Contents

1 Introduction and Background

Thermal spray is regarded as a key surface engineering technology that underpins the competitiveness of many critical manufacturing and engineering industries. It is being developed continuously to meet market evolution and new requirements. This evolution raises challenges that must be addressed for the advancement of thermal spray processes and coatings, and to direct academic research into promising industrial applications that offer opportunities for R&D investment.

Experts in academia and industry were surveyed by the Thermal Spray Advisory Committee to identify the scientific and technology issues facing recent and emerging spray processes. As well, they identified key areas for the future development of existing processes. The outcome is a list of priority items that will enable industry and academe to develop improved products in terms of quality and performance at a lower life cycle cost.

2 Recent and Emerging Spray Processes

2.1 The Cold Spray Process

Cold spray is a solid-state coating process that uses a high-speed gas jet to accelerate powder particles toward a substrate where particles plastically deform and consolidate upon impact. This technique is suitable for the deposition of oxygen- and temperature-sensitive materials and can produce thick coatings exhibiting wrought-like microstructures with near theoretical density. Cold spray is being used in the military, aerospace and energy industries.

The main research priorities identified are:

2.1.1 Powders

- Enhanced understanding of the effect of powder processing and characteristics on the properties of cold spray coatings,
- Manufacture of powders designed specifically for cold spray applications,
- Manufacture of innovative powders; e.g., coated powders; agglomerated, porous and ball milled feedstocks that meet the requirements of specific applications better than current powders.

2.1.2 Cold spray equipment

- Design of guns to spray on parts with complex geometries; including parts with internal diameters,

- Design customized guns for specific applications considering part geometry, coating material, deposition rate, gun wear and maintenance and operation cost.

2.1.3 Spraying onto real parts

- Experimental and numerical studies to elucidate the many factors involved when changing the geometry and size of parts,
- Transfer the information developed in the lab, on flat substrate coupons, to real parts of complex shape.

2.1.4 Process control to increase process reliability

- Monitoring gas flow, solid particle velocity and solid particle temperature.

2.1.5 Effect on Substrate

- Understand the effect of substrate temperature on the mechanism of coating build-up and properties,
- Relate newly-developed spray systems; which operate at higher gas pressure, temperature and powder feed rate, with respect to the substrate properties,
- Understand the effect of the cold spray coating on substrate mechanical properties such as fatigue debit due to the amount of cold work imparted by the coating to the substrate.

2.1.6 Bow shock

- Understand the bow shock phenomenon that is generated by the impingement of the supersonic gas on the substrate, in particular for non-flat surfaces,
- Development approaches to mitigate the bow shock phenomenon, thus allowing the spraying of finer particles,

2.1.7 Opportunities to embrace

- Creation of nano-structured and amorphous coatings,
- Cold spraying of ceramic materials,
- Including cold spray as an additive manufacturing technique.

2.2 Suspension and Solution Precursor Thermal Spray

The demand for fine-structured coatings has led to the development of thermal spray processes that are based on plasma and HVOF. Thus, the use of liquid feedstock in the form of suspensions or solutions enables the production of coatings with unique microstructures; e.g., columnar, segmented, highly porous/high specific surface area, and dense features. Potential applications include thermal barrier coatings with stress relieving structures and lower thermal conductivity for aerospace and gas turbines. Other applications include fuel cells; photocatalytic and anti-microbial coatings, and biomaterials or biotechnology uses.

These technologies are not sufficiently mature to meet industrial standards and customer needs. However, collaboration among researchers will provide understanding of the scientific principles and behavior of a process. In this fashion, equipment manufacturers will develop processes that are reliable, robust and easy to adopt within an industrial environment.

The research priorities identified to ensure a rapid increase in technology readiness include:

2.2.1 Feedstock

- Formulation of stable suspensions and solutions.
- Choice of the suspension particle size to achieve nanostructured coatings.
- Handling and storage of suspensions.

2.2.2 Spray process

- Design of stable spray guns adapted to liquid feedstock and fine particle processing.
- Proper and stable injection of the liquid feedstock into the high-energy gas flows.
- Experimental observations and numerical simulations to understand liquid feedstock / high-energy gas interactions,
- Experimental observations and numerical simulations to understand the mechanisms of coating formation,
- Increase in stand-off distance,
- Increase in deposition efficiency and deposition rate.

