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

April 2023| Vol. 3| Issue 1

SPRAYTODAY™

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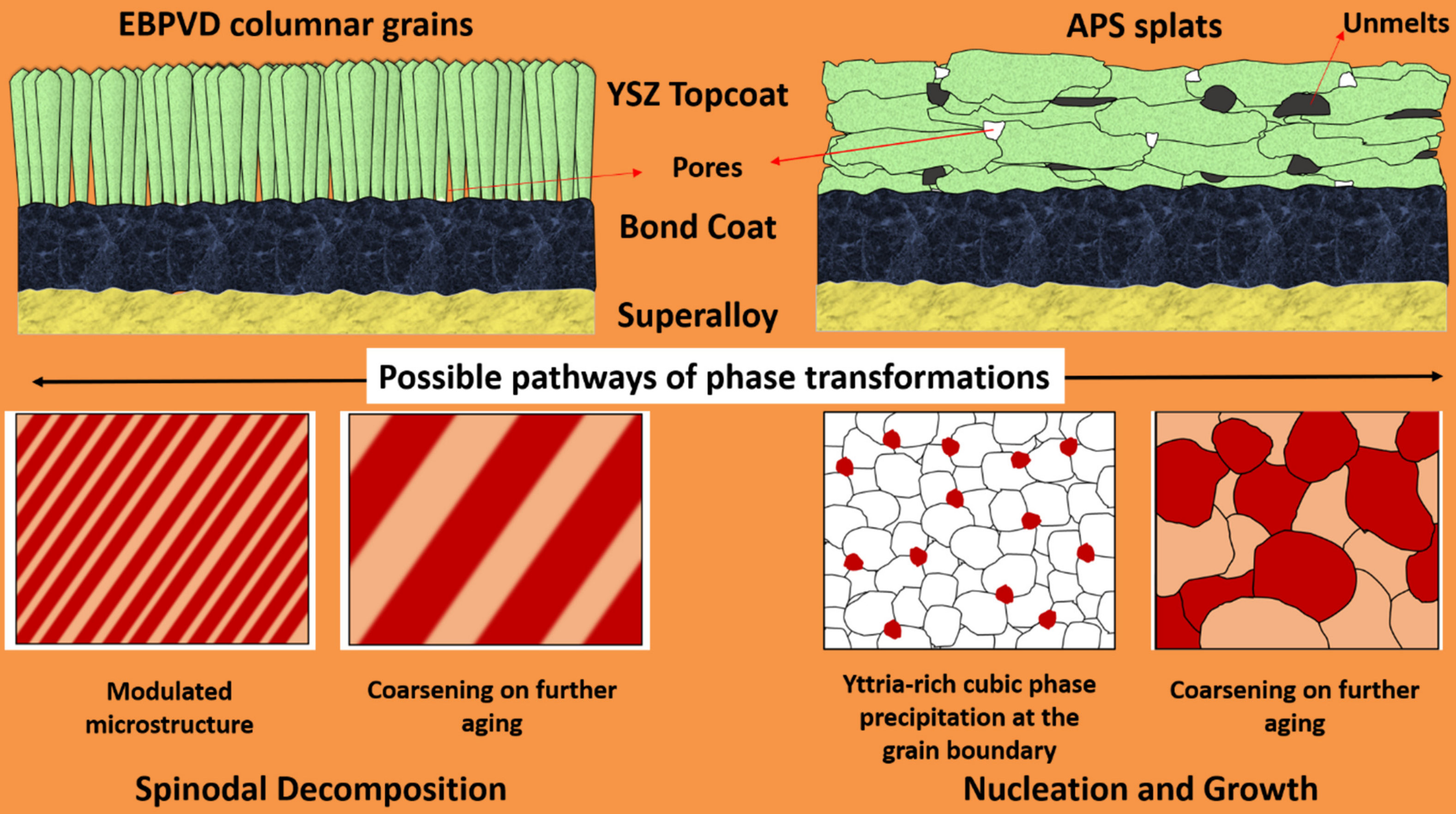

Issue Highlights

- **Featured Article**: Phase Transformation Pathways in YSZ TBCs On High-Temperature Thermal Exposure
- **Technical Note**: Numerical Investigation of Tamping Effect on the Inter-Splat Bonding in Cold Spray
- **Academia Research**: Development of Alumina Based Ceramic Coatings on Steels Using Thermal Spray Process
- **Industrial Research**: Metallurgically Formed Niobium Carbide Composites for Corrosion, Erosion and Wear Protection

