Center for Thermal Spray Research

The Center for Thermal Spray Research at Stony Brook University

Stony Brook University has had a long legacy in thermal spray technology from its initial formation as the Thermal Spray Laboratory within the Materials Science Department under the leadership of Professor Herbert Herman to its evolution as a national center of excellence established in 1996 through the prestigious US National Science Foundation (NSF) Materials Research Science and Engineering Center (MRSEC) program. Today, the *Center for Thermal Spray Researc*h (CTSR) in conjunction with its industrial consortium partnership continues to be the focal point within the US of thermal spray research, knowledge transfer and human resource development.

The roots of the thermal spray program at Stony Brook date back to the late 1970s. Professor Herman and his research group as a scientific curiosity were trying to rapidly quench oxides to form metastable phases. While the traditional piston-anvil quenching method worked well for metals, they needed higher temperature thermal sources to melt refractory oxides for subsequent splat quenching. At the suggestion of the late Dr. Volker Wilms, then a PhD student, and with the help of the local company "Metco", the group tried to plasma spray splat-quench alumina onto polished substrates for transmission electron microscopic examination of phase structure. They realized that plasma spray offered a rich platform of scientific research opportunities in materials beyond the original mission of splat quenching. The visually impressive nature of the process immediately grabbed the attention of fellow researchers in the group and soon everyone in Prof. Herman's group was infected with plasma spray research interests. There was no turning back. In fact this visual appeal was aptly described "*it's so hot its cool*" by one of the visiting high school students on a field trip to the Center in the late 1990s.

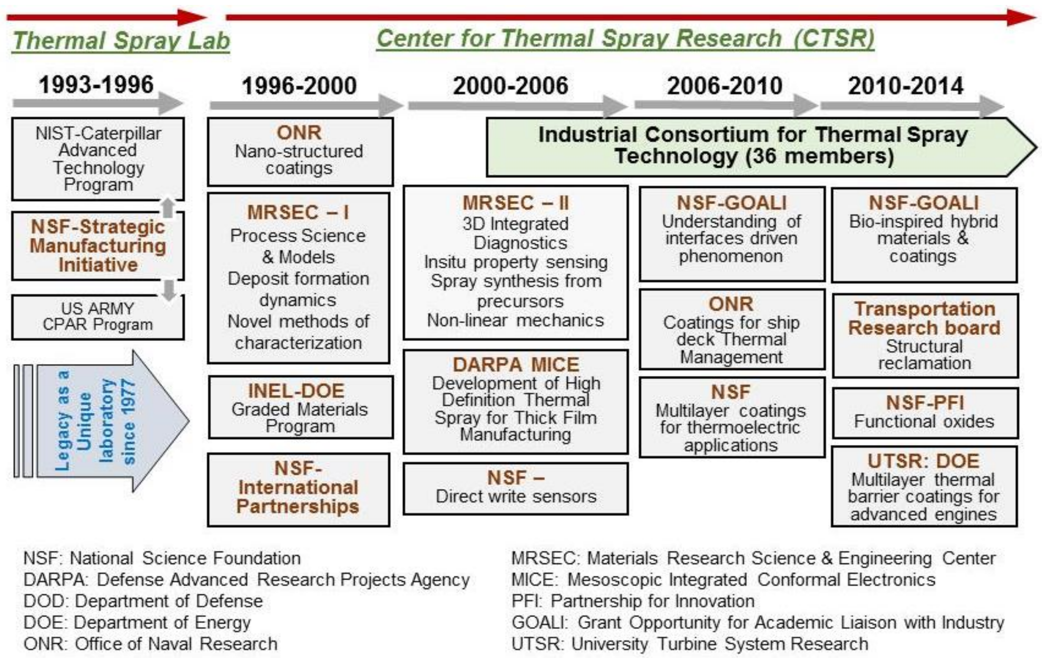

Figure 1: A time-line illustration depicting evolution of the thermal spray program at Stony Brook University including major sponsored programs from federal agencies and industrial organizations. Details of the Center's partnership program and research strategy is available in reference [1].