2.2.3 Process control to increase process reliability:

- Development of sensors that measure fine particle velocity, temperature and size.

2.2.4 Opportunities embrace

- Benchmark this technology against conventional thermal spray processes and other coating techniques,
- Investigate potential for improved performance coatings for power generation and aerospace industries,
- Investigate potential for corrosion and wear resistant coatings under extreme conditions.

2.3 Very Low Pressure Plasma Spray

Very Low Pressure Plasma Spray, or VLPPS differ from traditional thermal spray processes in that coatings are deposited at chamber pressures typically less than ~1000 Pa. Deposition may be in the form of very fine molten droplets, vapor phase deposition, or a mixture of vapor and droplet deposition. The coatings exhibit similar quality to those produced by physical vapor deposition (PVD) or chemical vapor deposition (CVD); however, the VLPPS deposition rates can be an order of magnitude higher.

VLPPS can be used to produce dense, high quality coatings in the 1 to 100 micrometer thickness range with lamellar, columnar and mixed microstructures.

Specific questions to be answered to further industrial acceptance of this technology include:

2.3.1 Plasma spray process

- A better understanding of:
    - Properties and physics of D.C. plasma jets at reduced chamber pressures,
    - Phase transformation pathways for the feedstock (e.g., melting, vaporization, ionization, solidification, condensation, chemical reaction, …),
    - Mechanisms responsible for columnar microstructures.
- Increase in the process thermal efficiency.

2.3.2 Opportunities to embrace

- Benchmark this technology against thin film technologies (PVD, CVD),
- Benchmark this technology against EB-PVD (electron beam physical vapor deposition), which has a long history of success for deposition of thermal barrier coatings in aerospace and gas turbine industries,
- Investigate VLPPS as an alternative to electroplated coatings,
- Manufacture and production of wear- resistant metal-ceramic composite coatings.

3 Thermal Spray Markets and Applications

Thermal spray is used by a large spectrum of manufacturing industries. It is vital to improve the performance of components and industrial products to maximize their life cycle. However, some sectors are still unexplored; e.g., electronics applications. Also, traditional sectors are facing the global pressures on prices, regulatory demands, and global shortage of critical raw materials.

The main research needs to respond to these challenges are:

3.1 Electronics Industry, Semi-conductors Manufacture

Thermal spray technology can be further explored for electronic materials and electronics applications; keeping in mind that these sectors employ existing, competitive coating technologies. There is potential for a wide range of electronics applications; including sensors, wiring, antennas and RF, energy storage and energy harvesting. The high throughput, material versatility and processing at ambient conditions are attractive features of thermal spray for these applications.

In order to be competitive, particularly with regard to the very high quality standards of electronic materials, thermal spray coatings must exhibit:

3.1.1 <u>Good electrical properties</u>

- High electrical conductivity to minimize resistance losses, high mobility for potential semiconductor applications, high purity with low concentrations of undesirable materials, ability for doping for sensing, semiconductor, and thermoelectric applications,
- Stable properties under thermal or mechanical cycling, aging, humidity, or service history,
- Repeatable properties, to consistently reproduce the coating properties for a given device.

3.1.2 <u>Consistency between feedstock powder and final coating,</u>

3.1.3 <u>Capability to deposit patterns without the use of masks by designing micro plasma spray torch.</u>

3.1.4 <u>Opportunities to embrace</u>

- Wide range of materials that can be deposited on conformal (non-flat) surfaces,
- No need for post-processing (no firing, curing, etc.),
- High deposition rates: fast processing time, large areas, low cost,
- Processing done at ambient conditions.

3.2 Automobile Industry

Advanced mechanical and automotive engineering is crucial for most national economies in order to compete in the global markets and, also, in value adding and creating jobs for people with higher academic education. Automotive engineering and industrial manufacturing are basic to mass production of thousands of parts per day. Manufacturing engineering in these industries requires a complex and deep knowledge base with a distinct interdisciplinary approach. High quality and productivity can only be achieved by process automation with highly sophisticated control systems.