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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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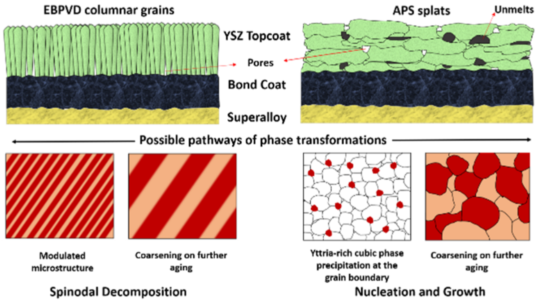

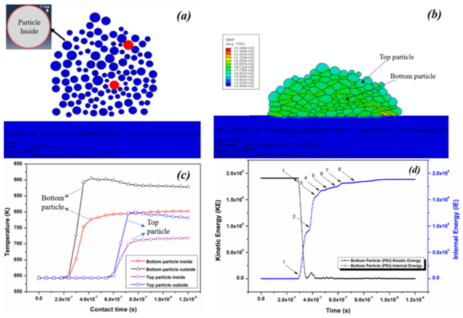

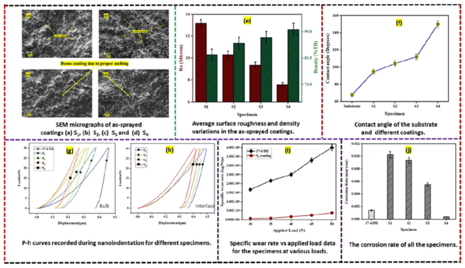

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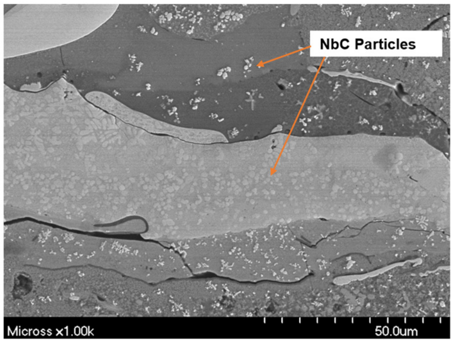

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ABOUT THE COVER

Phase Transformation Pathways in YSZ TBCs On High-Temperature Thermal Exposure

Editor’s Note

Dear Readers,

The Indian Thermal Spray Association (iTSA) organized the 1st National Thermal Spray Conference (NTSC 2023) in the historical city of Jodhpur on 18-19 Feb 2023 and it was an absolute pleasure and privilege to host 120+ delegates from different parts of the country and abroad. We were overwhelmed by the academic vibrancy and research enthusiasm of delegates from both industry and academia. We are deeply honored to have iTSA President Prof. Prof. Harpreet Singh, Chief Guest Prof. Ladislav Celko, Guest of Honor Professor Tanvir Hussain, Dr.S. Rangaswamy and Mr. MD Modi (Co-convenor Metallizing Equipment Co. Pvt. Ltd.), Prof. Sanjay Sampath, Prof. Vikram Jayaram, Prof. Christopher Berndt, Prof. Arvind Agarwal, Dr. Anand K., Dr. Aruna TS, Mr. C. Rajesh Kumar and many more as Keynote speakers and iTSA committee. It was great to see such an auditorium after a long day's session at 7.00 pm on both days. Sincerely acknowledge support from our sponsors. Thanks to all who made NTSC 2023 the India's first success story in Jodhpur!
The Picture Gallery is now available! Watch the great moments!
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I am particularly pleased to be allowed to recommend to you the latest issue of the **SPRAYTODAY based on NTSC2023**. This issue includes invited innovative featured articles from industry and academia experts on the Phase Transformation Pathways in YSZ TBCs On High-Temperature Thermal Exposure, Numerical Investigation of Tamping Effect on the Inter-Splat Bonding in Cold Spray, Development of Alumina Based Ceramic Coatings on Steels Using Thermal Spray Process, Metallurgically Formed Niobium Carbide Composites for Corrosion, Erosion and Wear Protection; 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.

