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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.

Thermal Spray Research at Boston University

M. Gevelber; E-mail: gevelber@bu.edu; D. Wroblewski and S.N. Basu

The goal of the Plasma Spray Research Group at the College of Engineering at Boston University (BU) is to develop improved plasma spray processing capabilities to engineer the next generation of advanced coating systems, as well as to improve manufacturing capabilities in terms of yield and process optimization. This will not only improve the performance of existing plasma deposition applications (such as coatings for engines and turbines), but also facilitate newer applications such as solid oxide fuel cells.

The plasma spray process features complex plasma/particle and particle/substrate interactions, which involve significant distributions and variations. The research is focused on understanding the sources of these distributions and their effect on coating quality and using this knowledge base to mitigate these effects through development of an intelligent control system. This requires a deeper understanding of the fundamental processing/structure relationships, which are studied using a combined experimental and modeling approach. A major focus of the research is on the development of new sensing capabilities to more effectively study the fundamental processing/structure relationships and to enable feedback control schemes that exploit those relationships.

An interdisciplinary team addressing these issues includes Prof. Michael Gevelber, with expertise in process control; Prof. Soumendra Basu, with expertise in materials; and Prof. Donald Wroblewski, with expertise in thermal-fluid interactions. The group has also developed relationships with industry experts to ensure industrial relevance to the ongoing research and that the ''theory'' developed is practicable on the shop floor. The Plasma Spray Group continues to seek collaborative efforts with industrial and academic partners.

Need for Improved Control

Variations in the particle state that occur run-to-run and during a long deposition run limit process capabilities, in particular, since plasma spray is currently operated in an open loop with empirically developed actuator set points. Research at BU is focused on developing closed-loop control capability for plasma spray since it offers the ability to compensate for the inherent process variations as well to more directly maintain the required conditions to achieve a desired coating structure.

Benchmark experiments have been conducted in collaboration with several industrial coating companies to better understand the need for control. Figure 1 shows the variation in coating thickness (±10%) and density (±15%) for flat substrates sprayed over 400 h of torch operation in a production cell. The lack of correlation between thickness and density suggests that different control strategies need to be developed to reduce variations for both objectives. Other experiments reveal that variations for curved surfaces are even more sensitive to variations in the spray state.

The benefits of developing better closed-loop control for plasma spray include: (a) variation reduction, minimizing impact of perturbations and drift on coating thickness and coating structure; (b) explicit control of deposition rate, which more directly provides a basis for optimizing the process relative to deposition rate and efficiency; (c) tighter control of resulting coating structure since control strategy is based on measurement of physical quantities more closely related to coating structure (e.g., particle state instead of torch current/voltage); and (d) automatic compensation for the slow variations (torch aging) and fast jumps (bifurcations) observed in the plasma spray deposition process.

To develop an effective control system, it is critical to determine what particles states are most related to the critical process objectives, what sensing schemes are required to measure those states, and how to best adjust torch inputs to control those states to meet the objectives.

Sensor Requirements for Control

Research at BU is focused on looking beyond averages of individual particle temperatures and velocities or those based on ensemble averaging by the measurement of radiation intensity from the whole plume, by introducing the importance of distributions into the control strategy. More specifically, the research involves the analysis of critical subdistributions, such as the distribution of molten particles that are actually incorporated into the coating, to best map the coating features to the deposition conditions (Ref 1). The result of this effort has been a new plume flux sensor, the output of which shows good correlation with deposited coating

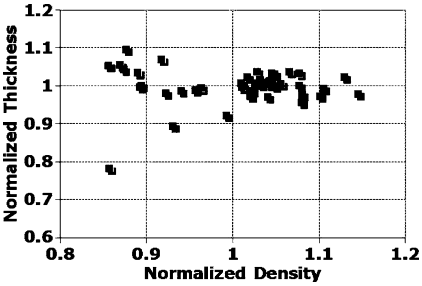

Fig. 1 Variations in coating thickness and density for flat substrates sprayed over 400 hours in a production cell (YSZ)

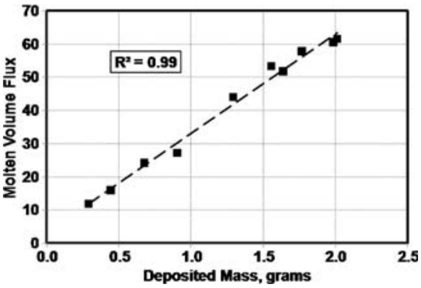

Fig. 2 Good correlation between the molten volume flux rate and deposited coating weight for new plume flux sensor (PFS), developed at BU

weight (Fig. 2). Evaluation of the benefits of this sensor and the development of advanced capabilities to control other coating qualities such as coating microstructure are major thrusts of sensor-related research efforts at BU.

