Sep. 2021| Vol. 1| Issue 3

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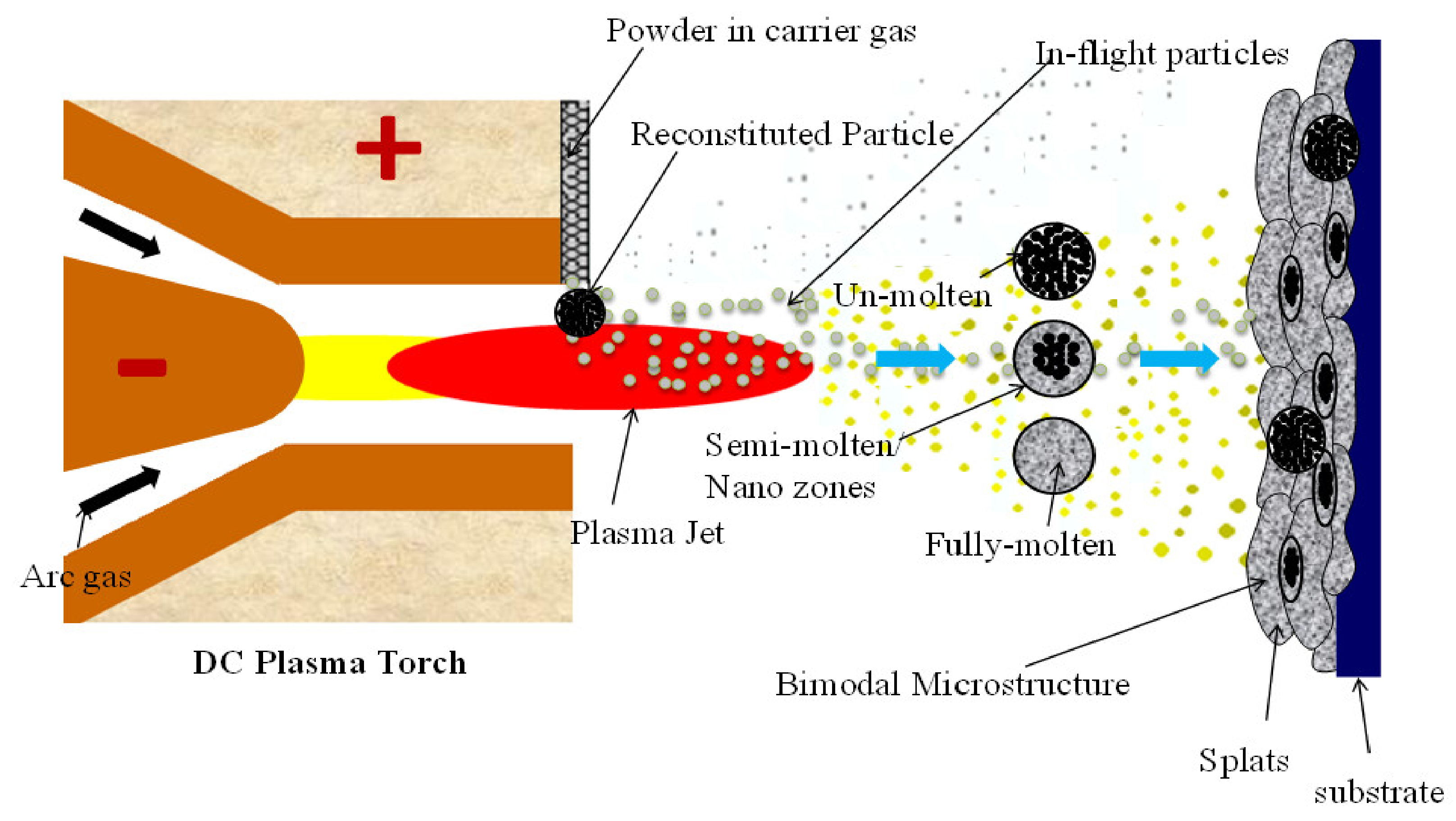

Issue Highlights

- Featured Article: Zinc Spraying - Advantages and Applications
- Technical Note: Preparation for a Huge Leap Forward in Coating Technology
- Industry Research: Advanced Metallic Composite Niobium Carbide Cladding for Power Plant Corrosion and Erosion Protection
- Academia Research: Plasma Sprayed Nanostructured YSZ Coatings Doped with Rare Earth Oxides: A state of the art

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EROSION & CORROSION PREVENTIVE COATING ON HYDRO - TURBINE PARTS

'MEC' - HVOLF SYSTEM

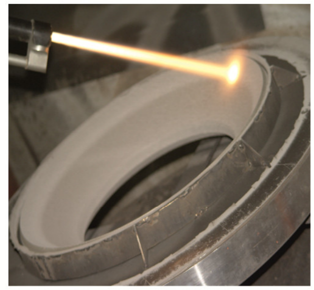
XPOJET SPRAY GUN

XPOJET 5000

XPOJET 5250

MJP - 6000

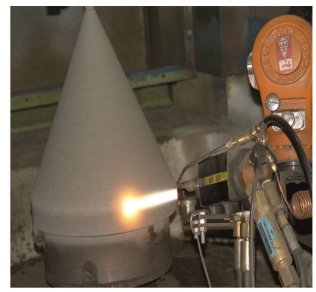
APPLICATIONS



HARD SURFACING OF SEAT RING

HARD SURFACING OF RUNNER

HARD SURFACING OF PELTON WHEEL



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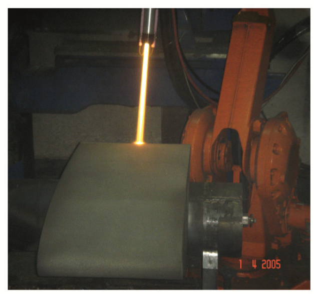


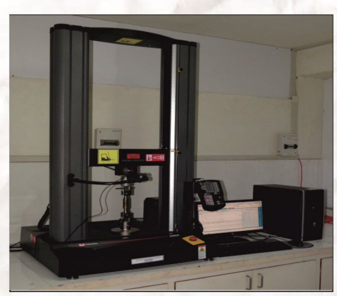
HARD SURFACING OF GUIDE VANE

HARD SURFACING OF TOP COVER

TESTING FACILITIES - NABL ACCREDITED

SEM Machine

XRD Machine



Adhesion Testing Machine

Vickers Hardness Tester

CERTIFICATIONS

ISO 9001:2015

AS 9100C, CE

API SPEC Q1

ISO/IEC 17025:2005

CRISIL RATINGS MSE2

ASM INTERNATIONAL

OFFICIAL SYSTEM PARTNER KUKA ROBOT

Metallizing Equipment Co. Pvt. Ltd.

