iTSA
The Indian Thermal Spray Association
ITSA ASSOCIATION FOR THERMAL SPRAY TECHNOLOGY AND RESEARCH

Dec 2022| Vol. 2| Issue 4

SPRAYTODAY™

An INSCIENCEIN publication | Affiliated to the Indian Thermal Spray Association® as its official Newsletter

Issue Highlights

- **Featured Article**: Development of Spray Parameters for Sustainable Thermal Spray
- **Technical Note** : Plasma Spray Coating Activities Related to Solid Oxide Fuel Cells at CSIR-National Aerospace Laboratories
- **Academia Research**: Facile Fabrication of Superhydrophobic Surface Through Flame Spraying
- **Industrial Research**: Investigation of Dense Sinkor® Coating Performance in Molten Zinc
- **Knowledge Point**: Thermal Spray Powder Types, Manufacturing Process & Characteristics

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Mission: Our mission is to deliver the most recent thermal spray industry news and keep up to date to thermal spray community by providing company, event, people, product, research, and membership news of interest to industrial leaders, engineers, researchers, scholars, policymakers, and the public thermal spray community.

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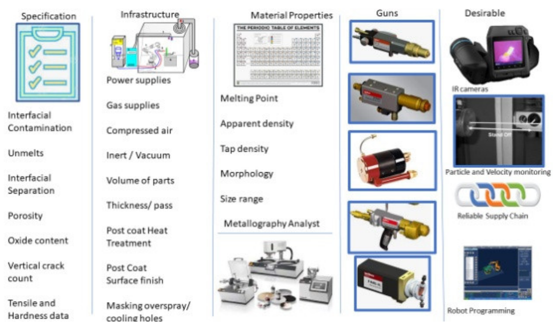

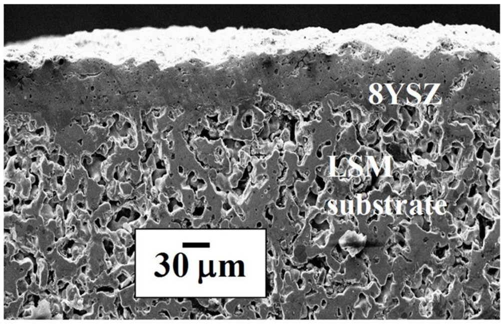

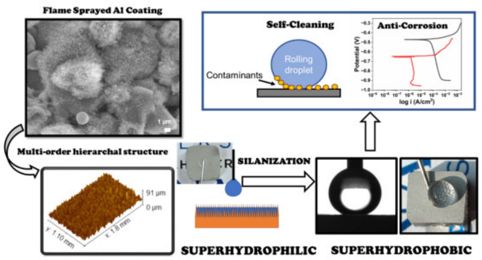

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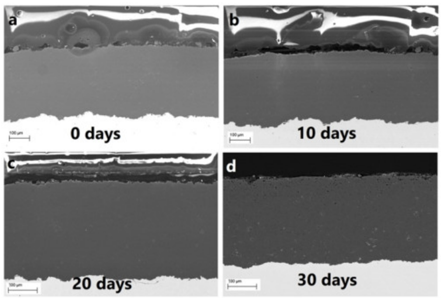

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ABOUT THE COVER

Facile Fabrication of Superhydrophobic Surface through Flame Spraying

Editor’s Note

Dear Readers,

The global Thermal Spray Market is projected to be worth USD 17.68 Billion by 2027, registering a CAGR of 8.0% during the forecast period (2021 - 2027). During this forecast period Asia-Pacific Thermal Spray Market is expected to expand at a projected CAGR of almost 11.5%. India has a growing economy and thermal spray has a bright future. Due to the global conditions all the key players are investing in India for their future projects which will definitely increase the thermal spray market in the country.

Now there is few thermal spray OEMs as well as manufacturers of thermal spray grade powders & wire in India. Tata group has come forward to produce indigenous HAP powder for orthopedic implants. There are also some good companies producing quality thermal spray grade ceramic powders. The need of the hour is to produce carbide powders now as market share is higher than all other feedstock materials. I hope we will achieve this in the near future. Government of India is promoting Atmanirbhar Bharat and Made in India campaign.

The Indian Thermal Spray Association is organizing 1st National Thermal Spray Conference (NTSC2023) on Feb. 18-19, 2023 at Jodhpur City. For more info please visit https://www.indtsa.org/ntsc-2023

I am particularly pleased to be allowed to recommend to you the latest issue of the **SPRAYTODAY**. This issue includes invited innovative featured articles from industry and academia experts on the Development of Spray Parameters for Sustainable Thermal Spray; Plasma Spray Coating Activities Related to Solid Oxide Fuel Cells at CSIR-National Aerospace Laboratories; Facile Fabrication of Superhydrophobic Surface through Flame Spraying; Investigation of Dense Sinkor® Coating Performance in Molten Zinc; that illustrate current research trends in thermal spray development.

Looking at the future of thermal spray in India, it will be pleasing if the **SPRAYTODAY** can also inspire the spirit of thermal spray research in the country by providing the latest information on thermal spray technology.

Be healthy, active and curious.
Merry Christmas & Happy New Year 2023!

Best Regards,

(Dr. Satish Tailor)

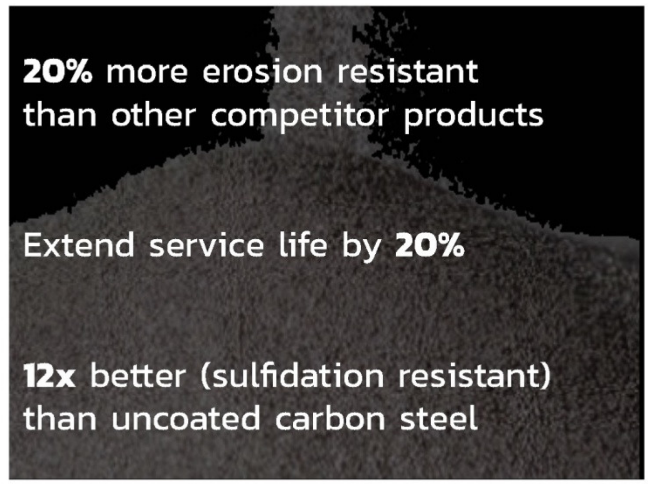
ADVANCED METALLIC COMPOSITE NIOBIUM CARBIDE CLADDING

US Patent Application No: 63/248,885 (patent pending)

