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News from Research and Technology Institutes Worldwide

This column informs *JTST* readers of activities in research and technology institutes active 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 complementary partnering relationships to increase the fundamental understanding of thermally sprayed materials and to 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 at: Los Alamos National Laboratory, P.O. Box 1663, MS G-770, Los Alamos, NM 87544; e-mail: kjhollis@lanl.gov.

Research Activities of the Laboratory of Reliability Research on Materials for Ultrahigh Temperature at the Fracture and Reliability Research Institute, Tohoku University, Japan

The Fracture and Reliability Research Institute (FRI) at Tohoku University, located in northeast Japan, originated from the Research Institute for Strength and Fracture of Materials established in 1964 as one of the specializing institutes in safety sciences. FRI is composed of five divisions and more than seven laboratories. Its research activities cover several fields such as the physics and chemistry of fracture, environmentally assisted cracking, high-temperature materials and coatings, long-term reliability, strength assessment of nanoscale structures, and nondestructive evaluation techniques. FRI has been conducting a number of international and domestic cooperative research programs as an international research center of safety science, which is concerned particularly with environmentally assisted cracking and material aging for the integrity of energy-related structures and systems.

The High-Temperature Materials (HTM) laboratory carries out innovative R&D work on surface modification, degradation-resistant coatings, and nondestructive evaluation (NDE) followed by transfer of the developed technologies to industry. Activities aim at improving the understanding and preventing the degradation of structural materials by overlay coatings and optimizing the coating performance for targeted industrial applications.

Recently, cold spraying and thermal spraying have been the main focus of the HTM laboratory's activities. The group is composed of three researchers, four technicians, and students from various districts of Japan and foreign countries. Their research spans:

- Process and coating optimization for industrial applications
- Cold spray repair technique development
- Cold spray adhesion mechanism investigation
- Formulation of novel coating systems to limit oxidation
- Development of in situ monitoring systems for thermal barrier coatings (TBC).

The group has developed a strong expertise in coating characterization and performance evaluation of oxidation, bond strength, and residual stress. Some of the current research programs are described.

Repair Technique Using Cold Spray

The cold spray technique provides a dense, low-oxide metallic coating without the need for a processing vacuum chamber. Therefore, it is possible to apply cold spray to the repair of metallic components including aluminum. In case of low-pressure type (LP) cold spray, the equipment is compact and portable. Consequently, LP cold spray is suitable for the on-site repair of aluminum components. HTM laboratory has a Dymet 403j LP cold spray system and has succeeded in depositing dense, pure-aluminum coatings. To achieve the practical use of aluminum repair by the LP cold spray technique, HTM laboratory is studying two topics: one is to understand the fundamental aluminum deposition mechanism of LP cold spray and the other is to investigate the novel application of aluminum and aluminum composite coatings. From the results, the LP-deposited samples showed higher compressive strength than the similar bulk material.

To develop a technique for repairing high-temperature components of land-based gas turbines, HTM laboratory introduced a high-pressure (HP) type cold spray system manufactured by Plasma-Giken, Japan, in 2007. The HTM laboratory is carrying out physical experiments as well as computational analysis such as finite element method (FEM) and molecule dynamics (MD) tools to understand the adhesion strength and other mechanical properties of the deposited coatings.

Improvement of Crack Resistance and Oxidation Inhibition for TBC Systems

In TBC systems, thermally grown oxide (TGO) forms at the interface between the top coat (TC) and bond coat (BC) during service. Delamination or spallation at the interface occurs due to the TGO formation and growth. Modification of the bond coat material is one means to inhibit the TGO formation and to improve the crack resistance of TBC system. HTM laboratory has developed modified BC materials by adding Ce and Si to the conventional materials. As a result, HTM laboratory succeeded in producing a high-strength TBC system of CoNiCrAlY with Ce and Si (CoNiCrAlYCeSi) with improved resistance to crack propagation.