Since the initial establishment of a small "glove-box" DC plasma spray system, the Center has emerged as a *tour-de-force* in thermal spray research and education, contributing some 300 refereed publications, numerous book chapters, over a dozen patents and having graduated over 100 PHD and MS students. Noteworthy is that majority of the graduates continue to participate in thermal spray technology around the world creating an international network of Stony Brook thermal sprayers.

The Center's critical evolution is illustratively captured through a time-line chart identifying key programs and events. Following the early years as a legacy laboratory under Professor Herman from the late 1970s to the early 1990s, the program grew rapidly with first the addition of Professor Chris Berndt and subsequently Professor Sanjay Sampath. Following initial support from the US-NSF to enhance the fundamental science base of thermal spray technology, the group received a major boost in 1996 through the establishment of the prestigious *Materials Research Science and Engineering Center* (MRSEC). The MRSEC program provides substantial multi-year financial support to bring an interdisciplinary group of researchers to address pertinent materials problems important to science & industry. During the first phase of the MRSEC award from 1996-2000, the Center brought together researchers from materials science, chemistry, geoscience and mechanical engineering as well as alliances with other institutions such as MIT, and various federal laboratories for advanced testing and characterization. Several international linkages further expanded the interdisciplinary activity portfolio. The MRSEC also catalyzed new opportunities including pioneering programs in nano-engineered coatings and functionally graded materials. The project pushed the frontiers of thermal spray fundamentals through integrated process models (with the Idaho National Laboratory), novel X-ray and neutron characterization of defects (with the National Institute of Standards and Technology) and physics of deposit formation dynamics (with the University of Limoges, France). These developments led to a successful renewal of the MRSEC in 2000 for an additional 7 years, enabling rapid developments in science, technology, human resources. Concurrent to the MRSEC efforts, under the leadership of Prof. Sampath the Stony Brook team through support from US Department of Defense created disruptive new concepts including high definition thermal spray systems for mask-less direct writing of thick film electronic circuits and sensors. Key technical developments in this era along with their implications for thermal spray industry are detailed the following sections.

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Research Strategies and Notable Contributions

Given its long legacy in thermal spray technology the Stony Brook research program has multifaceted attributes addressing both long-term foundational agenda as well as short-term problem solving for industry. Since the formation of the MRSEC, two key attributes of research that emerged were integration and multi-disciplinarity. The underlying theme was fundamental, addressing the four Ms: Methods, Measurements, Mechanisms and Models, with an emphasis on development of advanced strategies for process enquiry and materials characterization that will provide new insights into process control, property optimization and prime-reliant design.

