac{T_g - T_{ps}}{\pi d_p} \quad \text{(Eq 2)}$$

where Nu is the Nusselt number; λ_g is the gas thermal conductivity; T_{ps} is the particle surface temperature; $T_g\ (X,Y)$ is the ambient gas temperature. The function $T_g\ (X,Y)$ is considered to be known like $\vec{V}_g(X,Y)$ in Eq 1. The drag coefficient and the Nusselt number are known functions of the Reynolds and Prandtl numbers.

The temperature distribution and phase transformations in the particle are described by:

$$\frac{\rho_p\, \partial h(T_1)}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \lambda_1(T_1)\frac{\partial T_1}{\partial r}\right),\ r \in (0;\gamma) \quad \text{(Eq 3)}$$

$$\frac{\rho_p\, \partial h(T_2)}{\rho t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \lambda_2(T_2)\frac{\partial T_2}{\partial r}\right),\ r \in (\gamma;\xi) \quad \text{(Eq 4)}$$

$$T_1(\gamma,t) = T_2(\gamma,t) = T_m \quad \text{(Eq 5)}$$

$$\rho L_m \frac{d\gamma}{dt} = \lambda_1(T_m)\frac{\partial T_1}{\partial r}\bigg|_{r=\gamma+0} - \lambda_2(T_m)\frac{\partial T_2}{\partial r}\bigg|_{r=\gamma-0} \quad \text{(Eq 6)}$$

$$\rho L_v \frac{d\xi}{dt} = \lambda_2(T_2)\frac{\partial T_2}{\partial r} + Q(T_2),\ r = \xi \quad \text{(Eq 7)}$$

where t is the time; r is the radius; $T_1(r,t)$, $T_2(r,t)$ are the temperature distributions in the solid and liquid phases, respectively; L_m is the latent heat of melting; L_v is the latent heat of evaporation; T_s is the particle surface temperature; T_m is the melting point; $h(T)$ is the specific enthalpy of the particle material; $\lambda_1(T)$, $\lambda_2(T)$ are the known thermal conductivities for the solid and liquid phase, respectively. The problem is characterized by the two mobile bounds: evaporation interface $\xi(t)$ and solid/liquid interface $\gamma(t)$. These bounds divide the calculation domain into two parts [0;γ] and [γ, ξ], respectively. Expressions 3 and 4 are the heat conduction equations in solid and liquid phases written in spherical geometry (the particle is assumed to have a spherical shape). The temperature at the solid/liquid interface is always constant and equal to T_m (Eq 5). Equation 6 represents the Stefan boundary condition at the solid/liquid interface. Equation 7 is the boundary condition at the particle surface, which involves energy flux Q through the surface of the particle (Eq 2).

As an example of the obtained results, Fig. 2 shows calculated particle temperature in its center and at the surface.

A considerable expertise in combining characterization and modeling allows DIPI to address development challenges in the field of novel materials for composite, graded and nanostructured coatings deposition.

Contact: Dr Philippe Bertrand, ENISE DIPI lab., 74 Rue des Aciéiries 42000 Saint Etienne, France; Tel. +33 4 77 91 01 60; Fax +33 4 77 74 34 97; E-mail: bertrand@enise.fr.

