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Center for Thermal Spray Research

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Stony Brook University

LINKING RESEARCH TO PRACTICE

Going Beyond the Surface

Message from the Director

I am pleased to introduce our 13th annual newsletter 'Going beyond the surface', providing a snap-shot of our technical accomplishments, industrial partnerships and personnel/alumni updates. As this newsletter goes to press, we are excited about the upcoming fall industrial consortium meeting due to be held at Mitsubishi Hitachi Power Systems USA at their Savannah Machinery Works location in Savannah GA. Mitsubishi Heavy Industries is a leading supplier of advanced energy systems. We are grateful to our hosts Maxim Konev and Andrew Hague for supporting this event.

Since 2010 we have rotated the fall consortium meeting around industrial partner sites around the country. This allows for more people not only from the specific host company to participate but also provide shorter travel opportunity around the host site. For instance, this meeting was targeted at the "industrial turbine belt" of southeast United States. Gas turbine coatings continue to be one of the most important application sectors for thermal spray. We look forward to presenting our developments and engaging in fruitful discussions to enhance thermal spray utilization in this important industrial sector.

This past year has been one of transitions. As it occurs every three to four years we undergo a change in the research group with graduation and gainful employment of our students. This past year saw four PhDs and two MS students graduate. Most of the graduates have found gainful employment in the thermal spray field and will continue to support our industry.

The Center continues to innovate in all aspects of materials and process technologies related to thermal spray. We have active efforts in high temperature ceramic coatings, damage tolerant surfaces and functional materials. Our partnership with Oak Ridge National Laboratory has allowed us to continue to advance our multilayer TBC work. During this current year, we are focusing on substrate geometry effects (concave and convex shapes) on TBC durability. A highlight of this work is presented in this newsletter.

Our efforts at understanding thermal spray remanufacturing of metallic structures inadvertently led us to reexamining adhesion of spray coatings and associated testing methods. The original remanufacturing work addressed load bearing capability of spray clad laminates. This study suggests that beyond the intrinsic strength of the sprayed layers, a key element of such load recovery coatings is the ability to transmit load across the coating-substrate interface which is connected to adhesion. We have now seen clear correlation between tensile measurements of spray coated laminates and the classic ASTM C633 data. This is also highlighted in this newsletter. This research has major implications as it points to a more robust and sophisticated way to interpret adhesion particularly in high velocity sprayed systems where the bond pull evaluation is not adequate.

Building on our prior work to harness microstructure design ideas from nature and to engineer damage tolerant coatings, the focus has shifted to critically examine fracture toughness and crack propagation resistance curves for sprayed ceramic coatings. As will be noted in this newsletter, we provide a framework to robustly measure toughness of spray coatings along with their sensitivities to processing and microstructure. This work will have implications in both materials and process selection for various applications.

Finally, following up on our report last year in the development of thermally sprayed thermoelectric materials, we have expanded our work to fabricate complex multilayer power harvesting devices with potential applications in waste heat recovery. Our initial work has been based on TiO_2 where through novel processing conditions, one can create sub-stoichiometric phases which provide duality in properties, namely Seebeck coefficient and electrical conductivity. Building on these advances, multilayer power harvesting modules have been prepared via an all plasma spray approach and tested with encouraging results.

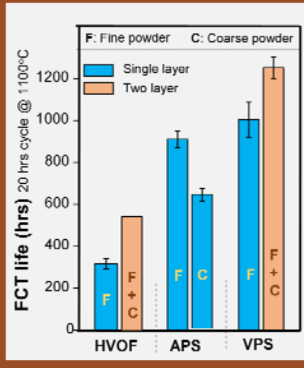
As always, I invite you to join the CTSR team to realize our common goal, to make thermal spray a household word.

