JTTEE5 16:475–479
DOI: 10.1007/s11666-007-9135-3
1059-9630/$19.00 © ASM International

In The News

News from Research and Technology Institutes Worldwide

This column informs JTST readers of activities in research and technology institutes in the field of thermal spray technology. Technical overviews help the reader to understand the primary focus of the institution and the needs driving their thermal spray research and development. Getting to know the research interests and professional experience of our thermal spray colleagues allows us to better recognize experts in specific fields of study. Knowledge of institutional expertise is important for developing complimentary partnering relationships to increase the fundamental understanding of thermally sprayed materials and increase the quality and breadth of practical applications.

This column includes articles giving an overview of current activities or a focus on a significant breakthrough. To submit an article for this column, please contact Kendall Hollis, JTST Associate Editor, address: Los Alamos National Laboratory, P.O. Box 1663, MS G-770, Los Alamos, NM 87544; e-mail: kjhollis@lanl.gov.

Thermal Spray Research at the University of Auckland, New Zealand

Thermal Spray Research at the University of Auckland is carried out within the Department of Chemical and Materials Engineering, Faculty of Engineering, and our research programs are naturally influenced by the local strengths and national interests. The Thermal Spray Research Group has strong links with intra-University centers such as the Light Metals Research Centre, the Polymer Electronics Research Centre, and most importantly, the Research Centre for Surface and Materials Science, which reflect the research backgrounds of the principal academics (Hyland and James) and give our thermal spray research programs a unique flavor. In addition, our work has benefited enormously from collaborations with NZ companies—Holster Engineering and Metal Spray Suppliers—and international groups such as Paul Munroe's Electron Microscope Unit at the University of New South Wales and Sanjay Sampath and the Center for Thermal Spray Research.

Carbide Cermets

Our initial research centered on high-velocity sprayed cermets, and the evolution of microstructure as a function of spray parameters and in-service conditions. The high-velocity techniques, especially high-velocity air fuel, are particularly suitable since the lower jet and particle temperatures minimize decarburization during deposition. Variations in microstructures of HVAF and HVOF WC-Co coatings were correlated with sliding wear performance (Ref 1, 2). The mechanism of the decarburization process and the formation of decarburized halos has also been elucidated (Ref 3).

Parallel work in our lab has confirmed similar behavior for HVAF and HVOF as-sprayed Cr_3C_2-NiCr coatings. These coatings are used in moderate to high-temperature erosive-corrosive environments, such as turbines in fluidized bed combustors. Under these extreme in-service conditions, the microstructure can be expected to change, but too commonly, testing is carried out under conditions that do not adequately mimic these conditions. Our goal was to study the erosion-corrosion of Cr_3C_2-NiCr coatings under turbine conditions, understanding the evolution of the microstructure and its influence on the mechanism of erosive-corrosive wear.

Figure 1 demonstrates the evolution of microstructure and hardness with heat treatments mimicking the early service life temperatures of turbine coatings. The obvious change is the precipitation of fine carbide structure from the matrix. During coating deposition, some carbide is dissolved in the matrix, which occurs to a greater extent in deposition technologies that heat the particles to higher temperatures (Ref 4). This dissolved carbide precipitates as very fine particles, which grow with longer heat

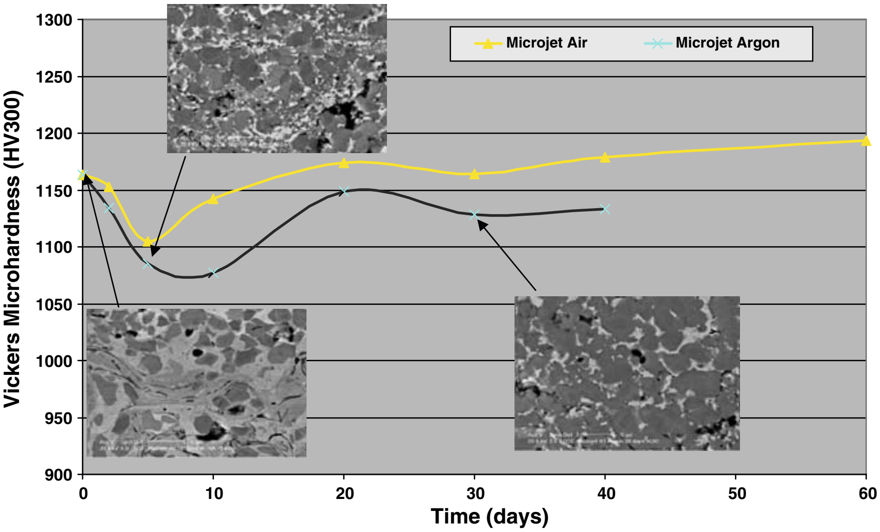

Fig. 1 Change in microstructure of HVOF sprayed Cr_3C_2-NiCr coatings heat-treated at 900 °C and the corresponding change in hardness