One challenge of measuring particle flux is the accurate measurement of particle diameter, which is typically obtained from temperature and intensity information. However, proper calibration of measurements is complicated by the fact that within the wavelength range typically used for two-color temperature measurements, the optical thickness is of the same order as the particle diameters for ceramics, coatings such as yttria-stabilized zirconia (YSZ). The result is that radiation from smaller particles (<10 μm) tends to be proportional to volume; for larger particles (>100 μm), it is proportional to surface area; and for particles in the critical range in between, it is a combination of the two. A current research focus is to better understand this relationship for incorporation into sensing schemes.

Development of Closed-Loop Strategies for Coating Thickness Control

Research efforts at BU have focused on evaluating the performance of different monitoring and control strategies relative to the objective of maintaining better coating thickness control. One strategy that has been developed and evaluated is to directly measure and control both the molten flux as well as the centroid position of the spray pattern (Ref 2). Figure 3 summarizes the experimental performance of this control strategy compared with open-loop test for deposition of YSZ sprayed with a SG 100 torch. Using the closed-loop control strategy reduced the variation measured by standard deviation relative to no control by a factor of 3.

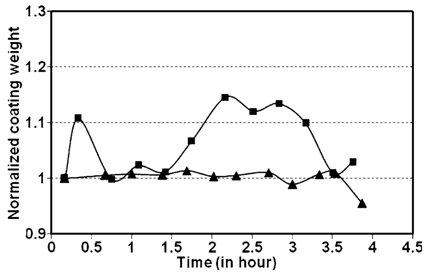

Fig. 3 Coating weight (normalized to initial weight) variation for deposition rate control (triangles) compared to open loop runs (squares)

The current control research is focused on evaluating alternative control strategies, developing appropriate strategies to respond to torch arc fluctuations, as well as strategies that more specifically control those degrees of freedom that determine coating structure (e.g., porosity, and crack density and orientation).

Particle/Substrate Interactions

One key feature of plasma sprayed microstructures is microcracks. In order to be able to either engineer them in thermal barrier coatings (TBCs), or eliminate them in electrolytes for fuel cells, it is critical to fundamentally understand microcrack formation This requires a much deeper knowledge of how cracks are initiated under real topologies.

Thus, a major research focus is the study of the particle/substrate interactions to identify critical factors that affect the stresses during splat solidification that lead to microcrack formation. Using the controlled plasma torch, the density and orientation of microcracks has been mapped as a function of particle states (Ref 3). The geometries of real surfaces have been critically examined, and surface roughness features at different length scales that affect crack formation have been identified (Ref 4) (Fig. 4). Algorithms have been developed to identify stress concentration sites based on the magnitude and sign of the second derivative of the surface profile. The goal is to incorporate such experimentally observed complexities, including roughness features at different length scales and distributions in the molten particles, into particle/surface interaction models to determine how ''real'' plasma sprayed microstructures evolve and to determine to what extent they can be controlled to engineer crack and pore structures.

A non-dimensional parametric analysis has been developed to better understand the important length scales for various stages of the development of the coating microstructure. A common observed phenomenon in plasma sprayed microstructures is the continuation of grains across splat boundaries, suggesting that remelting and growth of the grains in the new splat often occurs using the grains in the splat below as a template. Figure 5 shows the characterization of the basic physics of the remelting process using a single non-dimensional temperature, *U*, which is a combination of splat temperature, substrate temperature, and the melting temperature of ZrO_2 (Ref 5). The significantly different levels of remelt for the different length scales highlights the importance of multiple length scales.

