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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 Avenue, Argonne, IL 60439; e-mail: JTST.Ilavsky@aps.gov.

Research in Advanced Joining Process Laboratory

Toyohashi University of Technology

Toyohashi city is located in the central part of Japan, close to Nagoya and easily accessible from both Tokyo and Osaka by Shinkansen Super Express. Toyohashi University of Technology, TUT, one of the newest national universities in Japan, was established in 1976 as a unique and novel concept, different from the conventional national universities. The purpose of TUT is to conduct research of advanced tech-nologies and to educate students in such technologies with an emphasis on graduate studies. The most skillful students from other national technical colleges in Japan form the majority of the students at TUT. The Department of Production Systems Engineering was also established in 1976. It encourages studies relevant to industrial problems in all aspects of production. Research extends from challenges in mechanical engineering and industrial engineering to cutting edge materials research. The department covers three major areas of study: materials, material processes, and systems engineering. Division of material processes covers forming, welding, and allied processes, as well as new manufacturing processes.

Prof. Masahiro Fukumoto's Research

Professor Masahiro Fukumoto joined the faculty of the Department of Production Systems Engineering in TUT as an Assistant Professor in June 1984, with interest in research on materials joining and welding, including the thermal spray process. Prof. Fukumoto received his Doctor's degree in 1984, from Keio University, Tokyo, Japan, where he studied the fatigue properties of heat-resistant steel materials at elevated temperatures. At TUT he achieved full professorship in 2002, and currently he is also Director of Research Center for Future Vehicle. From 1989 to 1990, he visited Prof. Boulos's laboratory at Sherbrooke University, Canada, where he studied mainly fabrication of composite coatings by plasma spraying. He established the Advanced Joining Process (AJP) laboratory at TUT in 1995. Dr. Toshiaki Yasui joined AJP as Associate Professor in 2002, coming from Osaka University, Japan, and Dr. Motohiro Yamada became Assistant Professor in 2006, after obtaining his Ph.D. degree from the AJP laboratory at TUT.

AJP laboratory carries out education and research in the fields of joining, welding, and surface modification processes. The laboratory has a regular research budget from Japanese government and is frequently supported by the Grant-in-Aid for Scientific Research of the Ministry of Education, Science, Culture, and Sports in Japan. Further, collaborative research with local companies on various up-to-date research problems brings in industrial funding as well.

Research History from 1984 through 2002

Selected scientific problems conducted in AJP laboratory by Prof. Fukumoto. In a historical order:

- Diffusion bonding of metal/ceramics bulk materials and nonlinear thermal stress analysis in metal/ceramic bonded structures
- Fabrication of functionally graded thermal sprayed coatings and evaluation of their thermal shock resistant properties
- Evaluation of abrasion, corrosion, and erosion behavior of thermal sprayed metallic/ceramic coating
- Diffusion bonding of YBCO superconductors
- Fabrication of fine, homogeneous metal/ceramic coating structures by thermal spraying of metal/ceramic mechanically alloyed (MA) composite powder
- Nonlinear, unsteady-state thermal stress analysis in metal/ceramic functionally graded thermal sprayed coatings
- Fabrication of Cu fine pattern less than 25 μm width on alumina plate by using microplasma torch
- Feasibility of $MoSi_2$ coatings by low-pressure plasma spraying
- Fabrication of nitride, carbide coatings by reactive RF plasma spraying
- Synthesis of diamond coating by thermal plasma chemical vapor deposition (CVD)
- Fabrication of high-performance SOFC anodes by thermal spraying of metal/ceramic MA composite powder
- Fabrication of IMC composite coatings by thermal spraying of metal/metal MA composite powder
- Fabrication of $FeSi_2$, SiGe thermoelectric coatings by thermal spraying of metal/metal MA composite powder
- Flattening behavior of thermal sprayed particles onto flat substrate surface
- Fabrication and evaluation of TiO_2 photocatalytic coating by HVOF spraying
- Rapid prototyping by means of thermal spraying
- Fabrication of nanostructured coating by HVOF spraying of nanostructured MA powder
- Joining between dissimilar metals by friction stirring