Best Regards,

Satish

(Dr. Satish Tailor)

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Phase Transformation Pathways in YSZ TBCs on High-Temperature Thermal Exposure

*By **Vikram Hastak** and **Ashutosh S. Gandhi,** Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai, India.*
Email: vikramhastak@gmail.com

t'-YSZ (~7-8 mol% $YO_{1.5}$. ZrO_2) based air plasma sprayed TBCs are widely utilized in hot sections of aeroengines and gas turbines to enhance thermal stability [1], [2]. However, the metastable t' experiences phase transformations with prolonged thermal exposure which might lead to TBC failure. There exists a long running debate on the mechanism of thermal decomposition of t'-YSZ [3]–[5]. On thermal exposure, the t' phase slowly decomposes into yttria lean tetragonal (t) and yttria rich cubic (c) phase. Owing to slow cationic diffusion even at temperatures as high as ~1400°C, the equilibrium is established only after long aging periods. The yttria lean tetragonal phase undergoes martensitic transformation by forming monoclinic phase as it crosses T_0(t/m) line on cooling. This tetragonal to monoclinic transformation involves increase in the molar volume ~5% which in turn induces high stresses leading to TBC failure. In addition to this, yttria-rich cubic phase can also transform to t''-phase through a displacive partitionless transformation which is also composition invariant. This may give rise to a complex phase assembly consisting of 5 different phases at room temperature. Hence, in order to assess the lifetime of TBCs, it is very important to understand the phase transformation pathways in relation to the temperature and time excursion.

The presence of two tetragonal phases i.e., the non-transformable t' phase and transformable yttria lean t phase along with the yttria rich cubic phase was first reported by Miller in plasma-sprayed 8.6 mol% $YO_{1.5}$. ZrO_2 [6]. The transformable tetragonal phase appeared to be monoclinic at room temperature. Following this, Azzopardi et al. [4] examined the changes in microstructure of yttria-partially stabilized zirconia (Y-PSZ) EBPVD coating with varying aging temperature (in the range 1100-1500°C) and aging time (in the range 10-300 h) followed with air quenching. The appearance of band structure after aging at 1500°C for 100 h was suggestive of spinodal decomposition. The microstructural evolution studies on 7YSZ EBPVD coatings at 1482°C by Krogstad et al. [7] also revealed modulated microstructures which is a characteristic of spinodal decomposition. These microstructures appear to coarsen on further aging. High resolution TEM images showed fully coherent t'' phases with t matrix for samples aged for 0.26 h. The multiple tetragonal phases (t, t' and t'') were observed in all aged samples. Monoclinic phase was barely observed even after higher aging periods. The retained t' phase observed even after aging was suggested as an impression of t-t'' coherency.

Synchrotron X-ray diffraction studies were carried out by Lipkin et al. [3] on APS 8YSZ coatings heat treated at several aging times and temperature. The phase evolution studies were carried out based on Holloman-Jaffee time-temperature correlation parameter i.e., $HJP = T[27 + \ln t$. The monoclinic phase that appeared after HJP of 51000, reached to a maximum of ~36% above 54000 HJP and saturated at 57000 HJP. Similar to the microstructures observed in EBPVD coatings, the modulated structure was also observed in APS coatings. However, some grains after phase transformation did not show any compositional gradient of yttria in the microstructure.

In a similar study by Lughi and Clarke [8], the t' phase was found to be coexisting with t and c phases on annealing t' 8YSZ EBPVD TBC at 1200°C and 1425°C from 7 h up to 195 h. The precipitation of cubic phase happened through nucleation-growth mechanism (diffusional transformation). Both Raman spectroscopy and X-ray diffraction (XRD) established the absence of monoclinic phase. However, coating samples annealed at 1425°C experience the formation of monoclinic zirconia after