Plasma Spray Facilities

The Plasma Spray Facility in the Advanced Materials Process Control Laboratory at BU is a fully automated, research-oriented resource designed to parallel the capabilities of a modern industrial plasma spray shop. The facility uses two plasma torches: the Praxair SG-100 (Fig. 6) and Sulzer-Metco 9MB. Either torch can be mounted on the computer controlled two-axis gantry robot capable of achieving velocities up to 500 mm/s in each axis. Torch power levels and gas flow rates are computer controlled. A sensor motion control system can automatically track torch plume centroid.

A diagnostics and control system, shown schematically in Fig. 7, is used for real-time measurement of particle states, including volumetric average particle temperature, plume trajectory and width, and individual particle temperature, velocity, and diameter. The sensors include an inflight pyrometer and torch diagnostic system (IPP/TDS) and an individual particle monitor (IPM) for particle state diagnostics and control. A CCD camera has been developed to obtain real-time intensity distribution of the particles, which is used to determine the spray pattern centroid, and spatial distribution. The spray pattern centroid (i.e., location of the particle flux concentration) is

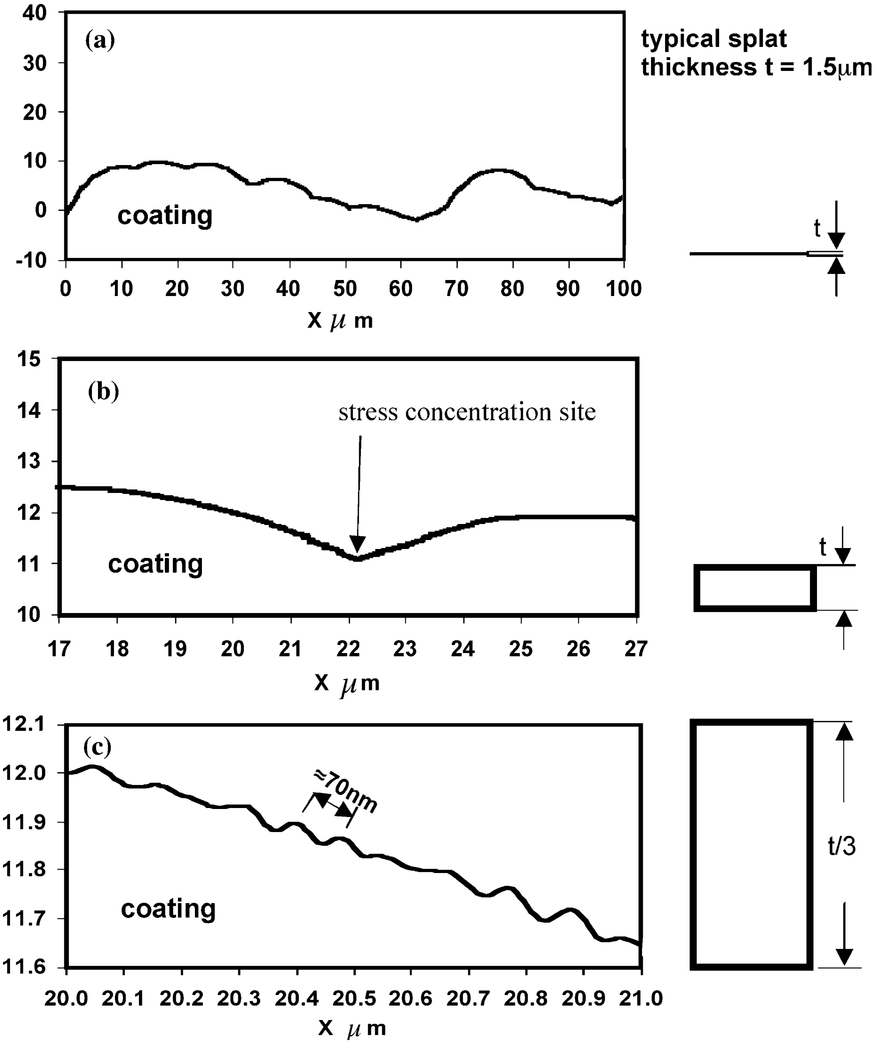

Fig. 4 Surface roughness profiles at different length scales of (a) 100 μm, (b) few microns, and (c) 100 nm wavelengths. The relative thickness of a typical splat (~1.5 μm) is shown adjacent to each surface roughness length scale. Source: S.N. Basu, G. Ye, M. Gevelber, and D. Wroblewski, *Int. J. Refract. Met. Hard Mater.*, 2005, **23**, p 335-343