Fig. 1 Students on tour at AJP laboratory in the summer of 2006

Recent Research Topics in AJP Laboratory

AJP laboratory has now three permanent staff members and usually around 16 graduate and six under-graduate students, as shown in the photo taken during laboratory tour in summer 2006 (Fig. 1). Current research subjects can be divided into four major areas: (a) thermal spray, (b) cold spray and aerosol deposition, (c) solid-state joining of dissimilar materials by friction stirring, and (4) plasma processing. Among the surface modification process, thermal spray and cold spray are attractive and promising ways for fabrication of thick coatings. However, these processes are complicated and need to be established as more controllable and reliable. The aim of AJP laboratory is to establish controllability and reliability of these surface modification processes, as well as of a new solid-state friction stir-welding process. To achieve this goal, we have investigated deposition processes such as HVOF, APS, LPPS, and so forth, and evaluated them by in-flight particle measurement system (DPV2000), ultra-high-speed camera and video, optical emission spectroscopy system, and so forth. Further, coatings and welding specimens are analyzed by characterization techniques, such as SEM, TEM, AFM, XRD, XPS, and so forth. Recent research of surface modification processes is discussed in more detail.

Control of Thermal Spray Process by Analysis of Flattening Behavior of Individually Sprayed Particles

In order to establish the reliability and controllability of the thermal spray process and to obtain the desired coating properties, fundamental study on the flattening phenomenon of an individual particle on the flat substrate surface was undertaken. In particular, flattening

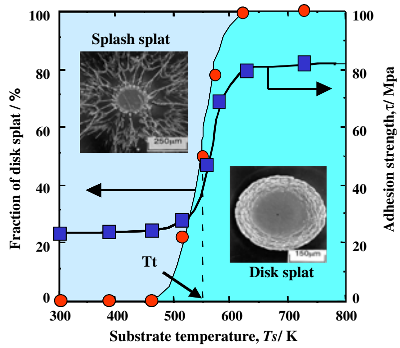

Fig. 2 Definition of transition temperature, Tt. Source: *Proc. of Int. Thermal Spray Conf.*, **95**, 1995, p 353-358; *Mater. Trans.*, **45**(6), 2004, p 1869-1873

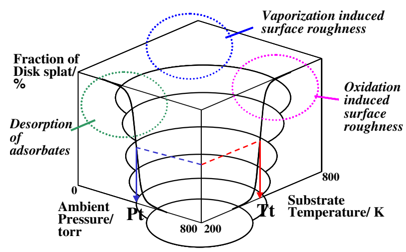

Fig. 3 Three-dimensional transition map. Source: *Pure Appl. Chem.*, 2005, **77**(2), p 429-442

behavior of both metallic and ceramic particles plasma sprayed onto the substrate surface was systematically investigated by changing the substrate temperature. A transition phenomenon from a splashing splat to a disk splat in the flattening pattern for each particle material was identified as shown in Fig. 2. Moreover, similar transition behavior in flattening related to changing the ambient pressure has been recognized by Prof. Fukumoto's group as well. Both transition temperature, Tt, and transition pressure, Pt, have been defined and proposed as critical information for the process control. Consequently, the relation between fraction of disk splat and both substrate temperature and ambient pressure was summarized as three-dimensional (3-D) transition maps for each studied material. The relationships between physical properties of the materials sprayed and character of these 3-D maps has been investigated (Fig. 3). The research has been supported by the Grant-in-Aid for Scientific Research of the Ministry of Education, Science, Culture and Sports in Japan.

Photocatalytic Coatings Manufactured by Thermal Spraying

Photocatalytic materials, such as TiO_2 and ZnO, are effective for the elimination of NO_x present in low concentration, but in large quantities, in natural atmosphere. Thermal spray process is feasible for manufacturing large area, thick coating on the surface of large structures. Especially, direct coating of TiO_2 by thermal spraying is a promising way to fabricate a practical coating on to the existing surface of the infrastructure. TiO_2 coatings manufactured by thermal spray process were investigated, and their NO_x elimination characteristics were evaluated (*Proc. Int. Conf. on Surface Modification Technologies*, 2000, p 51-56).

Metallic Glass Coating by Thermal Spraying

Metallic glasses are prom-ising materials due to their extremely high corrosion resistance—up to 100 times higher than that of the normal stainless steel. However, thermal spray-ing of metallic glasses induces thermal effect on the metallic glass during spraying, and this usually results in deterioration of the properties. Thus, highly controlled spray process is needed for formation of metallic glass coatings by thermal spray. The authors suc-cessfully manufactured metallic glass coatings by both highly controlled gas flame spray and HVOF spray processes. The corrosion properties of the coatings obtained were evaluated and usability of the coating has been verified (Fig. 4).

