



LINKING RESEARCH TO PRACTICE

Message from the Director

I am pleased to introduce our 12th 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 Applied Materials in Silicon Valley, California. It is noteworthy that this meeting is being hosted by Applied Materials, the world's leading manufacturer of semi-conductor processing equipment, as it demonstrates not only their interest in thermal spray technology but to the need for continued industry-university research cooperation in emerging areas of thermal spray technology. We are grateful to Drs. Jennifer Sun, Yikai Chen and Om Nalamasu of Applied Materials for facilitating this opportunity. The meeting will provide an opportunity to introduce to a wider audience of materials specialist the capabilities of thermal spray technology.

This newsletter contains snap-shots of celebrations and sorrow. The Center mourns the loss of our dear colleague Prof. Richard Gambino. Dick was a world renowned materials scientist with expertise in electronic and magnetic materials and has brought novel ideas and applications to the thermal spray industry. A brief obituary about Dick, his contributions and his legacy is included in this newsletter.

This past summer, in conjunction with our spring consortium meeting, we had the opportunity to celebrate the 80th Birthday of our beloved colleague, CTSR founder, Prof. Herb Herman. CTSR alumni from the 1970s to present were in attendance and participated in a special symposium honoring

Prof. Herman.

The Center continues to make significant progress in research, knowledge transfer and human resource development. Breakthrough advances in multifunctional, multilayer thermal barrier coatings have been demonstrated incorporating novel coating designs based on new materials, advances in process engineering and performance assessment. Several papers have been published with additional work underway. A brief overview of the project is highlighted in this newsletter. Activities aimed at demonstrating the efficacy of *in-situ* load bearing repair of infrastructure steels is also showing very good promise. Optimized coatings are not only able to offer dimensional restoration but recover load bearing capability of parent metal both under static and fatigue loading. A field demonstration activity is being explored with New York State Department of Transportation. The implications of this work goes beyond infrastructure into the entire field of material reclamation and remanufacturing. Expanded industrial interactions have been initiated. We have also continued to expand the process-property assessments of functional oxides for applications in fuel cells, thermoelectrics and dielectrics. Finally, our work on hybrid composite (metal-polymer and ceramic-polymer) coatings harnessing biomimetic design strategies has shown significant progress.

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

Establishing process-property relations in functional oxides

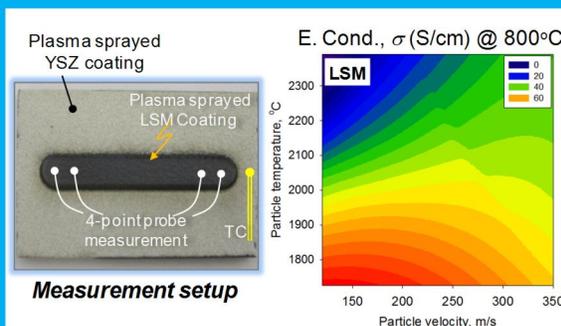
Thermal spray processes and coatings are now becoming main stream technologies for functional oxides. Functional oxides are materials that impart electrical, electronic, and sensory functions rather than just protection. For instance, oxide based electrical conductors are sought as high temperature interconnects in solid oxide fuel cells. Traditional approaches to characterizing thermal spray materials and coatings (microstructure, adhesion) as well as their process linkages (particle properties, spray environment) are not readily translatable to these applications. Through support from the National Science Foundation Partnership for Innovation program the CTSR team is developing a complete framework to enable expansion of thermal spray into the arena of thick film functional oxides.

In one part of this study, process diagnostics and mapping concepts were applied to two conductive oxide compositions of interest to the fuel cell community. Strontium doped Lanthanum Manganite ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, LSM) a rare earth based perovskite oxide and manganese cobalt spinel ($\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$,

MCO) a cubic composition. Plasma processing resulted in preferential loss of Mn and O in both materials which were linked to process temperatures and dwell time of the particles.

Oxygen recovery was possible upon low temperature annealing while Mn loss was irrecoverable. The results also showed that through judicious selection of an appropriate processing window it is feasible to limit/suppress Mn loss yielding deposits that have high degree of crystallinity, stoichiometry with reasonable electrical properties. LSM and

MCO coatings with conductivities of 55 and 40 S/cm respectively at 800C were achieved with excellent durability and protection to the metallic interconnect. The LSM results have been recently published in the Journal of Power Sources Vol259 (2014) 245. The MCO work is now being prepared for publication.