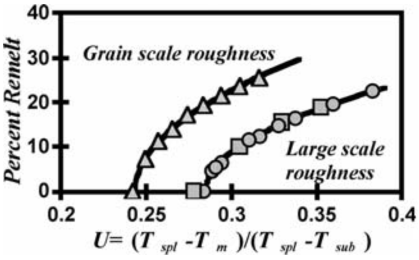

Fig. 5 Plots of percent remelt as a function of the non-dimensional temperature parameter, *U*, showing the effect of different surface roughness length scales. Source: D. Wroblewski, R. Khare, and M. Gevelber, *J. Thermal Spray Technol.*, 2002, **11**(2), p 266

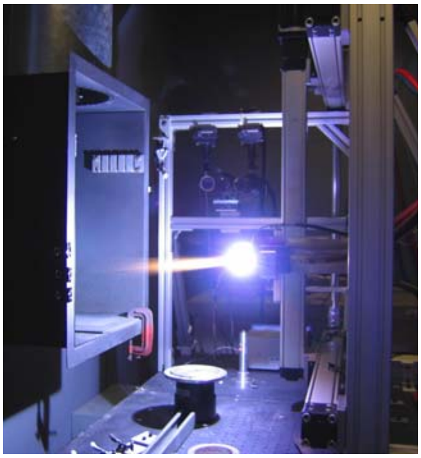

Fig. 6 Plasma spray booth at Boston University

particularly important since the centroid rarely coincides with the gun centerline. In addition, an IR sensor system provides thermal imaging of the substrate for temperature control. The high-frequency characteristics of the torch voltage and the acoustic emission from the torch are monitored simultaneously to characterize torch life and its effect on particle states.

Acknowledgments

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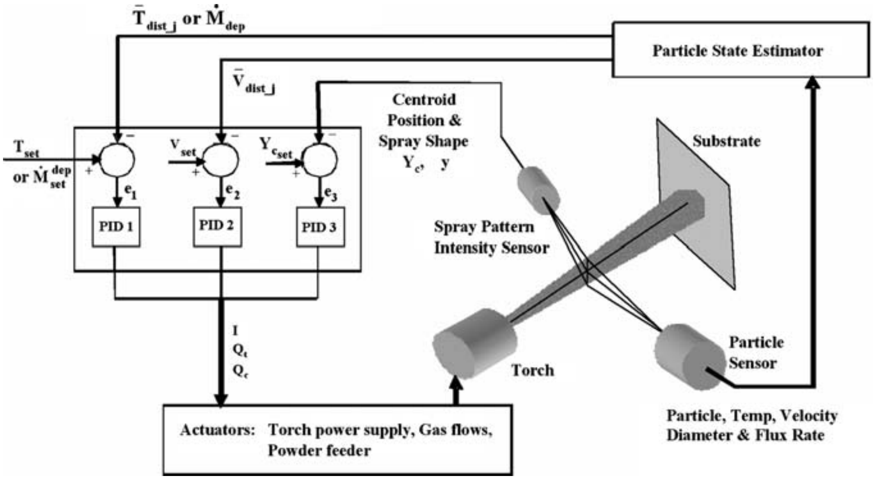

Fig. 7 Schematic of closed-loop control system for plasma spray

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High-Speed Thermal Imaging of Plasma Sprayed Particle Impinging on Substrate

The National Institute for Materials Science (NIMS), Japan, recently succeeded in capturing the evolution of an yttria-stabilized zirconia droplet impinging on a substrate in plasma spraying in collaborative research with Kinki University. (See the related article, K. Shinoda, H. Murakami, S. Kuroda, S. Oki, K. Takehara, and T. Goji Etoh, High-Speed Thermal Imaging of Yttria-Stabilized Zirconia Droplet Impinging on Substrate in Plasma Spraying, *Appl. Phys. Lett.*, 2007, **90**, Art. No. 194103). NIMS developed an in situ monitoring system to capture the droplet impacting phenomena under atmospheric dc plasma spraying conditions. This system utilized a high-speed video camera of 1 million fps (a prototype of HSV-1, Shimadzu Corp., Japan) coupled with a long-distance microscope (QM100, Questar Corp., USA).