- Sanjay Sampath, Director, CTSR

Bond Coat Processing Method on TBC Durability

As advanced gas turbines move to higher and higher operating temperatures with efforts to incorporate more complex low thermal conductivity top coat compositions, the need for improvements to bond coats continues to be importance particularly related to thermal barrier coating durability. As such bond coat compositions are becoming more complex incorporating reactive elements such as Re, Hf and Si. One can anticipate that these reactive elements by their very nature can be affected by processing. Given the many variants of thermal spray processes, which are equally suitable for bondcoat processing, the selection of an optimal one has always remained a challenge and of particular importance to emerging compositions. From processing point of view, three properties are desired to be in a bond coat, roughness, chemistry and mechanical strength, which are strongly dependent on the selection of process and the process parameters. For example, atmospheric plasma spray (APS) produces coatings with higher roughness and is economically attractive, but have a drawback of heavy oxidation of particles in-flight. On the other hand, processes such as high velocity oxy-fuel (HVOF) and vacuum plasma spray (VPS), offer to reduce the oxidation but lack in terms of coating roughness, and require a flash-coat with coarser powder to enhance the roughness.

Researchers at CTSR have conducted a process comparison study on a single bond coat material (NiCoCrAlHfSi) with two different powder size distributions. The TBC durability results (shown in the adjacent figure with identical top coats) suggest that enhancement in roughness using two-layer bond coat approach invariably shows significant improvement in the TBC durability. Furthermore although VPS remains the best performer attributed in part to minimum change in chemistry, the coatings with APS bond coats performed equally well in some cases despite extensive inflight oxidation. This finding suggests that understanding and predicting process-microstructure-performance relationships in TBCs continues to be a challenge.



There are many aspects of these bond coat microstructures that needs careful studies including coating chemistry, oxide content, stiffness, thermal expansion coefficient etc. Of importance is the stress evolution in the thermally grown oxide (TGO) during thermal cycling and its dependency on processing. Our ongoing efforts include the measurements and understanding of stress evolution on these bond coat with various degree of high temperature exposure. The stresses, which are primarily generated due to TGO at the bond coat and top coat interfaces, are being measured at Oak Ridge National Lab using photo-stimulated luminescence spectroscopy (PSLS). The preliminary measurements suggest not only a significant differences in the stresses on different bond coat architectures, but also points to a strong effect on the TGO stresses from the topcoat stiffness. These results are being examined in detail and will soon be reported in a publication.

Center for Thermal Spray Research
Department of Materials Science and Engineering
130 Heavy Engineering, Stony Brook University
Stony Brook, NY 11794-2275, USA

www.ctsr-sunysb.org
Ph: (631) 632-8480
Fax: (631) 632-7878
Email: sanjay.sampath@stonybrook.edu

Industrial Consortium News

The Consortium for Thermal Spray Technology hosted by CTSR continues to expand and provide benefits to industry across the supply chain. This year's addition to the group is Eutectic Castolin. This Swiss company has been a household name in surface engineering for many decades and is expanding its coating services through acquisitions. The Consortium is entering its 15th year starting from some 10 companies in 2002 to the present membership of 30 international companies. Each company contributes $12,500 annually as membership fees to the consortium enabling self-sustaining operations following the 11 year National Science Foundation Materials Research Center grant from 1996 to 2007.