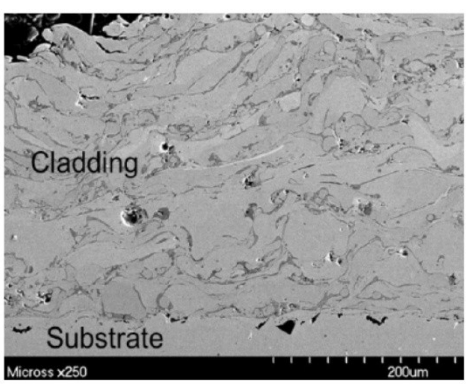
Composite Cored Wire Cladding Containing Hard Niobium Carbide

Key Features of this New Innovative Cladding

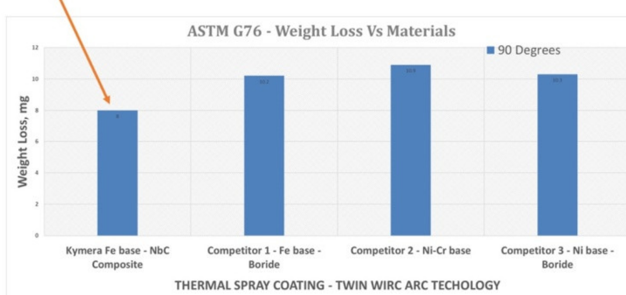
- Corrosion & erosion resistant
- Non-permeable with treatment
- Cladding easily measurable - Ni base
- High bond strength: > 4000 psi
- Easily repairable
- Porosity: < 4%
- Total oxide content: < 3%
- Hardness: average 56 HRC
- Deposition efficiency: ≈ 68%
- Cladding thickness typically between 6 mils to 125 mils



Innovative Wire Feed Stock



LESS WEIGHT LOSS - BETTER EROSION RESISTANCE



20% MORE EROSION RESISTANT THAN COMPETITOR PRODUCTS IN THE MARKET

NC100 CLADDING - EROSION RESISTANCE	
DISTANCE	10 MM
ORIENTATION	90 DEGREES
VELOCITY	30 M/S
PRESSURE	8 PSI
SCFH	15
MEDIA	ALUMINA: ANGULAR SHAPE, 50 µm

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Development of Spray Parameters for Sustainable Thermal Spray

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Email: venkatav@lsbu.ac.uk

Abstract
A structured approach is needed to develop spray parameters considering the modern requirements to produce high volume of complex shaped parts while retaining the spraying efficiency. Coating specification needs to be understood thoroughly for the microstructural and mechanical property requirements, current infrastructure, materials physical properties of the substrate and the powder, choice of guns and the need for monitoring and diagnostics. A good understanding of the robust supply chain of powders is required to invest time and develop parameters for those powders that are available uninterrupted. Statistical software such as Minitabcan guide the development of process parameters to obtain high quality coatings and a database concerning this can be shared through online platforms as a healthy practice to share knowledge.

Introduction
Thermal Spray Industry caters to a wide variety of sectors ranging from aviation, power generation to precision life supporting bio implants[1]. Many corporations develop their coating technologies in house to keep them proprietary or rely on external supplier's base to outsource the work. Spray parameter development could take months or even years. Although, the spray parameters may comply with the specifications but there could be room for further optimisation of the process as an effort to save costs, materials and energy.
Thermal spray costs incurred are a zero-sum game. It could be that customer is paying exorbitant rates for a coating process or the supplier is incurring losses to keep the customer base intact. The success of developing coatings to comply with a certain specification depends on a lot of factors such as volume of parts to be coated annually, post coating finish required, base material type, base material melting point. The tendency of the coating material to oxidize, its melting point, density of the powder and the surface roughness of the coating desired needs to be factored in. There could be limitations on the equipment or the gases that could be available due to geographical or budget constraints. Material physical properties, microstructural features, mechanical properties, and end application of the coating need to be considered prior to starting the development. Selection of equipment such as guns, coating process controller, powder feeder is paramount since it will have long term maintenance and operation costs. Whole process development might have to recur should there be a need to change the equipment later due to cost factor. Choice of wheel feeders Vs fluidized bed feeders could be done upfront considering the feeder maintenance.
This article will elaborate on the factors, and nuances of the process parameter development to aid practicing engineers with a view to standardise these practices. The article does not focus on a single thermal spray process but in general air plasma, HVOF, wire arc and flame spray processes. The objective is to create a subtle understanding of parameter development for engineers and thermal spray operators alike.

Critical steps in coating parameter development
It is prudent to pay attention to coating specification as a first step to understand the microstructural features needed such as unmelts, interfacial contamination, porosity, oxide content, vertical crack counts (in case of segmented coatings), the hardness and tensile strength requirements. Test requirements such as erosion or thermal cycling tests are contingent upon the microstructure, hardness and tensile properties. Hence, it is not mandatory to target compliance with these tests in the first place. In other words, if we get the microstructure, hardness, and tensile properties to comply, the rest of the testing requirements will comply by itself. The second requirement is to understand the infrastructure where the parameter will be used for production. Potential availability of high energy guns, access to inert, combustible gases and liquid fuels would

provide a wide variety of process options to choose from. For example, presence of acetylene and oxygen would be suitable for flame spray and availability of hydrogen would open up HVOF capability while presence of liquid fuels would be even better for high throughput metal and alloy coatings with HVOF. Availability of post coat heat treatment infrastructure would enhance the capability of applying bond coats that can diffuse into the base material on heat treatment. Ability to mask cooling holes with metal, tape masks or cooling holes masks is important to choose the processes accordingly. For example, we cannot design a HVOF process for WC-Co, if there are no feasibility of metal masking on the part. A plasma spray with tape masking is an alternative for such scenarios.

The third and most important step is to understand the physical properties of coating material as well as the base material. Properties such as apparent density, tap density, morphology, size range, melting point are important to consider for powder while selecting process, guns and gases and standoff distance. Properties of the base material such as melting point, coefficient of thermal expansion are worth noting before starting development especially when choosing standoff distance and choice of gases and guns.

The next most important step is the choice of guns. Choice of gun is dictated by the geometry of the part, whether the inside or outside of the part is to be coated, availability of gases and the throughput needed. Thickness / pass needed is a consideration to be given while choosing guns.

For high throughput, a high kw gun with radial external injection is a natural choice with large nozzle bore diameter. With doublet or triplet injector that can uniformly channel the powder across the circumference of the plume, these guns can manufacture production parts faster and consistent in their coating quality.

Fifth step is to understand the need for monitoring and diagnostic tools such as IR camera, particle temperature and velocity monitoring devices, having a good offline robot software such as robcad, robo guide or robot studio. Open-source codes with python/ GitHub support are also available to perform offline programming of robots such as KUKA. A parameter developed on samples coated with a ladder program is going to be significantly different from the parameter developed on parts with complex profiles. It is wise to attach samples on actual parts to study the efficacy of such parameters on such profiles. Besides all these, a significantly important need is to have a good metallography analyst which can give consistent and reliable feedback to the process parameters developed so that tweaking the parameters is in line with the feedback. Wrong feedback from the analysis lab would confound and delay the development of parameters.

