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Center for Thermal Spray Research

Stony Brook University

www.ctsr-sunysb.org

Linking Research to Practice

Going Beyond the Surface

Message from the Director

I am pleased to introduce our annual newsletter "Going Beyond the Surface". 2021 was another challenging year due to Covid and it appears that Covid will continue to linger and affect our lives in the foreseeable future. It is also encouraging to see how well the world has adapted to this new way of living with an endemic virus. Despite challenges, the CTSR team has persevered and, in fact, thrived over the last year. The team made outstanding progress on many fronts in research and knowledge transfer. A number of high quality papers were published with more in the works. The laboratory has been working normally for the past year with appropriate care to ensure health and well-being.

The Consortium activities have continued successfully online. Similar to 2020, webinars have become the effective forum for communication. Sixteen webinars were conducted in 2021 covering topics from tutorial talks to research developments. These have been well received by the community. Of course, we miss the in-person sessions, especially the off-line conversations over coffee/lunches which allow people to get to know each other in a more personal way. We hope that we can revert to at least one in person event in 2022 and reconnect.

The Center research continues to push both a fundamental agenda and expanding thermal spray opportunities. Our work with the US Army on thermal management coatings for diesel engines is now in its 5th year. Some 20 engine tests have been completed with promises and challenges. Notable is that coatings are durable but the thermal benefits are not yet completely clarified. We expect continued activities in 2022-23 to shed further light into the opportunity. On the fundamental side, we have done a deep dive on the tensile adhesion test and unraveled its capabilities and challenges. This led some 6 of the webinars presented in the past 2 years and a major publication is in preparation. Our work on TBCs and EBCs have continued. In the TBC arena, we now have compelling theoretical basis to describe how *vertical (segmentation) cracks* form in plasma spray. In the area of hard coatings, much of the emphasis has focused on HVOF process dynamics especially relating to torch combustion pressures and oxy-fuel ratios. The goal is to produce process maps that can be linked both to properties and performance enabling linking manufacturing with design. *Oxidation, hot corrosion and aqueous corrosio*n are additional topics that have been examined both from fundamental and applications point of view. In the case of oxidation and hot corrosion, the temperature of interest is in the intermediate range of 500-800C where ferrous alloys suffer from significant degradation. In the case of aqueous corrosion both cemented carbide and metallic overlays (steels, Hastelloy's) have been carefully investigated examining process-property-performance correlations. Many of the developments have been presented to the community through consortium webinars or conference presentations.

This past year, CTSR has engaged in conversations with industry about the future of the technologies. A number of challenges have emerged in part due to covid related reorganizations. There has been a significant number of "retirees" from our industrial organizations with concomitant implications on corporate knowledge and experiences. Renewals are sought with new workforce in some cases and automation in others which has the expected growing pains. CTSR will continue to monitor the developments and attempt to push the frontier in both pedagogy and expanding application opportunities. We welcome dialogue with the membership in the months to come.

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

-Sanjay Sampath

CTSR Celebrates a milestone: 25 years as a Center of Excellence

Thermal spray research and education started in the late 1970s at Stony Brook when Prof. Herman along with his then graduate student the late Dr. Volker Wilms explored ways to rapidly quench oxides using plasma spray. As Prof. Herman describes it, it was love at first sight. The plasma spray process captivated the interests of students then, and the ones that followed later (including current director Prof. Sampath). During the early years, Prof. Herman and the group were engaged in topical projects related to thermal spray science or applications. In the early 1990s there was a realization that thermal spray required interdisciplinary thinking. This led to an intense effort by Profs. Herman, Berndt and Sampath to establish a National Center of Excellence through the National Science Foundation, Materials Research Science and Engineering Centers program. This highly competitive and prestigious grant resulted for a multistage competition and finally in 1996 the team was rewarded with an initial $4M, 4 year grant to pull together an inter disciplinary group of scientists with background in mechanics, thermal sciences, modeling, and chemists along with opportunities to engage with unique facilities within the National Laboratories. The team's premise was that thermal spray allows materials synthesized from extreme conditions with novel microstructures that allow important functionalities in engineering systems. The Center was extended for another 6 years with additional $6M in funding, following which the Center has been operating in a self-sustaining mode through the Consortium.