E–101, MIA, Phase–II, Basni, 342005, Jodhpur, Rajasthan

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Sep. 2021| Vol. 1| Issue 3

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SPRAYTODAY™ is a quarterly publication of the INSCIENCEIN Publishing,

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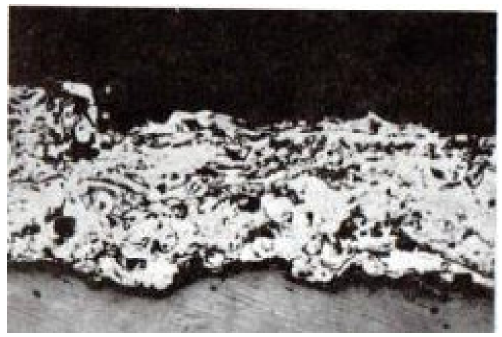

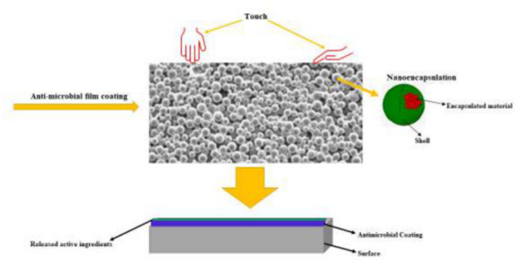

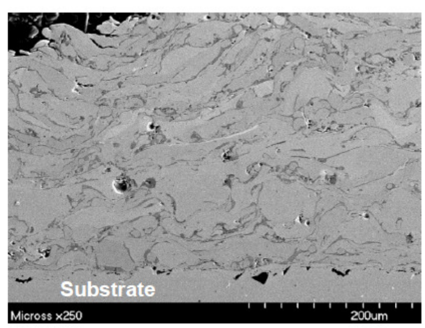

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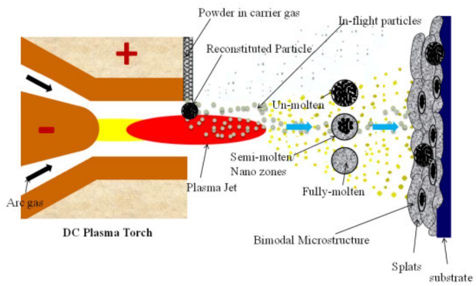

Research NEWS from Academia: **Plasma Sprayed Nanostructured YSZ Coatings Doped with Rare Earth Oxides: A state of the art**

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ABOUT THE COVER

Plasma Sprayed Nanostructured YSZ Coatings Doped with Rare Earth Oxides

Editor’s Note

Dear Readers,

The Corona period has affected almost all industries and 2020-21 so far has been unimaginable and full of surprises. The coating industries have also affected particularly thermal spray job shops. While the first restrictions in schools, universities and institutions already had a massive impact on everyday life at an early stage and brought about, among other consequences, digital learning, the crisis is also showing dramatic long-term consequences in the economic sense, particularly in our thermal in the spray coating area.

India is dealing very well with this corona situation and is organizing the world's largest vaccination program. India is producing the corona vaccine in large quantities and is committed to helping other countries. In this situation, India has emerged as a hope for the world. In this unclear situation, Indian coating companies are showing great courage and trying to exploit the problem as an opportunity, at least partially. In particular, the subject of digitization is experiencing a high reach in this regard. Happily, countless telephone conferences and web meetings have allayed the initial concerns of loss of personal contact due to Corona. Even better, new forms of working digitally were tried and in many cases successfully implemented. A healthy mix of old and new ways of exchanging information and knowledge seems to support this positive development.

I am particularly pleased to be allowed to recommend to you the latest issue of the SPRAYTODAY. This issue includes invited innovative featured articles on the subject of thermal spraying received from industry and academia experts that illustrate research trends in thermal spray development.

Looking at the future of thermal spray in India, it will be pleasing if 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.

Best Regards,

(Dr. Satish Tailor)

Zinc Spraying - Advantages and Applications

By **L. Pugazhenthy**, *Executive Director, India Lead Zinc Development Association & Past President of The Indian Institute of Metals*
Email: ilzda.info@gmail.com

Introduction

Globally of all the metallic coatings Zinc will be the largest volume wise. Zinc is applied on steel products and structures for corrosion prevention through several methods: hot dip galvanizing, zinc-aluminium alloy coating, spraying, electroplating, zinc-rich paints etc., Tonnage wise hot dip galvanizing and Zinc-aluminium alloy coating (galvalume, galfan etc.,) will be the largest. Next in order would be zinc spraying method.

Zinc Spraying

Zing spraying mainly consists of the following steps: a) degreasing to remove oil grease etc., b) mechanical cleaning through grit blasting (to remove rust, scale etc.,) and to make the surface rougher for better coating adhesion and c) spraying of Zinc (with either wire or powder of purity 99.5% or 99.95%). Zinc spraying is mainly a manual operation although automatic installations are also available for tonnage production of similar jobs.

Advantages

Of all the materials, zinc inherently has excellent corrosion resistance, both as barrier protection as well as sacrificial protection. In case there is any small holiday in the coating, surrounding zinc sacrifices itself and protects the exposed area which is vulnerable for corrosion to begin. Sacrificial protection is also known as cathodic protection. This is a well known value added property of zinc. The coating metal is applied on to the job with the help of a spray gun: the coating will consist of droplets of zinc surrounded by a layer of zinc oxide formed while the metal is molten. They combine together and bond with the steel surface giving the required adhesion (Fig-1).

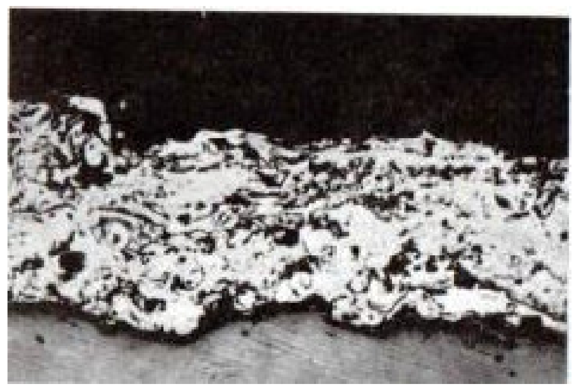

Figure 1: Zinc Sprayed Coating on Grit Blasted Steel

Zinc-aluminium alloys are also used for better corrosion protection. Originally 65% Zinc -35% Aluminium alloys were used and nowadays 85% Zinc - 15% Aluminium alloys are common and widely used in the industry.

Zinc spraying has the following inherent advantages:

- excellent corrosion resistance
- adequate adhesion
- can be applied in the factory or at site
- can avoid to and fro transport costs
- very thick coatings possible (> 1000 g/m2)
- no limitation on the size of the job
- carried out at low temperatures
- no adverse effect on the mechanical properties
- no distortion of the job
- can be sealed to avoid porosity
- can be painted to give aesthetic appeal
- duplex coated products can withstand higher temperatures
- most economical for larger surface areas

Applications

Zinc spraying is a very versatile process because of the above advantages. Worldwide originally a large number of steel bridges were zinc sprayed and they all gave a long life too. Well known Zinc sprayed bridges are Clifton suspension bridge in UK, Ridge Avenue bridge in Philadelphia, Pierre-Laporte bridge in Canada and Bosphorous bridge connecting Europe and Asia. Unlike hot dip galvanized coating, very thick coatings can be applied. In India steel bridges, both in railways as well as highways, should adopt zinc spraying instead of painting to obtain longer maintenance free service lives.

Duplex coated products ie., Zinc sprayed with an over coat of paint can be used in industrial atmospheres, coastal areas, chemical units, fertilizer plants, pipelines etc., Among chemical units, acidic atmospheres should be avoided for zinc sprayed products which will perform well under alkaline conditions. High mast lighting columns, foot over bridges, crash barriers, telecom towers etc., can also be zinc sprayed. If there is any size limitation because of the dimensions of the available galvanizing bath or if there are no galvanizers nearby, then it is always better to go in for zinc spraying at the sites.

