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Stony Brook University

Center for Thermal Spray Research

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Linking Research to practice

Going Beyond the Surface

Message from the Director

I am pleased to introduce our annual newsletter "Going Beyond the Surface", highlighting our scientific and technical achievements, industrial interactions, and personnel/alumni updates. As I write this newsletter, we are gearing up for our Fall Consortium Meeting which will be hosted by our colleagues at Caterpillar Inc. in Peoria, Illinois. We are grateful to Dan Sordelet and Andrew Steinmetz for their leadership in organizing this. Fall meetings allow topical discussions in areas relevant to a major OEM. This year's theme will address diesel engine coatings, remanufacturing, and structurally integrated coatings as highlights, in addition to reporting general progress in Center research. These consortium "road shows" also allows exposure of thermal spray science and technology to a broader group of engineers involved in the host companies. We look forward to welcoming the consortium group to Peoria IL in mid-November.

The CTSR team continues to push the science and innovation agenda. Our advanced TBC research has focused on bond coat processing, geometry effects, multilayers, and CMAS effects on different TBC microstructures. To establish robust correlations our research has focused on microstructural pedigree and robustness enabled through advanced processing protocols. This allows identification of key structure-property attributes that govern the various failures.

Working closely with US Army Tank Automotive Research Center in Michigan, CTSR students have developed thermal management coatings for application on diesel engine piston crowns. This work involves material development, thermal property measurements, spray optimization on complex piston geometries, followed by engine testing at Army. Recent engine results are encouraging and point towards pathways to develop coating solutions for this application.

Our work on thermoelectric waste heat harvesting is also yielding positive dividends. Following our successful work with plasma spray synthesized sub-stoichiometric TiO_2, we have expanded to other oxides and will report on our recent success with Calcium cobaltate.

In the arena of environmental barrier coatings development, our work has focused on processing science of complex silicates. These materials are prone to stoichiometry shifts through silica losses and easy glass formation which affects the microstructural integrity. Through careful phase analysis, we have identified the key embodiments that enable a robust/functional coating.

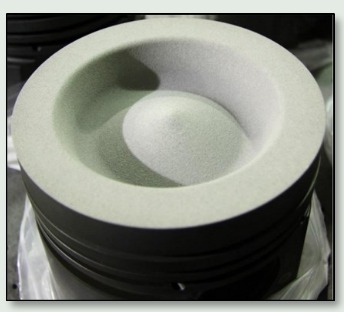
We have also worked aggressively on property measurements of coatings. Notably fracture toughness of sprayed ceramics through a variety of techniques probing microstructure and anisotropy. These techniques are easily translatable to industrial testing and incorporation into coating design. Industry is already adopting some of these methods in their day to day practice.

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

Diesel Engine Thermal Management Updates

More than 40 years have passed since the beginning of the Cummins-TACOM adiabatic engine program, which demarcates the introduction of coatings to thermal management in diesel engines. While these and many subsequent works attempted to use thick (on the order of 1mm or greater) thermal barriers made from various forms of stabilized zirconia to increase combustion temperatures and reduce the effective heat flux through engine wall components, many years of research and development have shown that intrinsic aspects of periodic combustion are detrimental to this approach. Despite these decade-old limitations, this field has seen renewed interest with the introduction of new and exciting insulation strategies and the potential to turn these previous limitations into benefits using alternative fuels.



For the same ease of refractory processing, scalability of manufacture, and process-driven control of material properties that researchers turned to in producing thick TBC's, researchers in the automotive industry are again turning towards thermal spray to produce thin thermal swing insulation coatings. The idea behind these thermal swing coatings is simple; wall temperatures should closely match gas temperatures at every point during the combustion cycle.

This will reduce heat flux by minimizing the gas-wall thermal gradient in combination with minimizing conducted heat, rather than simply reducing the TBC thermal conductivity. This also works to ensure that the wall temperatures do not rise to the point that they inhibit engine performance by heating incoming gasses and reducing volumetric efficiency. Interestingly, contemporary reports of mechanical failures in these studies are also abundant, despite being easily overcome in other fields through robust process controls and consideration of thermal and residual strain.

Research is currently underway at CTSR, through sponsorship and collaboration with the US Army's Tank and Automotive Research and Development Center (TARDEC), to identify optimal materials and coatings to best facilitate this behavior while maintaining sufficient traditional insulation. The physics of this define an ideal material to have minimum thermal conductivity and maximum diffusivity, leading to minimum density and heat capacity. Besides the breadth of thermophysical testing required to evaluate these properties, two prominent issues arise in this endeavor: the temperature dependence of these qualities and the static nature of standardized thermophysical testing itself. To accelerate this selection process a benchtop test was developed to directly measure a coatings thermal swing through at a variety of speeds and temperature ranges.