Going Beyond the Surface

Industrial Consortium News

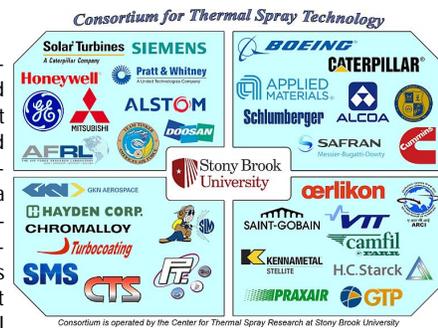
The Consortium for Thermal Spray Technology hosted by CTSR continues to expand and provide benefits to industry across the supply chain. Recent additions to the group includes Oil and Gas giant Schlumberger, Diesel Engine Manufacturer Cummins, Korea's leading heavy equipment manufacturer Doosan, thermal spray materials supplier HC Starck and spray coating applicator TurboCoating of the United Coating group. The Consortium is entering its 12th year starting from some 10 companies in 2002 to the present membership of 36 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 70 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. As noted earlier, since 2010 the fall meetings are rotated around OEM partner sites to facilitate interest within large

equipment integrators.

Fall 2014 meeting will be held on Nov.12th at the Applied Materials facility in Santa Clara California. This meeting follows successful past events at Naval

Research Lab (2010), GE Aviation Learning Center (2011), Boeing Museum of Flight (2012) and Tinker AF Base in Oklahoma city (2013). 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.

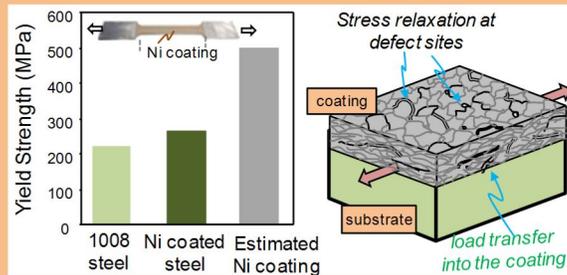


Spray-remanufactured steel shows improved mechanical properties than bulk metal

In the past newsletters, we have shown that engineered thermal spray coatings can impart enhanced structural functionality to reclaimed or remanufactured metallic components.

Ongoing studies into the loading bearing capability of such structurally integrated thermal spray coatings have led to novel approaches for extracting effective properties of the coating-substrate system. The results show that a well fabricated HVOF Ni coating on steel can actually carry a tensile load of about 500 MPa when connected to the substrate.

This allows the laminated composite of the parent metal (1008 or 1018 steel) and the sprayed HVOF coating complete load recovery of the lost metal due to corrosion damage and in fact even enhance functional capability. This beneficial effect is in part attributed to synergistic load transfer and sharing as illustrated in the attached figure. A key contributing factor is the process induced residual stress in the coatings. The measurement concept and the interpretation



have far reaching implications not only for this specific application but to the design, synthesis and characterization of this entire class of structurally integrated coatings. Preliminary

results also indicate both fatigue and corrosion benefits of such a clad metal composite.

This work on Structurally Integrated coatings at CTSR has garnered interest from both the Re-manufacturing community as well from the state transportation authority responsible for steel bridge overhaul. In the former, the interest stems from recovery and refurbishing of machine elements to initial

production conditions or better, while the latter many enable strategic on-site repair of steel structures potentially saving millions of dollars in removal and reassembly of structures. CTSR has initiated interactions with several companies and organizations including the Remanufacturing council, NY State Department of Transportation and the Motor Equipment Remanufacturers association

Outreach efforts continue through CTSR's field trip program

CTSR students and staff continue to promote thermal spray technology and materials engineering to both K-12 and under-represented college students. Over the past year, CTSR hosted visits from the National Society of Black Engineers, Society of Hispanic Professional Engineering and students enrolled in the Women in Science and Engineering program. The tours include live demonstrations of thermal spray processes, description of processes and applications.

Through these interactions, students are exposed to the research center and industrial partnerships, giving students the opportunity to see the application of materials science and engineering core concepts and curriculum to real world industrial applications. We have introduced them to thermal spray processes and techniques and conveyed to them the impact our research center contributes to the industry.