In the case of 0.5Ce addition to the BC, TGO morphologies showed the formation and growth of the mixed oxide (gray region in Fig. 1) were fully developed. In the case of a 1.5Ce1SiBC material, it seems that the mixed oxides grow into the BC downward to the substrate along the grain boundaries in the BC. The addition of Ce led to the generation of rootlike oxides inside the BC. As a result of high-temperature exposure, Ce in the BC is oxidized and Al_2O_3 is formed at the interface between the TC and BC. It is not easy for oxygen to penetrate to the inside of the BC because of the formation of a porous Al_2O_3 layer at the interface. From the results, the rootlike oxides can improve crack resistance under pure bending load.

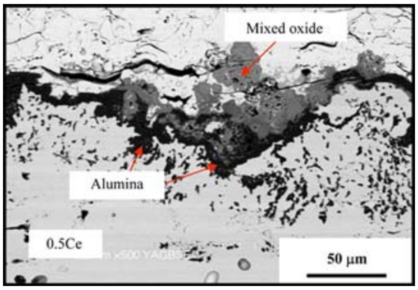

Fig. 1 Cross-sectional SEM image of TBC aged at 1373 K with Ce addition to the BC

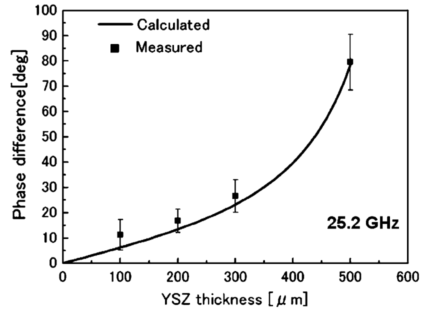

Fig. 2 Measured and calculated in-contact results of phase difference by microwave NDE at 25.2 GHz

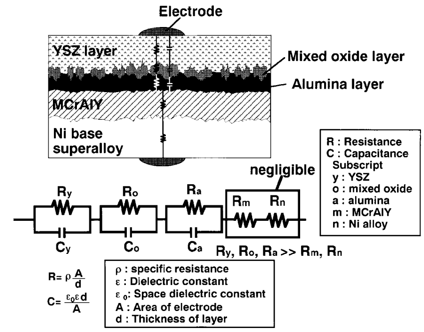

Fig. 3 Schematic of TBC and equivalent circuit for IS technique

Microwave NDE Technique for Degraded TBC

TBC failure, which is attributed to the BC oxidation and TC degradation, will result in rapid substrate material degradation. At present, more reliable and sensitive nondestructive techniques are required to monitor TBC integrity over the component lifetime. Therefore, to detect TC and TGO thicknesses, a microwave nondestructive technique was developed.

Microwave NDE is simply based on wave reflection from a dielectric media interface. According to the dielectric properties of the TBC (permittivity and loss factor), a part of this incident wave will be reflected from the interface and another part will be transmitted and propagated through the TBC layer. These forward and backward traveling waves inside the TBC layers can be formulated by enforcing the appropriate boundary conditions. Finally, TC and TGO thicknesses can be derived by measuring the reflection coefficient, which is the ratio of the reflected and transmitted waves. The measurement system consists of a network analyzer (Agilent N5230A 10 MHz to 50 GHz) feeding signals to a rectangular waveguide and a computer manipulating the waveguide's position. In general, when dealing with thin and low-loss dielectric materials, information from the phase of the reflection coefficient is much more useful than that of the magnitude of the reflection coefficient. For instance, Fig. 2 shows the measured and calculated in-contact results of phase difference (with respect to the case without YSZ) versus YSZ thickness at 25.2 GHz. The results showed a very good resolution of 1° change in phase for 15 μm YSZ thickness. Microwave NDE has the potential to be one of the most accurate methods for composite material evaluation, and therefore further studies will be conducted to better understand this technique.

Impedance Spectroscopy NDE Technique

The aim of this research is to develop a novel nondestructive technique for evaluation of the reaction layer using the impedance spectroscopy (IS) method. In this IS method, defects such as delamination, spalling, cracking, and other damage can be detected using voltage and current response with alternating current and frequency. Changes of both resistance and capacitance associated with the degradation can be measured. Thickness reduction of TBC, initiation of defects, formation of oxide film, and coating delamination can be detected by the resistance and capacitance data.