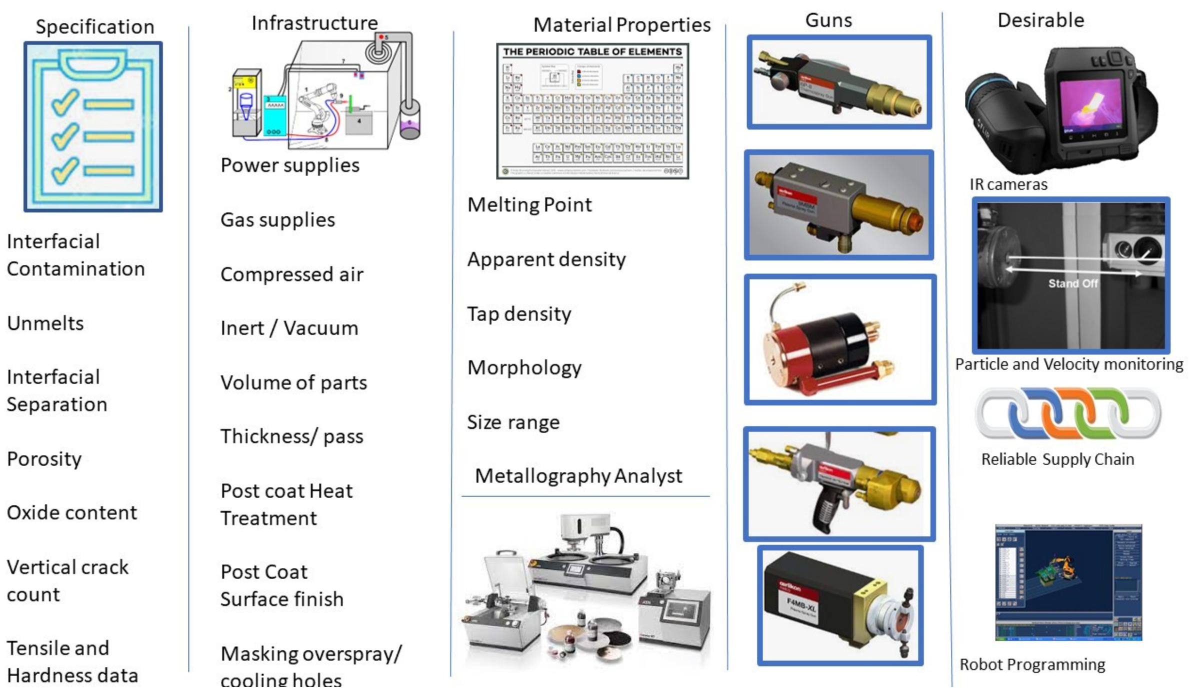

Figure 1: Steps involved in the development of spray parameters for thermal spray.

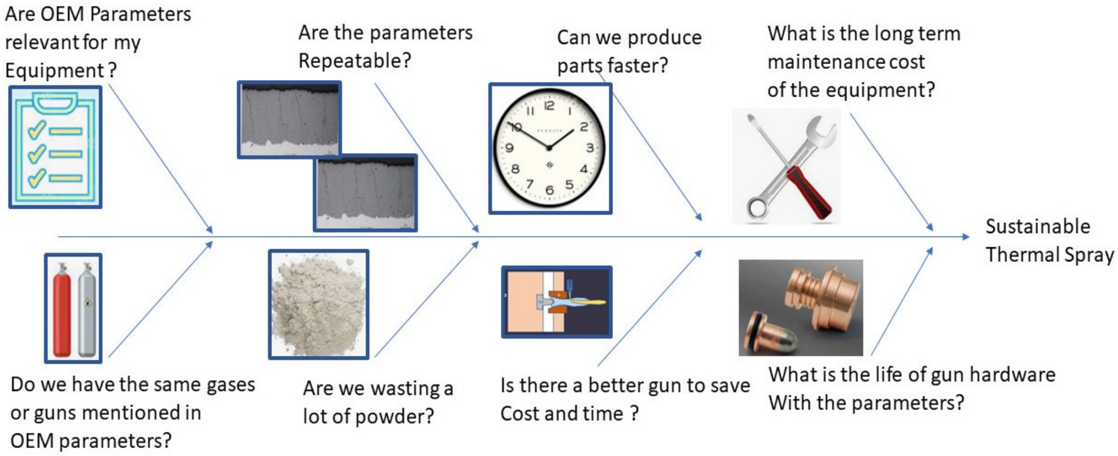

Figure 2: Checklist to consider before starting the development of spray parameters

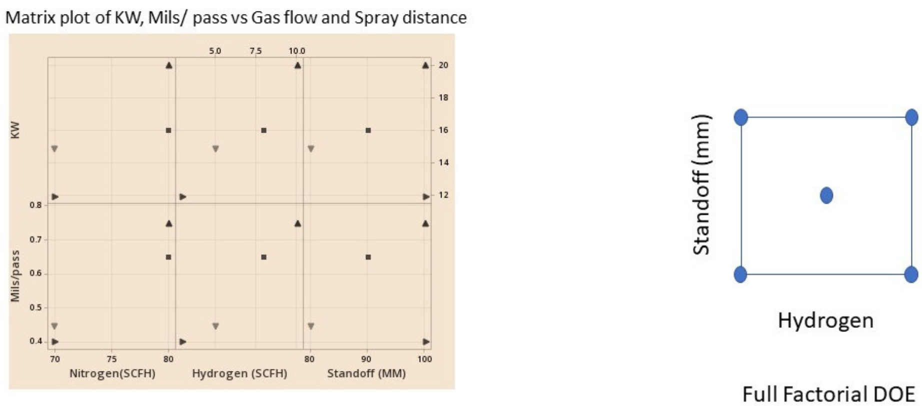

Figure 3: (a) Matrix plot of parameters vs two important coating requirements (kw and mils/pass). (b) A full factorial DOE with the two important parameters

Table 1: Parameters trials with four set of parameters on 8YZ with 9MB gun

Nitrogen(SC...	Hydrogen (S...	Standoff (MM)	Carrier gas (...	Amps	Volts	KW	feed rate (g/min)	Unmelts	Porosity	Mils/pass	Tensile (PSI)
70	3	100	7	400	30	12	35	3	4.0	0.40	800
70	5	80	8	400	37	15	35	2	3.0	0.45	900
80	8	90	8	400	40	16	38	1	2.5	0.65	1000
80	10	100	8	400	50	20	45	0	2.0	0.75	1100

Importance of Design of Experiments and Statistical Analysis

Development of parameters starts with a full factorial Design of Experiments (DOE) and a good statistical analysis tool is essential to be applied. An example case is shown below wherein it is important to understand and finalize the DOE with two or three most important parameters that significantly contributes to the coating properties. For instance if 8YSZ powder is to be sprayed with a 9MB gun, then it is important to note that hydrogen and standoff distance were finalized as predominant parameters to change, leaving all other parameters constant.