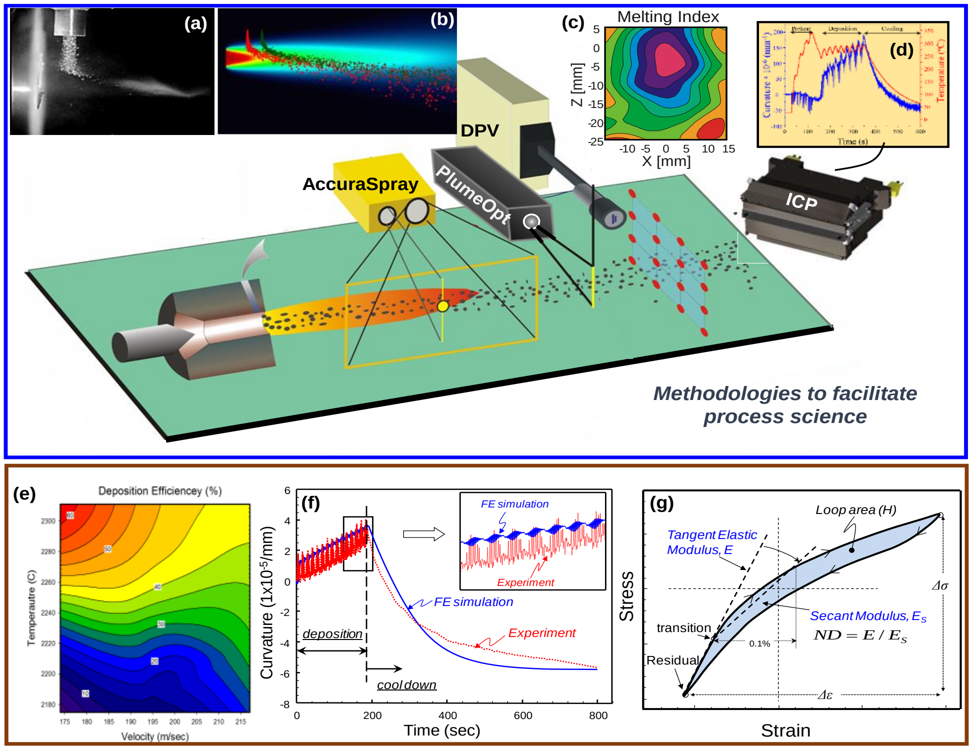

Figure 2: *Illustration of integrated thermal spray process diagnostics and modeling capabilities developed during the National Science Foundation MRSEC program. The program sought to address particle behavior in thermal sprays, in-situ monitoring of coating formation dynamics and novel methods to interpret microstructure property relationships. (a) Laserstrobe image of particle image into a plasma [2]. (b) Visualization of particle behavior in thermal sprays with two injectors (one for metal and one for ceramics) [3,4] (c) 3D cross-section of particle melting states described via non-dimensional group parameter, melting index [5]. (d) in-situ monitoring of residual stresses through beam curvature monitoring through the ICP (in situ coating property) sensor [6,7] (e) 2nd order process maps overlaying deposition efficiency as a function of particle temperature and velocity. [8] (f) simulation of ICP beam curvature evolution using finite element methods [9] (g) non-linear stress-strain behavior of porous ceramic coatings obtained from beam curvature measurements [10,11] .*

Figure 2 provides an illustrative outcome of one of the Center's accomplishments: a fully integrated, in-booth, diagnostics and modeling strategy incorporating particle trajectory monitoring/control, 3D plume cross-section analysis and *in situ* coating property assessment through a novel adaptation beam curvature theories. The associated descriptions of particle behavior in thermo-fluids and coating formation dynamics were concurrently modeled to provide enhanced interpretation of the sub-processes and enabled model-guided design of the processes.

The outcome of such integrated 3D diagnostics, modeling and Coating formation sensing are described through the concept of *process maps*. 1st order maps describe the interplay play between thermal state and kinetic energy of the particles in relation to process parameters, which, in turn, affect the ensuing coating properties (2nd order overlays) and ultimately coating performance (3rd order extensions). These design maps are useful to both researchers and industrial practitioners as they not only provide physical descriptions of the operating phenomena but also allow for application specification optimization and reliability assessment. These developments have now been set-up in all of the process cells (spray booths) at Stony Brook providing both development and training opportunities to graduate researchers, undergraduate students and industrial engineers. The concepts are now routinely being used by Stony Brook's consortium partners.

Advanced processing capabilities and know-how have also allowed new concepts in coating design, through microstructure and property optimization. The core elements of the diagnostics and modeling efforts result in a forward process design strategy where-in coating layers can be strategically optimized to exacting microstructural requirements. These, in turn, provide a reverse opportunity for tailoring coating properties based on specific performance requirements based on location and geometry. This connection between bottom-up understanding of the process and top-down design embodiments is applicable across the entire spectrum of thermal spray applications, including high temperature thermal barriers, damage tolerant wear and corrosion control coatings, load bearing reclamations of damaged structures and functional multilayers for sensing and energy applications. Examples of these developments are captured illustratively in Figure 3 and described within the associated caption.