Conclusion

Of late India has gone for massive investments in public infrastructure which are national assets; these investments are bound to go up in the coming years. The country should prevent avoidable corrosion losses and instead go wisely for zinc sprayed or zinc coated steel structures.

Money saved is money earned!

Preparation for a Huge Leap Forward in Coating Technology

*By **Dr. Reza Javaherdashti**, General Manager, Eninco Engineering BV, Netherlands.*
E-mail: Javaherdashti@enbincoating.com

Of the five ways by which corrosion (more correctly, electrochemical corrosion) can be controlled is use of coatings. In fact, one of usages of techniques such as thermal spraying is to create a barrier between the electrolyte (the corrosive atmosphere) and the vulnerable metal particularly to avoid CUI -that is to say, corrosion under insulation.

Coatings are effective mainly because they either do not let anode and cathode on the substrate see each other and therefore no electron emission (from anode) and electron acceptance (by the cathode) will take place. Therefore, the electron flow which is a necessary element in facilitating electrochemical corrosion is disturbed.

In addition, coatings do not allow any contact between the anode-cathode pair with the outside moisture in the air that would act as the electrolyte. This is particularly important to control atmospheric corrosion.

However, coatings such as galvanising do another function which is cathodic protection via sacrificial anode where zinc “sacrifices” itself to save the steel substrate. In any case, what makes coating to survive is the adhesion that exists between the coating material and the substrate. Adhesion is so important that one can have the best quality coating ever, however without a strong adhesion, the coating will not “stay” on its place, and this will be leading into spalling of the coating and peel off so that after some time, the coating will come off the substrate. The worse case scenario is that this peel off procedure takes place in a non-uniform way so that some parts of the substrate are covered and some parts remain bare. The areas where there is still a coating coverage would act as cathode with respect to the areas where coating spalling has happened and therefore can be considered as “bare” and with no coating.

It follows that even a poor-quality coating that adheres strongly to its substrate is more preferable to a very high quality coating that shows a poor quality in adhesion.

It follows that one direction we see coatings generally will generally take in the future as a trend will be developing coatings with very high adhesion forces to their substrates that can also be applied very easily. This way the costs associated with both application and maintenance will highly be reduced. In addition, as we see it, all these coatings must show features that would render them as eco-friendly as possible. This is a very important feature that while these days in some developing or underdeveloped countries may not be taken that seriously about the type of coatings they use, in the future will definitely become a compulsory criterion.

Apart from showing high adhesion, ease and economy of application as well as being eco-friendly, there is yet another feature that particularly these days have been even too important and it is the development of the so-called antimicrobial coatings.

In the same way that CUI is an electrochemical corrosion process which can be controlled by thermal spray method, microbiologically influenced corrosion (MIC) is an electrochemical corrosion in which living micro-and macro-organisms can affect the severity of corrosion. These organisms contain a class of bacteria that like sulphate reducing bacteria (SRB) are capable of inducing typical corrosion rates such as 1.75 mm/year or in some exceptional cases to 10 mm /year (1 cm/year)!

There are five methods currently in use or having the potential of use against corrosion:

1. Mechanical measures (e.g. pigging, this way by removing the debris and scales, likelihood of conditions leading into corrosion in the form of under deposit corrosion is highly lowered),

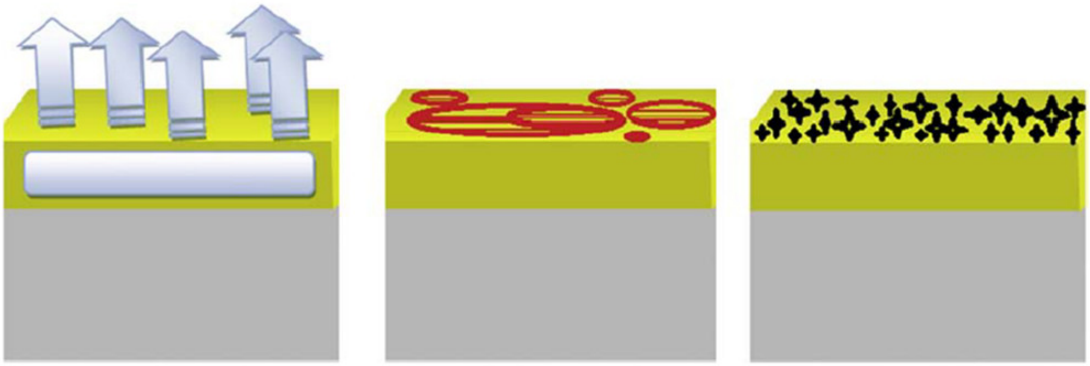

Figure 1: General categorization of coatings that can be used against MIC, from left to right: impregnated with biocide (biocide leaching strategy), with very low surface tension that will be too "slippery" for biofilm to be formed (adhesion resistance strategy) and with physical barriers/spikes (positively charged compounds) that destroy corrosion-related bacteria/archaea (CRB/CRA) approaching the coating to form a biofilm (Contact killing strategy).

2. Chemical measures (e.g. application of corrosion inhibitors with anodic, cathodic, or mixed effect mechanisms)
3. Physical measures (e.g. application of protective coatings and paints)
4. Electrical measures (such as cathodic protection and anodic protection)
5. General purpose and design measures (for example, material selection and/or modification of design so that condition leading into corrosion will not be encouraged)

In case of microbiologically influenced corrosion (MIC), these measures will show a little bit of modification, for instance in item 2, chemical measures will be expanded to also include biocides or a sixth measure, biological measures, will also be added examples of which could be bio-competitive exclusion and bio-augmentation.

Physical measures when it comes to MIC can be grouped into three categories:

2-1- Coatings that are impregnated with a biocidal material which releases over time,

2-2- Coatings that have such a low surface tension that makes them too "slippery" to let biofilms form on it

2-3-Coatings that have localities on them that carry different electrical charges thanks to their special functional groups

These three coating types can be schematically seen in Figure 1.
However different these may look like; they are all the same in that they form a layer on the substrate that is far different from the fabric of the underlying substrate. Being as such, frequent problems with paints/coatings such lack of adhesion happen. We at Eninco Engineering B.V. have solved this problem by inventing a technology that would allow the coat to literally become a part of the substrate itself and due to this fusion between the coating and the substrate, we have solved the paramount problems other coatings have from drying and handle time to the service life. We have discussed this somewhere else.

However, with COVID19 pandemic becoming a bitter fact of life nowadays, we though to develop a technology that using nano-particles in the levels approved by Environment Protection Agency (EPA), would allow to produce a new generation of smart coatings that due to their antimicrobial effects (effective against bacteria and viruses), we call them "Antimicrobial coating".