Thermal Spray with Mechanical Alloyed Powder

Major improvements in selected properties achieved by refining the feedstock grain size to nanocrystalline level has become lately of interest in the material science. In this study, the authors try to fabricate new materials, such as nanostructured NiAl, TiAl, Fe-Cr/TiB_2 coatings by thermal spraying of mechanically alloyed nanostructured powders (*Mater. Trans.*, 2003, **44**(12), p 2678-2687; *Mater. Trans.*, 2006, **47**(7), p 1717-1722). In particular, the authors successfully developed a TiAl coating for diamond polishing by using LPPS.

Reactive Plasma Spraying

Reactive plasma spraying is an attractive process to fabricate nonoxide ceramic coatings with high deposition rate. Reaction between feedstock powders (metal element) and surrounding active species in

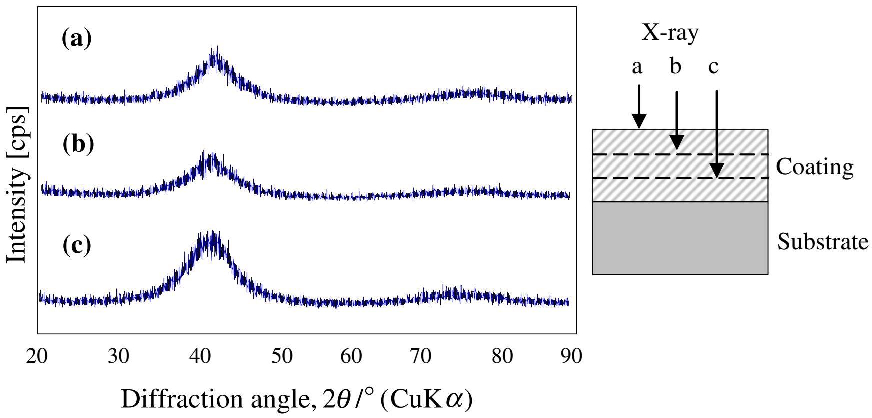

Fig. 4 X-ray diffraction spectrum for metallic glass coatings. Source: *Proc. ICCCA-2006*, 2006, p 6-9

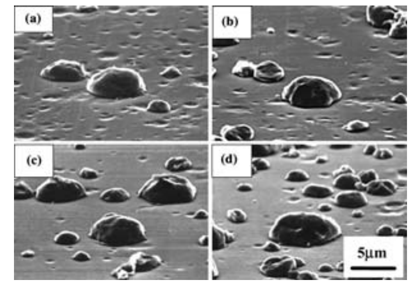

Fig. 7 Morphologies of collected particles. Gas pressure, 0.3 MPa; gas temperature, room temperature; particle size, 5 μm. Substrate temperature: (a) 373 K, (b) 473 K, (c) 573 K, and (d) 673 K

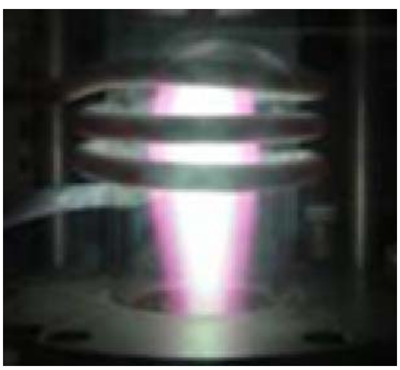

Fig. 5 Appearance of radiofrequency plasma. Source: *Mater. Trans.*, 2004, **45**(12), p 3304-3308; *Surf. Coat. Technol.*, 2006, **201**, p 1745-1751

the plasma enables fabrication of nonoxide ceramic coatings without thermal decomposition of nonoxide ceramic phase during spraying. Among the nonoxide ceramics, titanium nitride (TiN), titanium carbide (TiC), chromium nitride (CrN), silicon nitride (Si_3N_4), aluminum nitride (AlN), and iron nitride (Fe_4N) were successfully fabricated by reactive plasma spraying by using RF (radiofrequency) plasma spray apparatus (Fig. 5).