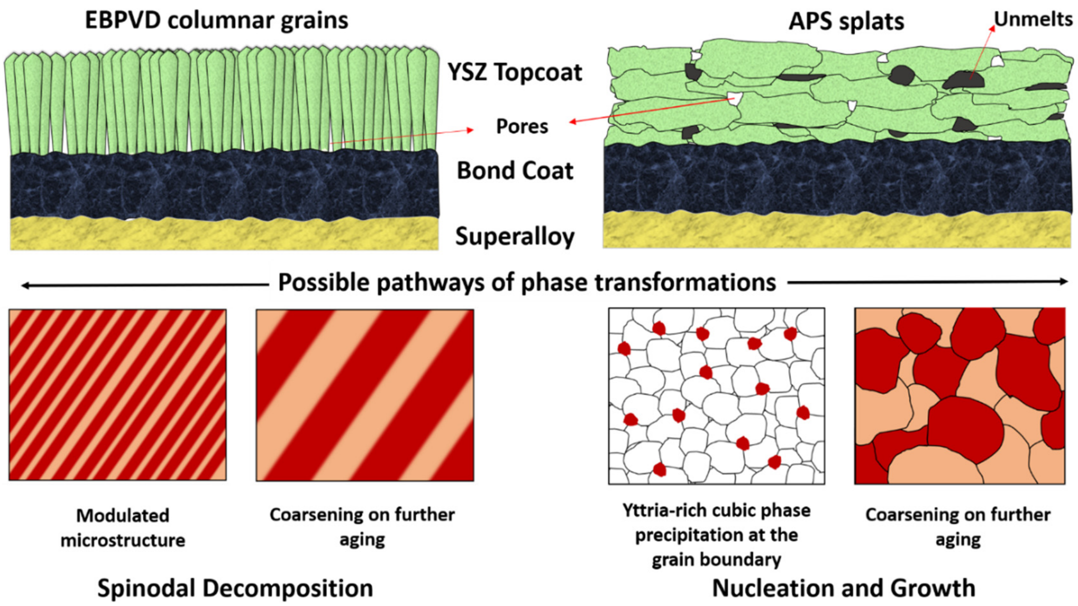

Figure 1: Schematic representation of EBPVD and APS TBC cross-sections and possible pathways of phase transformations

several months as a result of isothermal martensitic transformation. Limarga and Clarke [9] made use of Raman spectroscopy which proved to be effective for studying phase transformations. Based on their findings, blue shift in the characteristics Raman lines could be attributed to the formation of coherent mixture of yttria lean tetragonal and yttria rich cubic phases, whereas the sharpening of peaks corresponds to the decrease in oxygen vacancies.

Interestingly, the sintered YSZ compacts, prepared by coprecipitation technique showed a different phase transformation behaviour. The t' phase was not retained at room temperature i.e., only t + c phase assembly was observed in the aged specimens. The yttria rich cubic phase in such microstructures appeared to precipitate at the grain boundary via nucleation and growth mechanism [5], [10]. This yttria-rich cubic phase is susceptible to transform to a t''-phase, as it crosses T0(c/t) line, via two possible mechanisms; ‘displacive transformation’ leading to twinned microstructure and ‘ordering’ resulting in mottled microstructure. The possibility of different mechanisms of microstructural evolution and phase assemblies, therefore, depends upon the starting microstructure, type of coating deposition technique and the aging parameters.

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Numerical Investigation of Tamping Effect on the Inter-Splat Bonding in Cold Spray

*By **Gidla Vinay, Ravi Kant** and **Harpreet Singh**,*
Indian Institute of Technology Ropar, Rupnagar, Punjab 140001, India.
Email: harpreetsingh@iitrpr.ac.in

Introduction

Cold Spray is a solid-state coating deposition process where micron size particles are bombarded on to a suitably prepared substrate. These impacted particles undergo severe plastic deformation and the heat generated is highly localized at the interface due to the adiabatic heating [1]. This localized heat generation results in localized melting at the deformed particle interface which further helps in adhering of the particle to the substrate. Subsequent particles deposit on to the previously deposited particles thereby forming the coating. Since it involves no melting of materials, cold spray is the most appropriate technique for depositing thermally sensitive materials and materials with low melting temperature. Thickness of each layer depends on the factors like nozzle transverse speed, feedstock feed rate and nozzle angle. Owing to its unique deposition mechanism, cold spray is also used in additive manufacturing in the form of depositing standalone parts or for repairing the worn-out structures and coatings.

