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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 and Capabilities in Plasma Sprayed Coating Preparation and Characterization

Introduction to Purdue University and Prof. Rodney Trice's Research

Purdue University, a land-grant institution in northern Indiana, was established in 1869. The College of Engineering, ranked sixth overall in the recent *U.S. News and World Report,* comprises 12 different schools. In 1959, the School of Metallurgical Engineering at Purdue University was formed as a separate identity from the School of Chemical Engineering. The name was changed in 1973 to the School of Materials Engineering to reflect the broader research interests and specialties of the faculty. The school has recently experienced growth in its number of faculty—from 12 in 2000 to 21 in 2006. The school will be moving to the Neil Armstrong Hall of Engineering in summer 2007 to accommodate this growth and the need for increased research space.

Rodney W. Trice joined the faculty in the School of Materials Engineering as an Assistant Professor in Aug 2000 after completing a two-year postdoctoral research fellowship at Northwestern University. His research there focused on investigating the processing-structure-property relationships of plasma sprayed coatings using mechanical testing and transmission electron microscopy. Prior to Northwestern, Prof. Trice received his Ph.D. from the University of Michigan (1998) where he studied the high-temperature properties of a novel ceramic composite. From 1989 through 1995, he worked in the defense industry, employed at Lockheed Martin and later Northrop Grumman. He received his Master's degree in 1989 (Materials Science) and his B.S. degree in 1987 (Mechanical Engineering) from the University of Texas at Arlington.

Prof. Trice's work in plasma spray at Purdue University is primarily supported by two National Science Foundation Grants. The first, funded by the division of materials research (DMR-0134286) is titled, "CAREER: High Temperature Deformation of Stand-Alone Plasma Sprayed 7 wt.% Y_2O_3-ZrO_2 Coatings." The second grant, funded by the design and manufacturing innovation division (DMI-0456534), is "Plasma and HVOF Spray of Colloidal Solutions to Produce Nano-Scale Features in Coatings." The capabilities and expertise developed through these two grants is explained here.

Suspension Spray: A New Way to Prepare Coatings with Nanocrystalline Features

The most significant limitation of the conventional spray process is that only large (i.e., >10 μm), nonagglomerating powders can be fed into the plume via gas flow. Suspension spray overcomes this physical limitation by placing the powders in a liquid media and using dispersants to keep adjacent powders from being attracted to one another (i.e., flocculation). By dispersing the powders prior to injection, they can easily be carried through a nozzle via a liquid medium. Upon evaporation of the solvent carrier in the plume, the powders remain in a non-agglomerated state. Prof. Trice's research group has been developing and maturing suspension spray since 2002.

The first step to prepare a coating via suspension spray is to prepare the suspension. The suspension consists of nano-sized powder mixed in a bottle with a dispersant, milling media, and ethanol. The dispersant is added so that the small particles, which would normally be attracted by Van der Waals forces to form agglomerates, will repel each other and thus stay suspended in the solvent. Next, the bottle is turned on a ball mill in order for the tumbling action of the milling media to disperse the powder and break apart any agglomerated clusters. The milling media are removed after this step. Finally, the suspension is poured into a pressurized vessel. The pressurizing gas is most often nitrogen. Using a regulator and solid stream nozzle, the suspension is injected into the hot plume at pressures ranging from 20 to 100 psi. Figure 1 shows the interaction of the suspension stream and plume. During its short time in the plume, the solvent used to disperse the powder is quickly vaporized; the powder is then melted, and the liquid droplets are propelled against the substrate to form the coating.

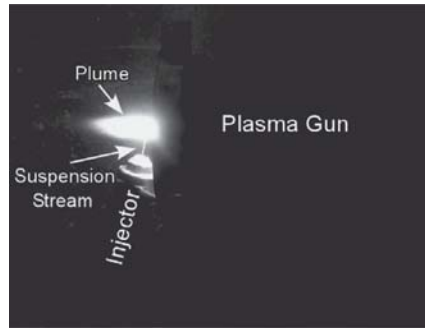

Fig. 1 Ceramic-loaded suspension stream and its interaction with the plasma plume. The processing-structure-property relationships of suspension spray are being investigated in Prof. Trice's research group.