Atmospheric Pressure Microwave Plasma Spray

Conventional plasma spray systems, such as DC plasma and RF plasma spray, are difficult to operate at less than 1 kW power at atmospheric pressure condition. Microwaves easily generate high electric field and efficiently ignite discharge at atmospheric pressure condition under 1 kW power. Microwave

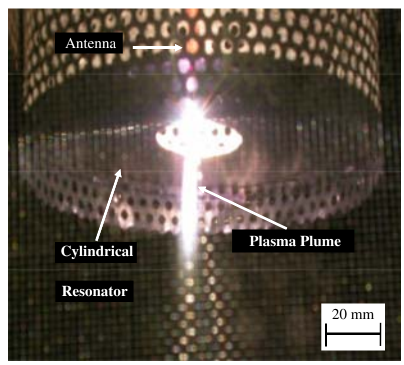

Fig. 6 Appearance of microwave plasma

discharge is characterized as an electrode-less discharge. Thus, the process can be operated with reactive gases, such as nitrogen and oxygen. The authors developed an atmospheric microwave plasma spray apparatus operating under 1 kW (Fig. 6). The maximum temperature of 5000 K and thermal efficiency of 16% were obtained at 20 L/min of argon gas. Plasma spraying of aluminum, copper, and hydroxyapatite powders was successfully achieved by this atmospheric pressure microwave plasma spraying (*Proc. of ATSC-2006*, 2006, p 62-63).

Cold Spray and Aerosol Deposition Process

Both cold spray and aerosol deposition are newly developed coating processes that can deposit both solid metallic and ceramic particles by high velocity. The deposit on a substrate is formed due to kinetic energy of particles while keeping the substrate at low temperature. Although these are promising technologies for fabrication of high-quality metal and ceramic coatings, their deposition mechanisms have not been fully clarified yet. The particle deposition mechanism has been fundamentally described by investigating the deposition behavior of individual particles onto the substrate surface (Fig. 7). To perform this, inhouse developed spray equipment and operating systems were installed in the laboratory (*Proc. ATSC-2006*, 2006, p 85-86).

Others

TUT provides a special English curriculum for a Master's degree, in which foreign students can earn all credits in classes given in English language as well as perform their research activities—getting from entrance to graduation—without the need for mastering the Japanese language (see: http://www.tut.ac.jp/english/admission/master.html). For postdoctoral researchers, a JSPS scholarship can be available (see: http://www.jsps.go.jp/english/e-fellow/main_qa.htm). Both English-course students and JSPS postdoctoral researchers are welcomed at AJP laboratory.

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News from NASA

Marshall Space Flight Center Engineers Aiming for Engine Life Revolution

Marshall Space Flight Center engineers are heading to a crucial test stage for what is described as new component alloy combinations and innovative ceramic liner technologies, designed to extend engine life. Their evaluations are initially based on potential viability for use in reaction control system thrusters, although the development process could grow toward larger workhorse engines such as the J-2X, which is currently baselined on the upper stage of the Ares I Crew Launch Vehicle. Similar technology could impact the design of larger engine systems. These include innovative liquid oxygen/liquid-methane rockets now in development at Marshall and even the J-2X engines that will power the upper stages of the Ares launch vehicles. While reusability on the J-2X will not be a requirement—it could aid reliability and even reduce the weight of components. Such a technology could also prove to be vital in extending engine life on vehicles that will be tasked with long-haul exploration, which NASA is aiming for over the coming decades.

Currently the sustained heat from engine operation quickly wears out certain components, such as the injector system and the thrust chamber. To mitigate such issues, components are traditionally "bulked up," increasing both the thickness and mass, which in turn adds weight. Since 1999, Marshall engineers have been examining new materials and fabrication processes for resolving these issues, in order to deliver lightweight, long-lasting thrust chambers and injectors, designed to withstand higher temperatures and operate for longer periods of time. In their tests, they used reaction control system thrusters to test out the two-metal combination currently used on the RCS systems. The first, rhenium, is a "refractory" metal that can withstand sustained high temperatures much more effectively than conventional alloys. The second, iridium, protects against metallic oxidation, a common chemical breakdown process that can speed up engine deterioration over time. In their findings, the engineers concluded that the current fabrication of thrusters using these two metals produce a "less-than-optimum" strength and durability, noting that over time, the iridium protection diffuses away, exposing the rhenium and reducing the life of the thruster. They also observed that their test article failed to reach the ideal operating temperature margins of 2500 °C.