Knowledge and Technology Transfer: The Industrial Consortium for Thermal Spray Technology

Thermal spray is a platform manufacturing technology targeting a diversity of applications. Although there are significant differences in operating mechanisms among various thermal spray materials and processes, the fundamental elements such as particle dynamics, stress evolution and property characterization have substantial commonalities, enabling development of integrated test methods. The knowledge gained through the various government-funded basic research initiatives still required transitioning to industry through effective communication. Of further importance is to distill the

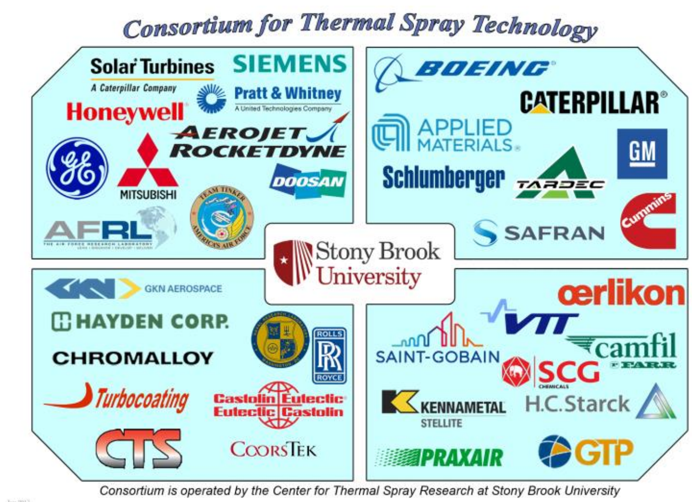

Figure 4: *Participants engaged in knowledge transfer partnership through CTSR's Consortium for Thermal Spray Technology Program.*