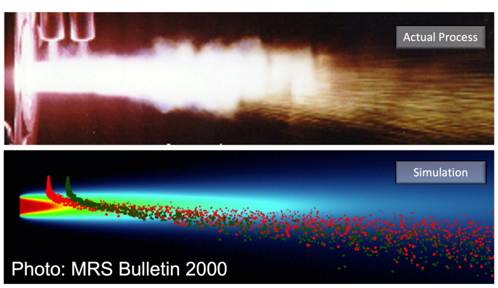

Photo: MRS Bulletin 2000

The Center's output has been significant. Some 50 PhD, 40 MS, 30 Post doctoral fellows and hundreds of undergraduates have been engaged in the program. Notable further is the recognition by the Materials community related to the virtues of thermal spray as a tool not only for applications but also an approach to study novel material formulations.

Notable further is that 2022 will represent the 20th year of the Consortium Partnership. A celebratory workshop is planned for the summer of 2022 coincident with a Consortium meeting.

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Industrial Consortium News And Updates

The Consortium for Thermal Spray Technology, hosted by the CTSR continues to expand and provide benefits to our industry across the supply chain. The Consortium is now starting its 20th year 2022, starting from some 10 companies in 2002-03 to the present membership of 30 leading international companies.

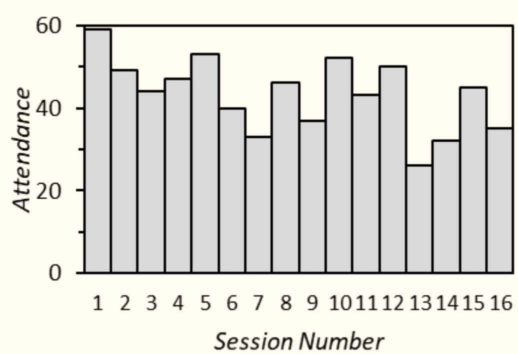
The Consortium is a pre-competitive research and knowledge transfer partnership between CTSR Researchers and Industrial Partners. The goal is to provide *Methods, Measurements, and Models* that will allow the industry to more effectively design and manufacture with Thermal Spray. Each company contributes $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. A large number of students have been exposed to thermal spray through the consortium.

While we did not have a face-to-face Consortium Meeting in 2020 and 2021, the meetings were kept ongoing through a virtual platform. These webinars touched hundreds of participants. We look forward and are hopeful to hosting a face-to-face meeting in 2022 with the members and continuing to find innovative and unique ways to implement the highly successful virtual platform in the future.

CTSR Consortium Webinars Update

Continuing the webinar based virtual meetings started in March of 2020, the CTSR Consortium Webinar Discussions hosted sixteen additional Zoom based meetings between April 1st and December 16th of 2021.

These discussions allowed the CTSR team to share recent developments in thermal spray technology along with ongoing work at the CTSR and topical reviews. Nearly 200 individual participants from 52 member companies and affiliated universities attended the 2021 CTSR Consortium webinar series with an average of 43 participants attending per session. These meetings were all successfully recorded and stored in a SharePoint location for Consortium Member access anytime from any device for post-meeting viewing and many participants avail this opportunity.