To date, Prof. Trice's group has successfully used this technique to produce coatings of 4.5 mol% yttria-stabilized zirconia (YSZ) that contain nanocrystalline grains (*J. Mater. Sci.,* 2004, **39,** p 4171-4178). In particular, 75 nm YSZ powder was dispersed in ethanol using 1 wt.% dispersant. Approximately 25% by weight of powder was added to the solvent; this colloidal suspension was then plasma sprayed at Ames National Laboratory in collaboration with Dan Sordelet, Ph.D. An atomic force microscopy image of the resulting microstructure in cross section is shown in Fig. 2. The lamellae from suspension spray are on the order of 30 to 50 nm thick. The individual colum-

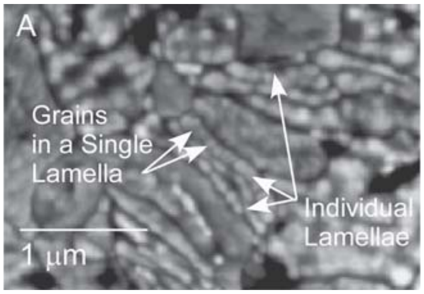

Fig. 2 Cross-sectional AFM image of a coating made using suspension spray. The starting powder size was 75 nm diameter 7wt.% Y_2O_3-ZrO_2 powders. Note the 30 to 50 nm thick lamella and smaller grains that comprise each lamella. Adapted from *J. Mater. Sci.,* 2004, **39,** p 4171-4178

nar grains that make up each lamella from suspension spray are difficult to resolve, but are on the order of ~20 to 40 nm. Ongoing work is determining the processing-structure-property relationships as a function of key variables such as solids loading in the suspension, starting powder size, spray distance, and power.

Sintering and Thermomechanical Characterization: Determining How Temperature and Stress Affect Plasma Sprayed Coating Properties

Sintering Characterization: As has been well established in the literature, thermally sprayed coatings contain various microstructural features that contribute to its unique mechanical and thermal behavior. These features include microcracks that originate from thermal stress and porosity that is due to gases trapped in the melted droplets during solidification. Because many applications require the coating to be immersed in a high-temperature environment, as in the case of thermal barrier coatings, substantial changes to the as-sprayed microstructure can occur via sintering. Because coating properties can vary substantially as a result of exposure to heat, Prof. Trice's research group has developed a powerful technique that can be used to progressively observe changes in the microstructure.

Using atomic force microscopy, Prof. Trice's research group has developed an experimental protocol for returning to the exact same coating area after subsequent heat treatments. Thus, this affords direct observation of changes in coating microstructure after various heat treatments, as demonstrated in a recent publication on plasma sprayed YSZ (*J. Am. Ceram. Soc.,* 2006, **89**(5), p 1673-1678). Figure 3 shows the progressive changes in micro-

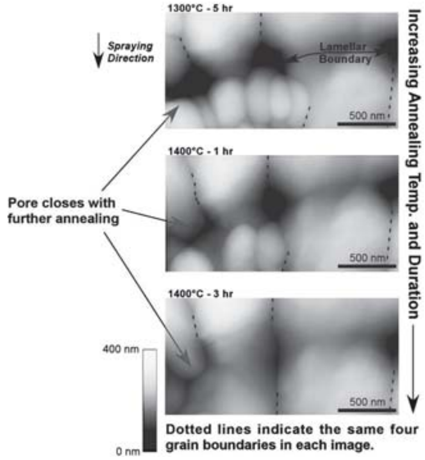

Fig. 3 Cross-sectional AFM images showing the effect of heat treatments on the same region of microstructure between two lamellae. Note that by returning to the same area, the progression of pore closure and other microstructure features can be investigated. Adapted from *J. Am. Ceram. Soc.,* 2006, **89**(5), p 1673-1678

structure of the same area after annealing at temperatures ranging from 1200 to 1400 °C. By returning to the exact same area, the mechanisms of pore closure can be discerned.

Thermomechanical Characterization: There are many applications in which the mechanical performance of thermally sprayed coating determines the success of the underlying structure. For example, YSZ topcoats used in thermal barrier coating applications are under in-plane compressive stresses during engine start-up due to differential heating effects. As a result, the YSZ will compressively deform (or shrink) via several temperature-, stress-, and time-dependent mechanisms. Upon engine cool-down, the densified YSZ coating is under tension, generating through-thickness cracks in the YSZ that can extend to the YSZ/bondcoat interface and deeper. The effect of this network of cracks is to diminish the mechanical integrity of the YSZ and provide an easy path for corrosive species deep within the TBC system. Because the amount of compressive deformation determines the tensile stress that develops in the coating on cooling, it is key to quantify and mechanistically understand the high-temperature deformation mechanisms in plasma sprayed YSZ under compressive stress. Because of these concerns, Prof. Trice's research group has developed some unique capabilities to measure the mechanical response of plasma sprayed coatings in a stand-alone (i.e., no substrate) cylindrical configuration.