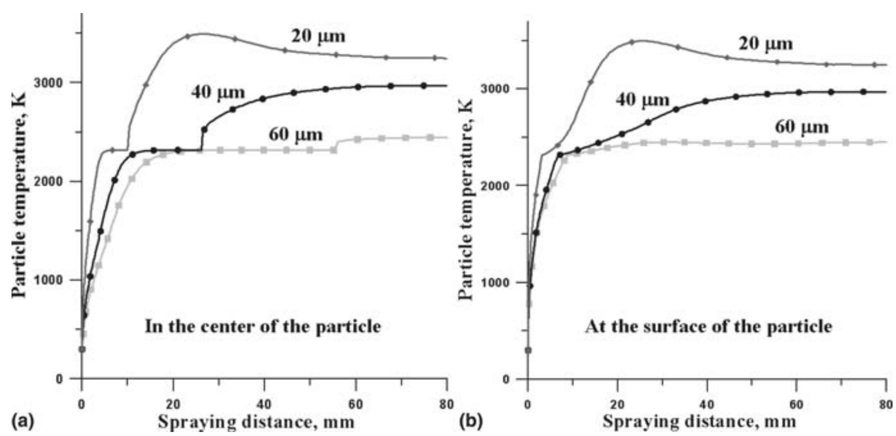
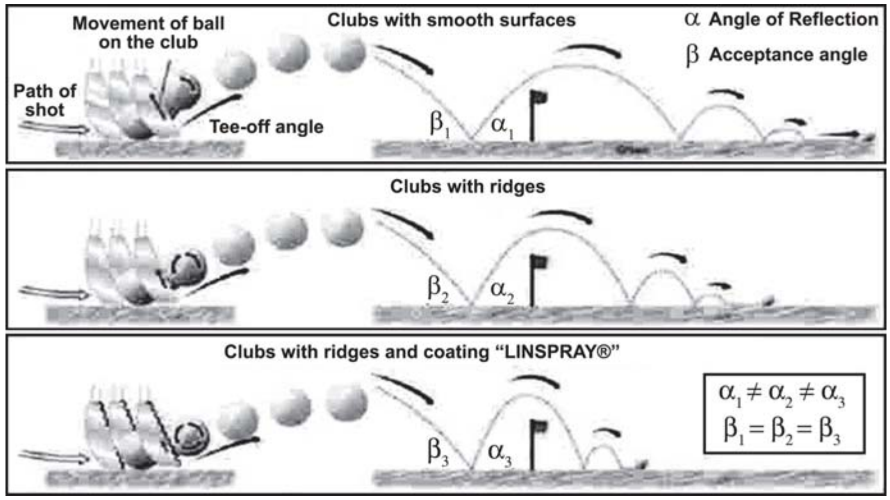


Fig. 2 Temperature evolution of Al_2O_3 particles with several diameter values in Ar plasma jet versus the distance from the powder feeder. Plateaus in the center (left) and salient points at the surface (right) correspond to melting.

Thermally Sprayed Golf Clubs Achieve Improved Backspin

SpinPro, a technologically advanced hard and wear-resistant coating applied to the clubface of short irons and wedges to improve backspin up to 2.5 times, delivers high spin rate through a unique texture, definitive surface roughness, and an optimized microstructure and modulus of elasticity. LinSpray technology was developed by Linde AG, Linde Gas Division, then put into practice at Linde's Application Technology Centre. The faces of different clubs were coated and the process optimized to obtain the best possible result by using a special spraying material and the required industrial gases as carriers of thermal and kinetic energy. Sulzer Metco is the exclusive licensee of SpinPro golf club coatings.



The effect of a SpinPro coated club

Contact: Peter Heinrich, Linde AG, Linde Gas Division, Carl-von-Lind-Strasse 256, 85716 Unterschleissheim, Germany; Tel: 0049 89 31001 564; E-mail: Peter.Heinrich@Linde-Gas.com; Web: www.spinpro.de.

News from NASA

Blanch-Resistant and Thermal Barrier NiAl Coating Systems for Advanced Copper Alloys

U.S. Patent 6,838,191. Sai V. Raj, John Glenn Research Center

Copper alloys containing chromium and niobium are being considered for use as combustor and nozzle liners in reusable launch vehicle applications. Unprotected copper alloys degrade during use in rocket engines in a process called blanching. Repeated exposure to the hydrogen/oxygen combustion mixture causes oxidation and reduction of the alloy, leading to failure or reduced useful life of the component.

This method forms an environmentally resistant thermal barrier coating on a copper alloy. In particular, the present invention addresses issues related to the design and deposition of suitable coatings and bond coating technology for protecting an advanced copper alloy known as GRCop-84. The steps include cleansing a surface of a copper alloy, depositing a bond coat on the cleansed surface of the copper alloy, depositing a nickel aluminide (NiAl) top coat on the bond coat, and consolidating the bond coat and the NiAl top coat to form the thermal barrier coating.

Excerpted from *NASA Tech Briefs,* July 2006.