Alumni workshop and reunion held on the occasion of Prof. Herman's 80th Birthday

This past June, our colleague and founder of the Stony Brook thermal spray program, Prof. Herman celebrated his 80th Birthday. On this occasion CTSR alumni and friends were at hand to honor their beloved Professor and to pay tribute to his contributions not only to the field of thermal spray but also to the development of human resources in the field. The event was held in conjunction with the spring consortium meeting and featured lectures from alumni spanning some four decades of graduates. Noteworthy is the continued association of many of the alumni in the



field of protective coatings and thermal spray technology. A celebratory dinner event sponsored by the Materials Science Department was held with friends and family following the two day workshop. The CTSR family wishes Herb, a very happy birthday and wish him and his wife Barbara the very best in their golden years.

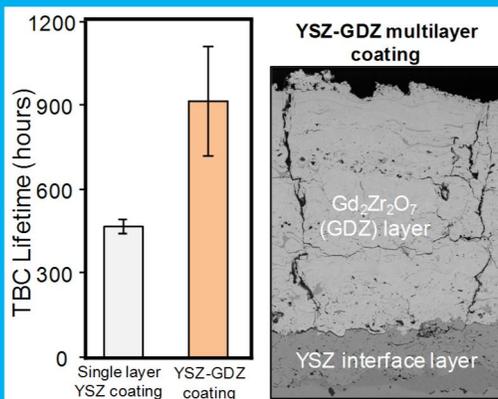
Multilayer, Multifunctional TBCs demonstrated

The quest for continued improvements in gas turbine engine efficiencies has resulted in the increase in engine operational temperatures requiring improvements and new considerations for thermal barrier coatings. Future needs not only include traditional requirements of low conductivity, but also materials that are sinter resistant, survive erosion damage and resistant molten silicate deposit (CMAS). To meet these varied requirements, the coating needs to be multifunctional which is possible through carefully designed multilayer coatings using both conventional ceramics (yttria stabilized zirconia) and low conductivity zirconates – $Gd_2Zr_2O_7$. However, synthesis of such multilayer coatings require not only the linkage to various performance and damage scenarios, but also the ability to achieve and control requisite microstructure and properties via processing.

Using extensive past knowledge on process-property relationship for the zirconia system, CTSR researchers optimized microstructures of $Gd_2Zr_2O_7$ TBC compositions as well as strategies for layered microstructure optimization. The attached figure shows an example of one such multilayer coating comprised to two layers of ceramics based on YSZ and GDZ systems. Such a location specific optimization enables not only multifunctional capability

but is also intrinsically enabled via thermal spray processing. For instance, the microstructure of the YSZ layer near the interface is optimized not only for chemical compatibility with the thermally grown alumina but also to impart high toughness to resist crack propagation. The surface GdZ layer is made simultaneously dense and compliant to meet the dual needs of durability and erosion resistance. The utilization of process maps and advanced diagnostics enable the identification of scope for processing induced functionalities for each constituent layer in such systems. Ongoing tests are currently focused on optimizing these coating architectures to arrive at a design strategy for such multimaterial TBC systems. The utilization of thermal

spray technology to deposit such multilayered coatings could translate to significant cost benefits for the gas turbine industry. This work was supported by the Department of Energy through the National Energy Technology Laboratory and conducted in cooperation with several Consortium partners (Siemens, St. Gobain, Oerlikon Metco, Praxair and GE Aviation) as well as with the Oak Ridge National Laboratory.



In Memoriam: Richard J. Gambino

It is with deep sadness that his colleagues at Stony Brook University inform the materials community of the passing of Dr. Richard Gambino on August 3, 2014. Dick was 79 years old. Dr. Gambino was a beloved professor and revered advisor for students, a highly-respected researcher and scientist, and a warm and devoted family man. His valued presence and endless contributions to Stony Brook University's Center for Thermal Spray Research will remain a part of the Center's history, its lasting footprint and future impact on the entire materials science community.