Mechanism and features:

The antimicrobial coating has been formulated based on using nano silver phosphate and copper oxide in the resin and co-reactant. The nano particles are light and heat sensitive agents. The method we have used to keep the nanoparticles together and balanced in the coating structure is encapsulation of the active ingredients. Using this method, incompatibility among different particles will be highly prevented. To produce the microcapsules, cross-linking method has been used whereby adding an active ingredient to the cross-linkable aqueous solution, cross-linking will happen. Figure 2 shows schematically the mechanism by which antimicrobial coating as developed by us works:

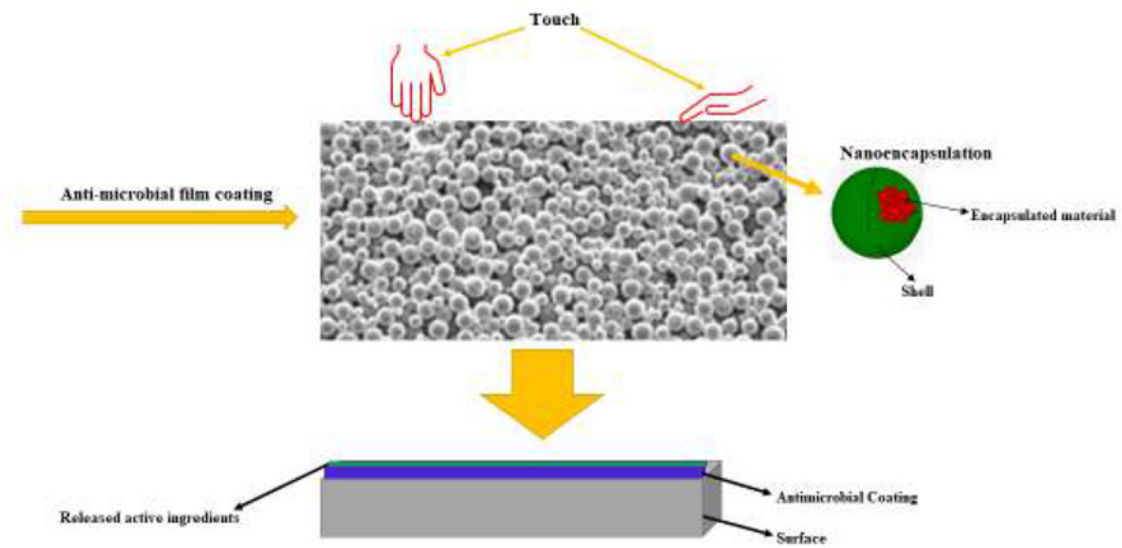

Figure 2: Working principle of antimicrobial coating technology as developed at Eninco Engineering B.V.

As shown in the figure, some layers of nano-size capsules (encapsulated particles) are introduced into the structure/fabric of the paint. Each encapsulated particle has been filled with antimicrobial agent. Upon touch or being exposed to a temperature of 37oC, the nano capsules are fractured and thus release the antimicrobial agent that will disinfect the surface. While by each touch, a layer is gone, due to calculated layers required, we have achieved the results that a total thickness of about 35 microns DFT (Dry Film Thickness) of the coating will suffice to give a disinfection rate of 99.99% and it will last for one year and will not be lost during this time. The film thus produced also serves to make the surface completely hydrophobic so that biofilm formation will be avoided. This one component, transparent paint has very low VOC % (Volatile Organic Compounds percentage).

Advanced Metallic Composite Niobium Carbide Cladding for Power Plant Corrosion and Erosion Protection

By ***Leo Antony*[1], *David Rigg*[1], *Edward Lewis*[2]**,
[1] *Kymera International-SCM Metal Products Division, RTP, NC 27709, USA.*
[2] *Independent Engineering System Consultant.*
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ABSTRACT
Boiler corrosion and erosion are a serious concern when the power plant components are exposed to by products of coal, biomass, municipal and industrial waste combustion. An advanced metallic composite niobium carbide cladding applied by twin wire arc spraying was developed to protect power plant components from boiler corrosion and erosion. Cost effective feedstock materials were strategically designed to produce niobium carbide in the final cladding matrix. Aggressive corrosion and erosion testing were conducted on this cladding to evaluate its corrosion and erosion performance. The results of the corrosion testing revealed that this cladding performed 12X better than the uncoated steel under aggressive sulfidizing environment. Relative erosion ranking revealed that this cladding outperformed other competing products by 20%. Also, the cladding revealed no cracking when subjected to aggressive thermal gradients.

Keywords: Twin wire arc spraying, Fireside corrosion, Niobium carbide, Erosion, Thermal cycling testing

Introduction

Of the several thermal spray coating techniques available, the twin wire-arc spraying technique has many key advantages that are particularly well suited for in-situ applications involving large power plant components. An example of an advantage of twin wire-arc spraying is a faster cladding application rate. In addition, twin wire-arc spray systems are portable; the equipment is robust; and cored wire can be used as feed stock, which offers greater flexibility in the composition of the final cladding materials that can be repaired in-situ if needed. Using thermodynamic analysis, cored wires can be strategically designed to produce advanced metal carbides using relatively in-expensive feedstock materials. An example of metallic composite cladding system involving niobium carbide is listed in Figure 1.

Metallic matrix composite cladding has been of interest for use as protective claddings due to their high hardness, high chemical stability, erosion and wear resistance. These claddings benefit from the ductile matrix of the metal but are reinforced by a hard ceramic phase. Niobium carbide has incredible hardness (17GPa - 22GPa), high wear resistance, and a high melting temperature 3873°C. It is a group VB element which are known to make very hard phases in many common alloys. Unlike other carbides between group IV to VI such as titanium, vanadium, and chromium, NbC has been given little attention towards hard coatings application. In the past, NbC has been researched to be used to make wear resistant coating using thermal reactive diffusion (Ref 1 - 3).

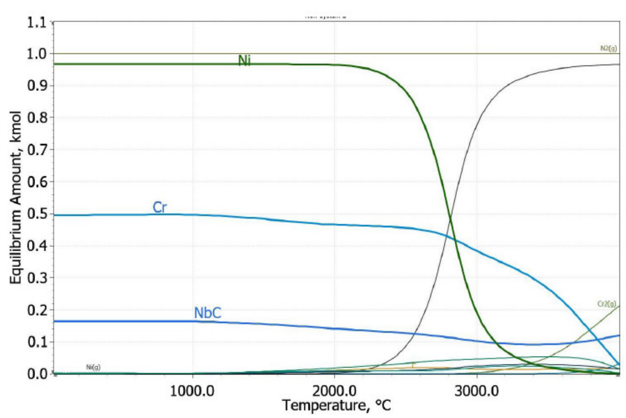

Figure 1: Gibbs energy minimization plot for the cermet cladding system with niobium carbide.

Good corrosion resistance is the most fundamental requirement for any applied coating/cladding material used in a boiler environment. When selecting a suitable material, it is important to understand all the possible corrosive environments and the associated mechanism of attack. Furthermore, both local and general forms of corrosion attack should be considered, since either can compromise the underlying tube.

Erosion resistance is an important characteristic of thermal spray coatings/claddings. Tube material wastage due to fly-ash erosion is a common phenomenon in the boiler, so an erosion resistant coating/cladding with sufficient thickness and minimal defects can prevent the underlying tube material from erosion.

Innovative metal matrix niobium carbide cladding applied by twin wire arc spraying will definitely be an unique advanced material in the thermal spray processing field. This innovative cladding will be a promising material for both corrosion and erosion protection of powerplant components.