Aiming for solutions, NASA engineers started to test new fabricating options, which began back in August of this year. Two options showed promise, both involving the same metals, but applied using a different fabrication process. In the first, the iridium/rhenium liner is formed using a patented "electrodeposition" process called El-Form, in which a metal solution is introduced via electrical current to a material surface, leaving behind a thin, uniform liner coating—one hopefully more durable than materials bonded via vapor deposition. The second option is an innovative vacuum plasma spray process that transforms the material elements into "functional gradient materials," blended composites that smoothly transition at the molecular level from one material at one surface to another material at the opposite surface. This change in the way the components are fabricated eliminates the distinct bond joints between the material layers, thus creating an extremely strong and durable component. The next challenge was to address the necessary increase in temperature margins. The goal was to increase the tolerance margins for the required temperature of 2500 °C—which is required for future vehicle concepts.

This goal involved testing ways to combine the two fabrication processes and add a durable ceramic layer to the interior of the thruster. The iridium layer will still prevent oxidation, but adding the ceramic layer will help reach the heat tolerances required.

Achieving this higher temperature limit will provide a safer margin of error and longer life for existing thruster designs. It also will enable engineers to pursue new thruster designs and consider alternative propellant options, often supporting more powerful engines that can burn hotter and offer higher system performance. They will know if their concept works when they carry out the hotfire test next month. The hotfire will be conducted on a small thruster with the ceramic layer, increasing the temperature margin to demonstrate the durability of the new fabrication process and combination of materials. NASA engineers expect to present these results to fellow propulsion engineers next May in Colorado.

Adapted from article by Chris Bergin, published on http://www.nasaspaceflight.com/ on Nov 23, 2006.

News from ITSA

The International Thermal Spray Association at 2007 Fabtech International & AWS Welding Show in Chicago

The International Thermal Spray Association (ITSA) plans to host a Thermal Spray Pavilion at the 2007 Fabtech International & AWS Welding show in Nov 2007 at the McCormick Place in Chicago. The Pavilion will feature informative events and presentations as well as demonstrations on the benefits of the thermal spray technology. The FABTECH International & AWS Welding show is cosponsored by American Welding Society (AWS), Society for Manufacturing Engineers (SME), and Fabricators and Manufacturers Association (FMA) and attracts about 17,000 attendees annually. It is the largest event in North America dedicated to full spectrum of metal forming, fabricating, tube and pipe, and welding equipment and technology.

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2006 ASM Fellows from Thermal Spray Field

In 1969, ASM established the Fellow of the Society honor to provide recognition to members for their distinguished contributions to materials science and engineering and develop a broadly based forum of technical and professional leaders to serve as advisors to the Society. Following are the members recognized by their colleagues in 2006 in Thermal Spray Field.

Frank Hermanek

Frank Hermanek, Consultant, FJH and Associates, Indianapolis, IN. Hermanek's carrier in the thermal spray field spans more than 40 years and includes a number of publications, patents, and mainly successful novel applications of the technique close to his heart. He has guided the industrial development and application of thermal spray technology as a manager of various engineering groups at a number of companies, most notably, perhaps, in the gas turbine engine industry. He was the chair of the Awards committee for 9 years and originator of the Hall of Fame. He is also a member of various committees, Chair of the Glossary Committee as well as the primary author of the Glossary itself. Previously, Hermanek was very active in the AWS C2 Thermal Spray Committee and authored two chapters of the AWS Thermal Spray Handbook. Hermanek has left lasting footprints in our field that are difficult to enumerate.

His citation reads: "For long term activities in thermal spray, in particular the conceptualization and nurturing of the thermal spray glossary and the creation of the Thermal Spray Hall of Fame."

Christian Moreau

Dr. Christian Moreau, Group Leader, Surface Technologies, National Research Council Canada, Quebec, Canada. Moreau has an approximately 20-year-long, distinguished career at the National Research Council of Canada and in the field of thermal spraying in general. He is author of numerous high-quality publications in respected journals and holds seven patents on optical sensing techniques for thermal spray processes. He is currently Editor-in-Chief of the *JTST* and served also as co-editor of *Thermal Spray 2003, Proceedings of the International Thermal Spray Conference 2003*, guest editor of *JTST*, Vol 10 (No. 3) issue, and so forth. He has actively participated in ASM life by organizing or co-organizing conferences, sessions, workshops, and meetings over last 20 years. He was elected to Thermal Spray Society Board of Directors in 2006.

His citation reads: "In recognition of his invention and development of novel sensor technologies for thermal spray processes, and for strong support of ASM Thermal Spray conference activities."