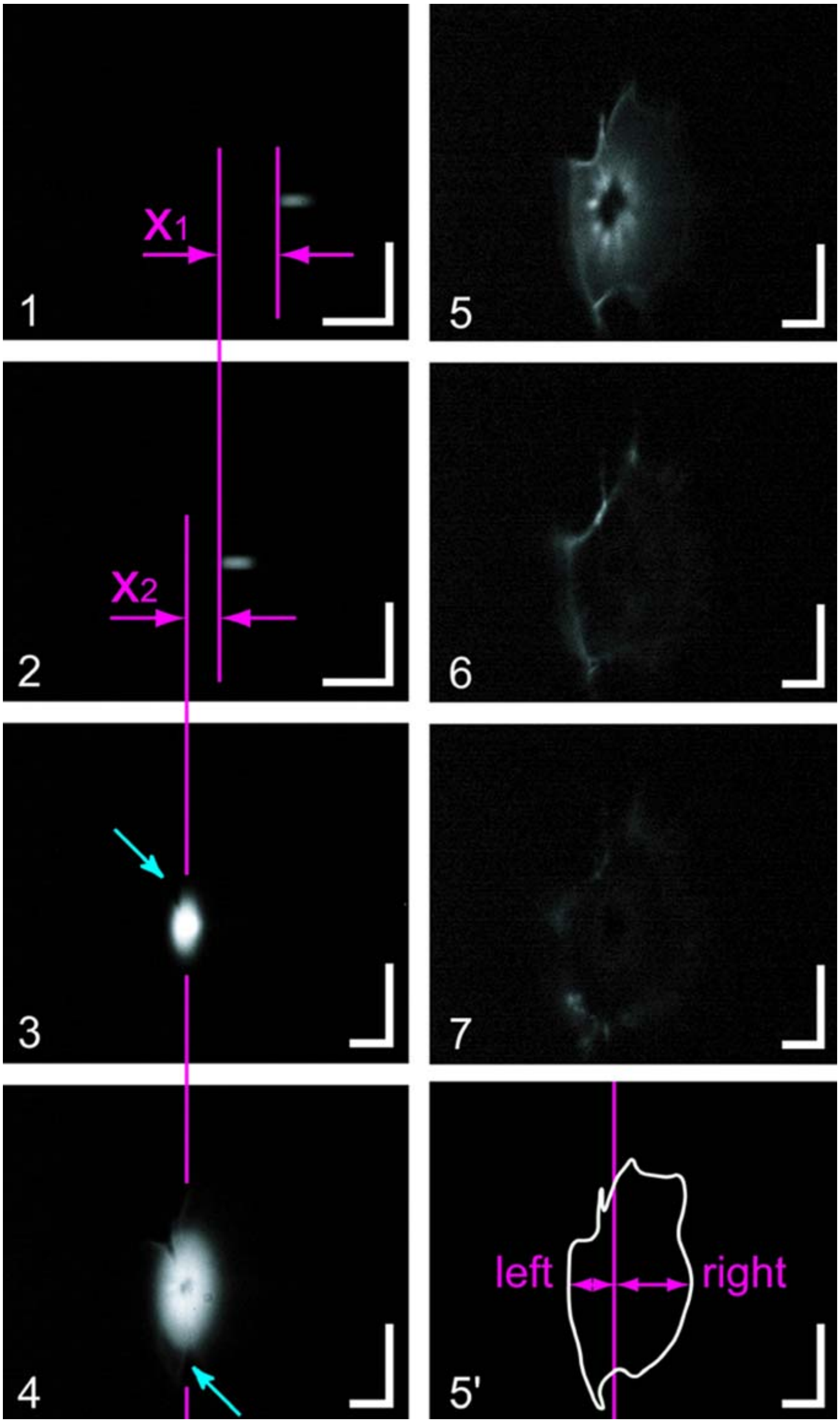

Fig. 1 The evolution of an yttria-stabilized zirconia droplet impinging on a substrate in plasma spraying. Source: Reused with permission from K. Shinoda, *Appl. Phys. Lett.*, 2007, **90**, 194103