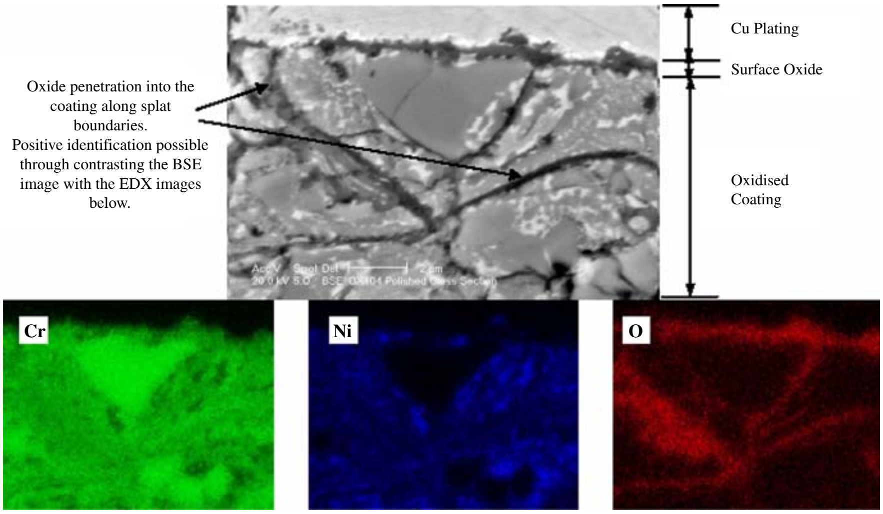

Fig. 2 Cross section of an HVOF sprayed Cr_3C_2-NiCr coating oxidized at 700 °C for 48 h; electron micrograph (*top*), and elemental maps of the same area (*bottom*). Oxidation extends into the coating along splat boundaries

Fig. 3 The Kratos Axis DLD XPS system in the Research Centre for Surface and Materials Science at the University of Auckland

treatments. The precipitation restores the ductility of the matrix, and this effect dominates in the early treatment stages, resulting in an initial drop in hardness. The later increase in hardness tracks the increasing volume and size of carbides (Ref 5). This effect is not as pronounced for HVAF coatings where the extent of carbide dissolution into the matrix is less.

Oxidation processes of Cr_3C_2-NiCr coatings are also influenced by the as-sprayed microstructure. Higher-temperature processes that give thin lenticular splats with large splat areas are more prone to oxidation, since the oxygen can diffuse along the splat boundaries into the coating (Fig. 2). Weight gain during oxidation curiously is greater at lower temperatures, because the surface passivates slowly, allowing oxygen to penetrate more extensively into the coating (Ref 6).

Surface Oxides and Splat Formation

More recently, the focus of our research program has shifted from bulk microstructure to the interface—taking advantage of our expertise in surface characterization to probe the influence of surface chemistries and structures on the formation and structure of splats. Of particular interest is the role of the substrate on the splat formation process, especially the surface oxide layer.

Substrates are inevitably covered with an oxide layer that must play a role in controlling the bonding process. The influence of oxide structure and chemistry on interfacial bonding in other coating technologies is well documented (for example, Ref 7). Strong bonding is achieved by careful control of the oxide thickness, structure, and degree of hydration. Durability of bonds to metals is directly related to the stability of the oxide layer. Aside from the well-known effect that oxides have in controlling the substrate temperature at which splats switch from splash (undesirable) to disk (desirable) splats, there is little known about the role of the oxide layer in thermal spray systems. Suggestions about the role of oxides are sometimes contradictory—on the one hand, it is proposed that the oxide layer must be disrupted in order for solid splats to bond to the substrate (Ref 8); on the other hand, bonding has been shown to involve the formation of an interfacial oxide (Ref 9). Bill Trompetter, who has recently completed his Ph.D. (Ref 10) at the University of Auckland, has shown that disruption of the oxide and direct contact between the splat and substrate metal occurs for molten splats. With nonmolten splats, disruption of the oxide and direct splat/substrate contact does not always occur. However, the splat will make strong conformal contact with the oxide layer, which probably gives rise to bonding through dispersive forces.