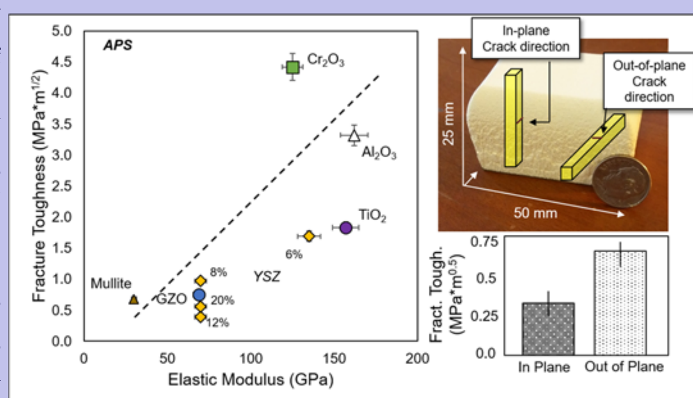
The spring consortium meeting held on Stony Brook University campus was attended by more than 90 participants from the member companies. Over the span of two-days, CTSR staff, students and collaborators presented updates on both science and technology as well as their value to industrial operations. This year's thematic contributions included industrial presentations in suspension plasma spray and in hot corrosion coatings. As noted earlier, since 2010 the fall meetings are rotated around OEM partner sites to facilitate interest within large equipment integrators. Fall 2016 meeting will be held on Nov.15th and 16th at the Savannah Machinery Works of Mitsubishi Hitachi Power Systems America. This meeting follows successful past events at Naval Research Lab (2010), GE Aviation Learning Center (2011), Boeing Museum of Flight (2012), Tinker AF Base in Oklahoma City (2013), Applied Materials, Santa Clara (2014) and Cummins Engine Co, Columbus, IN (2015). This allows larger participation of design and manufacturing engineers from these organizations which will be crucial to enhance thermal spray coating utilization in engineering systems. This particular meeting is targeted at the industrial turbine industry which is prevalent in America's south.

Consortium for Thermal Spray Technology

Consortium is operated by the Center for Thermal Spray Research at Stony Brook University

Fracture Toughness of Sprayed Ceramic Materials

Coupling mechanical, thermal, and electrical properties of various materials often requires deep searches into various literature sources and "connecting the dots" to establish a reliable material property. When making the jump to thermal spray, not only is such information difficult to find, the correlations in many cases do not follow. Given the importance of such data for sprayed materials, especially with their known sensitivity to chemistry and processing, developing both measurement methodology and establishing a database can be very useful to both industrial designers and manufacturing engineers. For example, the roles of processing and parametric effects can be realistically discerned for specific material groups (e.g. TBCs with varying compositions) or where entirely different groups of materials are being investigated.



The CTSR team has been at the forefront of such data generation efforts for complex thermal sprayed materials for more than two decades. Initial efforts aimed at measurement of thermal conductivity of porous ceramic coatings, following which efforts were concentrated to measure compliance of thermo-structural coatings using non-linear elastic property measurement. Recent efforts have focused on measuring fracture toughness and energy release rate of sprayed ceramic coatings and their sensitivities to processing and orientation. A large number of sprayed ceramic coatings have been tested using the single edge notch beam technique in the through thickness orientation and their toughness are shown in the following figure.

Since spray coatings can be anisotropic, it is of importance to see if there are differences in properties depending on sample test geometry. In a collaborative effort with GKN Aerospace of Sweden, orientation dependence of fracture toughness was conducted through the single edge notched beam technique. GKN provided an ultra-thick YSZ coating of ~ 25 mm thick and also sliced these coatings into vertical and horizontal test specimens allowing for robust and reliable measurement using the three-point bend toughness test. Data from this work is shown in the inset figure. The results confirm that spray coatings are indeed lower in toughness (20% or so) in the in-plane direction. Such information can be very useful to assess potential failure mechanisms in ceramic coating.