Figure 1 shows deformation and cooling processes of an impinging droplet taken by the high-speed video camera. Each frame interval was 1 μs, and the exposure time was 500 ns. An yttria-stabilized zirconia droplet of 50 μm in diameter impinged on a smooth quartz glass substrate kept at room temperature. The images showed that the liquid sheet jetting out sideways from the droplet detached from the substrate and kept on spreading without disintegration until its maximum extent. While the sheet was spreading, the center region of the flattened droplet cooled down much more rapidly.

Contact: Seiji Kuroda, Coating Materials Group, Composites and Coatings Center, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan; Tel: +81-29-8592405; fax: +81-29-8592401; e-mail: kuroda.seiji@nims.go.jp; web: http://www.nims.go.jp/cccenter/coating/homeeng.htm.

News From NASA

Increasing Durability of Flame-Sprayed Strain Gages

Thermally sprayed dielectric ceramic coatings are the primary means of attaching strain and temperature gages to hot-section rotating parts of turbine engines. As hot-section temperatures increase, lifetimes of installed gages decrease and seldom exceed 1 h above 2000 °F (~1100 °C). Advanced engine components are expected to operate at temperatures approaching 2200 °F (~1200 °C), and the required high-temperature lifetime is 10 h minimum.

Typically, to enable a ceramic coating to adhere to the smooth surface of an engine component, a thermally sprayed NiCrAlY or NiCoCrAlY bond coat is applied to the smooth surface, thereby providing a textured surface to which the ceramic coat can adhere. The main failure mechanism of this system is decohesion and/or delamination at the interface between the ceramic top coat and the bond coat, caused by oxidation of the bond coat and stresses from the mismatch between the coefficients of thermal expansion of the ceramic top coat and the metallic bond coat.

The approach taken to increase the high-temperature lifetime of a gage attached to an engine component by the method described above involves (1) selective oxidation of the bond coat by means of a heat treatment in reduced oxygen partial pressure followed by (2) the application of a noble-metal diffusion barrier. In experiments to test this approach, heat treatments of NiCoCrAlY bond coats were carried out in a tube furnace in which, in each case, the temperature was alternately (1) increased at a rate of 3 °C/min and (2) held steady for 1 h until the desired temperature was reached. The tube furnace was continuously purged with dry nitrogen gas. A final heat treatment temperature range of 1600-1800 °F (871-982 °C) proved most beneficial.

Test coupons were made to enable evaluation of the cycle lives of various bond coats, including some made from the commercially available coating materials Praxair 171 (an NiCoCrAlY formulation) and Praxair 343 (an NiCrAlY formulation). Each test coupon included a base-metal coupon of Inconel 718 nickel alloy. One of the bond-coating materials to be tested was thermally sprayed on the metal, the coupon was subjected to the aforementioned heat treatment at reduced oxygen partial pressure, then a ceramic dielectric top coat was thermally sprayed onto the bond coat. To provide a basis of comparison for evaluation of the relative merits of the various surface treatments and heat treatments, some of the NiCoCrAlY and NiCrAlY bond coats were incorporated into the coupons in the as-sprayed condition; that is, the affected coupons were not subjected to the heat treatment at reduced oxygen partial pressure.

Each coupon was mounted on an Inconel 718 nickel-alloy fixture and placed in the tube furnace, wherein it was heated to 1150 °C and held at this temperature for 1 h. The test fixture was then retracted from the furnace (see Fig. 1) and allowed to cool to 150 °C. The cooling process took approximately 5 to 6 min. Upon reaching 150 °C, the test fixture with the coupon was placed back in the furnace and reheated to 1150 °C. The entire heating-and-cooling sequence was considered one cycle, and the lifetimes of the coupons were assessed on the basis of the numbers of cycles to failure.