The deformed particle is known as splat and the interface between the splats is known as Inter-splat boundaries. Inter-splat boundaries are important to determine the bonding state between the splats. As the bonding state between the splats is difficult to quantify, researchers often rely on inter-splat dependent properties for quantifying the inter-splat bonding. Such properties are electrical conductivity, elastic modulus, corrosion resistance and tensile strength [2,3,4]. To increase the inter-splat bonding, often used approach is the heat treatment of the deposited coatings, which is a post processing technique where the substrate also undergoes heat treatment. Researchers have applied techniques like shot peening as a post processing technique for improving the bonding and observed an increase in corrosion resistance. It overcomes the substrate effect problem (which occurs in heat treatment) but accuracy, surface finish, delamination of coating from substrate are some of the drawbacks [3]. The layer-by-layer deposition in cold spray results in higher mechanical properties like hardness in the bottom layers due to the strain hardening of the already deposited particles by the incoming particles. This effect is often known as tamping effect. In-situ hammering, which is a combination of shot peening and tamping effect has gained popularity as a promising technique to improve inter-splat bonding.

In in-situ hammering, large sized hard particles are mixed with the feedstock and are propelled along with the feedstock by letting them impact on the deposited coating. Due to the higher particle size and mass, these hard particles achieve less velocity due to which they will not stick to the coating however their impact on the deposited particle further improves the compaction thereby decreasing the porosity and increasing the inter-splat bonding [5]. H Zhaou et al. [6] used single particle simulation of large size shot peening particle impacting on a smaller Ti6Al4V feedstock particle and observed an increase in the interface temperature (of selected nodes) which helps in improving the bonding during In-situ hammering. Thus, making the deposition of Ti6Al4V easy otherwise would be difficult considering the higher critical velocity of Ti6Al4V [6]. The drawbacks in using in-situ hammering are that higher size particles used are of different material and there is a fair chance for trapping of higher size shot peening particles in the coating. Another drawback is that the process is not efficient as the higher size particles are mixed with the rebound particles which makes the recycling of rebound particles difficult. Wu et al. [7] observed that parameters like nozzle angle, scan offset, and nozzle retreat distance plays important role in CSAM (Cold Spray Additive Manufacturing) depositing complex structures and thick repairs. The applicability of in-situ hammering with the strategies given for CSAM complex structures is rather challenging. Other techniques such as mixing a large range of powders, segregating powders according to the sizes have also been explored and they have their own advantages and disadvantages.

All the above methods have special aid for improving the inter-splat bonding. At Surface Engineering Lab, Indian Institute of Technology Ropar (IIT Ropar, India) the current research is focused in a way to reduce the special aid for improving the inter-splat bonding using the tamping effect which normally occurs in the cold spray deposition. To understand the effect of tamping effect on the bonding, a finite element-based simulation approach is chosen. The short note tries to highlight the effect of tamping effect on the inter-splat bonding taking interface temperature as reference.

Methodology

For the current analysis, a multi particle simulation is used where particles are arranged in several layers. Commercially available ABAQUS/Explicit software was used, and feedstock material used is IN718. Johnson-cook plasticity model which has the effect of strain hardening, strain rate hardening and thermal softening is employed and the properties of the IN718 used can be found from G. N. Devi et al. [8]. The multiparticle simulation (2D plane strain) consisting of 120 particles with an average particle size of 45 µm were created using the average particle size distribution data (Fig.1a.). CPE3T element type is used for defining the element in the current analysis. As suggested by Schmidt et al. [9] 60% of feedstock material thermal conductivity is applied in the current multiparticle simulation. An outer periphery of 0.5 µm thickness was sectioned in all particles of multiparticle simulation for estimating the inter-splat boundary temperatures. Interactions between the particles is given by penalty contact algorithm and total run time for multiparticle simulation is 1.2 µs. Particle velocity of 500 m/s and particle temperature of 593 K are given as input parameters for the particles used in multiparticle simulation.

Results

To understand the effect of tamping, two approaches were used. In the initial approach, a particle in the 4th layer namely bottom particle and a particle in 11th layer namely top particle (shown with red color in Fig.1a.) are observed for their temperature evolution during the deposition process. Fig.1b. shows the deformed particles at the end of simulation run time. As mentioned in the methodology, each particle sectioned has an outer periphery which is named as particle outside and the rest of the particle is named as particle inside (Fig.1a). From Fig.1c. it is clearly observed that the temperature inside the particle is much less than the particle outside (outer periphery) for both bottom and top particles. This shows that the particle boundaries are experiencing more temperatures which helps in bonding. The low temperature inside the particle helps in making strain hardening effect more dominant which often observed from the increase in hardness of the cold sprayed coatings. Among the observed two particles, the bottom particle is showing higher temperature (both inside and outside) when compared with the top particle. These higher temperatures in the bottom particle are due to the transfer of energy from the top layers to the bottom layers which helps in further deformation.