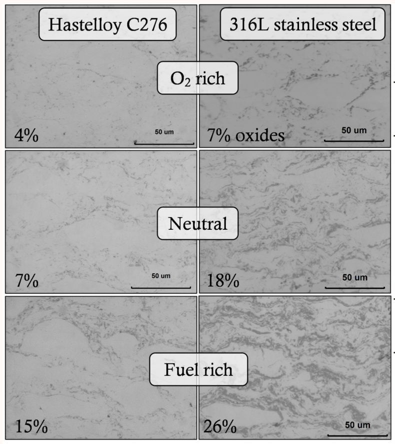


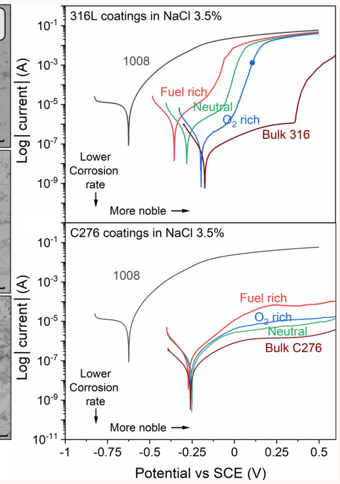
General review sessions were held covering topics ranging from thermal spray basics, specification for thermal spray coatings, process diagnostics, fundamental of coating adhesion, and splat formation. While focused topical session covered applications of thermal spray coatings ranging from corrosion protection, the use of cermets, TBCs, and oxidation barrier coatings.

Consortium 2021 Webinar Topics			
1: Thermal Spray Basics	2: Thermal Spray Process Dynamics and Diagnostics	3: Contemporary Understanding of Coating Adhesion	4: Understanding Thermal Spray Process and Coating Reliability
5: Factors Affecting the Corrosion of Thermal Spray Coatings in Aqueous Media	6: Contemporary Understanding of TBCs on Diesel Engines	7: Thermally Sprayed Cermets - A New Look at an Old Idea	8: Thermal Cyclic Testing of Thermal Barrier Coatings
9: Specifications in Thermal Spray	10: Thermal Spray - Knowns and Known-Unknowns	11: Implications of Flame Stoichiometry on HVOF Processing of Materials	12: Thermal Gradient Testing of Plasma Sprayed Thermal Barrier Coatings
13: Contemporary Understanding of the Tensile Adhesion Test	14: Thermal Spray Splat Formation	15: Oxidation of Alloys and Coatings under Isothermal and Impulse Heating	16: Elastic Measurements of Plasma Spray Refractory Metal Coatings

HVOF Metal Cladding for Corrosion Protection

Machinery/components operating in harsh corrosive environments are often manufactured of stainless steels and Hastelloy over mild steel, accounting for a high material cost. As an effort towards the development of cost-effective alternatives, an investigation on the corrosion performance of 316L stainless steel and C276 Hastalloy coatings processed by HVOF on mild steel substrates is being studied. Coatings were sprayed with different flame stoichiometries (oxygen rich, neutral, fuel rich) and the corrosion response studied in mild-harsh solutions, including deionized water, neutral(pH7) and acidic (pH4) salt (3.5wt% NaCl).



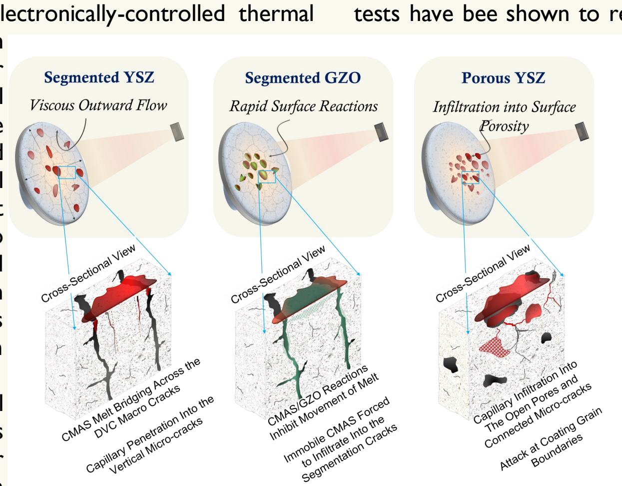


As shown in the inset, processing with fuel rich conditions resulted in a higher degree of inflight oxidation associated to a higher heat input. Nevertheless, in the corrosion tests carried out in deionized water, coatings performed similarly to one another. In fact, the corrosion performance of 316L stainless steel coatings was found to be equally good or superior to that of bulk stainless steel. This may be attributed to the presence of internal oxide lamellae resulting from oxidation.