The heat treatment of the NiCoCrAlY bond coats at reduced oxygen partial pressure yielded a significant increase in lifetimes: Coupons heat treated to 1750 °F (954 °C) at reduced oxygen partial pressure exhibited more than double the cycle lives of those containing as-sprayed NiCoCrAlY. This considerable increase in life can be attributed to the fact that selective oxidation of the aluminum and chromium in the bond coat yielded a graded interface. The heat treatment of the NiCrAlY bond coats yielded little or no increase in lifetimes.

The failure mechanisms of the coupons containing NiCoCrAlY bond coats differed from those of the coupons containing the NiCrAlY bond coats: The NiCoCrAlY-bond-coated specimens failed by decohesion and/or delamination at the interfaces between the top and bond coats. The NiCrAlY-bond-coated specimens underwent cohesive failure within the bond coats. Evidence of failure by these mechanisms can be seen in Fig. 2(a) and (b), respectively.

In an effort to reduce the extent of internal oxidation in the bond coats, platinum and rhodium coats were

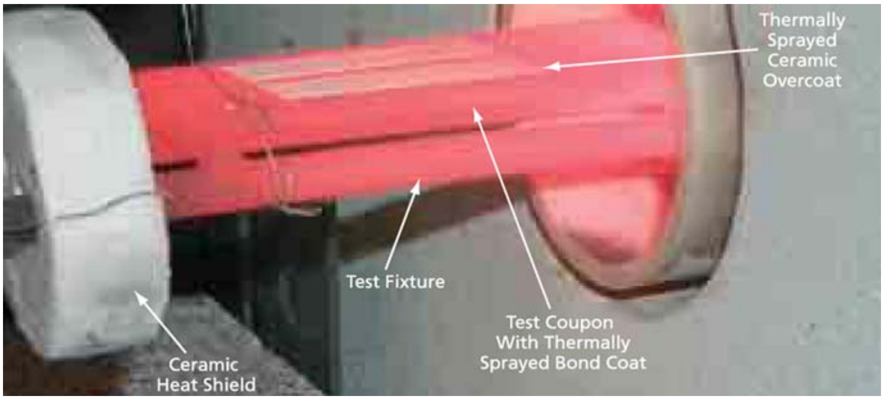

Fig. 1 A test fixture is depicted here during removal from a horizontal tube furnace maintained at a temperature of 1100 °C. A coupon is fastened to the fixture with platinum wire

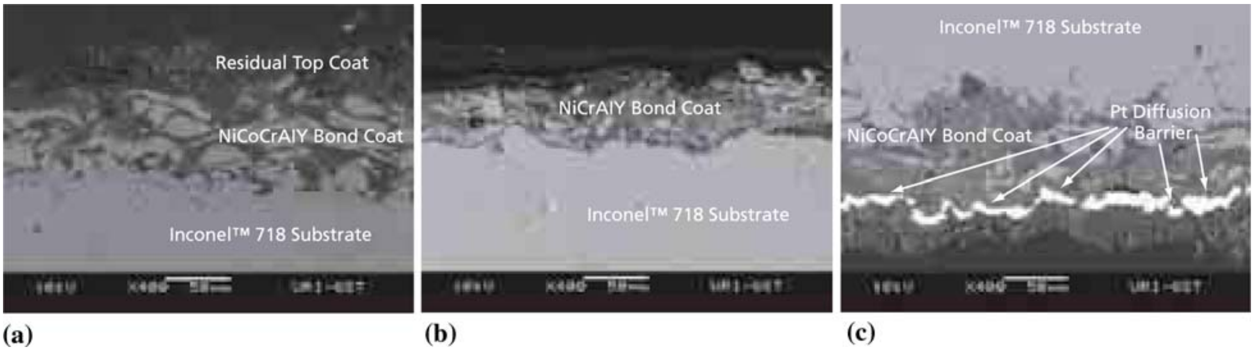

Fig. 2 These scanning electron micrographs of cross sections of representative coupons illustrate three different conditions. (a) As-sprayed NiCoCrAlY bond coated specimen that failed by decohesion and delamination at the top-coat/bond-coat interface. (b) As-sprayed NiCrAlY bond coated specimen that underwent cohesive failure in the bond coat. (c) NiCoCrAlY bond coated specimen containing a Pt diffusion barrier

employed as diffusion barriers. Initially, as-sprayed NiCoCrAlY-bond-coated coupons were coated with platinum to a thickness of 2 μm by physical vapor deposition (PVD). An example of a platinum diffusion barrier can be seen in Fig. 2(c). The platinum-coated Inconel coupons were heat treated to 1800 °F (982 °C), then magnesium aluminate spinel top coats were thermally sprayed over the platinum coats. Rhodium diffusion barriers were applied to the surfaces of NiCoCrAlY-bond-coated coupons by pen electroplating. (Pen electroplating was investigated as a means of forming diffusion barriers because it is easy to perform and does not entail costly capital investment.)