Experimental

Innovative cored wires were designed, fabricated and sprayed through Kymera vendor companies onto various steel substrates to confirm the effectiveness of the cladding. For confirmation, various validation testing involving aggressive sulfidation testing, erosion testing and thermal cycling testing were performed. Brief metallurgical characteristics of this cladding are listed in Table 1.

Table 1: Brief metallurgical characteristics of the cladding

Characteristics	Values
Porosity	< 4%
Cohesive Bond Strength	~4400 psi
Hardness	584 ± 98 HV0.1

For sulfidation testing, a lab simulated sulfidation attack by pyrite decomposition was considered. This testing is the most detrimental of all corrosive microclimates along the waterwalls of coal-fired boilers (Ref 4 - 6). Both bare and Kymera cladded steel coupons were exposed to this aggressive sulfidation testing.

Erosion testing was performed at an outside lab per ASTM G76. The test parameters are listed in Table 2.

Thermal cycling testing was performed using an oxyacetylene torch. The cladded samples were cycled from 200°C to 550°C to 200°C. The time for an individual cycle was approximately 10 minutes and a total of 100 cycles were performed.

The results of the sulfidation, erosion and thermal cycling testing are discussed in the next section.

Table 2: Erosion Test Parameters

Test Parameters	Values
Distance	10 mm
Orientation	90 degrees
Velocity	30 m/s
Pressure	8 psi
Flow	15 SCFH
Media	Alumina: Angular shape, 50mm

Results and Discussions

SEM micrograph of the metallic composite niobium carbide cladding is listed in Figure 2. XRD analysis is shown in Figure 3. Iron carbonate and iron oxide were detected due to surface contamination since the as-sprayed surface was not polished. NbC presence were indicated by orange arrows.

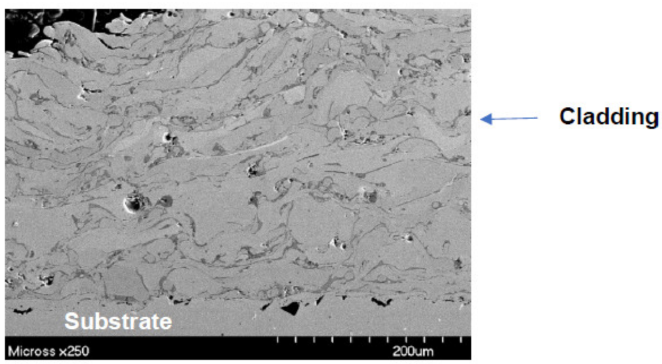

Figure 2: SEM photograph of the metallic composite niobium carbide cladding is shown.

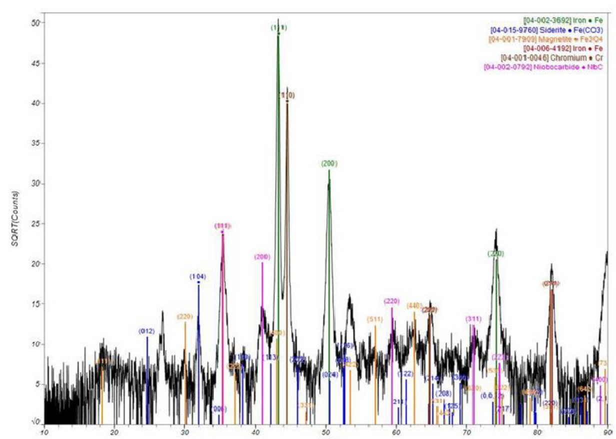

Figure 3: Background subtracted phase identification results for metallic composite niobium carbide cladding. NbC peaks were indicated by orange arrows.

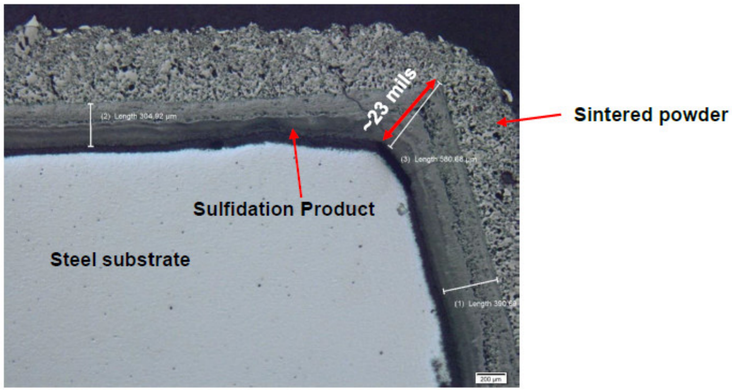

Figure 4: Condition of the bare steel substrate exposed to sulfidation testing is shown.

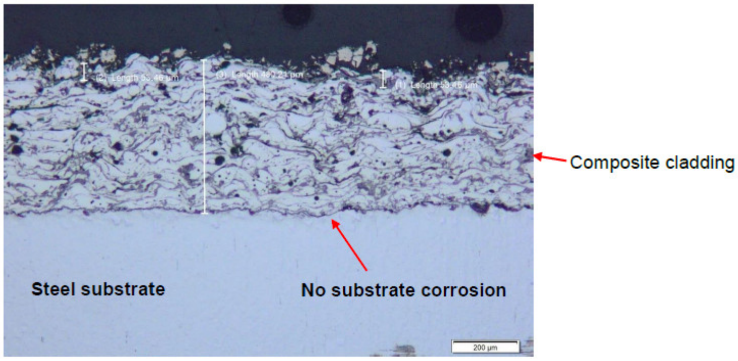

Figure 5: Condition of the cladded substrate after sulfidation testing is shown.
Superficial corrosion product on the outer surface seen and no substrate corrosion attack observed.

Corrosion Resistance

The results of the sulfidation testing are shown in Figures 4 and 5. The bare steel substrate suffered a significant corrosion attack and showed a maximum corrosion product of ~23 mils. Whereas, the cladded steel substrate showed a superficial corrosion product (~ 2 mils) on the outer surface and the substrate showed no corrosion attack.

The metallic composite niobium cladding performed 12X better than the bare steel substrate.

Erosion Resistance

The erosion resistance of various thermal spray coatings/cladding was measured in accordance with ASTM G76 (Ref 7&8). The test results are shown in Fig. 6.

Lower weight loss – Better erosion resistant

The results from this testing can be used to rank the erosion resistance of various thermal spray coatings/claddings under a specified test condition; however, it should be noted that any single lab experiment may not be sufficient to evaluate the expected boiler service performance of any coating/cladding. Field performance should be evaluated in addition for better understanding of the erosion performance. Per this tested erosion ranking criteria, Kymera composite cladding outperformed other competing thermal spray products by 20%.

Thermal cycling performance

Thermal fatigue failures are a concern in the furnace wall tubes of the supercritical boilers due to an increment of boiler tube wall temperatures and frequent thermal spiking of tube crown surface under certain operating conditions. Thermal spikes in certain cases can exceed 100°C due to potential slag shedding and under certain operating demands (Ref 9). A thermal spray cladding that can minimize slag deposition and can act as a buffer to the tube material with no cracking potential will benefit the tube life of the boiler components.

Although, simulating actual boiler thermal fatigue mechanism is complex, a simple thermal gradient exposure study was performed with this cladding material. The results are shared in Figure 7. The cladded material did not show any cracking and there was no substrate corrosion observed. Cladding was well adhered to the substrate.