To a certain extent, the thermal spray business and technology is still dominated by traditional small and medium size enterprises and spray shops. Their focus is on materials engineering and coating process technology that will add value to the products of their customers.

The main challenges in meeting the requirements of the automotive sectors are:

- Integration of the necessary analytical instrumentation, steering and control systems for the coating process to ensure stability, reproducibility, dimension tolerance,
- Integration of the control systems of thermal spray and robot systems with the ability of tailored sprayed particle trajectories and heat release to substrate,
- Knowledge gain by deep scientific exploration is essential and the basis for planning and operating modern factories by means of virtual reality (VR) engineering.

Opportunities to deal with:

- Environmental concerns and legislation are powerful drivers for technology change (environmentally-friendly coating processes and products),
- Advanced tribological systems for reduction of friction, oil consumption and pollutant emissions, and improved performances: power train (engine and gear), wheel suspension, drive and brakes. Many sub-systems which need lubrication are actually re-designed and engineered with the aim of operational safety,
- Thermal barrier coatings,
- Coatings with functional properties: electrophysical, physicochemical, optoelectronic, etc.,
- Emerging thermal spray processes (suspensions and solution precursors) for improved surface functionality and performance.

3.3 Land-based and Aero Gas Turbines

Thermal spraying is a well-established surface engineering technology in the gas turbine sector, especially in producing thermal barrier coatings (TBC) that can withstand the high fuel gas temperature needed for efficient engine operation and low pollutant emissions.

TBCs for land-based and aero gas turbines are one of the current key market segments of thermal spraying. However, it is now facing new challenges such as increased firing temperature, longer service life of components, use of non-conventional fuels (syngas , low-BTU gases…), global shortage of “Rare” Materials (Y, Yd, He..), larger and more complex parts.

The key researches identified to address these challenges are:

- Novel TBC coating architecture and compositions to withstand higher temperatures, longer life and various fuels,
- Coating systems with improved resistance to silicate deposits (CMAS : Calcium-Magnesium-Alumino-Silicate), vanadium, water vapor and erosion,
- Coating deposition with non-He spray parameters,
- Higher deposition efficiency to reduce the use of strategic materials,
- Overspray recycling,
- Coating deposition on parts with complex geometry with better/faster robotic manipulation system.

Opportunities to deal with:

- New thermal spray coating technologies: suspension and solution precursor plasma spraying, plasma spraying-PVD, advanced air plasma spraying,
- Mechanisms-based modeling of TBC failure under service conditions (CMAS under thermal gradient).

3.4 Energy Conversion and Harvesting

Both population growth and economic development are accompanied by an ever-increasing consumption of energy. However, the use of fossil fuels to meet this increasing demand has resulted in the rapid increase of carbon dioxide in the atmosphere, which in turn translates into climate changes and extreme weather events. It is therefore necessary to develop renewable energy sources and also to increase the thermal efficiency of fossil fuels.

Thermal spray technology has the potential to contribute to energy conversion and harvesting, in particular in the following applications:

3.4.1 <u>Thermoelectric Energy Converters (TEC)</u>

Thermoelectric devices can convert thermal energy to electricity in a variety of applications (e.g. *waste heat* from power stations and vehicle *exhaust pipes*). Many materials exhibit high thermoelectric effects but generally within a narrow temperature range. Current developments involve the combination of several thermoelectric elements efficient at different temperature levels, in order to broaden the useful temperature range and increase the output voltage. They are typically produced by powder metallurgical methods including sintering processes, which involve relatively long processing times at high temperatures, limiting hence the spectrum of applicable materials.

In principle, thermal spraying allows for the production of near-net shape multi-layered structures with constant or functionally graded composition of material and porosity. Therefore, multi-layered TECs present an interesting challenge for plasma technology with potential for a large field of R&D and new applications.

3.4.2 <u>Alkaline Water Electrolysers (AWE)</u>

Hydrogen is becoming increasingly important as energy carrier and energy storage medium in particular in connection with renewable energy sources. Up to now most hydrogen is produced from reforming of hydrocarbons (e.g. natural gas). An alternative is the production by water electrolysers using electricity from wind, solar or nuclear energy. Alkaline water electrolysers with standard pure metal electrodes have a long history. However, to make the hydrogen production more efficient new electrodes with activated surfaces should be developed, suited for intermittent operation as required by renewable energy sources. In small size such electrodes have already reached the desired quality, but electrodes in technical size (larger than 1 m^2) represent still a significant challenge for thermal spray in an economical and reliable way.