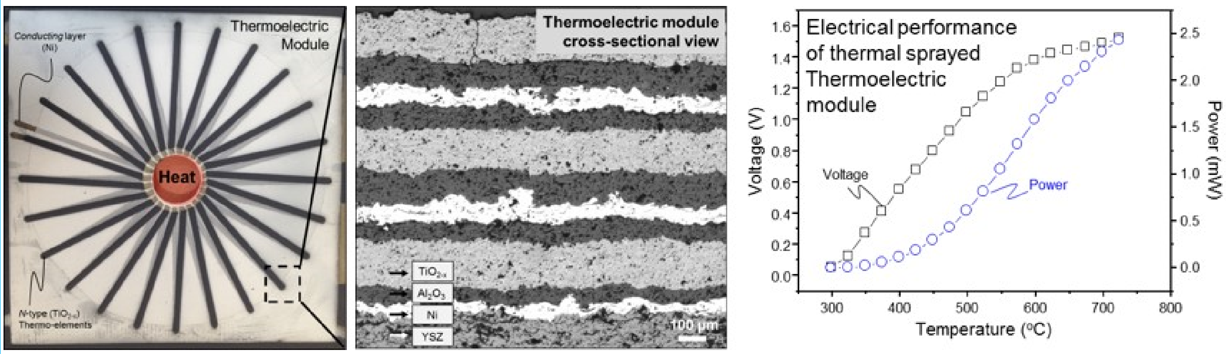
CTSR Student Road Trip, 2015

On their way to and from last year's consortium event at Cummins Engine Co. in Columbus, Indiana, the students and staff had the opportunity to visit a number of consortium member sites and see first-hand spray practices in use during their long drive from Stony Brook to Columbus. The team of some 12 road warriors also included several undergraduate students who got a chance to see 'gee-whiz' stuff like aero-engines on display at GE Learning Center to Diesel Engine assembly. Tours were graciously offered at Cincinnati Thermal Spray and Praxair Surface Technologies, as well as visit to the GE Aviation Learning Center and Cummins Engine Plant, which gave the group a glimpse at the broad processing arena – transitioning from powder manufacture up to coated engineered components and turbines. We are grateful to Tom Lewis (Praxair), Kirk Fick (Cincinnati Thermal Spray), Doug Konitzer (GE Aviation) and Roger England (Cummins) for their help organizing the tours.

Harnessing Waste Heat Through Novel Thermal Spray Based Device Engineering

Energy from heat generated through turbocharger, exhausts, power plants and steam pipes can be a significant energy source for waste heat conversion. Solid state waste-heat to power conversion based on thermoelectric devices are attractive to solution for such a strategy due to their passive operation, and simplicity of having no moving parts. A thermoelectric device relies on Seebeck effect that generates voltage in material in presence of a temperature gradient. Although many materials demonstrate Seebeck effect, the efficiency of power generation relies on a complex interplay among absolute temperature, temperature gradient, intrinsic Seebeck coefficient, electrical and thermal conductivities Often these properties do not scale in the same direction leading to challenges in efficient thermoelectric power generation in conventional materials and require unique structural characteristics.

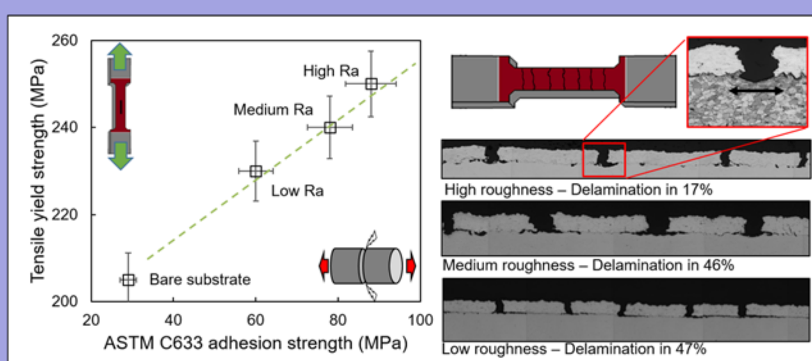
Recent work has shown through judicious process parametrization it is possible to produce a reasonable quality thermoelectric coating through controlling stoichiometry in TiO_2 (TiO_{2-x}) via atmospheric plasma spray. The APS TiO_{2-x} deposits has shown a thermoelectric figure-of-merit of 0.132 at operating temperatures of about 500 ^oC. Although as an absolute value this number is not that high, the material is inexpensive, easy to process and easy to scale into devices. A multilayer energy harvesting concept was devised and fabricated through selective masking and spraying of various functional elements. The produced devices have 13 layers of thermal sprays along with 24 individual elements in each layer resulting in a 72-junction thermoelectric device. The device produced a thermoelectric voltage and power when a thermal gradient between the center and edge was applied. Additional work is underway to not only scale these systems, but also incorporate more promising thermoelectric oxide compositions. This study shows potential to expand thermal spray into novel functional applications.