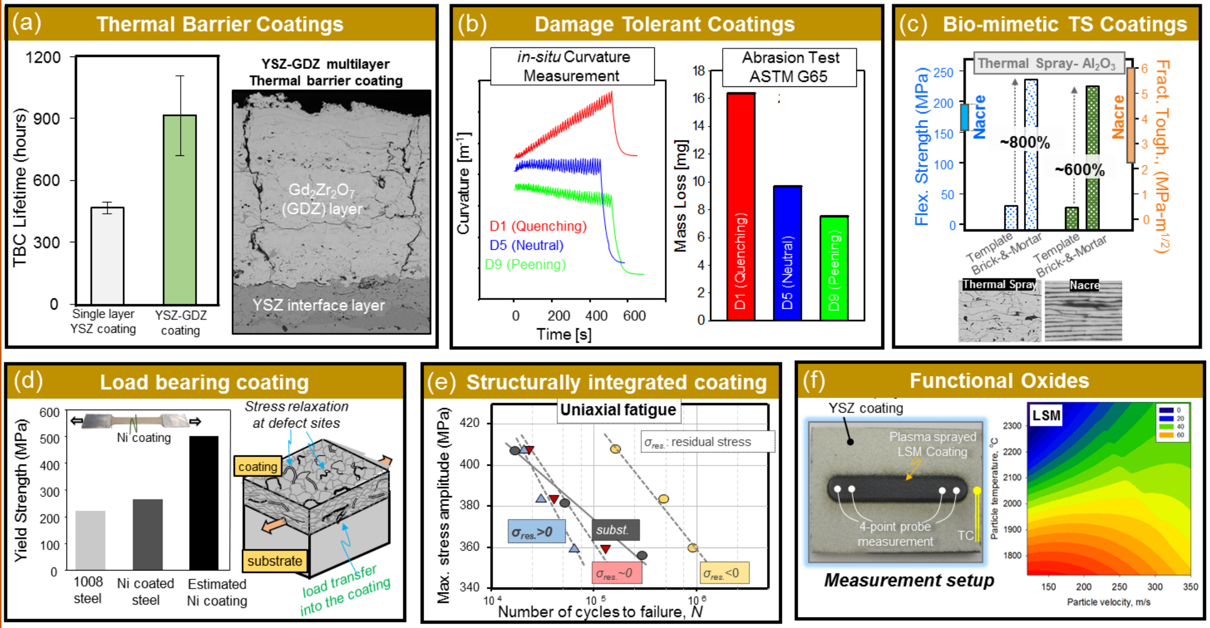

Figure 3 Examples of notable recent results arising from Center research: (a) Durable, multilayer, multifunctional thermal barrier coatings comprising of yttria-stabilized zirconia interface layer over which a dense vertically cracked gadolinium zirconate coating is applied. These coatings protect against harsh thermo-chemical environments in additional to oxidation induced failure modes [12]. (b) The connection of formation stresses during coating deposition as measured through the ICP sensor with coating wear behavior obtained via dry sand abrasion tests [13]. (c) bio-mimicry via thermal spray. The polymer treated thermal spray alumina coatings shows mechanical properties matching those of the tough natural material, 'nacre', present in sea shells. Strategically designed lamellar/staggered microstructure of coatings can have more than 600% increase in mechanical property after polymer (epoxy) infiltration [14]. (d) Demonstration of load bearing capability of dense metallic reclaimant coatings applied onto metallic substrates subjected to corrosion and wear loss. The load bearing capability is associated with unique load transfer mechanisms around coating defects [15]. (e) Structural integration and assessment of coated specimen in terms of their fatigue life. Higher compressive stresses in coatings are shown to offer fatigue credit to the coated structure [16]. (f) Optimizing functional properties of oxide based electrical interconnects [La(Sr)MnO_3] through process map strategies and electrical characterization [17]. These examples provide a snap-shot of current areas of Center's research agenda.

fundamental findings into relevant and specific themes for each of the interested industrial segments and to connect the scientific enhancements to system-level thinking. To foster this interaction, CTSR in concert with NSF established a formal knowledge-transfer partnership with multiple industrial organizations under the framework of a Consortium program. The mission of the Consortium is to provide a pre-competitive forum allowing interactions among various competing organizations in a neutral framework. Starting with 10 companies in 2002, the Consortium is entering its 12th year, currently comprising more than 35 leading industrial organizations. Each company provides a financial contribution to the university in the form of an annual membership fee, which allows the NSF center to continue as a self-sustaining entity to promote research, knowledge transfer, and human resource development. The companies benefit from research advances that enable enhanced coating design, improved process optimization, robust methods of testing and overall enhancement of process and coating reliability. The Consortium meets twice annually and provides an excellent forum for researchers and students to interact with industry practitioners and coating specifiers.

The consortium partnership continues to advance the cause of establishing efficient, reliable and controllable thermal spray processes together with enhanced confidence via advanced materials knowledge. A secondary, but important outcome, is developing a workforce with advanced skills having a strong scientific knowledge-base.

Disruptive Innovations

The traditional role of thermal spray has been in the domain of broad-area protective coatings. However, the ability of thermal spray to deposit a wide range of materials offers opportunities in thick film functional materials and multilayers. Indeed, this capability has been investigated extensively for the fabrication of solid oxide fuel cell multilayers for more than two decades, but a wide range of further opportunities exist in thick film electronics, electromagnetics, sensors and patterned structures. History suggests that many attempts were made in the past to use thermal spray to fabricate thick film integrated circuits and radio frequency devices, but these attempts were met with limited success. Recent scientific advances suggest targeted opportunities for thermal spray in this arena.

Since 1999, the Stony Brook CTSR team, through support from the US Defense Advance Research Project Agency, embarked on a major initiative to develop thermal spray-based 3D direct writing capability for mesoscale electronics and sensor structures. The goal here was multifold: identify electronic /sensory device concepts uniquely enabled by thermal spray technology, develop methodologies for high definition, mask-less patterning of mesoscale traces and producing an integrated platform combining direct writing and blanket deposition for an advanced thermal spray electronics deposition system.

The program resulted in major innovations in high definition thermal spray, mask-less 3D direct writing of sensor traces directly onto components, multilayer thick-film electronics and sensor assemblies. The technology received several international patents and was the recipient of the prestigious R&D 100 award in 2007. The technology has also seen commercial success through the Stony Brook based spin-off Mesoscribe Technologies. Numerous papers have been published on this subject with key papers identified in the listed references. The impact of these continuing achievements will hopefully be realized in the coming decade.