Energy analysis of the bottom particle over the whole simulation time is observed where most of the kinetic energy of the particle converts into internal energy (summation of plastic deformation energy (EPD) and recoverable elastic strain energy (ER)). Fig.1d. shows the change in internal energy (of bottom particle) with successive impact of the incoming particles. It is observed that the successive impacts have caused change in the internal energy, and it reached near the kinetic energy. This is surprising, as some part of the kinetic energy of the particle is utilized to deform the substrate or its below particles. This increase in internal energy is due to the successive impact of the incoming particles.

To understand this effect on the temperature evolution of the particle, a multiparticle simulation which can show the effect of top layers on the bottom layers is created. For this purpose, a bottom particle is chosen and strategically removed all the subsequent particles to be impacting it. The multiparticle distribution which shows the effect of top layers and without the effect of top layers are shown in Fig.2a,2b. Both the simulations are run for the same parameters i.e., 500 m/s and 593 K. Fig.2c. shows the temperature evolution in the outer periphery of the particle with and without the effect of

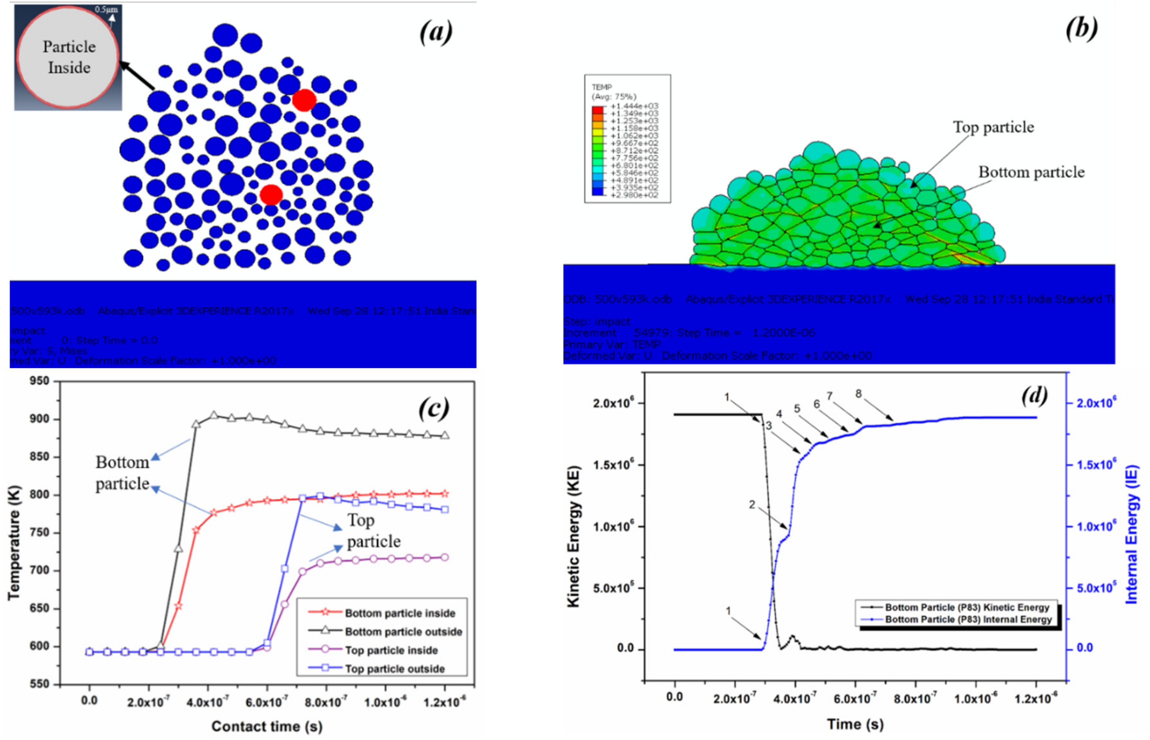

Figure 1: (a) Multiparticle simulation showing particle distribution, top & bottom particle (red color) and the particle sectioning; (b) Coating after 1.2μs; (c) Temperature evolution in particle inside and particle boundary for top and bottom particle; (d) Kinetic energy and Internal energy plot for the bottom particle indicating successive impact from subsequent layers