Dr. Gambino joined the *Center for Thermal Spray Research* during the early years of the National Science Foundation *Materials Research Science and Engineering Center* (MRSEC) program. As part of the NSF program he used electrical and magnetic measurements to characterize metastable and defect structures in thermal spray deposits. In 1999, he became part of the *Defense Advanced Research Project Agency's Mesoscale Integrated Conformal Electronics (MICE)* program within the MRSEC, which introduced thermal spray into the arena of electronic circuits and sensors. The *MICE* project led to the formation of *Mesoscribe Technologies*, which he co-founded and served as its President and CTO. Under Dick's scientific leadership the company developed a breakthrough materials processing technology enabling the fabrication of embedded sensors, flexible electronics, antennas, and electronic circuit components directly onto complex surfaces. This new technology will allow unprecedented structural health sensing capabilities for gas turbine engines and aerospace structures operating in harsh environments. This technology received the R&D 100 Award in 2007.

Dr. Gambino was the recipient of the 1995 National Medal of Technology for the invention of magneto-optical



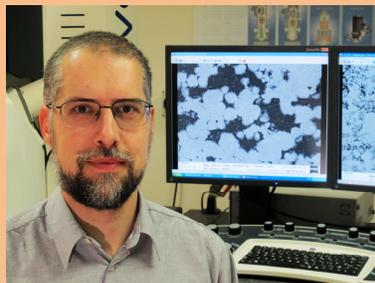
To Richard
Congratulations,
Bill Clinton Al Gore

recording (picture in the inset is from the medal ceremony in the White House with then President Clinton and Vice President Gore). In 2004, Dr. Gambino was inducted into the National Academy of Engineering as well as the Long Island Technology Hall of Fame in 2007. He received the SUNY Medallion of Distinction along with an honorary doctorate from Stony Brook in 2013 and subsequently achieved the rank of Distinguished Professor Emeritus.

Dr. Gambino was a gifted and natural teacher. Whether it was science, sailing or painting, he loved to share these gifts with all those around him. His kindness, humility, warmth, inspiration and enthusiasm for life were contagious, and he will be greatly missed by all those people whose lives he touched.

Alumni Focus: Dr. Jiri Matejcek

In this newsletter, we are pleased to recognize our international alumnus Dr. Jiri Matejcek of the Czech Republic. Jiri joined Stony Brook University in the mid 1990s, facilitated through the extended collaboration between the Center and the Institute of Plasma Physics, in Prague. He completed his Master's degree at the Czech Technical University prior to conducting Ph.D. research under the guidance of Prof. Sampath. His thesis focused on understanding residual stress evolution in thermal sprayed coatings using a variety of tools including beam curvature measurements, X-ray and neutron diffraction studies. During his graduate work, he made numerous trips to the National Institute of Standards and Technology to use their neutron diffraction beam line to probe through-thickness residual stress profiles in sprayed coatings. This novel study for the first time revealed the complex residual stress profiles in layered spray coatings and related this to the process dynamics. He also conducted microscale residual stress measurements on single thermal spray "splats" using advanced microfocus diffraction experiments. Together, these two methods provided a glimpse into the events associated with thermal spray deposit formation dynamics and coating formation. Concurrently, he was also instrumental in expanding the use of beam curvature measurements for insitu monitoring of residual stresses. Following the original work of Dr. Kuroda at NIMS Japan and combining the analytical models of Prof. Clyne at Cambridge Jiri, working with other researchers



at Stony Brook bridged the fundamentals of stress evolution with process dynamics. These fundamental concepts are now becoming part of industrial lexicon through the development of the *in-situ* coating property sensor. Jiri's work also closely coupled with other partnership between Prof. Sampath's group and that of Prof. Suresh at MIT in using coupled curvature and neutron diffraction measurements for residual stresses in layered and graded materials. Jiri's publications will leave a lasting legacy in our understanding of residual stresses in coatings and their implication both for processing and performance.

Following his doctorate, he spent several months at NIST further expanding the use of neutron stress measurements beyond coatings and then returned to the Institute of Plasma Physics in Prague in 1999 where he serves now as a senior scientist. These days he continues his research in thermal spray through both Czech and European Union programs. His specific interests are in development of materials for plasma facing components in thermonuclear fusion, where he is applying concepts of graded materials design using plasma sprayed tungsten composites.

Jiri is married to Irena with whom he has three boys Vit (14), Petr (9) and Jonas (7). His hobbies include photography, travels, rock music and Wikipedia.