Ongoing work has focused on coating material and microstructure development at Stony Brook with instrumented engine testing at TARDEC. Initial engine test results point to a complex interplay of combustion gases and the coating surface and suggests benefits only for select microstructures and testing conditions. The team is encouraged with the initial results and have several on-going activities to harness the potential of this technology.

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Industrial Consortium News

The Consortium for Thermal Spray Technology hosted by CTSR continues to expand and provide benefits to our industry across the supply chain. This past year has seen the addition of two OEM members: Lam, a major manufacturer of semiconductor processing equipment and IHI–Japan are now part of the group. IHI is a leading manufacturer of Aviation turbine sub-systems and materials. This is a testament to the continued interest in the consortium program and in Stony Brook thermal spray activities. The Consortium is completing its 15th year starting from some 10 companies in 2002-03 to the present membership of 30 international companies.

The consortium is a pre-competitive research and knowledge transfer partnership between CTSR Research and Industrial Partners. The goal is to provide Methods, Measurements and Models that will allow industry to more effectively design and manufacture with thermal spray. Each company contributes $12,500 annually as membership fees to the consortium/ CTSR enabling self -sustaining operations following the 11 year National Science Foundation Materials Research Science and Engineering 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 coating design & manufacturing. Fall meetings are usually hosted by a member organization.

CTSR Student Road Trip to Member Sites

The 2017 Fall Consortium Meeting was hosted by Oak Ridge National Laboratory in Oak Ridge, Tennessee. Since 2010, Fall meetings are hosted by a member company or collaborating partner. Oak Ridge and CTSR have and continue to collaborate on several research projects coupling advanced expertise in testing and characterization of materials at Oak Ridge with processing science and synthesis at CTSR. This two day meeting was attended by over 70 consortium participants. The participants had the opportunity to visit the Manufacturing Demonstration Facility (MDF), which is a national resource on additive manufacturing technologies. Additionally, the National Transportation Research Center and the Spallation Neutron Source for characterizing materials in neutron beams, mechanical and corrosion science laboratories were visited. Presentations featured both updates on CTSR research as well as relevant Oak Ridge capabilities and demonstration of research synergies.

It was a highly successful event. We are grateful to Oak Ridge staff Edgar Lara-Curzio, Bruce Pint, Allen Haynes, Michael Lance, Wim Bloklund and others and especially to Christine Goudy who worked tirelessly to provide access to the participants to the national laboratory.

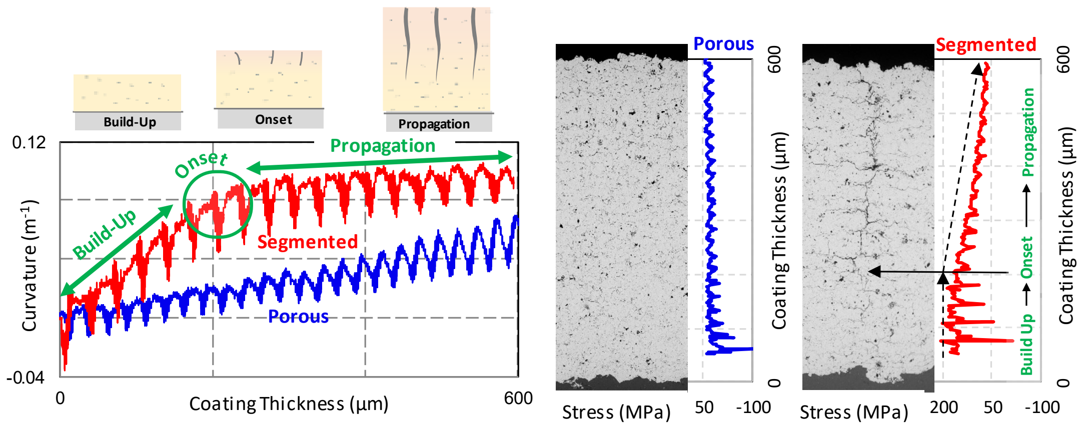
Typically CTSR staff, graduate students, and several undergraduates use these off-site events to conduct road trips allowing a large group of young participants to visit these unique facilities and even consortium member sites. Pictured is the attendees of the Fall Consortium at Oak Ridge's High Temperature Materials Laboratory. We expect to continue this tradition.

Edward Gildersleeve wins Oerlikon Metco Young Professionals Award

CTSR PhD student Edward Gildersleeve won the 2018 Oerlikon Metco Young Professionals Award at the International Thermal Spray Conference. The competition engages about a dozen international students and scientists engaged in thermal spray research in a five-minute presentation session at ITSC. The participants are judged by distinguished group of academic and industrial panelists who grade the performance on several metrics including intellectual depth, presentation style and communication. Edward's presentation was titled 'Process-Property Relationships of YSZ and GDZ Air Plasma Sprayed Thermal Barrier Systems Regarding CMAS Attack'. Pictured is Ed receiving the award from Dr. Richard Schmid CTO of Oerlikon Metco. The award carries a $1000 cash prize and a trip to any Oerlikon Metco facility in the world. Edward plans to visit Oerlikon's facilities in Switzerland in coming months. Congratulations Edward.