For this purpose several issues have to be addressed including optimization of (i) spray material with respect to composition and powder particle size and of (ii) electrode layer structures; (iii) preparation/activation of substrate surface for stable bonding of coating, (IV) means and methods for preventing deformation of large metal substrates during the spray process and (V) industrialisation of the production process, which also means improvement of spray equipment.

3.4.3 <u>Solid Oxide Fuel Cells and High Temperature Electrolysers of Solid Oxide Electrolyser Cell-Type (SOEC)</u>

Fuel cells directly convert chemical energy into electricity with an efficiency much higher than that of other energy conversion processes. Different fuel cell types exist in the whole temperature range between ambient temperature and about 1000 °C. The lower temperature types need mostly hydrogen as fuel gas, which has to be produced first by reforming of hydrocarbon fuels, whereas the high temperature types, like SOFCs, have intrinsic reforming qualities and can use hydrocarbon fuels directly. Therefore, the latter are of great interest for combined electricity and heat supply in stationary application with outputs from 100 W to 2 MW.

They can also be used as electricity source in vehicles as “Auxiliary Power Units” (APU). Hundreds of cells are then arranged electrically to form SOFC stacks and units.

Thermal spray techniques are of potential interest to produce cells with limited or no post treatment. For planar “Metal Supported Cells” for car APUs, the multi-layered cell structure is sprayed directly on the surface of the metal base sheet This concept involves cells with an overall thickness of about one millimetre. However, the production of thin and fully dense electrolytes is one of the issues faced by thermal spraying for the production of SOFCs.

High temperature solid oxide electrolyser cells (SOEC) which need less specific electric power due to involved thermal energy have significant potential for hydrogen production and energy harvesting when they are coupled to a renewable or nuclear heat source. Their operation principle is the inverse of that of SOFCs with operating conditions even more demanding than those of SOFCs. The materials and processing methods are similar and therefore, thermal spray techniques may also be of interest for their production.

3.5 Wear Resistant and Corrosion Resistant Coatings

The cost of wear and corrosion are estimated to be a significant fraction (up to 3-5%) of developed nations’ Gross Domestic Product. They result in the degradation and eventual failure of components and systems both in the processing and manufacturing industries and in the service life of many components.

Thermal sprayed coatings prevent, or limit, the effects of corrosion and wear by providing protection against chemical and physical interactions of a material with its environment. However, there is still much room for the development of cost-effective coatings that can resist under specific conditions. In addition, the search for reliable coatings that improve the performance and extend the operating range of applications of structural materials has accelerated because of the **world-wide concerns for reducing** energy consumption, **conserving resources and minimizing the emission of the products of corrosion to the environment.**

Thermal spray coatings exhibit a microstructure that is different from coatings produced by other coating technologies: highly oriented structure with lamellae of different sizes and shapes parallel to the substrate surface; variable quality of contact and bonding between lamellae interfaces; some porosity, cracks and possible inclusions of partially melted particles. This morphology has important implications with regard to the performance of coatings used against corrosion and wear.

The research areas identified for further development of thermal sprayed coatings are:

- Characterization of inter-splat interface, bonding formation mechanisms and effect of physical, chemical, thermal, and metallurgical reactions of impacting droplet with the underlying layer,
- Relationships between process operating parameters, coating structures and product performance in order to be able to tailor coating architectures to the service conditions.
- Modeling the microstructure and properties of thermal spray coatings taking into account inter-connected pores and permeability to fluids,
- Relationship between wear performance, microstructure and properties of splats, processing parameters for low stress and high stress wear conditions,
- Establishment of database for thermal spray coatings applicable to different service environments.