The rhodium diffusion barriers yielded only a marginal increase in the lives of NiCoCrAlY-bond-coated coupons. However, platinum diffusion barriers applied by PVD in conjunction with reduced-oxygen-partial-pressure heat treatment yielded substantial increases in lifetimes. The platinum films were thick enough to constitute oxygen-diffusion barriers that slowed the growth of internal oxides by promoting the formation of alumina-rich scale at the interfaces between the top and bond coats. The best results achieved to date were realized by use of sputtered platinum diffusion barriers in conjunction with heat treatments to 1800 °F (982 °C) at reduced oxygen partial pressures. This combination yielded a fourfold increase in the fatigue lives of NiCoCrAlY-bond-coated coupons.

This work was done by Otto J. Gregory and Markus A. Downey of the University of Rhode Island, and Steve Wnuk and Vince Wnuk of HPI Inc. for John H. Glenn Research Center, Cleveland, OH. 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-17530-1. Adapted from *NASA Tech Briefs*, May 2007.

News from TSS

JTST Best Paper Award 2006

The *Journal of Thermal Spray Technology* contains worldwide coverage of the latest research, products, equipment, and process developments and covers all fundamental and practical aspects of thermal spray science, including processes, feedstock manufacture, and testing and characterization. Every year, the Best Paper Award recognizes the quality of an exceptional paper published in the Journal.

For Year 2006, the JTST Volume 15 Best Paper Award winner was selected by a panel of 16 international judges who commented that this paper presented "original work" and "demonstrates the advantages of using a novel method for generating and depositing nanoparticles to form nanocrystalline films and patterns. The paper is very well structured, and the results are presented in a nice fashion."

Professor Joachim Heberlein is awarded for the *Journal of Thermal Spray Technology* Volume 15 Best Paper Award by Dr. Christian Moreau, Editor-in-Chief. The award was presented at the International Thermal Spray Conference 2007 Banquet Ceremony in Beijing, China

The JTST Volume 15 Best Paper is "Hypersonic Plasma Particle Deposition—A Hybrid between Plasma Spraying and Vapor Deposition," written by Joachim Heberlein, J. Hafiz, R. Mukherjee, X. Wang, P.H. McMurry, and S.L. Girshick, University of Minnesota, Minneapolis, MN (Vol 15 (No. 4), Dec 2006, p 822-826).

Chris Berndt Inducted into Thermal Spray Hall of Fame

The Thermal Spray Hall of Fame was established by the ASM Thermal Spray Society in 1993 to recognize significant contributions to the science, technology, practice, education, management, and advancement of thermal spray.

Prof. Christopher C. Berndt, FASM, 2007 inducted to TSS Hall of Fame

The 2007 inductee into the Thermal Spray Hall of Fame is Prof. Christopher C. Berndt, FASM, Professor of Surface and Interface Engineering at James Cook University, School of Engineering, Townsville QLD, Australia. His involvement in many of the research areas precede the time when these research areas became ''fashionable,'' showing him as a genuine pioneer. This is due for his mechanical property measurements, his involvement in biocompatible coatings, and his microstructure analysis.

Colleagues have noted that his innovations in mechanical property measurements remain the standard for assessing the mechanical properties of spray coatings. Additionally, his R&D on dental materials and hydroxyapatite coatings on orthopedic implants led to an appointment as Adjunct Professor in Orthopedics at Stony Brook. His many innovations have led to facilitating the bridge between academia and industry, effecting numerous collaborations. Also, he was among the first to use solution plasma spraying, an area that is emerging as a very promising technology.

Please read the Commentary in this issue with Chris Berndt's extended acceptance speech.