Key questions remain concerning the role of the oxide layer:

- Does the oxide chemistry (which changes rapidly with humidity) affect splat wettability and spreading?
- How does the presence of the oxide affect the substrate deformation process?
- How does the oxide affect the heat transfer from splat to substrate and the rate of splat solidification?
- Can the oxide participate in formation of interfacial compounds?

In this work, access to the facilities and expertise in the University of Auckland Research Centre for Surface and Materials Science has been invaluable. Using x-ray photoelectron spectroscopy (XPS), we have been able to characterize the chemistry of the outermost 1-5 nm of the surface, revealing more than just the elemental composition, but the chemical functionalities as well. For example, it is possible to distinguish between metallic aluminum and aluminum oxide and between oxygen present as oxides, hydroxides, or adsorbed water. The Kratos Axis DLD (Fig. 3), is a state-of-the-art XPS instrument equipped with heated analysis stages in both the preparation and analysis chambers and two ion guns for sample cleaning and depth profiling. It has allowed us, among other things, to follow the change in surface chemistry as the substrate is heated, thereby tracking the

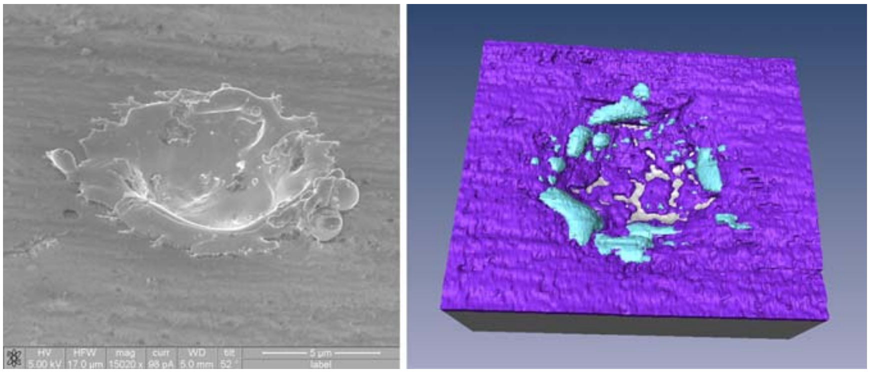

Fig. 4 Electron micrograph of a NiCr splat on Al (*left*) and a processed slice-and-view FIB image of the same region, with the splat digitally removed to expose the substrate below and show the extent of the splat/substrate contact (*right*). Purple, undisturbed oxide; *light blue*, intersplat/substrate porosity; *gray*, Al below the oxide layer

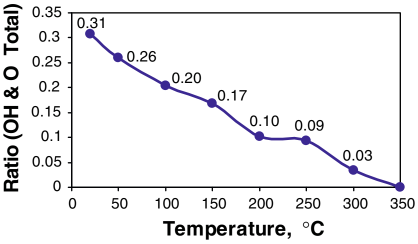

Fig. 5 The change in hydroxide content in the surface layer of a polished aluminum substrate. By 350 °C, the hydroxide has converted completely to oxide

changes that occur when substrates are heated prior to or during spraying.

Focused ion beam milling in combination with TEM has proved to be a powerful tool for probing the interface with minimal disturbance of the region and introduction of artifacts that frequently plague other microstructural characterization techniques that rely on polished cross sectioning. In a very productive collaboration with Professor Paul Munroe at the University of New South Wales, we have been able to cross section the critical interface, identify novel bonding features in solid splats such as interfacial jets, probe the disturbance of the oxide layer (as described earlier), and build up 3D images across the entire splat/substrate interface (Fig. 4). In this way, we have gained new insights into the nature of the splat/substrate contact, nature and number of voids, the extent of substrate deformation or melting, and the deformation and disruption of the oxide.