Four different parameters were sprayed with 9MB and 8YSZ powder on Super alloys and the microstructure and tensile properties were all put together in one table format as show in Table 1. Then, a Statistical software such as Minitab was used to obtain a matrix plot of the data to compare the two most important parameters (hydrogen flow and spray distance) affecting two critical to quality requirements (kW and the thickness/pass.) It was thus concluded based on the matrix plot that hydrogen and standoff distance are the change makers for the coating properties needed and it was decided to make a full factorial DOE with two parameters shown in Fig. 3.

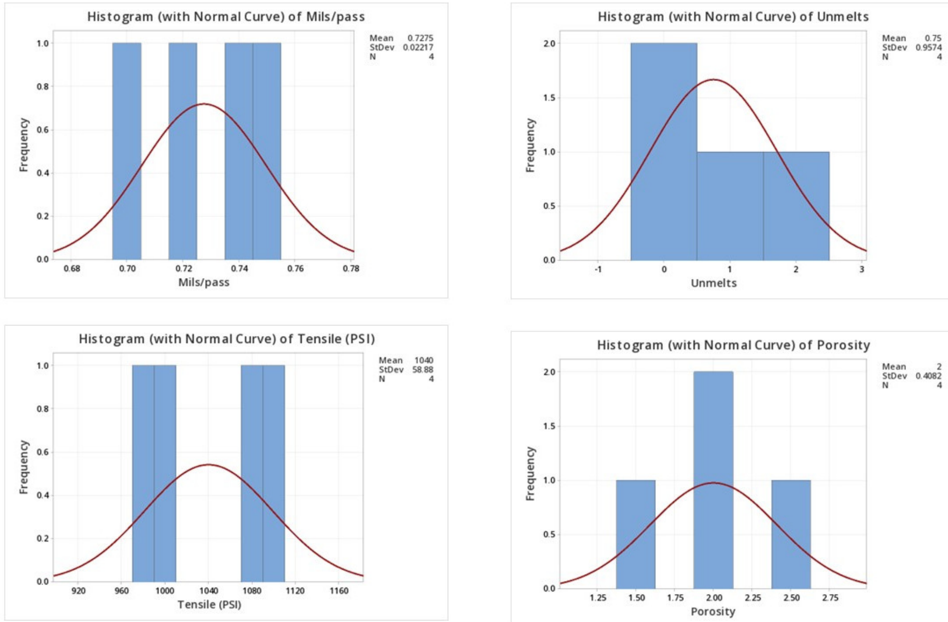

Figure 4: Histogram showing plots with coating properties and the range of values that are expected

Table 2: Repeat of trials to ensure that the parameters are statistically repeatable

Repeatability Check

Nitrogen(SC...	Hydrogen (S...	Standoff (MM)	Carrier gas (...	Amps	Volts	KW	feed rate (g/...	Unmelts	Porosity	Mils/pass	Tensile (PSI)
80	10	100	8	400	50	20	45	0	2.0	0.75	1100
80	10	100	8	400	50	20	45	1	1.5	0.72	1000
80	10	100	8	400	50	20	45	2	2.5	0.70	980
80	10	100	8	400	50	20	45	0	2.0	0.74	1080

Statistics

Variable	N	N*	Mean	SE Mean	StDev	Min	Q1	Median	Q3	Max
Unmelts	4	0	0.750	0.479	0.957	0.000	0.000	0.500	1.750	2.000
Porosity	4	0	2.000	0.204	0.408	1.500	1.625	2.000	2.375	2.500
Mil/pass	4	0	0.7275	0.0111	0.0222	0.7000	0.7050	0.7300	0.7475	0.7500
Tensile (PSI)	4	0	1040.0	29.4	58.9	980.0	985.0	1040.0	1095.0	1100.0

Based on the full factorial DOE it was finalised to use 100mm standoff with 10 SCFH hydrogen parameter. Now, it is time to do the repeatability check and check if all properties such as porosity, tensile strength are consistently meeting the requirement. A histogram plot of the properties such as porosity, unmelts, thickness/ pass, tensile could help us identify if the process is within the compliance window before releasing it to production. It is important to publish a range instead of a specific number for users to achieve it without any difficulties. Hence it is important to get mean, median and standard deviation from such repetitive studies as shown in Table 2.

Conclusions

Thermal spray parameter development engulfs interdisciplinary approach from materials engineering, mechanical engineering, and robotics expertise. The developer of such parameters must vet the properties that can be achieved by repeating the parameters development before publishing it. This will make it easier for the thermal spray manufacturing professionals to use the parameters in real-applications and report back on further improvement which could iterate continuous evolution of knowledge in this arena.

Acknowledgments

The authors acknowledge the financial assistance from the EPSRC NetworkPlus in Digitalised Surface Manufacturing (EP/S036180/1).

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1. V. Viswanathan, N.K. Katiyar, G. Goel, A. Matthews, S. Goel, Role of thermal spray in combating climate change, Emergent Materials 4(6) (2021) 1515-1529.

Plasma Spray Coating Activities Related to Solid Oxide Fuel Cells at CSIR-National Aerospace Laboratories

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Introduction

Plasma spraying is an important, old, well-establishedand widely used thermal spray technique for a myriad of applications [1]. It is a much sought-after process as it can be (i) used to coat a wide range of materials including metals, refractory ceramics, cermets, etc. to meet a variety of needs, (ii) coated on a variety of substrates, (iii) used to develop different functional coatings for a variety of applicationsand (iv) it is a relatively cheaper technique. The plasma spraying technique is used in different industries starting from biomedical to aerospace(Fig. 1).

Figure 1: Schematic showing various industries where plasma spraying is employed.