Based on the data from the impedance measurements, an equivalent circuit of an aged sample is proposed as illustrated in Fig. 3. In practice, the electrical resistance of MCrAlY and Ni alloy can be neglected because these two metallic materials have a smaller resistivity than the other ceramics layers. A reaction layer containing two layers of dark alumina and gray mixed oxide is observed. YSZ and the two oxide layers formed can be represented by three impedance elements. It is possible to estimate the impedance behavior using sensitivity analysis. The thickness of the alumina layer is calculated from the largest impedance value obtained at a saturated phase region. It is possible that the thickness of the TGO alumina layer can be evaluated nondestructively with less than 30% error.

Oxidation-Resistant Coating for Carbon/Carbon Composites

Due to its superior specific strength at high temperature, carbon/carbon (C/C) composite is one of the candidate materials for the engine wall of air-breathing rocket or ramjet engines, the extendible nozzle of rocket engines, and the turbine blades for a more highly efficient gas turbine generator. Because the C/C composites are easily oxidized at elevated temperature, an oxidation-resistant layer on the C/C surface is required. Silicon carbide (SiC) coating by cold spraying and thermal spraying along with silicon (Si) infiltration are being tried to protect the C/C composites. Surface modification of C/C composites is also being researched to enhance their apparent elastic modulus at the same time. C/C composites are usually coated with SiC or Si to protect them from surface degradation. However, the effective heat-resistant temperature of a SiC coating is below 1800 K in practical use under an oxidizing environment, so a cooling system embedded in the combustor structure is necessary when an engine wall is exposed to combustion gas with a temperature of around 3000 K. In the design of oxidation-resistant coatings, the physical and chemical adaptability of the coating to the substrate is the crucial factor. During the investigations, novel processes will be adapted to optimize the bonding layers between the C/C composite and the ceramic outer layer. Currently, many unsolved challenges remain in this investigation.

National and International Collaborations

In addition to conducting R&D projects with many industrial partners in Japan, the HTM laboratory works in close collaboration with several universities and research centers in foreign countries:

- France: Ecole des Mines de Paris (School of Mines-Paris)
- Russia: Institute of Theoretical & Applied Mechanics, Russian Academy of Sciences
- Korea: Chosun University
- Germany: Technische Universität Darmstadt (TUD)
- United States: Northwestern University

Equipment

The HTM laboratory integrates the following equipment for the deposition, characterization, and evaluation of coating performance.

- Sulzer Metco-based low-pressure plasma spray (LPPS) system
- High-pressure type cold spray system (Plasma Ginken, Japan) with robot control
- Low-pressure type cold spray system (Dymet 403j)
- NDE systems based on microwave, impedance spectroscopy, remote-induced current potential drop, and high-frequency signal transmission characteristics techniques
- Focused ion beam (FIB) and ion milling machine
- Atomic force microscope (AFM) and scanning tunneling microscope (STM)
- X-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS)
- Atomic emission spectroscopy (AES) and dynamic secondary ion mass spectrometry (D-SIMS)
- Field emission scanning electron microscope (FE-SEM) with energy dispersive spectroscopy (EDS) and orientation imaging microscopy (OIM)
- Various evaluation systems of high-temperature corrosion and oxidation resistance
- Various servohydraulic universal testing systems and creep test systems
- Various microscale and nanoscale indentation systems
- Various optical microscopes and image analysis systems

Contact: Prof. Kazuhiro Ogawa, Fracture & Reliability Research Institute, Tohoku University, Aoba 6-6-01, Aramaki, Aobaku, Sendai 980-8579, Japan; tel: +81-22-795-7542; fax: +81-22-795-7543; e-mail: kogawa@rift.mech.tohoku.ac.jp; web: http://www.rift.mech.tohoku.ac.jp

EPA Issues Final Air Emissions Standards for Plating and Polishing Area Sources

On July 1, 2008, the Environmental Protection Agency (EPA) published the final regulation for plating and polishing area sources in the Federal Register (73 Fed. Reg. 37728). The final rule, 40 CFR Part 63, Subpart WWWWWW, is effective immediately for new affected sources (i.e., those that begin operations on or after July 1, 2008). Existing plating and polishing operations must comply with the new regulatory requirements by July 1, 2010.