Segmentation Crack Formation Dynamics

Segmentation cracked or the so-called *Dense Vertically Cracked* (DVC) Thermal Barrier Coatings produced by Air Plasma Spray have been successfully used in gas turbine engines for more than two decades. DVCs have important attributes such as high in-plane strain tolerance, limited microstructural changes during service, and significantly enhanced fracture toughness, all of which impart enhanced durability. The formation and control of such cracked coatings occurs at special regimes of processing involving high plasma power and small particle size to produce high coating density along with increased deposition temperatures in excess of 500°C that allow generation and control of crack patterns. The formation dynamics and the underlying mechanisms remain unresolved. However, recent studies using *in-situ* beam curvature monitoring during deposition provides interesting observations. In the figures below, the curvature evolution of segmented and porous coatings are compared. One can note that the segmented coatings show a sharp change in the curvature beyond a certain thickness. Converting the curvature into quenching stresses is also described in adjacent figures and one can observe that the onset of cracking can be clearly related to the curvature change and reduction in quenching stress evolution. These results suggests that crack initiation occurs sometime during deposition and once initiated, the propagation follows in the successive layers over the pre-formed crack. The mechanism is still under more detailed investigation but these measurements provide insights. The data shown below is for 7YSZ although similar observations have been made for other ceramics including GZO, Yttria, and Titania.

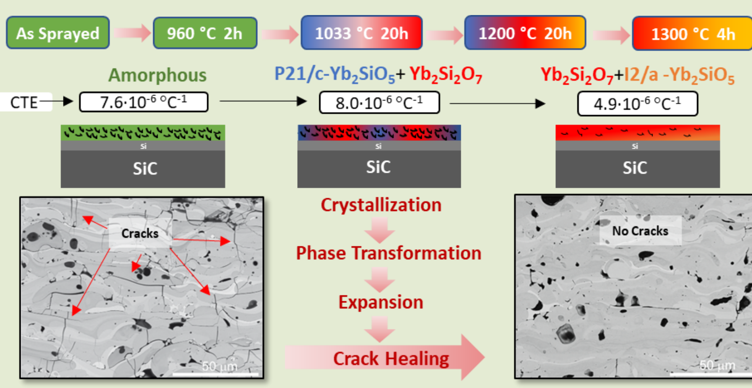


Processing Effects on EBC Phase Evolution

Rare earth silicates, notably Ytterbium Disilicate ($Yb_2Si_2O_7$) is being developed as environmental barrier coatings (EBCs) on SiC/SiC ceramic matrix composites to protect against water vapor attack and associated SiO_2 volatilization and coating recession. Since EBC compositions must fulfil a litany of requirements, including similarities in thermal expansion coefficient with the composite substrate, phase and chemical stability in combustion environments, processing of these silicate materials via plasma spray is a challenge. $Yb_2Si_2O_7$ is a line compound and any deviation from stoichiometry can result in multiphase coatings.

Unfortunately, as-sprayed Yb-silicate coatings are mainly amorphous, associated with the rapid solidification of splats. Obtaining as-sprayed crystalline Yb-silicate coatings require unique modifications to the process, such as plasma spraying on substrates kept inside furnaces. This approach, while effective, can be considered impractical for industrial applications where the size and shape of real components may limit this as a cost-effective option.

CTSR researchers have systematically studied the phase evolution and thermal properties of APS $Yb_2Si_2O_7$.



Through deliberate variations in processing conditions, coatings with slight to significant silica loss were produced. Silica loss increases with increasing plasma thermal energy and H_2 content. The as-deposited coatings are predominantly amorphous when generated at high plasma enthalpy. However, at milder spray conditions, a mixture of molten and unmolten splats are interspersed as amorphous and crystalline phases.

Research has further brought light to understand the crystallization dynamics of the coatings and the importance of different silicate content. For instance, coatings with silica loss show the presence of the Ytterbium Monisilicate (Yb_2SiO_5) phase during the crystallization and phase evolution process, leading to higher thermal expansion coefficient and a permanent expansion after thermal treatment. On a constrained situation this two-phase mixture when fully evolved can heal cracks resulting in an improved coating for durability. The illustration below describes the phase evolution in this system.

Work on thermal cycling with and without moisture exposure is underway.