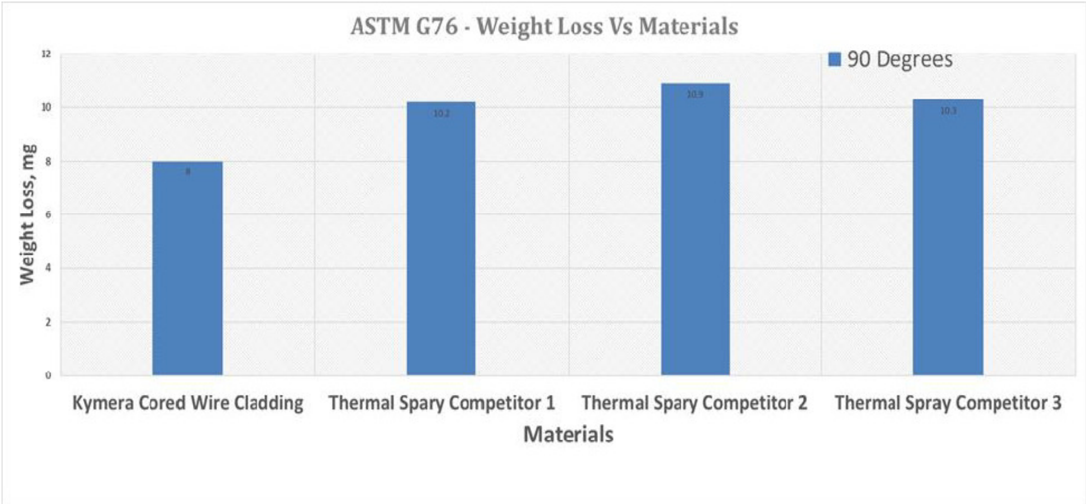

Figure 6: Relative erosion performance of tested thermal spray materials.

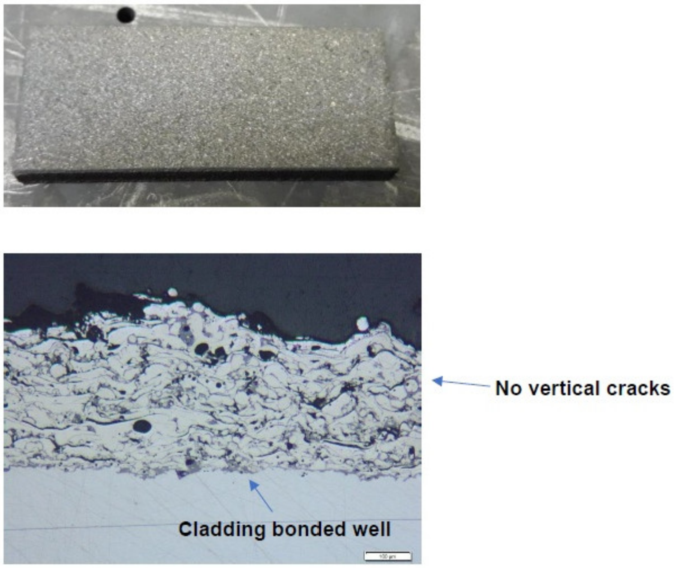

Figure 7: Cladded sample (top) and a micrograph (bottom) post thermal cycling testing is shown. No vertical cracks were observed and the substrate revealed no corrosion.

Conclusions

Advanced metallic composite niobium carbide cladding was successfully obtained through wire arc spraying. The resultant cladding showed exceptional performance in both corrosion, erosion and thermal cycling test conditions. Corrosion performance of the cladding was 12X better than the bare steel substrate and the erosion performance of the cladding was 20% better than other competing thermal spray products in the market. This innovative cladding exceeded the expected performance and can be deployed for powerplant corrosion and erosion protection.

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

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Plasma Sprayed Nanostructured YSZ Coatings Doped with Rare Earth Oxides: A State of the Art

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Abstract
The motivation for the present work on nanostructured plasma sprayed Yttria Stabilized Zirconia (YSZ) arises due to the superior properties exhibited by such nanostructured coatings over conventional coatings. However, the greatest challenge lies in retaining the nanostructure phases, both during the processing of these coatings at high temperatures as well as their application at elevated temperatures. Thermal spray coatings have found immense application, both in aviation and automotive sector, owing to the intense research that has gone into this area for the past two decades. Plasma sprayed YSZ coatings have attracted the research community due to its good thermal, mechanical and tribological properties. Plasma-sprayed YSZ coatings with tetragonal prime (t') structure is one of the most commonly used thermal barrier coatings (TBC) because of its low thermal conductivity and phase stability at operating temperatures below 1200°C. However to increase the efficiency of TBCs, there is a need to develop materials with high temperature stability for long periods as well as lower thermal conductivity. This calls for designing a material with stable microstructure. Therefore, the present work has been aimed at developing a microstructure in which combined effect of nanostructure and doping of rare earth oxides such as La_2O_3, CeO_2 and $La_2Ce_2O_7$ on microstructure, mechanical, thermal and tribological properties of plasma sprayed YSZ coatings was explored.
Keywords: Plasma spraying, YSZ, LaCeYSZ, TBC, bimodal microstructure

Introduction
(Increased operating temperatures and hence, improved performance of gas turbines or diesel engines can be realized by using thermal barrier coatings (TBC) [1-3]. Plasma sprayed thermal barrier coatings based on yttrium stabilized zirconia (YSZ) have been applied to hot section components. Zirconium based ceramics are considered to be best suitable for thermal barrier & wear resistance application due to its low density, high hardness, low thermal conductivity. YSZ is the current industrial standard material of TBCs, owing to its low thermal conductivity, phase stability at relatively high temperatures, a relatively high coefficient of thermal expansion (CTE) and chemical inertness in combustion atmospheres as compared to other ceramics [4-5]. A major disadvantage of YSZ is the limited operation temperature (<1200°C) for long term application. At higher temperatures, phase transformations takes place from the t'-tetragonal to tetragonal and cubic (t+c) and then to monoclinic (m) occur, giving rise to the formation of cracks in the coating. The addition of CeO_2 and La_2O_3 to YSZ could improve the corrosion resistance, fracture toughness, and thermal insulation of the coating [6].

Bulk nanostructured material (grain size < 100 nm) have exhibited outstanding mechanical properties such as exceptional hardness, yield strength and wear resistance [7]. Thermal spray coatings obtained from nano structured powders (as shown in Fig. 1) also exhibits such outstanding properties. Spray conditions must be carefully adjusted to minimize the coarsening or alteration of the nano grains and to control the chemical reactions and phase stability of materials. It has been reported that nanostructured zirconia coatings show lower thermal conductivity, lower Young's modulus, higher CTE and higher toughness with respect to the microstructured conventional ones [8]. For the applications with more severe environments such as higher temperature, strains, and corrosion, doping of La_2O_3 and CeO_2 into YSZ coatings has resulted in reduce thermal conductivity and resistance to sintering [9-10] and doping of YSZ with multiple dopants has also been reported [11]. Y2O3-ZrO2-rare earth oxides composite coatings commonly look attractive due to their high temperature stability, high fracture toughness & better corrosion resistance & thermal insulation. In this context, the scope of present work describes the combined effect of nanostructure and addition of CeO2 on the microstructure and thermo-mechanical properties of plasma sprayed YSZ coatings.