The Clean Air Act mandates that the EPA must promulgate standards to control the emissions of hazardous air pollutants (HAPs) from small or area sources. An area source is a facility that emits less than 10 tons per year of a single HAP or less than 25 tons per year of total HAPs. Under the terms of a court order, the EPA was required to issue area source emissions standards for plating and polishing operations by June 2008. The order also set a schedule for the EPA to issue standards for 54 other area source industry categories.

The plating and polishing processes that are subject to the plating and polishing area source rule are those ‘‘processes performed at an affected plating and polishing facility that uses or has the potential to emit’’ any compound of any of the following metal HAPs: cadmium, chromium, lead, manganese, and nickel. This includes electrolytic and nonelectrolytic plating and coating processes (e.g., electroplating, conversion coating, sealing, and phosphating), electroforming, dry mechanical polishing, and thermal spray at approximately 2900 existing plating and polishing facilities.

The final rule does not apply to:

- Processes that are subject to the Chromium MACT standard (40 CFR Part 63, Subpart N)
- Processes that use cadmium, chromium, lead, and nickel in concentrations of less than 0.1 wt.% and manganese in concentrations of less than 1.0 wt.%
- Processes that use metals other than cadmium, chromium, lead, manganese, and nickel
- Tanks used strictly for educational purposes
- Thermal spraying processes to repair surfaces
- Dry mechanical polishing on a surface prior to plating

Applicable GACT Standards

The National Association for Surface Finishing (NASF) Government Relations (GR) program has been working closely with EPA officials by providing technical information on a variety of plating and polishing processes in developing the final rule. As a result of these efforts, the EPA did not establish emission limits for plating and polishing operations, but required plating and polishing facilities to follow management practices as the generally available control technology (GACT) standards. The management practices included using wetting agents in electroplating tanks, and the capture and control of emissions from thermal spraying and dry mechanical polishing.

According to the EPA, additional controls were not necessary because the industry had successfully reduced air emissions through the implementation of management practices and had reduced emissions by 95% since 1990. The EPA estimates the new standards will cost an average of $1100 per facility for the first 3 years.

In response to the industry’s comments, the EPA made some clarifications in the regulatory language of the final rule and provided a broader array of management practice options for facilities to implement to comply with the rule.

A copy of the final rule is available on the NASF website at www.nasf.org. Over the next several months, NASF will be working with EPA officials to develop compliance guidance for the final plating and polishing area source rule. If you have any questions or need additional information, please contact Christian Richter of Jeff Hannapel at crichter@thepolicygroup.com or jhannapel@thepolicygroup.com.

News from TSS

ASM Thermal Spray Society Issues Safety Guidelines on Personal Protective Equipment

A new safety document developed by the ASM Thermal Spray Society and available free of charge from the TSS website provides "Guidelines for the Use of Personal Protective Equipment in Thermal Spraying." "It is the belief of the Thermal Spray Society Safety Committee that every person is entitled to work in a safe and healthful environment," said committee chairman Gregory Wuest of Sulzer Metco (US), Inc. "People are the most important assets in the thermal spray community, and their health and safety are the community's greatest responsibility." These guidelines provide information consistent with the Occupational Safety and Health Administration's (OSHA) Personal Protective Equipment Standard (29 CFR 1910.132-138). All information is presented in the context of Thermal Spraying.

Personal protective equipment (PPE) is intended to protect individuals from the risk of injury by creating a barrier against workplace hazards. This document provides guidelines for establishing PPE programs, assessing hazards associated with thermal spray operations, and training workers about PPE, as well as guidelines for selecting, using, and maintaining PPE. Copies of the guidelines, designation SG003-03, may be downloaded free of charge from the Safety Guidelines collection provided by TSS at http://www.asminternational.org/TSS/safety.