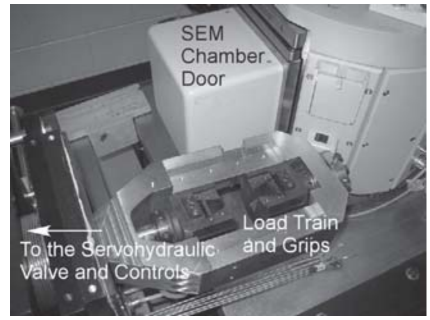

Fig. 4 Servohydraulic load frame that can be inserted into a specially equipped SEM for in situ experiments. The interaction of the unique plasma sprayed microstructure with the applied load can be viewed directly using this equipment.

One such capability is a specially equipped scanning electron microscope (Electo Scan 2020) with an Instron 8500 Plus load frame that can be inserted into the viewing chamber. This is shown in Fig. 4. Thus, load can be applied while simultaneously viewing the material response at high magnifications. Data (stress, strain, time) is recorded using a specially configured Lab View program. Figure 5 shows results from a recent study (*J. Am. Ceram. Soc.,* 2004, **87**(5), p 960-962) where a new crack nucleates (see arrow) and grows from an existing crack as stress is increased from 33 to 129 MPa. Using this capability, the mechanisms associated with deformation of plasma sprayed coatings are being observed in situ.

Prof. Trice's research group also has developed the capabilities to measure the creep and stress relaxation properties of stand-alone plasma sprayed coatings at temperatures ranging from 800 through 1400 °C. High-temperature compression testing has been performed using a MTS 810 servohydraulic load frame equipped with SiC pushrods and an Applied Test Systems high-temperature furnace. Strain is measured with a MTS high-temperature extensometer with a resolution of ±1 μm. The design of the extensometer is such that an alumina pushrod extends vertically through the center of the lower SiC pushrod, through a small hole in the lower SiC compression platen, through the hollow stand-alone YSZ sample, and to the surface of the upper SiC pushrod.

As an example of the type of thermomechanical data that can be collected, a representative experimental stress-relaxation response for as-sprayed YSZ coatings tested at 1000 and 1100 °C are

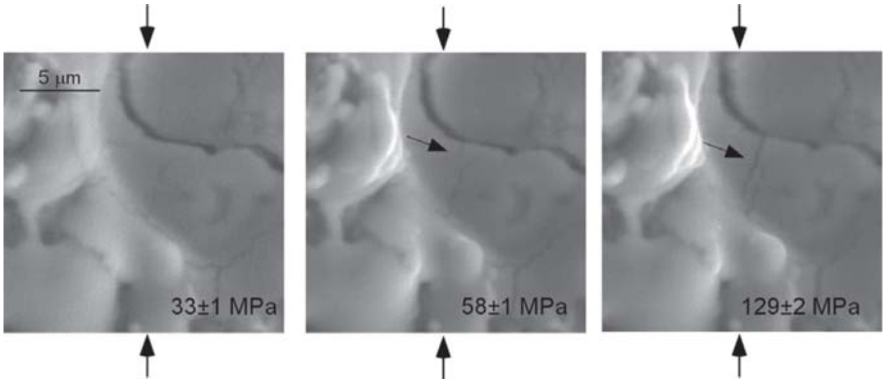

Fig. 5 Example of the experimental results obtained using the equipment pictured in Fig. 4. Note that as the external stress applied to the stand-alone YSZ coating was increased that a new crack nucleated and grew in a stable fashion. Adapted from *J. Am. Ceram. Soc.,* 2004, **87**(5)

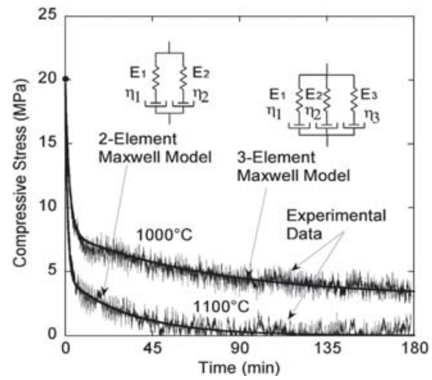

Fig. 6 An example of the type of thermomechanical data that can be measured at Purdue. The figure shows stress-relaxation data collected for two stand-alone YSZ cylinders tested at 1000 and 1100 °C. Modeling of the data can also be performed using a parallel arrangement of springs and dashpots; the modeled data are represented by the solid lines in the figure. Adapted from *J. Am. Ceram. Soc.,* 2005, **88**(8), p 2202-2208

presented in Fig. 6. The stand-alone coatings were relaxed from 20 MPa. Complete relaxation of the initial stress at 1100 °C was observed (i.e., the stress in the coating relaxed to within the measurement error of 1 MPa), while the YSZ coating tested at 1000 °C did not relax fully within 180 min test. As noted in Fig. 6, the experimental data from each coating tested at elevated temperatures exhibited at least two stress-relaxation regimes. At early times (~0 to 10 min), a fast stress-relaxation regime was observed, followed by a slower relaxation regime at later times. Using simple models of springs and dashpots in series and parallel, such as those shown schematically in Fig. 6, the behavior of plasma sprayed YSZ has been modeled by Prof. Trice's research group.