Lower-Conductivity Ceramic Materials for Thermal Barrier Coatings

Doped pyrochlore oxides of a type described below are under consideration as alternative materials for high-temperature thermal barrier coatings (TBCs). In comparison with partially yttria-stabilized zirconia (YSZ), which is the state-of-the-art TBC material now in commercial use, these doped pyrochlore oxides exhibit lower thermal conductivities, which could be exploited to obtain the following advantages:

- For a given difference in temperature between an outer coating surface and the coating/substrate interface, the coating could be thinner. Reductions in coating thicknesses could translate to reductions in weight of hot-section components of turbine engines (e.g., combustor liners, blades, and vanes) to which TBCs are typically applied.
- For a given coating thickness, the difference in temperature between the outer coating surface and the coating/substrate interface could be greater. For turbine engines, this could translate to higher operating temperatures, with consequent increases in efficiency and reductions in polluting emissions.

Thermal barrier coatings are needed because the temperatures in some turbine engine hot sections exceed the maximum temperatures that the substrate materials (superalloys, Si-base ceramics, and others) can withstand. Yttria-stabilized zirconia TBCs are applied to engine components as thin layers by plasma spraying or electron beam physical vapor deposition. During operation at higher temperatures, YSZ layers undergo sintering, which increases their thermal conductivities and thereby renders them less effective as TBCs. Moreover, the sintered YSZ TBCs are less tolerant of stress and strain and, hence, are less durable.

The materials that are sought as alternatives to YSZ are required to have and retain lower thermal conductivities and to be better able to withstand temperatures that degrade TBCs made of YSZ. The undoped versions of the type now under consideration as alternatives to YSZ are of general composition $Ma_2Mb_2O_7$, where *Ma* denotes a 3+ cation (for example, La to LU), and *Mb* a 4+ cation (for example, Zr, Hf, Ti). Doping has been investigated as a means of reducing thermal conductivities even further below those of YSZ coatings. In the doping approach investigated thus far, another cation is substituted for part of *Ma*, yielding a general composition of $Ma_{2-x}M_xMb_2O_7$, where x lies between 0 and 0.5 and M denotes a rare earth or other suitable element.

In experiments, powders of various compositions were synthesized by a modified sol-gel method and calcined at appropriate temperatures to convert them into compounds of pyrochlore structure as confirmed by x-ray diffraction. These powders were hot pressed into dense disks of 1 in. (2.54 cm) diameter. The thermal conductivities of the disks were measured at various temperatures up to 1550 °C by use of a steady-state laser heat flux technique. Figure 1 presents results of such measurements performed on several materials of general composition $La_{2-x}(Gd \text{ and/or } Yb)_xZr_2O_7$, where $x = 0$ or 0.3. The thermal conductivities of all doped samples ($x = 0.3$) were less than those of the undoped ($x = 0$) sample [$La_2Zr_2O_7$]. The lowest conductivity—ranging from 40 to 50% below that of undoped sample—was exhibited by the sample codoped with both Gd and Yb.