Plasma-sprayed coatings are commonly used for developing (i) tetragonal zirconia-basedthermal barrier coatings on gas turbine components; (ii) aluminum oxide and chromium oxide coatings on printing rolls; (iii) Mo-based coatings on diesel engine piston rings; (iv) biocompatible hydroxyapatite coating for implants, etc.
In the plasma spray process, the ceramic powders are fed onto or through the plasma flame where they get melted and traverse with high speed and get deposited on the substrate. The plasma spray process has the following variants: (i) atmospheric plasma spraying, (ii) suspension plasma spraying, (iii) solution precursor plasma spraying, (iv) low-pressure plasma spraying, (v) vacuum plasma spraying and (vi) plasma spray-physical vapor deposition. For atmospheric plasma spraying, flowable powders (20-100 μm) are a pre-requisite. On the other hand, for suspension plasma spray (SPS) application, very fine sub-micron (~1μm) size particles are required. For solution precursor plasma spray (SPPS) applications, a precursor solution containing stoichiometric amounts of constituent ions in solution form is required. Both SPS and SPPS yield thin coatings possessingnano-features. Depending on the requirement, different variants of plasma spraying can be used. Depending on the intended application of the coating, the plasma spray parameters like plasma power, spray distance, powder feed rate, powder properties, etc. can be adjusted to get coatings with the required porosity and density. For more details on plasma spray technology, readers can refer to the literature [2,3].
At CSIR-NAL, an atmospheric plasma spray facility was established in 2005 and later it has been suitably modified in-house for suspension and solution precursor plasma spraying applications. The work at CSIR-NAL has been focused on the indigenous development of plasma sprayable powders and plasma spraying them for different applications as illustrated in Fig.2. All the ceramic powders used for plasma spraying have been synthesized by a single-step solution combustion method or co-precipitation method [4,5]. Apart from that, the spray-drying process has been used to synthesize flowable powders [6]. In this report, the various plasma-sprayed coatings developed for solid oxide fuel cells (SOFC) are highlighted.

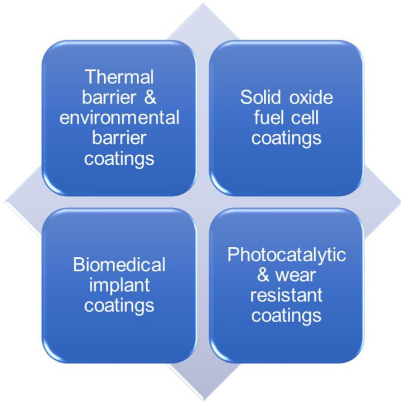

Figure 2: Schematic showing the plasma sprayed coatings prepared for various applications at CSIR-NAL.

Plasma-sprayed coatings for Solid oxide fuel cells

A solid oxide fuel cell (SOFC) is an electrochemical device that electrochemically combines hydrogen and oxygen to produce water and electricity at high temperatures. It consists of a dense electrolyte and a porous cathode and anode [7, 8]. Besides, the interconnect coating should be dense. The SOFC components are all ceramics and are listed in Table 1. It consists of a dense and ionically conducting electrolyte mostly made of 8 mol% yttria-stabilized zirconia (YSZ) cubic phase. The cathode is a porous LSM and the anode is also a porous electrode mostly made of Ni-YSZ cermet possessing higher electrical conductivity. The SOFC was initially developed in the form of tubular SOFC and in the past decade, the interest is towards the development of planar solid oxide fuel cells.

The review article by Hui et al. [9] provides the potential advantages, and challenges of thermal plasma spray (PS) processing for nanopowder production and cell fabrication of solid oxide fuel cells (SOFCs). The initial plasma spray activities at CSIR-NAL were focused on the development of plasma-sprayed electrolyte, anode, and interconnect coatings for tubular solid oxide fuel cell components as listed in Table 1. Due to thermal shock, the LSM tubes were breaking during plasma spraying. Usinga suitable inner fixture and also using gradual heating of the LSM tube before plasma spraying, facilitated the YSZ coating formation on the LSM tube without the breaking of LSM tubes [10].

The required YSZ, NiO-YSZ and LSM powders were synthesized in-house. To get flowable powders the, co-precipitation and solution combustion processes were tailored [4, 6]. The powders synthesized by the solution combustion method and co-precipitation method were mostly blocky angular in shape (Fig.3). The particle size distribution of 8 mol% YSZ showed the following size distri--bution: d10=18.193 µm, d50=63.328 µm, and d90=123.370 µm (Fig.4).

The cross-section of the plasma sprayed YSZ coating on a porous LSM substrate is shown in Fig. 5. The coating was nearly dense as evident from Fig.6, wherein the water drop did not penetrate the YSZ coating [11].

Table 1: Plasma sprayable SOFC powders and coatings developed at CSIR-NAL

Electrolyte	Cathode	Anode	Interconnect
Yttria stabilized zirconia (YSZ)	La0.6 Sr0.3 MnO3-δ (LSM)	NiO-YSZ	La0.6Sr0.2Ca0.2CrO3
Scandia stabilized zirconia (ScSZ)	La0.6Sr0.4Co0.8Fe 0.2O3-δ (LSCF)	NiO-GDC	Mn1.5Co1.5O4
Gadolinia doped ceria (GDC)			

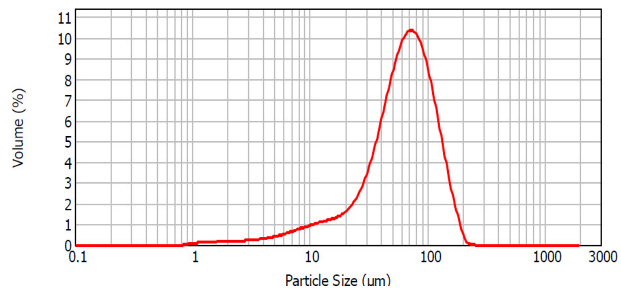

Figure 3: Particle size distribution for 8mol% YSZ obtained by co-precipitation method.

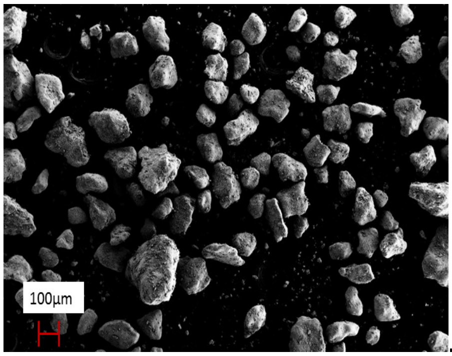

Figure 4: FESEM images of NiO-YSZ prepared by co-precipitation method at 100 X magnification.

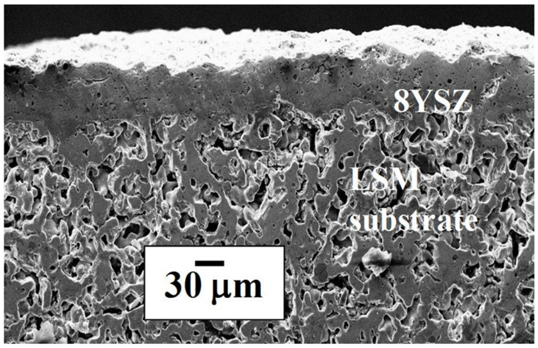

Figure 5: Scanning electron microscope image of a nearly dense YSZ coating on a porous LSM substrate.