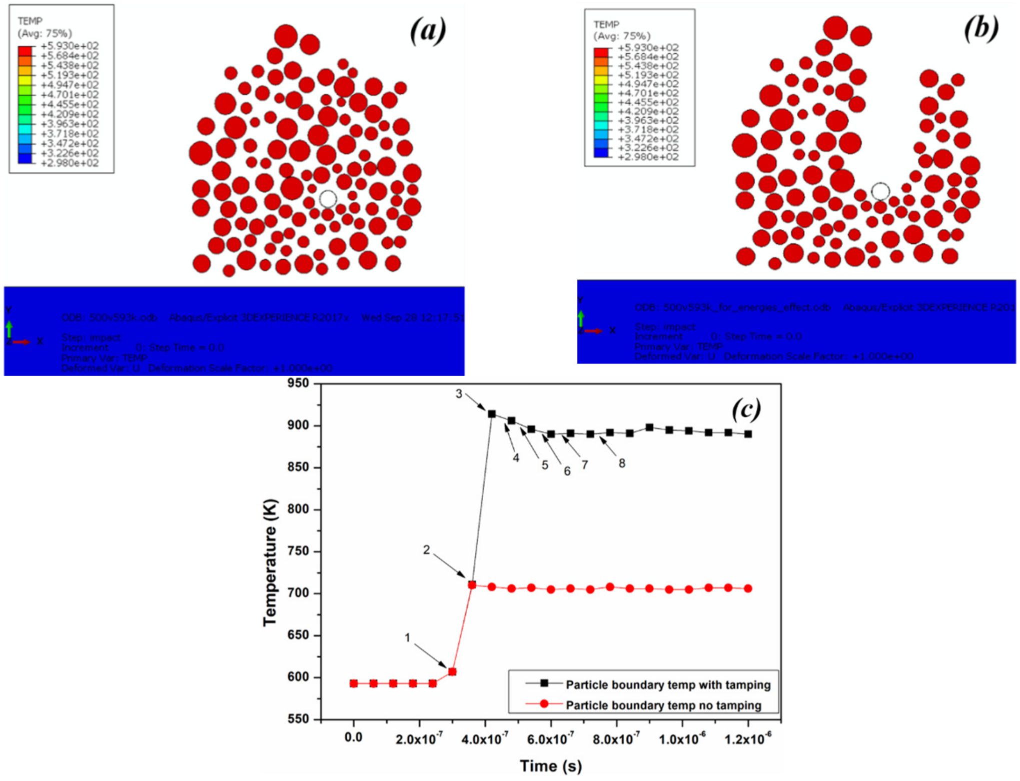

Figure 2: Multiparticle simulation distribution showing the boundary of the selected bottom particle (a) With successive layers impact (b) Without successive layers impact; (c) Evolution of temperature at the particle boundary with and without tamping effect

top layers throughout the simulation. It is observed that, with the effect of top layers, the average temperatures in the periphery of the particle are reaching 900 K while it is 700 K when there is no impact of the top layers. This shows that evolution of the temperature at the boundaries of the bottom layers are different when compared with the top layers and should effect the state of the inter-splat bonding.

Summary

Tamping effect is observed in cold spray coatings in the form of increase in hardness, however with the help of multi particle simulations it is observed that tamping effect may contribute in increase in inter-splat bonding considerably by increasing the interface temperatures.

Many different strategies are employed by different research groups to increase the inter-splat bonding using special aids. At Surface Engineering Lab, IIT Ropar, one of the ongoing research activities is focused on utilizing this tamping effect to optimize the post processing for improvement in inter-splat bonding of CSAM deposits which will be communicated in future.

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Development of Alumina Based Ceramic Coatings on Steels Using Thermal Spray Process

*By **Abhijit Pattnayak** and **Deepak Kumar**, Centre for Automotive Research and Tribology (CART)*
Indian Institute of Technology Delhi, New Delhi, Hauz Khas, 110016, India.
Email: ap22@iitbbs.ac.in

Introduction

Precipitation-hardened martensitic stainless steel like 17-4PH is widely used in aerospace, chemical processing, nuclear and medical devices due to its high strength, corrosion resistance, and excellent mechanical properties [1]. However, it fails prematurely in nuclear industry applications when it is used against EN31 steel under extreme environment conditions without application of lubricants. Galling, a special type of adhesive wear, at high temperature is the main cause of the same [2,3]. According to Archard's law, the wear resistance of any material depends on its hardness and is inversely proportional to the hardness [4]. Hence, improvement in the tribological properties by increasing the surface hardness, through surface modification techniques, can be a solution to this kind of problem of the 17-4PH steel.