Opportunities to deal with:

- Hard chrome plating alternatives,
- Development of metallic coatings with non-connected pores and sufficiently bonded inter-splat interfaces that are impermeable to corrosive fluids,
- Wear resistant coatings that can withstand the abrasive oil sands slurry during bitumen extraction and upgrading,
- Corrosion resistant coatings for high temperature processes, especially since the rates and efficiencies of many energy processes increase with higher temperatures: waste-to-energy systems, boilers, steam generators and gas turbines, nuclear energy plants…
- Coating microstructure design for high wear performance,
- Development of superhard nanostructured cermet coatings by cold spraying or warm spraying with high toughness,
- Development of smart thermal spray coatings with self-enhancing by environment (e.g., becoming strong with increasing operating temperature), self-repairing properties (e.g., rebuilding of self-lubricating film or self-protecting film),
- Wear protection for polymer composites (Aircraft leading edges, engine nacelles, radiomes, antennae, Wind Turbine Blades…).

4 Process Robustness, Reliability and Economics

As for every coating technology, the reliability and reproducibility of thermal-sprayed coating were essential for the early adoption of this technology in industrial manufacturing. The development of (i) thermal spray control systems that accurately control the gas, electrical and cooling water requirements and (ii) of diagnostic tools for the plume and/or the substrate have proven to improve process productivity, quality assurance and customer confidence.

The diagnostic tools are now well accepted in the thermal spray community. Over the last 20 years, they have been quite helpful, especially for spray parameters optimization, booth-to-booth parameter transfer, trouble-shooting, powder lot validation, go no-go monitoring, etc. However there is still a long way before those tools are systematically used for daily production.

The identified areas of research address:

- Determining the acceptable process windows for each material and taking actions (for example slightly readjusting the upstream parameters based on measurements) at the process level when the measurements do step outside the tolerance windows;
- Redesign method standards to reflect the resulting properties rather than the procedure;
- Evaluation of instrument’s measurement uncertainty versus achievable and desired coating capability;
- Improved basic understanding of splat formation and coating build-up to predict coating microstructures and properties;
- Fully predictive model of plasma torch operation as a tool to design stable and more efficient plasma torches, especially for the recent plasma torches operated at lower current and higher voltage than conventional plasma torches and with a relatively fixed arc attachment;
- Fully predictive model of thermal spray processes to optimize the process at very low cost;
- Fully predictive model of thermal spray processes to train sprayers and engineers.

Opportunities to deal with:

4.1 Thermal spray hardware

- Improved powder feeder technology: more stable injection, ability to better fluidize and feed fine particles without clogging, higher feeding rate.
- Improved plasma gun technology: higher thermal efficiency, more stable plasma jets, higher deposition efficiency and lower process variability due to hardware degradation.

4.2 Process Control

- Use of diagnostic tools on process spec sheets,
- Transparent integration of sensors with spray controllers,
- New sensors able to measure coating thickness on-line,
- New sensors able to measure coating properties online such as surface roughness, porosity and Young modulus. In some cases, the technology does exist but not as a commercial product ready for prime time,
- New sensors for the emerging thermal spray processes: suspension and solution thermal spray, very low pressure plasma spraying, cold spray,

4.3 Greening the thermal Spray Processes

Reducing energy and resource and minimizing waste and emissions contribute measurably to cost and environmental load cutting.

- Efficient energy use: minimize the total energy use per gram of deposited material,
- Efficient methods for the recovery and recycling of overspray.
- Life cycle assessment (LCA) of thermal spray processes and products for identifying, and reducing the environmental impacts of processes and products.

5 Contributors

The following people have contributed to identify the scientific and technological key issues in thermal spraying:

Armelle Vardelle (France)

Christian Moreau (Canada)

Christopher C. Berndt (Australia)

Dianying Chen (USA)

Pierre Fauchais (France)

Rainer Gadow (Germany)

Aaron Hall (USA)

Rudolf Henne (Germany)

Friedrich Herold (USA)

Éric Irissou (Canada)

Eric Jordan (USA)

Yuk-Chiu Lau (USA)

Klaus Landes (Germany)

Chang-Jiu Li (China)

Jon Longtin (USA)

André G. McDonald (Canada)

Luc Pouliot (Canada)

Mark F. Smith (USA)

Robert Vassen (Germany)

Jan Wigren (Sweden)

Motohiro Yamada (Japan)