In salt solution, however, differences start emerging. As conditions were shifted towards more fuel rich ones, 316 L stainless steel coatings develop more negative corrosion potentials, higher corrosion current densities, and pitting corrosion at more negative potentials, as results of a combination of higher pitting susceptibility (Cl- media) and processing induced oxidation, that causes Cr removal from solid solution leaving the oxide surroundings impoverished in Cr, and jeopardizing passivation. In contrast, coatings processed with the C276 feedstock showed a more robust performance with non-significant differences in corrosion and pitting potential, in addition to the development of low corrosion current and passivation for a wide range of potential. Results suggest that robust performance under corrosion can be obtained by means of HVOF cladding, with oxygen rich conditions giving overall better results.

Dynamic Interactions Between Molten CMAS and Multi-layer TBCs

The Center has been continuously working on developing its testing methodologies for Thermal and Environmental Barrier Coatings. Recently, the Center has built and developed an electronically-controlled thermal gradient cycling rig using an oxygen-propane burner torch. Simulative thermal gradient testing of these coatings is a growing field of study among the thermal spray community. To that effect, the Center has also developed a thermal gradient test which employs simultaneous injection of molten siliceous debris.



Using this test, novel single and multi-layer TBCs were evaluated for their resistance to molten CMAS. Three Plasma Sprayed architectures were tested: Porous 7YSZ, Segmented 7YSZ, and a multi-layered 7YSZ-GZO TBC (with a segmented GZO topmost layer). The coatings were surface-polished prior to testing.

From the test results, a unique response—different from what is conventionally observed in most CMAS testing—was observed. In some conventional CMAS tests, solid CMAS is applied to the surface of TBCs, and the whole system is put into a box furnace. These isothermal tests have bee shown to reveal that a TBCs resistance to CMAS is intrinsically related to their susceptibility to capillary infiltration of the melt.

However, these isothermal CMAS tests do not capture the complex interplay of mechanisms which can occur in a turbine engine environment. The CMAS thermal gradient test developed by the Center has been able to elucidate some of these mechanisms. Shown in the Figure is a pictographic summary of observations. Segmented coatings have a tendency to allow molten CMAS to be mobile, while porous coatings are more prone to infiltration into the interconnected porosity. Furthermore, the inclusion of CMAS-resistant GZO in this testing has shown that the rapid chemical interactions between CMAS and GZO inhibit melt mobility. A paper has been published on the topic

Awards and Honors

CTSR team continues to produce high quality publications as evidenced by its numerous best paper awards. The most recent award was received as a ***JTST Best Paper Honorable mention*** that resulted from the work done jointly between CTSR and US Army DEVCOM relating to the development of thermal swing coatings for diesel engines. The paper titled "***Thermal Swing Evaluation of Thermal Barrier Coatings for Diesel Engines***" is now in print in JTST and can be accessed online. Congratulations to the CTSR and Army teams.

Recent PhD graduate ***Dr. Edward Gildersleeve*** is one of the two CTSR alumni to receive the prestigious ***Alexander von Humboldt post-doctoral fellowship***. Edward will begin his fellowship in Germany under the guidance of ***Dr. Robert Vassen*** at the Forschungszentrun Jülich in Germany.

CTSR students continue to receive awards from the International Thermal Spray Association. This year's recipient is ***Emma Peleg***, a new joint PhD Student between CTSR and Sandia National Laboratories. Emma joins a long list of successful ITSA fellows since the 1980s, many of whom continue to be important members of the thermal spray community.

Mitchell Dorfman, an early alum from the Stony Brook thermal spray activities and a 42 year veteran at Oerlikon-Metco has announced his retirement from December 31, 2021. Mitch graduated with his MS in Materials from Stony Brook in the late 1970s. He worked with Prof. Herman and Prof. Clayton on Cavitation Erosion studies of coatings. Immediately upon graduation he went to work at then Metco-Perkin Elmer and stayed in that organization all these years.