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Industrial News

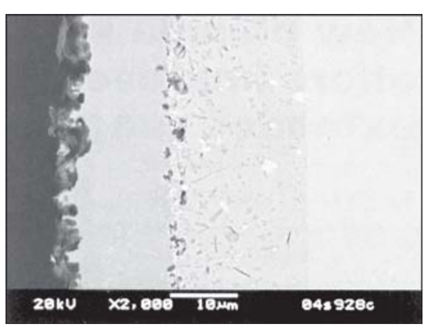
Sprayable Ceramic-Base Coating Protects Steel and Superalloys

A sprayable ceramic-based coating for steel and superalloys that prevents corrosion, oxidation, carburization, and sulfidation in gas, liquid, steam, and other hostile environments has been developed by researchers at Pacific Northwest National Laboratory (PNNL), Richland, WA.

The new coating bonds with the metal substrate and is "resilient, inexpensive, and simple." Because the coating is processed at temperatures significantly lower than typically required for conventional ceramic coatings, the new technology also can save energy and reduce harmful emissions.

The coating is produced on a steel part by mixing a liquid preceramic polymer with aluminum metal-flake powders to form a slurry that can be applied by dipping, painting, or air spraying. The coating is cured in a commercial ruthenium-base catalyst that dries the slurry to a green state and enables polymer cross linking.

The coated steel is then heated in air, nitrogen, or argon at 700 to 900 °C. The heat converts the coating into an aluminum diffusion/reaction layer that permeates the surface of the steel and forms an iron aluminide surface. According to PNNL Commercialization Manager Eric Lund, the diffusion reaction makes the coating so durable that it cannot be chipped or scratched off.



Electron micrograph of coated 316 stainless steel coupon in cross section showing the diffusion-reaction layers. From left (the surface of the steel), the following layers are visible: (1) aluminum oxide layer (not visible at lower magnifications), (2) FeAl layer, (3), Fe_3Al inner layer, and (4) 316SS

The reaction layer is much stronger than an external coating because it is an integral part of the steel. This layer develops even further during service as the coating is heated at very high temperatures, such as those during the heating of pipes in a process facility.

Unlike similar products, the liquid form of the coating can be applied with a spray gun. This feature makes the PNNL coating practical for protecting large areas.

Contact: Eric Lund, Pacific Northwest National Laboratory, Richland, WA 99352; tel: 509/375-3764; eric.lund@pnl.gov; Web: www.pnl.gov.

New Boron Nitride Spray Coating Eliminates Methylene Chloride

The Ceramics division from GE Advanced Materials has introduced a new grade of boron nitride (BN) spray coating that eliminates the use of methylene chloride. GE's Boron Nitride (BN) Spray II may be used as a release agent and lubricant in a wide range of applications, including metalforming, glassmaking, plastics molding, high-temperature sintering, and welding and brazing.

GE's Boron Nitride II spray coating offers several benefits:

- High-temperature resistance for demanding applications
- High-purity crystalline structure for improved lubrication
- Nonreactive formulation for excellent release qualities and chemical stability
- Easy application using a convenient aerosol package

Contact: Monica Ettamarna, GE Advanced Materials, Quartz & Ceramics, Strongsville, OH 44149; tel: 440/878-5740; monica.ettamarna@ge.com.

Awards Information

Best Papers for *JTST* Volumes 13 and 14

Journal of Thermal Spray Technology presented the best papers for Volumes 13 and 14 during the International Thermal Spray Conference 2006. The papers were selected by a committee of 14 judges. The awards were presented during the Thermal Spray Society open meeting by the president of the Thermal Spray Society, Richard Knight, FASM. During the same meeting, Kendall Hollis explained to the members the details on the selection process, criteria, and the voting process of this committee.

Jan Ilavsky accepts best paper award for *JTST* Vol 14.

The best paper selected for the *JTST* Volume 13 (2004) was "Neural Computation to Predict In-Flight Particle Characteristic Dependences From Processing Parameters in the APS Processes" authored by Sofiane Guessasma, Ghislain Montavon, and Christian Coddet from Université de Technologie de Belfort-Montbéliard (UTBM).