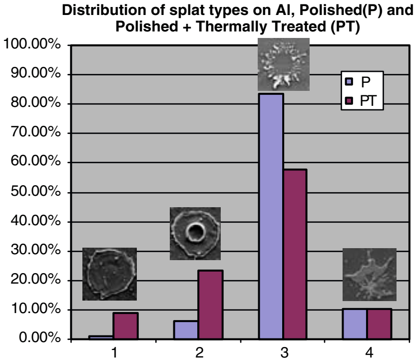

Fig. 6 A comparison of splat morphology for polished aluminum and thermally treated, polished aluminum. Thermal treatment prior to spraying reduces the hydroxide content and results in a reduction in splash splats

Surface Chemistry and Splat Morphology

Aluminum is a natural choice of substrate to explore the influence of oxide surface chemistry, since its surface oxide can be tailored by treatments to produce surface layers that range from hydroxide-dominated to fully dehydrated oxides. Surface treatments will also alter the morphology and roughness of the surface, and these need to be carefully controlled and characterized.

Aluminum surface oxides are usually a combination of oxide, hydroxide and physisorbed water; the proportions of each can be measured by deconvolution of the oxygen 1s XPS signal. A typical oxide on polished aluminum is about 63% oxide, 31% hydroxide, and 6% physisorbed water. These proportions change on heating: all of the physisorbed water is lost by 100 °C, and the hydroxide content steadily decreases as the temperature rises, finally converting completely to oxide by 350 °C (Fig. 5).

The presence of hydroxide affects the splat morphology. NiCr splats on polished aluminum sprayed at room temperature by plasma spray are dominated by highly splashed splats (Fig. 6). If the substrate is heated to 350 °C prior to spraying to remove the surface hydroxide, the proportion of splash splats drops, and disk splats increase, even though the plasma spray process is carried out at room temperature. Increased amounts of hydroxide are correlated with more splash splats. Stainless steel substrates show the same trend, and the effect is even more dramatic on aluminum substrates where the surface layer is a thick hydroxide: no splats adhere—it is impossible to deposit a coating, because the conversion of hydroxide to oxide that occurs dynamically as the hot splat hits the surface disrupts the splat formation process.

In the Future

This work is being extended to more fully understand the underlying influence of the surface chemistry. We are beginning modeling studies to compare the rate of the hydroxide conversion with splat spreading and determine its potential influence on the heat transfer to the substrate. We are also looking at the influence of surface chemistry on HVAF deposition of polymer coatings, PEEK in particular, with the aim of developing these wear-resistant coatings for food and dairy processing applications. Finally, we look forward to the anticipated expansion in our activities with the imminent return to New Zealand of a thermal spray colleague, Dr. Steve Matthews.

References

1. L. Jacobs, M.M. Hyland, and M. De Bonte, Comparative Study of WC-Cermet Coatings Sprayed via the HVOF and HVAF Processes, *J. Therm. Spray Technol.*, 1998, **7**(2), p 213-218
2. L. Jacobs, "Processing and Characterisation of Wear Resistant Coatings Deposited by High Velocity Air-Fuel Spraying," Ph.D. Thesis, University of Auckland, New Zealand, 1999
3. L. Jacobs, M.M. Hyland, and M. De Bonte, Study of the Influence of Microstructural Properties of the

Sliding Wear Behaviour of HVOF and HVAF Sprayed WC-Cermet Coatings, *J. Therm. Spray Technol.*, 1999, **8**(1), p 125-132

4. S. Matthews, "High Velocity Air Fuel Sprayed High Temperature Oxidation Resistant Coatings," Ph.D. Thesis, University of Auckland, New Zealand, 2005
5. S. Matthews, M Hyland, and B.J James, Microstructure and Hardness Evolution in Heat Treated Cr_3C_2-NiCr High Velocity Thermal Spray Coatings, *Acta Mater.*, 2003, **51**(14), p 4267-4277
6. S. Matthews, M. Hyland, and B.J. James, Long-Term Carbide Development in HVOF/HVAF Cr_3C_2-NiCr Coatings Heat Treated at 900 °C, *J. Therm. Spray Technol.*, 2004, **13**(4), p 526-536
7. M.M. Hyland, Surface Chemistry of Adhesion to Aluminum, *Handbook of Aluminum*, Vol 2, *Alloy Production and Materials Manufacturing*, G.E. Totten and D.S. MacKenzie, Ed., Marcel Dekker, 2003
8. T. Van Steenkiste, J. Smith, and R. Teets, Aluminium Coatings via Kinetic Spray with Relatively Large Powder Particles, *Surf. Coat. Technol.*, 2002, **154**(2-3), p 237
9. S. Barradas, R. Molins, M. Jeandin, M. Arrigoni, M. Boustie, C. Bolis, L. Berthe, and M. Ducos, Application of Laser Shock Adhesion Testing to the Study of the Interlamellar Strength and Coating—Substrate Adhesion in Cold-Sprayed Copper Coating of Aluminium, *Surf. Coat. Technol.*, 2005, **197**(1), p 18
10. W.J. Trompetter, "Splat-Substrate Interactions in High Velocity Thermal Spray Coatings," Ph.D. thesis, University of Auckland, New Zealand, 2007