Understanding substrate-coating adhesion: Using the age old tensile test to compliment ASTM C633

Although industrially relevant, the interpretation of ASTM C633 can get be convoluted due to issues such as glue penetration into porous coatings or glue failures in high adhesion coatings (such as sprayed by HVOF). In these cases, additional methods need to be contemplated to better understand substrate-coating adhesion and provide a quantitative framework for description of the results.

Recent work at CTSR related to thermal spray remanufacturing concepts involving tensile testing of coated laminates indicated there are circumstances under which dense HVOF coatings can provide load bearing capability when applied to low carbon steel in structurally integrated coating systems. This capability for the coating to support load was based on two premises: the coating is dense, and the coating-substrate bonding is sufficiently strong to promote load transfer across the interface. In other words, well bonded, dense coatings support load in structural situations while low bond strength coatings do not provide load support irrespective of how dense the coating itself is.



This interesting finding suggested an alternate evaluation strategy, one in which the tensile test and the resultant load transfer attributes between the coating and substrate can be used to gage the adhesion strength without the need for secondary processes such as application of a glue. The tensile test is easier to perform and generally more reliable than glue based tests and can be used to obtain data for high velocity sprayed coatings where the bond strength can exceed the glue strength.

In a recent study, both bond strength via ASTM C633 and tensile strength measurements were conducted on substrates with three different roughness, low (~2 µm), medium (~6 µm) and high (~9 µm) with application of HVOF Ni coatings under identical process conditions. A comparison of the strength data of the coated laminate obtained by the tensile test with that of the ASTM C633 results are shown in the figure here. The results show a strong correlation between tensile strength of the composites and the adhesion strength. This new approach may be a rigorous alternative for dense, high bond strength coatings.

Additionally, the cohesion of the coating can be evaluated by looking at a function of the crack density or how the coating cracks within that structure. The figure on the right shows the effects of three different substrate roughness on the formation of cracks as the tensile test progresses. As expected as the roughness increases, the remaining bonded area during tensile testing is larger. For example, the high roughness coating only shows 17% delamination compared to over 40% for the low and medium roughness coatings at equivalent loads. This suggests that this tensile test approach provides multiple ways to confirm adhesion in spray coatings not readily available in ASTM C633. Work is underway to validate these findings across a spectrum of materials and processes.

People and Places

The last 12 months has seen many changes to the makeup of CTSR. Three PhD students have since graduated and moved on to various positions in research and industry. Dr. SuJung Han now has a position at General Motors Power Train in Pontiac, MI. Dr. Andrew Vackel is at Sandia National Laboratory in a post-doctoral position, and Dr. Vaishak Viswanathan joined Praxair Surface Technologies, in Indianapolis, IN this past summer. Additionally, we had two master's students graduate, Amey Mohite is now at GE Energy in Greenville, SC and Michael Resnick is working nearby at ReliaCoat Technologies, in Setauket, NY. Undergraduate student Olivia Higgins completed a summer internship at GE Energy in Greenville, SC and back working in the Center.

CTSR PhD student Gregory Smith was chosen to serve as a student board member on the ASM Thermal Spray Society Board for the year 2016 to 2017. Greg also received the 2015-2016 ITSA Scholarship. Hot off the press, Prof. Sampath just received notification that he is the recipient of the prestigious TMS Application to Practice Award for 2017. This singular honor is given out to individuals who have successfully transitioned academic research ideas to industrial practice.