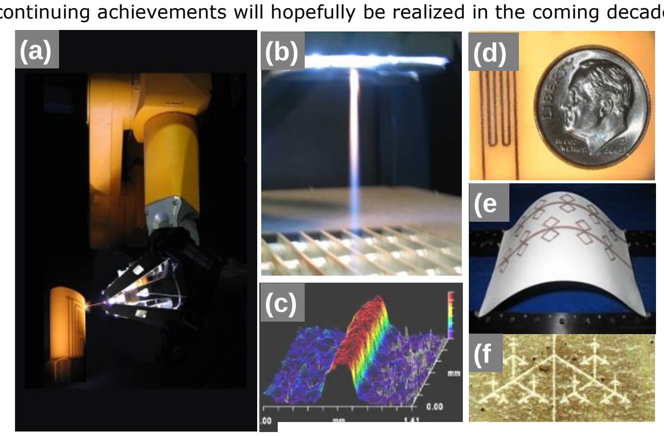

Figure 5: Illustrative description of high definition 3D direct write thermal spray technology (a,b) and prototype applications resulting from this unique capability. Up to a 250 micron line widths have been demonstrated (c, d) enabling patterning of a wide range of sensors (g) and antennae (e,f) Further details are available in references [18 and [19] .

Advanced Facilities for Research, Education and Knowledge Transfer

Large, integrated, interdisciplinary programs such as the NSF MRSEC and the direct writing project brought significant visibility to the Stony Brook group both within the University as well as the US. In recognition of these developments, the University in conjunction with New York State, built a dedicated thermal spray facility to house the Center. The building was dedicated in 2006, providing more than 10,000 square feet of high bay factory space with dedicated infrastructure to support thermal spray equipment. This facility presently hosts four advanced thermal spray cells with requisite automation and controls. Through support from industrial partners, such as *Oerlikon Metco*, fully integrated thermal spray equipment has been established in multiple spray booths capable of operation by both students and researchers. Other industrial partners such as *Caterpillar, Praxair, St. Gobain* and *Kennametal Stellite* have continued to provide equipment and materials support for educational research purposes, allowing a vibrant partnership and educational opportunities.

The team also continues to interact with federal laboratories and international organizations for access to advance testing and characterization facilities. For instance, close-cooperation with Oak Ridge National Laboratory has allowed innovation in thermal and mechanical testing of coatings. Access to sophisticated X-ray and neutron sources are sought periodically to provide insights into coating defects, phases and stresses.

Sustained Contributions to Human Resources

The key mission of the Center has centered around education and human resource development. Thermal spray has and will always require a "*hands-on*" approach to education and training. In addition, the unique attributes of the process, in particular, non-equilibrium phenomena, synthesis from extreme conditions, layered anisotropy and multiscale thermo-physical behavior all require new pedagogic strategies for both experienced and a new workforce. Starting from the initial formation of the Thermal Spray Laboratory in the 1970s, the Center has been at the forefront of this unique educational mission resulting in generations of trained graduates to support the thermal spray industry both within the US and internationally. The Center has graduated some 60 PhDs and equivalent number of MS graduates. In addition, each year at least 4-5 undergraduates participate in the program resulting in over 150 students, exposed to thermal spray technology. The majority of the graduates are involved either fully or partially with the thermal spray industry, a testament to the Center's effective and sustained contribution to human resource development. We expect this trend to continue. In addition, many of the alumni also represent their respective companies within the Consortium. The Center is grateful for financial support in the form scholarships from industry, federal agencies and the International Thermal Spray Association. Periodically, the Center hosts reunion events for the alumni, a photograph from the 2012 assembly is shown in Figure 6.

Figure 6: Photograph of participants from the 2012 alumni reunion event.

In closing, through sustained support from US federal agencies, industry and the university and through the dedication of faculty, staff and students, CTSR has and will continue to be the focal point of thermal spray research and knowledge transfer in the US.

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