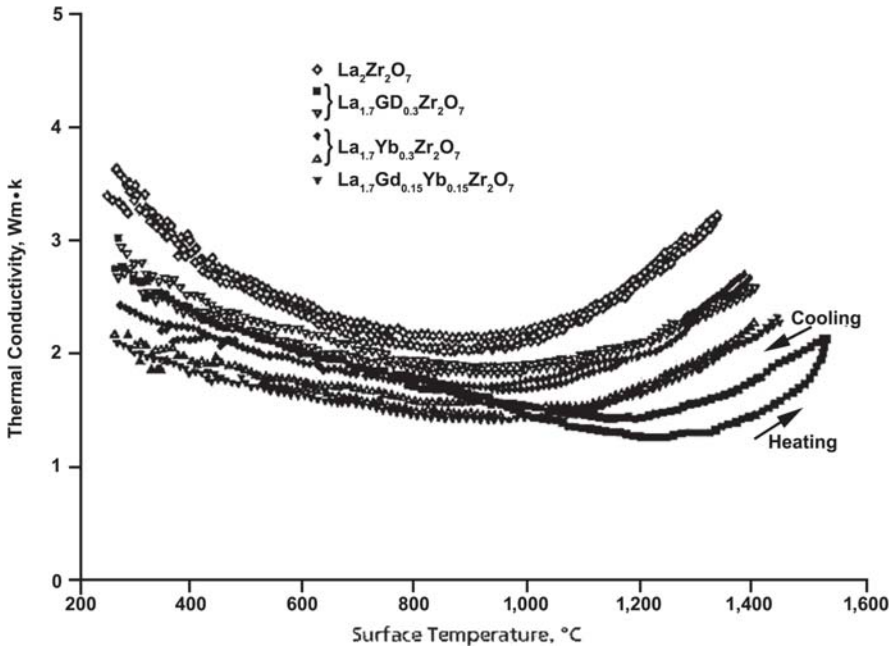


Fig. 1 Measured thermal conductivities of hot-pressed disks of several related pyrochlore oxide compositions illustrating the benefit afforded by doping

This work was done by Narottam P. Bansal of the John H. Glenn Research Center and Dongming Zhu of the U.S. Army Research Laboratory. 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, Innovative Partnerships Office, Attn. Steve Fedor, Mail Stop 4-8, 21000 Brookpark Rd., Cleveland, OH 44135. Refer to LEW-17469-1. Excerpted from *NASA Tech Briefs,* Sept 2006.

News from ITSC and TSS

United Nations of Thermal Spray

During the ITSC 2006 in Seattle, more than 20 top-level representatives from ten global thermal spray societies based in nine countries on four continents gathered for a general introductory meeting to give brief overviews of their respective organizations, get to know each other, and exchange ideas for cooperation. Many of the global industry societies engage in similar activities and also offer similar products and services to their membership and a commonly shared objective is to provide value to their members and to help the thermal spray industry grow beyond its current applications and customer base. Therefore, it was agreed upon that a certain level of cooperation between the global societies might be desirable. In fact, the concept of having an internationally representative group engaged in cross-border discussions related to the thermal spray industry and the opportunities that are presenting themselves triggered some further thought and discussions among some of the attendees. In order to facilitate communication, networking, cooperation, and coordination among the global societies and to foster industry growth it was suggested to create a general institution of global societies under the name "United Nations of Thermal Spray" (UNTS). There was a general consensus that a closer global cooperation would benefit individual societies and that a more formal approach could develop from the basic startup mode. The participants agreed to meet again during the ITSC 2007 in Beijing where further options and suggestions regarding this institution should be discussed. Societies who share the aforementioned objectives and views and who wish to engage in international cross-border communication and cooperation should contact Peter Hanneforth, ASM/TSS President Elect and Programming Chair, SpaCom, 223 Wall Street #160, Huntington, NY 11732, peterhanneforth@spacom.com.

TSS Board Election Results

In accordance with the Rules of Governance, the ASM Thermal Spray Society completed its 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 international thermal spray community. The Board is responsible to the members of the Thermal Spray Society and the ASM International Board of Trustees.

Peter Hanneforth

Peter Hanneforth, President, SpaCom LLC, Huntington, NY, becomes President for 2006-2008. He previously served on the Board as a member and most recently as Vice President.

Richard Knight

Dr. Richard Knight, FASM, Auxiliary Professor and CPPM Director, Drexel University, Philadelphia, Pennsylvania, remains on the Board for two years as Immediate Past President.

The following members were elected in 2006.

Mitchell R. Dorfman

Mitchell R. Dorfman, Director of Ceramics, Materials Development, Sulzer Metco (US) Inc., Westbury, NY, has been elected Vice President for two years and will automatically progress to President. Dorfman has served on the Board since 2004. He has more than 27 years of thermal spray material development experience and has been an active member in the thermal spray community for more than 18 years, serving as chairman of the ASM/TSS Information and Development Committee; participating in thermal spray related conferences as program organizer, session chair, and workshop instructor; and serving as reviewer of technical papers for *JTST*. He has authored more than 50 technical papers and holds 14 patents, and he received the Distinguished Alumni Award in 2003 from the Center of Thermal Spray Research at SUNY of Stony Brook. As ASM-TSS Society Vice President, Dorfman intends to promote thermal spray education, information dissemination, and membership through strong committees to create products and services for the membership, to improve the ASM-TSS website to strengthen global reach for new membership, and to continue to develop strong technical conference programs.