CTSR Alumni reunion was held in conjunction with the ITSC 2016 in Shanghai bringing together graduates who are currently living and working in Asia and continuing to contribute to the thermal spray field

CTSR Celebrates 20 years as a National Center of Excellence

In 2016 CTSR team celebrated 20 years of operation as a National Center of Excellence. Although thermal spray at Stony Brook goes back to the 1990s, CTSR won the prestigious Materials Research Science and Engineering Center award from the National Science Foundation during the fall of 1996. This provided over $10M in fundamental research funds to CTSR to bring advanced materials science to thermal spray technology. The Consortium evolved as a mechanism to continue Center support beyond the NSF term. During the spring consortium meeting, retrospective presentations were included by Profs. Herman and Sampath to show case the Center accomplishments over the last year including major milestones in research and knowledge transfer.

Alumni Focus: Dr. Rogerio S. Lima

In this newsletter, we are pleased to recognize, Dr. Rogerio S. Lima of the National Research Council of Canada (NRC). Rogerio is a native of Brazil and came to Stony Brook after completing his Bachelors degree in physics and a MSc degree in Materials Science from Federal University of Rio Grande do Sul. Rogerio joined the Center for Thermal Spray Research in January of 1998 to pursue his Ph.D. under the mentoring of Dr. Chris Berndt. During his Ph.D. at Stony Brook, he was able work on the development of thermal barrier coatings (TBCs) engineered from nanostructured agglomerated powders. The objective of this was work was to understand the effect of embedding semi-molten nano-agglomerated particles in the TBC microstructure with its mechanical behaviour. That was as a novelty and many of his Ph.D. papers are still being cited today. In addition, while as Ph.D. student, he had the opportunity to work in parallel projects that improved his experience and view of thermal spray. As an example, Rogerio spent 4 months at ASB industries during the early days of cold spray technology. He was also involved in the National Science Foundation Center Materials Research Science and Engineering Center activities during this period and led many of the outreach activities to middle and high school children promoting thermal spray and materials technology. As a student Rogerio was an active participant at the thermal spray conferences and this inculcated his interests in not only being a researcher but also someone who is constantly promoting virtues of thermal spray technology to both industry and to other disciplines.

After graduating in May 2001, Rogerio joined the Thermal Spray Team of the NRC in June of the same year where Rogerio was able to continue his thermal spray adventure. NRC gave him opportunities to be part of a large and integrated thermal spray team and had the chance to once again be exposed to multiple projects, process technologies and industrial interactions. He was fortunate to see the beginning stages of the development of suspension plasma spray (SPS) processing, to work on the complexity of environmental barrier coatings (EBCs) and dealing the "big challenges" of ID-HVOF spraying. His PhD experiences in both TBCs and cold spray were valuable to him especially, as the latter became a major activity within NRC in the last 10 years. After 15 years at the NRC, he achieved the position of Senior Research Officer, contributing to expertise is the R&D of aerospace thermal spray coatings (turbines and landing gears). Although his NRC position requires an important amount of time on planning and management, Rogerio loves to be in the trenches as he noted *"I may have a Ph.D., but deep down I consider myself as a job shop floor engineer, solving practical problems with the technicians at the spray booth. Someone who likes to use high-tech equipment, but at the same time an 'old school' who uses his eyes and ears to analyse the behaviour of the torch"*.

Notable is Rogerio's intense commitment to the field of thermal spray. He a tireless contributor through not only his publications and presentations (he has over 60 papers which have been cited over 1800 times), Rogerio plays a leadership role in the ASM thermal spray society. He was a lead or co-editor to various thermal spray conference proceedings and a coeditor some 9 special J.Thermal Spray Technology volumes and organizer of many symposia including a major surface engineering conference in Brazil in 2010.

Rogerio continues to a friend of Stony Brook. He maintains a strong intellectual and personal relationship with his mentor Chris Berndt, even after Chris moved to Australia. He cherishes his friendship with his classmates and successors at Stony Brook and has been a regular participant at the Center reunions both on site and during international conferences. He is incredibly responsive to requests from current Center students and is a cheer leader to them. We at Stony Brook are very proud of his accomplishments and look forward to seeing grow and contribute to the field of thermal spraying.