Kendall Hollis explains to TSS members how the best papers were selected.

For the *JTST* Volume 14 (2005), the best paper is titled "Advanced Microstructural Characterization of Plasma-Sprayed Zirconia Coatings Over Extended Length Scales" authored by Anand A. Kulkarni, Allen Goland, and Herbert Herman (SUNY Stony Brook), Andrew J. Allen (National Institute of Standards and Technology), Jan Ilavsky, Gabrielle G. Long, and Francesco DeCarlo (Argonne National Laboratory).

News from Down-Under

The Thermal Spray scene in Australia is the best kept secret of the national industry! Thermal spray is used throughout many mining and minerals primary industries as well as in the agricultural and animal husbandry sectors, yet it is rarely recognized, per se, as the technology that makes the whole system work efficiently and with productivity. The positive spin on this observation is that there are a host of potential applications that are assured of being successfully implemented if plant engineers and managers find the time to speak to sales engineers. The primary applications are for hard, wear-resistant coatings, as well as materials for anticorrosion applications.

The research agenda in Australia is set by the Australian Research Council, the ARC. All funded research must fit under what are termed as National Research Priorities. Coatings research, since it does not fall under any specific research priority is somewhat diffuse. Regardless, there are known research programs at the Commonwealth Science and Industrial Research Organization (CSIRO), as well as several universities. These research efforts are very much oriented toward solving practical problems that are being experienced by industries. The Australian military are known to be using TS coatings, for example as TBCs, but this work is kept very much under wraps. In summary, there is a great deal of opportunity for TS vendors from both the equipment and feedstock side of business, with emphasis placed on broadening the applications base of TS coatings used in Australia.

Australia is also a gateway to Oceania and Asia; for instance, interest has been generated within the chemical and petroleum industries. Several ventures are underway in the area of education; however, the need is at the technical level of an operator rather than concerning research and understanding. Thus, several companies and organizations in this part of the world have put out requests and tenders for quite basic training courses that might be oriented toward specific equipment, materials, and applications.

The future for "TS Down-Under" is tremendous. The economy has been booming for the last decade and there is no reason to believe that this will abate—in fact, the evidence is the opposite with multibillion dollar ventures hitting the open press quite regularly. There is a strong need for local organization of national and regional activities. For this reason, please contact Chris Berndt if you have an interest in participating in such an organization.

Contact: Christopher C. Berndt, professor of Surface and Interface Engineering, James Cook University, School of Engineering, Townsville, Queensland 4811, Australia; tel: 011 (617) 4781 6489; e-mail: Chirstopher.Berndt@jcu.edu.au.

ASM-TSS Recognizes the 2006 Hall of Fame Inductees

The ASM-TSS Thermal Spray Hall of Fame (HoF) was established in 1993 to recognize and honor outstanding leaders who have made significant achievements and contributions to the science, technology, practice, education, management, and advancement of thermal spraying. The 2006 HoF inductees are:

- Prof. Atsushi Hasui
- Dr. Mark F. Smith, FASM
- Donald M. Yenni

Professor Hasui has contributed immensely to the development of thermal spray technology through his pioneering and innovative research, his books and his leadership in the Japanese Thermal Spray Society, and in establishing industry standards. Professor Hasui was unable to attend the ITSC 2006 event, and his HoF award was accepted on his behalf by Professor Sachio Oki, VP of the Japanese Thermal Spray Society.

Dr. Mark Smith, FASM, from Sandia National Labs, Albuquerque, NM, was recognized "for significant and sustained technical contributions to advance the science and technology of thermal spray, especially process diagnostics and modeling, and for more than 20 years of service in professional society leadership as an active proponent of thermal spray."

The third HoF inductee of 2006 was Mr. Donald M. Yenni, formerly of Union Carbide (now Praxair) who was recognized for the invention of wire and powder fed plasma spray torches and deposition processes and the development of many ancillary thermal spray machines and thermal spray applications. Mr. Yenni was unable to attend the ITSC 2006 event, and his HoF award was accepted by Dr. Robert C. Tucker, Past President of the ASM Thermal Spray Society.

The 2006 inductees were officially recognized during the ITSC Plenary Session on Tuesday, May 16th, in Seattle, WA.

Suggestions for future HoF candidates are always welcome and should be forwarded to Daryl Crawmer at DCrawmer@tstcoatings.com and Joachim Heberlein at jvrh@me.umn.edu.

S. Oki accepts Hall of Fame award for A. Hasui

M. Smith

M. Smith receives his Hall of Fame award

R. Tucker

R. Tucker accepts Hall of Fame award for D. Yenni