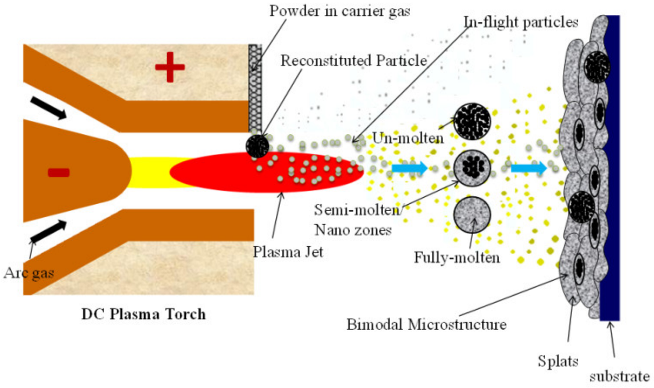


Figure 1: Schematic picture of plasma sprayed nanostructured coating process

Experimental

Synthesis of nanostructured powders by sol-gel route

The nanostructured YSZ powders employed in this study were synthesized through sol-gel technique [12]. Commercial nano La2O3 and nano CeO2 of particle size ~ 10-30 nm obtained from M/s Sky spring Nanomaterials, Inc.USA. Both the powders were mixed and heated at 1400 oC. The calcined powders were taken as the raw ingredients for the plasma spray process.

The transmission electron micrograph of as synthesized YSZ powders by sol-gel technique is shown in Figure 2(a-b). The average grain size of nanoparticles is in the order of 20-30 nm. Similar nanostructure has been obtained for the La2Ce2O7 compound, as shown in Figure 2 (c-d).

Both the powders were mixed properly and heat treated at 1400 oC. The calcined powders were taken as the raw ingredients for the plasma spraying process.

Reconstitution of nano powders

Nano-sized powder of 8LaCeYSZ [YSZ (5.4 wt. % Y2O3–ZrO2) + 8 wt. % La2Ce2O7] and 10CeYSZ [90 wt. % YSZ (5.4 wt. % Y2O3–ZrO2) + 10 wt. % CeO2] were plasma sprayed on Inconel 718 substrates. The finely dispersed nano particles was made agglomerated to a size of ~ 30–90 µm as required for plasma spraying. The nano particles were agglomerated by the spray-drying technique. The process is described elsewhere [13].

The final product is a feedstock of size ~50 µm spherical agglomerates containing nano grains of size 20-30 nm as shown in Fig.3.

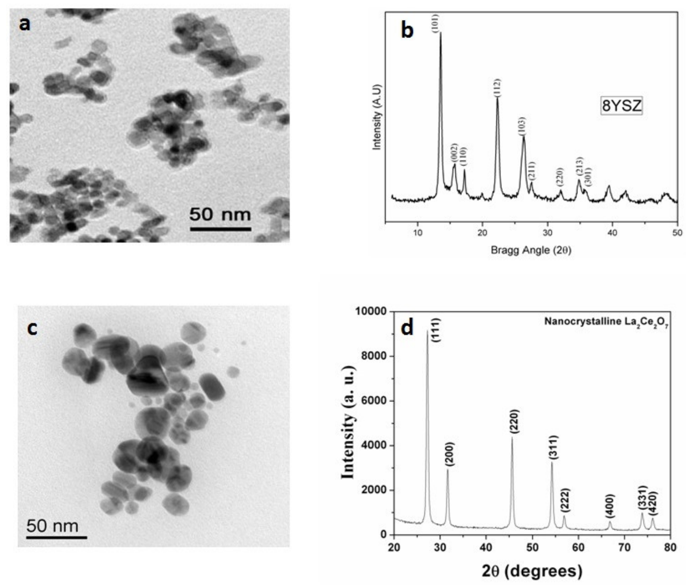


Figure 2: (a, c) TEM Micrograph and (b, d) XRD pattern of as-synthesized YSZ and La2Ce2O7 particles respectively

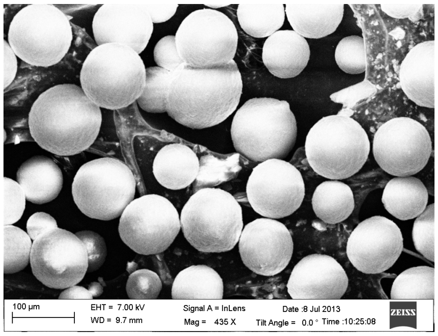


Figure 3: FESEM micrograph of spray dried LaCeYSZ particles

Table 1: Operating Parameters for Plasma spraying process

Parameter	Operating Range
Operating Power	38 kW
Current	865 amps
Primary gas (Argon) flow rate	40 lpm
Secondary gas (Hydrogen) Flow rate	0.5 lpm
Carrier Gas flow rate	5 lpm
Nozzle to substrate distance	80 mm
Powder feed rate	25 g/ min

Development of coatings

An important step in the plasma spray coating technique is preparation of the substrate surface to increase the mechanical anchoring between the substrate and the coating. The surface of the substrate was subjected to grit blasting to make the surface rough. A uniform roughness of 6-8 µm was maintained in order to provide better adhesion at the interface. The coating process was carried out using an 80 kW plasma spray system supplied by M/S Metallization, U.K. In this study, high purity argon and helium were used as primary and secondary plasmagen gases, respectively, at an outlet pressure of 4 kg/cm2. A roughened Inconel 718 substrate of dimension 120×60×5 mm3 was fixed on the turntable and LaCeYSZ nanocomposite powders was sprayed by varying process parameters. The process parameters are listed in Table 1. The number of passes was kept constant for each sample to produce coating thicknesses within a similar range. Particle temperature determination is based on the two-color pyrometry and in-flight particle velocities are measured from the length of the particle traces during known exposure times using a single high speed CCD camera [14].

Characterizations

The synthesized nanocomposite powders and coatings were characterized by X-ray diffractometer (XRD) to determine the crystal structure. The field emission scanning electron microscopy (FESEM: Make Zeiss, SupraTM55) studies have been carried out to investigate the microstructure and average grain size of the coating. A higher priority has been given to measure the thermal properties. The thermal diffusivity was measured at different temperatures using the laser flash technique (LFA 1000, LINSEIS).

Results and discussion

Structural Analysis

The XRD patterns of bulk YSZ, Nanocrystalline YSZ and the LaCeYSZ nanocomposite coatings are shown in Fig. 4. The commercial bulk polycrystalline YSZ Coating is taken as a standard to compare the change in XRD patterns of the nanocrystalline YSZ and LaCeYSZ nanocomposite coatings. The nanostructured coating obtained from reconstituted YSZ synthesized by chemical technique shows cubic structure of zirconia and impurity phase of Y2O3 is hardly observed in the XRD pattern. However, the higher intensified peak of (111) shifts towards the lower 2θ due to the development strain in the nano YSZ coating. The XRD pattern clearly represent that no monoclinic phase of zirconia is exist in the nano composite coating. It also indicates that no La2O3, CeO2 peaks appear in the pattern, which confirms La2O3, CeO2 is in solid solution with ZrO2 and doesn't cluster in the LaCeYSZ coating.