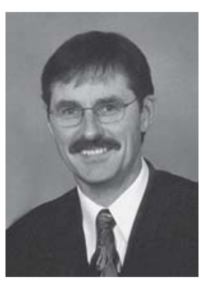
Raymond J. Sinatra

Raymond J. Sinatra, Senior Engineer, Rolls-Royce Corp., Indianapolis, IN. Sinatra has worked in the field of thermal spray coatings for 36 years and has been an active participant in the ASM TSS during the past ten years, serving on the TSS Board since 2003 and serving on the TSS Strategic Recognition Committee and Accepted Practices Committee on Metallography, as well as on the ASM Surface Engineering Congress Organizing Committee. Sinatra also has been reelected to a second term on the TSS Board from 2006-2009. He believes that the ASM Thermal Spray Society needs to be a strong resource for technical information required to support the ever-growing global business of coatings; that the information TSS develops and supplies to its members must be accurate, timely, and represent the latest advances in coating technology; and that training in all aspects of thermal spray will continue to be a strong member-driven need that TSS must address by developing the appropriate resources.

The following are newly elected Board members for 2006-2009:

Richard Bajan

Richard Bajan, Thermal Spray Coating Engineer, Turbine Component Services-Goodrich, Hodges, SC. Bajan has been an active member of the thermal spray community for the past 15 years, serving on the ASM Thermal Spray Division Committee on Testing and Characterization and the TSS Safety, Training, and Recommended Practices Committees, and he has participated in thermal spray related conferences both as a speaker and session chair. He also has authored articles for *Spraytime.* Bajan is looking forward to serving on the Board, particularly to encourage greater member participation on TSS committees, to work through ASM chapters to bring greater awareness about thermal spray technology, and to help organize technical programming at pertinent thermal spray related events.



Basil Marple

Dr. Basil Marple, Senior Research Officer, National Research Council of Canada, Boucherville, Quebec, Canada. Marple has been active in the field of materials research for 30 years, serving on a number of committees and serving in leadership roles in various professional societies. He has been active in the ASM TSS as member of the *JTST* International Board of Review, Panel of Judges, and Best Paper Award Committee; *JTST* guest editor, member of the TSS Nominating Committee, and he has participated in ITSC as a program organizer and proceedings coeditor. He also has served on the Board of Directors of the Canadian Ceramic Society. Marple views the ASM Thermal Spray Society as one of the prime motors to bring together stakeholders in the thermal spray community of researchers, powder and equipment developers and distributors, coating specialists, and end-users. He is interested in continuing to advance the field of thermal spray technology through sponsored events showcasing the latest breakthroughs and developments and by providing networking opportunities where the various players exchange ideas, discuss challenges, and work collectively to solve problems.

Christian Moreau

Dr. Christian Moreau, Group Leader Surface Technologies, National Research Council of Canada, Boucherville, Quebec, Canada. Moreau has been involved in ASM-TSS activities since 1999, contributing to *JTST* as an author and guest editor; serving as *JTST* Editor-in-Chief since 2004; participating in conference activities as a member of the ITSC Organizing Committee and ASM TSS Programming Committee, and symposium and session chair; and serving as member of *JTST* Editorial Committee, Information and Development Committee, and TSS Board Nominating Committee. He also has been active in a number of other technical societies. Moreau believes thermal spray will continue to evolve due to the close relationships among research scientists, application engineers, and practitioners at the national and international levels. He intends to promote these interactions, as well as the exchange of information and ideas among all members of the TS community to stimulate the growth of the industry.

Charles M. Kay

In addition, President Hanneforth has appointed **Charles M. Kay,** ASB Industries, Barberton, OH, as Secretary/Treasurer for 2006-2007. Kay has served on the Board since 2005 and will remain on the Board until 2008.