Contact: Margaret Hyland, e-mail: m.hyland@auckland.ac.nz and Bryony James, e-mail: b.james@auckland.ac.nz.

News from ITSA and TSS

News from ITSA

Nanomaterials—Health and Safety Concerns

As we all know, there are many efforts underway to develop, understand, and use nanomaterials on an industrial scale. The results of some of these efforts are already in commercial use. The thermal spray industry is no exception to this involvement with nanomaterials.

In parallel with these research and commercial efforts, many organizations and individuals have expressed concern about "unknowns" for these materials in the areas of health and safety. Some experts believe that due to their size, nanomaterials in particulate forms may pose greater risks than the same material in conventional particle sizes. Thermal spray processes can use nanosize materials as feedstocks; however, in addition, the spray process itself may produce nanosize particulates from more conventional feedstocks.

In order to stimulate more research on these safety and health concerns, the National Nanotechnology Initiative (NNI) developed a document, "Environmental, Health and Safety Research Needs for Engineered Nanoscaled Materials." Others have also spoken out about the need for more information and potential action. For example see "Thinking Big About Things Small: Creating an Effective Oversight System for Nanotechnology" authored by Mark Greenwood, former director of EPA's Office of Pollution Prevention and Toxics.

The EPA has awarded grants totaling over $30 million to investigate potential health and environmental effects of nanomaterials and applications and/or implications of manufactured materials. NNI has also funded similar studies.

In the interim, thermal spray researchers and commercial users of nanomaterials should have in place a good environmental health and safety program that takes into account the presence of nanosized materials in the workplace. One company's (Altairnano) efforts in this regard were reported on at a recent conference and are described in the *Occupational Hazards* e-journal (see http://www.occupationalhazards.com/News/Article/43536/Nanotech_Conference_Advice_for_StartUps.aspx).

Contact: Paul Kammer, Kammer Associates, Inc., e-mail: pakammer@suddenlink.net. Adapted with permission from *SPRAYTIME* 14(2); http://www.spraytime.org.

News from TSS

Rolls-Royce Licenses Jet Engine Turbine Coating Technology

Rolls-Royce Corp. acquired exclusive rights to use a coating invented by researchers at Iowa State University (Ames, IA) that helps turbines withstand the high temperatures in jet engines. The unique bond coating will be applied to engine turbine blades made of nickel-base superalloys, which require additional protection to enhance their high-temperature strength at hot section temperatures near 2100 °F. The bond coating improves the durability and reliability of a ceramic thermal barrier that is applied over the bond coat. The coating is based on a composition comprising platinum, nickel, aluminum, and hafnium and is said to offer significant advantages over existing coating technologies. It was invented by Brian Gleeson, Daniel Sordelet, and Wen Wang, a former Iowa State postdoctoral student. Gleeson, Sordelet, Dr. William Brindley of Rolls Royce, and Bingtao Li, a former Iowa State doctoral student and postdoctoral researcher, also developed a cost-effective method for applying the coating to engine parts.

The coating compositions grew out of basic research that began about 7 years ago and was supported by the Office of Naval Research. According to Sordelet, a key advantage to the technology is that it is mechanically compatible with the superalloys it covers and protects. It reacts to the heat and stress of an engine about the same way the superalloy does, enhancing engine part performance and extending service life. The Iowa State researchers continue to work on the coating composition project with goals of developing a better and less expensive way to produce the coating and developing new coating compositions.

Rolls-Royce will have an exclusive license to commercialize the inventions. Patents are pending for the inventions, and the term of the license agreement is for the life of any patents. For more information see http://www.iastate.edu.

This information was adapted from the TSS publication *International Thermal Spray & Surface Engineering*, **2**(3).