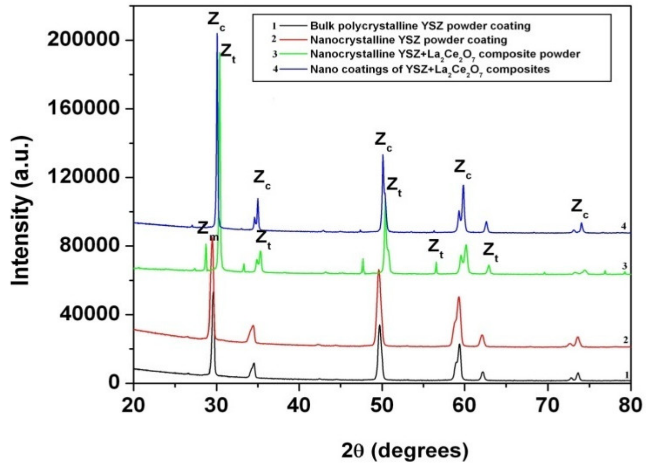
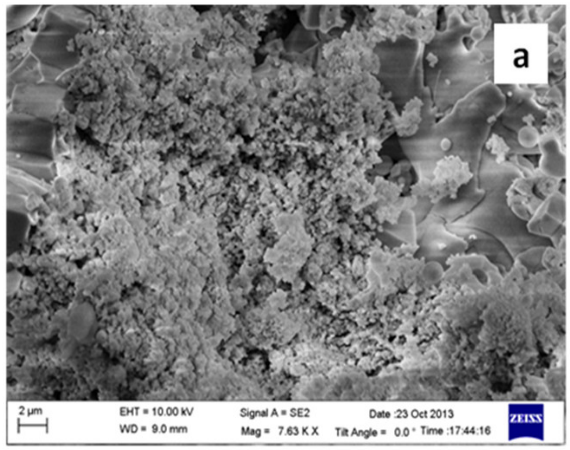


Figure 4: XRD patterns of bulk polycrystalline YSZ coating, nanostructured YSZ coating and LaCeYSZ nanocomposite coating

Surface Morphology Analysis

The field emission scanning electron micrographs are shown in Fig. 5. FESEM of fractured cross-section represents bimodal microstructure consisting of dense and smooth zones, indicating good molten state of particles and the rough and porous zones, indicating unmolten or semi-molten state of particles (Fig. 5a). The presence of nano-zones and micro-cracks enhances phonon scattering, which helps in reducing thermal diffusivity. When higher resolution micrographs have been taken, it is observed that the surface consists of densely packed nanograins having average grain size of ~ 90-120 nm. It is clearly observed from the micrographs that the grains are very closely packed with development of distinct grain boundaries. No voids and porous structure has been observed in the microstructure (Fig. 5b).



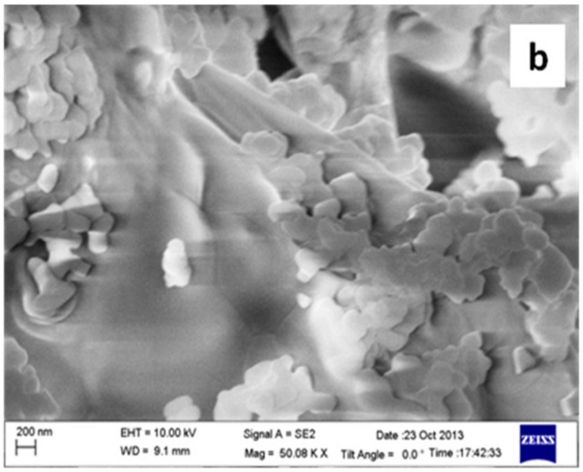
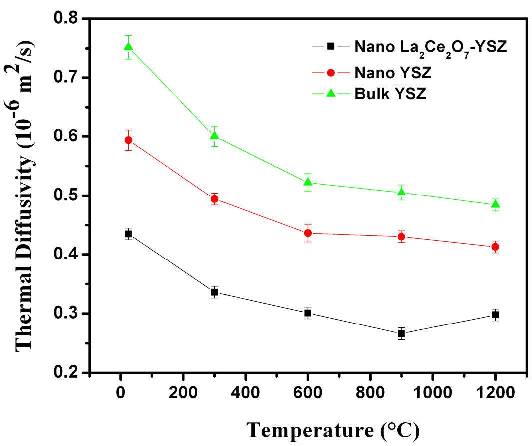


Figure 5: FESEM micrographs of YSZ- La2Ce2O7 nanocomposite coatings

Thermal characterization

The variation in thermal diffusivity values of bulk YSZ, nano YSZ and 8LaCeYSZ from room temperature to 1200 °C are shown in Fig. 6(a). It is observed that the thermal diffusivity of La2Ce2O7 –YSZ nanocomposite coatings is lower than both nano-YSZ and bulk YSZ coatings developed on Inconel 718 substrates. The thermal diffusivity value at room temperature was 0.4350 x 10-6 m2/sec and the value decreased up to 900 °C, where the value of thermal diffusivity was 0.2659 x 10-6 m2/sec and again gradually increased up to 1200 °C, where the value was 0.2979 x 10-6 m2/sec. This apparent increase at higher temperature may be attributed to the radiative heat transfer through the material. A similar trend is observed in the case of measurement of thermal conductivity of coated samples at different temperature, which is shown in Fig. 6(b). The same observation has been reported in case of 10CeYSZ nanocomposite coatings in Fig.6 (c,d).



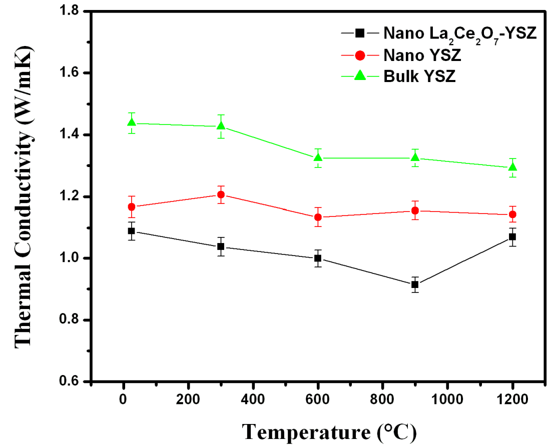


Figure 6: Variation in thermal diffusivity & thermal conductivity with temperature of as-sprayed conventional YSZ, nano YSZ and nanocomposite LaCeYSZ coatings

Conclusions

The atmospheric plasma sprayed nanostructured LaCeYSZ/ CeYSZ coatings on Inconel 718 substrates are characterized by molten particles, nano-zones, micro-cracks and higher inter splat porosity. The XRD patterns reveal the cubic phase transformation of tetragonal and monoclinic YSZ with a small percentage of tetragonal phases. La, Ce is in solid solution with ZrO2 and helps in stabilizing ZrO2 and does not cluster in as-sprayed nanocomposite coating.Micrograph of surface reveals the average grain size to be in the range of ~150-200 nm. The grains are closely packed with distinct grain boundaries. The thermal diffusivity of nano LaCeYSZ/ CeYSZ coatings is lower than that of nano and bulk YSZ. The reason may be attributed to scattering of phonons at grain boundaries, point defect scattering and higher inter-splat porosity.

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