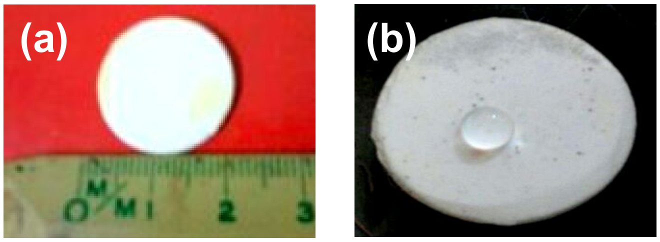

Figure 6: Photographs of (a) half cell coated with YSZ on a metal substrate and (b) water droplet on dense YSZ coating.

Scandia stabilized zirconia powders were also synthesized in-house and the plasma sprayed coating showed higher ionic conductivity (~7.19 × 10−4 S/cm @) 500°C) similar to that reported in the literature [12]. Similarly, Gd0.2Ce0.8O2-δ(GDC), which is used as an electrolyte for intermediate-temperature SOFCs, was synthesized by using different fuels [13]. Oxalyl dihydrazide yielded a very fine powder of GDC, which when sintered fully dense microstructure and exhibited an ionic conductivity of (3 x 10-4 Scm-1 at 400 °C). The mixture of fuels like glycine and ammonium acetate yielded plasma spray-grade powders.

Efforts were also made to develop coatings for metal-supported button cell SOFCs as they are considered low-cost material alternatives compared to traditional ceramic-based devices. These powders possessed the required flowability and phase purity for plasma spray application. The NiO-YSZ powder was synthesized by the single-step solution combustion method [14]. The particle size distribution of NiO-YSZ powder showed d10=7.3 µm, d50=60 µm, and d90=115 µm. The plasma sprayed coating showed a conductivity of 600 S/cm and it possessed a large number of triple phase boundaries and hence seems to be a promising route to use the plasma spray process.

Attempts were also made to deposit a thin LSCF layer using the SPPS process. This method does not require high-temperature temperatures for firing and avoids the formation of insulating phases [15]. Besides the SPPS process facilitated the formation of interlayer-free SOFC and it exhibited an area-specific resistance (ASR) of 0.1 ohm cm2 vis-à-vis the coating obtained from commercial LSCF powder 42.5 ohm cm2. LSM and LSM/YSZ coatings were developed by using the SPPS process [16]. The effect of plasma power on the composition of LSM/YSZ coatings was studied. The study revealed that the phase fraction of LSM and YSZ in the coating was dependent on the plasma powder. Interestingly, at low plasma powers, the composition of the final coating was close to the precursor composition.

Efforts were also made to develop metal-supported button cell SOFC. The performance of all plasma sprayed SOFC is shown in Fig. 7. From the figure it is evident that a maximum power density of 85 mW/cm2 was obtained. The lower power density of the metal-supported SOFC has been attributed to the thicker YSZ coating (500 µm).

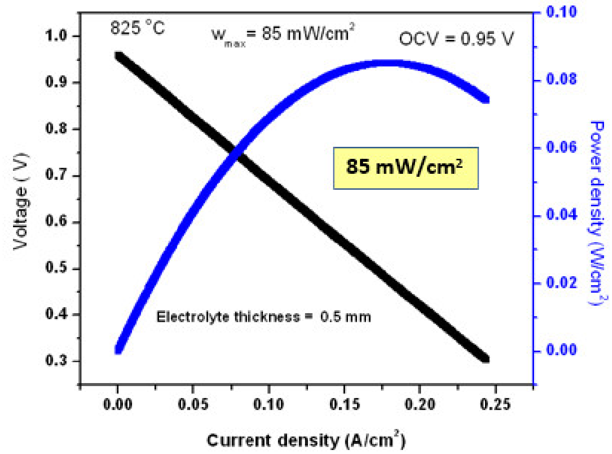

Figure 7: The power density curve of metal-supported SOFC.

In recent years there are efforts to develop protective interconnect coating on bipolar plates to avoid the diffusion of Cr onto the cathode side that deteriorates the cathode function. The protective interconnect spinel (Mn1.5Co1.5O4)coating has been developed from SPPS and atmospheric plasma spray processes [17]. This coating emerges as a promising coating for interconnect applications. Further, finer tuning of the plasma spray power and other parameters to achieve the metal-supported SOFC with improved power density.

Acknowledgments

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Facile Fabrication of Superhydrophobic Surface Through Flame Spraying

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Introduction

Nature is an eminent source of inspiration for many engineering systems. Among many, Lotus leafs are known for their self-cleaning ability [1]. The water droplet rolling on lotus leaf surface, removes all the contaminants. Similar characteristics are also displayed by taro leaf[2], salvinia[3], butterfly wings[4]. Fabricating such bioinspired superhydrophobic surfaces have gathered interest among researchers due to their extra-ordinary properties like self-cleaning[5], anti-corrosion[6], drag reduction[7], anti-icing[8], and anti-staining. The wettability is the inherent property of a surface dictating the interaction with the water droplet. The two extreme cases of wettability are superhydrophilic (water attracting surface) and superhydrophobic surfaces (water-repelling surface). The superhydrophilic surface have high spreading kinetics with contact angle approaching 0°, whereas superhydrophobic surfaces exhibits contact anglegreater than 150° and rolling angle less than 10°[9]. The very low contact of water with surface improves the corrosion resistance which is a desired property for any metallic surface. The surface topography with low surface energy plays a major role in making of superhydrophobic surfaces. The wettability of rough surfaces can be explained using Wenzel model (impregnating state) and Cassie-Baxter model (air entrapping). The models dictate the dependency of superhydrophobicity on surface topology[10]. The lotus leaf exhibits high superhydrophobicity due to multi-order hierarchal structures with epicuticular wax nanocrystalloids. The surface topography with hierarchal structures is essential for developing stable and resilient superhydrophobic surfaces. Many processing route has been adopted to manipulate the surface roughness such as soft lithography, hydrothermal, electrochemical method, sol gel etc. However, still there is a need to develop more durable and robust superhydrophobic surfaces for make them useful for real life applications. In the present work, we developedant-corrosion superhydrophobic surfaces through facile flame spraying technique. Development of superhydrophobic coatings throughcost-effective flame spraying method is a new add-on application in the list of thermal spray coatings.