In Memoriam: Dr. Rajan Bamola

We are deeply saddened by the sudden passing of CTSR Alumni and Colleague Dr. Rajan Bamola, President of Surface Modification Systems. Raj has had a long association with Stony Brook starting as an undergraduate in the early 1980s following which he stayed on to complete his Master's and PhD work. He initially worked with the late Prof. Les Seigle in the area of diffusion coatings and migrated to thermal spray, completing his PhD under the supervision of Prof. Herman in 1989 on the topic of vacuum plasma sprayed zirconium metal for corrosion protection. He moved west after graduation with a stint at Turbine Metal Technologies in Houston where he became VP within a few years. Following this, he continued west to California initially as a senior engineer at Bender Machine Company before venturing out as an entrepreneur.

Raj founded Surface Modification Systems (SMS) in his garage in 1993. Here, he brought together the two areas of coatings that he learned at Stony Brook: diffusion coatings and thermal spray coatings. This unique combination of technologies offered a one-stop-shop to many industries and led to Raj's great success through SMS. Through the 1990s SMS gained traction in the oil and gas industries treating stage sleeves and pump bearings, impellers and bowls for severe environment applications. The success continued in the 2000s with expansion into a 40,000 square foot facility in Santa Fe springs and an expanded market with big name Oil and Gas companies. Raj also pushed diversification of the SMS business into automotive, photovoltaics, electronics and space industries. SMS continues to be a thriving coating business based in southern California, carrying on Raj's legacy.

Raj was not only a successful businessman but also a hands-on coating practitioner. He personally built and maintained much of the processing equipment and also operated them for the company. He led the charge on challenging projects and was a innovator in bringing new materials and process technologies to the marketplace. Raj always had fond memories of Stony Brook and participated in CTSR through membership in consortium and also providing guidance to current students. He was always generous at conferences taking out CTSR researchers to dinners and reminiscing about the "good old days". Raj's heart was always in the Fiji Islands which is where he was born. He planned to return after retirement and even started building his future home before his untimely demise. He was truly a one-of-a-kind and will be missed. Raj is survived by his mother, father, two sisters, wife and two young daughters. Stony Brook and CTSR is proud to have had Raj as its distinguished alumni.

Alumni Focus: Joshua Margolies

In this newsletter, we are pleased to recognize Joshua Margolies of GE Power, Schenectady, NY. Josh completed his Bachelor's and Master's degrees from Stony Brook in 1998. Josh joined the CTSR group as an undergraduate researcher. As he was embarking on his Master's research, CTSR received word of an exciting donation of a $3M vacuum RF plasma spray system from GE Aviation in Lynn, MA. Josh led the extraordinary effort of spending 2 weeks with three other undergraduates dismantling the system in Lynn, labeling and tagging over 1000 wires and pipe connections, helping riggers bring it to Stony Brook, and then setting it up in the basement laboratory. He then had the system reconnected and functional within six months all on his own. This legendary accomplishment is still talked about in the Center today as an inspiration to young students and staff.

Following his MS thesis, Josh continued to stay at CTSR as a staff member and was involved in a number of innovative projects both with RF technology and other thermal spray techniques. Working closely with chemistry, Josh was the first to conduct precursor plasma spraying (now called solution precursor plasma spraying), wherein chemical precursors of inorganic oxides were injected in liquid form through the core of the axial induction plasma. The initial focus was on phosphoric materials, but spread to other complex oxides. He synthesized high surface area reactive materials, powder spherodization, etc. His most significant achievement was gas phase synthesis of Boron and carbon-doped boron nanoparticles using induction plasma. He designed the collector for these highly sensitive particles. This technology was adopted by Specialty Materials as feedstock for fabrication of MgB2 superconductors. He was instrumental in developing fine feature deposition technology under a major DARPA program and led the effort at setting up a one-of-a-kind thermal spray printing technology at Stony Brook. Josh's footprints continue to be seen everyday in many of our activities at CTSR.

GE Power had their eyes on Josh for a few years. As soon he was ready for greener pastures, he was recruited by GE and moved to Schenectady in 2005. At GE he contributed to many aspects of thermal spray technology, from bond coats to TBC fabrication on components. His recent leadership efforts have been in Environmental Barrier Coatings for Ceramic composites.

He was responsible for coating a complete set of composite shrouds that have now been in operation in a commercial power plant. He also performed multiple field demonstrations on low thermal conductivity TBCs. He continues to be a key player in the coatings team involved in TBC, EBC and processing technologies. He has 12 patents to his credit and was the recipient of GE's *Outstanding Technical Achievement Award* for Enabling Higher Efficiency through Low K Thermal Spray". He was recently promoted to Technical Leader in GE Power's Materials and Process Engineering Group.

He continues to interact with current Stony Brook students, providing them insights from his wealth of application experience and industrial knowledge. We at Stony Brook are very proud of his accomplishments and look forward to seeing him grow and contribute to the field of thermal spraying. Josh lives in Niskayuna NY with his wife Kendell and his children Jillian and Shaun. Jillian is a freshman at University at Buffalo, Shaun is a sophomore in high school.