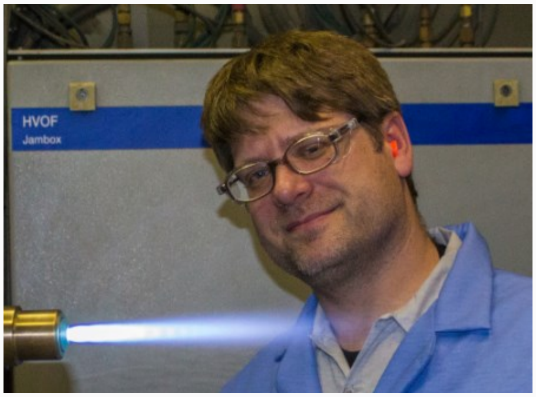
Mitch's sustained contributions to both industry and to the thermal spray community are well known. He was president of ASM TSS, recognized in the thermal spray hall-of-fame, and led many initiatives at the ITSC conferences. At the CTSR we always looked upon Mitch as a friend and mentor. He was very supportive of student research often providing support through materials and characterization, assistance and advise.

Mitch is a role model for someone who has stayed loyal to the industry, community all these years and has worked tirelessly to promote the technology. We wish Mitch all success in his golden years.

Alumni Focus: Jonathan Gutleber

In this issue of Going Beyond the Surface, we are pleased to introduce Jonathan Gutleber. Jon is currently a Senior Project Manager/Technical Expert within the Materials R&D group at Oerlikon Metco. Jon joined the thermal spray group in the mid 1990s working with Prof. Sampath in developing instrumentation for erosion testing of thermal spray coatings. As part of his senior design project, Jon spent a year designing, fabricating and validating a test rig that satisfied the ASTM G76 erosion test standard. This test is still being used today at CTSR some 25 years later.

Upon completing his Bachelor's degree in 1997, he continued for his MS thesis focusing on HVOF technology and (at the time) emerging in-flight particle diagnostics. One specific example of his work was examining the deposition of ceramic coatings using the HV-2000 HVOF torch. Jon's work in this area still stands out. It demonstrated it was feasible to deposit thin, dense high quality ceramics with excellent tribological and functional (dielectric) properties. This work subsequently led to almost a decade long collaboration with VTT Finland and several additional publications.



Following his MS, Jon stayed on at CTSR as a staff member supporting the then developing initiative on thermal spraying of electronics and sensors funded the through the major DARPA initiative under the Mesoscopic Integrated Conformal Electronics program. Concurrent to supporting the DARPA work, Jon also was a key contributor to the ONR nanostructured coatings program and in fact one of the initial evaluators of the early HVAF technology from Jim Browning commercialized by Praxair as JetStar. Through collaboration with University of Auckland in New Zealand, Jon's work showed that it was feasible to deposit carbides with minimal decarburization with HVAF technology. Much of modern HVAF technology implies this advantage.

The DARPA program led to the spin-off Mesoscribe Technologies to enable commercialization of the Direct Write Thermal Spray technology that emerged out of CTSR. Jon joined Mesoscribe in 2003 within a few months of its founding and spent 10 years as an engineer, a principal investigator and project manager. He was instrumental in developing many aspects of this emerging technology and pushed it through to commercial use where he developed sensors and processes for production.

In 2013, Jon joined Oerlikon-Metco (then Sulzer-Metco) as a senior project engineer, leading coating application development projects. His focus is in high velocity combustion processes and has pushed the boundaries of both materials and processes. Jon was recognized by Oerlikon as an emerging leader by being selected for the group's global Horizons development program in 2018. He has some 10 publications and 3 patents.

Over the years, Jon has remained a friend and resource to the CTSR team. He has made countless visits to the Center to help train new students and post-docs, participate in joint experiments, as well as hosted visits of students at Oerlikon. Generations of researchers have benefited from Jon's guidance and we expect these interactions to continue in the years to come.

Jon and his wife Samantha have two young boys and live on Long Island. They love the outdoors, enjoying hiking, snowboarding, travel and their dogs.