Methods

The aluminium powder was purchased from Metallizing Equipment Co. Pvt. Ltd. (MEC), India. The aluminium coatings are deposited on 10x10x5 mm^3 low-carbon steel coupons. The substrate was chemically etched in 5% HNO_3 solution for 2 minutes prior to flame spraying for better coating-substrate adhesion. The air pressure of the air-jet assembly and stand-off distance were varied from 0.5 to 2 bar and 50 mm and 125 mm, respectively. The surface chemistry of surface was modified by silanization. The morphological examination and elemental chemical distribution are conducted using a field emission scanning electron microscope, FESEM (JEOL, JSM-7610FPlus, Japan) with 15kV accelerating voltage equipped with energy dispersive spectroscopy, EDS. The contact angle measurements were performed on Goniometer (Apex, India). The adhesion force was measured using the force tensiometer (Sigma 701, Sweden).The mechanical durability was performed on Tribometer (Rtec, USA), against 2000 abrasive sheet as counter surface.The corrosion studies were performed in 3.5 % NaCl in potentiostat (Gamry, 100E) in a three-electrode system.

Results and Discussion

The micrographs reveal the multi-order hierarchal structures formed through flame spraying deposition. The spray parameters were optimized and micro-nano structures were clearly visible for large stand-off distance coatings. The coatings enhanced the surface roughness promoting the wetting behaviour.

Figure 1: Schematics showing superhydrophobic surface fabricated through flame spraying technique displaying self-cleaning and anti-corrosion behaviour after silanization. The multi-order hierarchal surface roughness enhanced de-wetting behaviour and imparted high durability

The lamellar structure is formed through the layer-by-layer deposition of molten/semi-molten powder particles on the substrate. The lamellar coating with inter-splat boundaries including un-molten particles, oxides, cracks, and pores leads to enhanced surface roughness. The as-sprayed coatings displayed superhydrophilic behaviour which was transformed into superhydrophobicity after silanization. The coatings with optimized parameters exhibited advancing contact angles greater than 155° and receding angles less than 152° with sliding angle less than 5°. Also, coatings displayed water surface adhesion lower than that of the lotus leaf. All the coatings exhibited water coating adhesion less than 20µN. The coatings displayed high resistance towards abrasion and showed enriched mechanical durability. The coatings displayed self-regeneration behaviour by repeating the surface morphology and properties even after some external damage. The self-regenerative behaviour of the coating was investigated using an abrasion test performed at 100mN load for more than two hours against 2000 SiC abrasive paper as a counter surface. The in-situ development of alumina nanoparticles was also responsible for high resistance to mechanical abrasion. The in-situ synthesis of nanoparticles in the aluminium coating was observed for coatings at a larger stand-off distance. Also, superhydrophobic coatings displayed low corrosion rates compared to the bare substrate. In potentiodynamic polarization and EIS studies coatings with large stand-off distance displayed low corrosion current density and high polarization resistance. The coating at optimized parameters improvised corrosion resistance by 121 times that of the substrate. The coatings at larger stand-off distances displayed multi-order hierarchal structures which were responsible for achieving a high de-wetting state. The effect of enhanced de-wetting was seen in improved corrosion resistance of samples at larger stand-off distances. The coatings demonstrated superior self-cleaning behaviour accomplished with anti-staining properties. The coatings were tested for dry and wet contaminants like chalk dust, muddy water, tea, coffee, cold drink. The dry contaminants were taken along the water droplet leaving the surface clean. The superhydrophobic coatings performed extremely well in the real environment, the samples maintained superhydrophobicity for several months when kept outdoors. Durability is one of the major concerns for superhydrophobic surfaces, however, the coatings fabricated through the flame spray technique are robust and durable.

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Investigation of Dense Sinkor® Coating Performance in Molten Zinc

By ***Satish Tailor*** and ***Ankur Modi*** , *Metallizing Equipment Company Pvt. Ltd. Jodhpur*
Email: dgm_rnd@mecpl.com

Surface treatment for sink rolls in continuous galvanizing line is an important issue due to the unfavorable environment of the molten zinc. The corrosion behavior of the four types of different thermal spray coatings of WC-12Co, Cr_3C_2NiCr, Al_2O_3-TiO_2, and Sinkor® (a MEC coating product) were tested in a static molten zinc condition for 30 days as shown in Fig. 1. WC-12Co and Cr_3C_2NiCr, coatings were prepared by HVOLF system (Make MECPL Jodhpur) equipped with MJP 5000 gun. Al_2O_3-TiO_2, and Sinkor® coatings were prepared by newly developed Hybrid-LVOF process equipped with CERAJET gun (Patented Technology). The full information about Hybrid-LVOF process is described by S. Tailor et al. [1-2]. The samples were analyzed for microstructure, phase and weight changes to understand the degradation mechanism of the coating after dipping in molten zinc. The results were checked and compared.

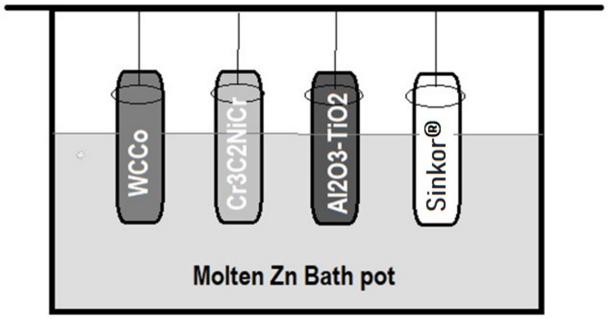

Figure 1: Molten zinc corrosion test setup

Cr_3C_2NiCr coating failed due to bulging and color changing effects and the sample remained in the vessel. It is clearly indicating that Cr_3C_2NiCr coating cannot survive in such environment. The corrosion mechanism of WC-Co coating showed Co-dissolution followed by carbide detachment from coating. Therefore, WC-Co coating is not suitable for molten zinc applications. The same results for both materials are reported by many researchers. Whereas, on the contrary Al_2O3-TiO_2 and Sinkor® coatings have shown good stability.

However, Zn accumulation was observed on the Al_2O_3-TiO_2 coating surface and Zn react with TiO_2 and form a Zn_2TiO_4, this leads to poor coating surface quality which can lead to poor surface quality of galvanized sheet. Therefore, Al_2O_3-TiO_2 coating also not suitable for sink rolls application.

Whereas, Hybrid-LVOF sprayed dense Sinkor® coating remained completely inert to molten zinc even after 30 days of exposure and maintains structural integrity. No visual defects and coating failure were observed even after 30 days test. The Sinkor® coating was stable without any defects and changes. No signatures were found to support in changing porosity, formation of any new phase and accumulation on the coating surface and grain growth. It is reported that Hybrid-LVOF sprayed ceramic coatings have better mechanical and structural properties in comparison to plasma sprayed a coatings [1-2], plasma sprayed coatings have more porosity and horizontal cracks after molten Zn test.

Further cross-sectioned SEM images of 0, 10, 20 and 30 days samples were also analyzed to investigate the penetration of molten Zn in the coatings. Microstructural analysis shows that no cracks were observed and no change in thickness was observed even after 30 days of molten zinc testing of Sinkor® coating. The coating remains non-reactive and Zn shows stability in corrosive environments. Due to dense coating microstructure no zinc penetration is observed in the coatings as shown in Fig. 2. Thus, it can be said that dense Sinkor® coating does not undergo any thickness reduction and does not loose coating integrity even after 30 days of test. Moreover, no phase changes were observed. Further no stress has been generated in the Sinkor® coating.