The Safety Guidelines Committee comprises expertise from across the thermal spray community. Members include Richard Neiser, Sandia National Laboratories; Aaron Hall, Sandia National Laboratories; Lysa Russo, SUNY at Stony Brook; Daryl Crawmer, Thermal Spray Technologies, Inc.; Douglas Gifford, Praxair Surface Technologies, Inc.; Donna Guillen, Idaho National Engineering and Environmental Laboratories; and Larry Pollard, Progressive Technologies, Inc.

People in the News

Thermal Spray Hall of Fame Inducts Albert Kay and Robert Gage in 2008

The Thermal Spray Hall of Fame (TSHOF), established in 1993 by the Thermal Spray Society of ASM International, recognizes and honors outstanding leaders who have made significant contributions to the science, technology, practice, education, management, and advancement of thermal spray.

At the recent ITSC 2008 in Maastricht, The Netherlands, TSS President Peter Hanneforth presented the TSHOF award to Albert Kay, FASM, President of ASB Industries and TSS Past President. Kay was cited for excellence in recognizing and commercializing emerging technologies such as HVOF and cold spray and for his proactive role in ASM and TSS committees leading to the spread of thermal spray in many industries.

Also inducted in to the TSHOF (posthumously) was Robert M. Gage, who was R&D Manager, Union Carbide Corp., Linde Division (now Praxair). Gage was cited for the initial invention and development of transferred and nontransferred arc plasma spray torches and coatings using powder or liquid feedstock, and seminal developments in the use of gases to effect reactions during spraying.

Chris Berndt Appointed Director of IRIS

IRIS, formally known as Industrial Research Institute Swinburne and located at Swinburne University of Technology for some 15 years, has a long and respected standing within the manufacturing sector of Australia. IRIS is a University Tier 1 Research Centre that resides within the Faculty of Engineering and Industrial Sciences. It has a staff of approximately 45 researchers, of whom 25 are postgraduate students, as well as professors, postdoctoral fellows, research engineers, technicians, and administrative support staff.

Professor Chris Berndt joined IRIS in December of 2007 under a university initiative that was designed to map future needs for manufacturing expertise. He brings several decades of international experience to Australia, primarily within the context of the United States. He assumed the role of Director of IRIS earlier this year.

The focus areas of Intelligent Manufacturing Systems, Laser Technology, Micro Technology, and Robotics & Non Contact Inspection have been hallmarks of prior success for IRIS. These will be brought under the umbrella of "surface science and interface engineering" by Berndt, as well as expanded and enhanced by his expertise in thermal spray technologies and biomaterials.

IRIS is currently participating in the Defence Materials Technology Centre, the Advanced Manufacturing Cooperative Research Centre, the Automotive Cooperative Research Centre, CAST Cooperative Research Centre, and the Melbourne Centre for Nanofabrication, among other large collaborative activities.

From its establishment in 1908 in Melbourne's eastern suburb of Hawthorn, Swinburne University of Technology has grown from being a local provider of technical education into a multidisciplined, multicampus provider of higher education of international significance.

Contact: Swinburne; Web: www.swinburne.edu.au.

Richard Knight Receives Drexel University Myers Award for Distinguished Service

Auxiliary professor Dr. Richard Knight, immediate past president of the ASM Thermal Spray Society, is the 2007-2008 recipient of the Drexel University Harold M. Myers Award for Distinguished Service. This is the highest service award at Drexel presented to a faculty or staff member of the Drexel community who has gone above and beyond their position in service to the university community. The award, consisting of a certificate of recognition and $2000, was presented earlier this year.

Rick was recognized by colleagues and students as an integral member of department, college, and university life in the area of service. He was particularly cited for his position as the Department of Materials Science and Engineering Chemical Hygiene Officer, his work in helping to transition the Centralized Research Facility from a departmental to a college and university facility, and his role as faculty advisor to student groups.