Samples were weighed before and after immersion in molten zinc to determine the weight change occurring in the coating.

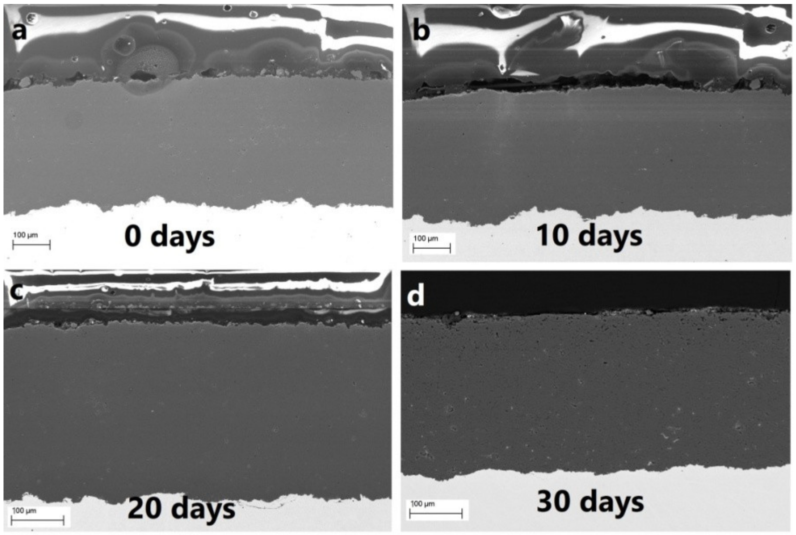

Figure 2: Sinkor® SEM microstructures after the molten zinc corrosion test for (a) 0, (b) 10, (c) 20 and (d) 30 days

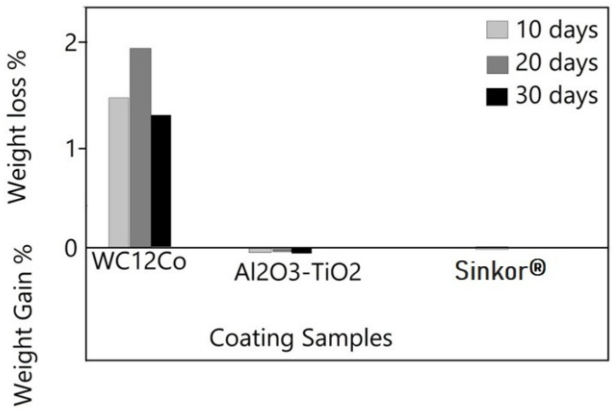

Figure 3: Weight change in coating after molten zinc corrosion test

Before weighing, samples were cleaned in acid solution to remove any solidified zinc followed by rinsing with water and hot air drying to avoid any false indications of weight gain. The WC-12Co coating showed a decrease in weight as the dipping time increases due to Co dissolution but it was observed that weight loss percentage is less in comparison to traditional HVOF sprayed coating.

Whereas, Al_2O_3-TiO_2 coating showed a very marginal weight gain with the increase in dipping time due to formation of Zn_2TiO_4 on the coating surface. Sinkor® coating has shown no change in weight which shows the chemical inertness of the Sinkor® coating. The weight change data is shown graphically in Fig. 3.

Conclusions

The findings of this study may solve an existing major corrosion and wear problem of the steel industry associated with pot rolls, including a sink roll and two stabilizer rolls, during Galvanizing process. MECPL Jodhpur has developed a special process and coating Sinkor® to solve this problem and it could be greatly improved the service life of a sink roll.

Hybrid-LVOF process is a new patented technology, mainly designed for thin and dense ceramic coatings. Hybrid-LVOF sprayed dense Sinkor® coating could be a very good candidate for protecting galvanizing pot plant hardware for a prolonged duration.

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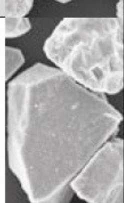
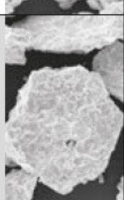
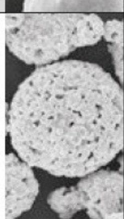
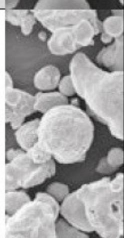
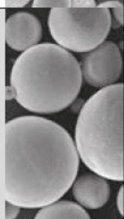
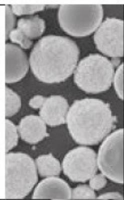
Thermal Spray Powder Types, Manufacturing Process & Characteristics

Powder type	Fused and crushed	Sintered and crushed	Agglomerated and sintered	Gas atomized	Water atomized	Spheroidized	Blended
							
Process	Fusing in arc furnaces, followed by cooling and crushing	Sintering of raw materials, crushing	Spray drying of a suspension consisting of fine powders and organic binder and subsequent sintering	Atomizing molten metal or alloy with high pressure gas (Ar, N_2) stream into a chamber	Atomizing with water into a chamber and subsequent drying	Feeding of agglomerates into a plasma flame to produce spherical particles	Mixing of 2 or more powders
Characteristics	Blocky, irregular, dense	Blocky, irregular, relatively dense	Spherical, porous, constituents homogenously distributed	Spherical, dense, high purity, low oxygen content	Irregular, dense, increased oxygen content compared to gas atomized	Spherical, porous or hollow, partly open (shells)	Different morphologies, segregation possible
Examples	Al_2O_3; Cr_2O_3; ZrO_2-Y_2O_3	WC-CoCr	WC-CoCr; Cr_3C_2-NiCr; ZrO_2-Y_2O_3	MCrAlY; Ni-, Co-base alloys; NiAl	NiCr; NiAl	ZrO_2-Y_2O_3	NiSF+WC-Co; Mo + NiSF; Cr_3C_2-NiCr; AlSi-Polys

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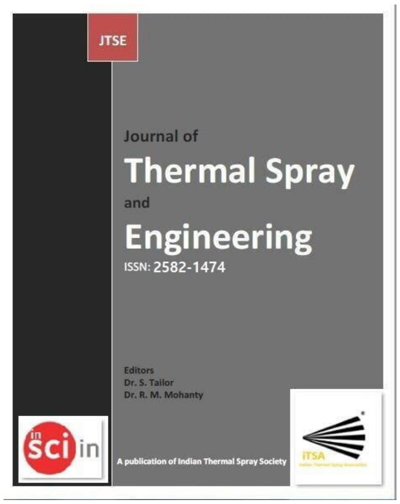

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