Surface deposition technique, particularly deposition of hard and dense ceramic coatings on the surface of a substrate, is widely used in industries to mitigate the wear of a component. Ceramic coatings provide several benefits, including improved wear resistance, corrosion resistance, and thermal protection when applied on a substrate [5-7]. A ceramic coating based on nano cerium oxide for 17-4 PH steel was developed by Singh [8] and its corrosion resistance was investigated. Ceramic coating by high velocity oxygen fuel (HVOF) spraying is a popular method due to its high spraying velocity, high particle kinetic energy and low oxide content, resulting in dense and uniform coatings [9,10]. In the process of applying ceramic coatings using HVOF thermal spraying, ceramic powder is heated in a combustion chamber where it is mixed with a fuel gas (usually hydrogen or propane) and an oxidant (usually oxygen or air). The resulting mixture is ignited and ejected at high velocity from a nozzle where it impinges on the steel surface and forms a dense, highly adherent ceramic coating. In addition, HVOF coatings can be applied to complex shapes and geometries, making them a widely used process for ceramic coating applications. It is worth noting that the HVOF spraying process can induce residual compressive stresses on the surface of 17-4 PH steel. This further improves the mechanical properties and performance of coated parts [11]. According to Ward et al. carbon steel (AISI1020) substrate was modified with a WC-based cermet coating using the HVOF thermal spray process [12]. Voyer et al. also modified the steel surface with a cermet coating containing a solid lubricant by the HVOF process [13]. Common ceramic materials used for coatings include alumina, titania, zirconia and silicon carbide. The choice of ceramic material depends on the availability, accessibility, desired properties, cost and specific application of the coating. Alumina based coatings are gaining significant attention now a days due to its cost to material ratio with significant wear and corrosion resistant properties. Kumar et al. [14] studied the surface and interfacial properties of alumina-ceria ($Al2O3-CeO2$) coatings on AZ91-Mg alloy. The optimum cerium oxide content is specified as 0.8 wt.% for improved mechanical and tribological properties compared to pure aluminum oxide. Gupta et al. proposed that alumina-based coatings with high hardness, wear resistance, and chemical inertness can be applied to steel using the HVOF thermal spray process [9,10]. It is also possible to develop Al2O3-CeO2 based coatings on the surface of 17-4PH steel using HVOF process where reduced graphene oxide (rGO) is added to the powder mixture [15].

Further, the limitation of the HVOF process for depositing ceramic coatings lies in the short dwelling period of the powder mixture in the combustion chamber results in lower melting of the particles and thereby producing relatively less dense coatings. On the other hand, powder flame spray (PFS) process is generally used for ceramic coatings owing to higher combustion temperature and longer dwellings of powders inside the camber which promotes better melting. There are some limitations with PFS that reduces the importance of the PFS technique significantly. The PFS is generally accompanied by post fusion process to get the denser coatings. Hence, the PFS process is a two-step process. The post fusion is done with an oxyacetylene flame, inductive heating, laser treatment or in a furnace [16,17]. Further, the lower particle velocity in PFS attributes to the moderate properties in coatings due to high porosity, low cohesion among the splats and inferior coating-substrate adhesion. Hence, a novel and modified PFS, known as Hybridized Flow Flame Spray (HFFS), process is proposed to develop dense ceramic coating on steels [18].

Materials and methods

The main materials that were used in this study are substrate and coating powders. In the study 17-4 PH steel is used as substrate. Alumina (Al2O3) powder of purity of 99%, Ceria (CeO2) powder of purity 99% and reduced graphene oxide (rGO) powder are used as raw materials for development of feedstock powders for the coatings. Four compositions of feedstock powders are finalized for the development of coatings as indicated in Table 1. Prior to coating, the powders are milled/mixed in a high energy ball mill to get a uniform coating and the substrates are grit blasted to have better mechanical interlocking with the splats. Figure 1 shows the sequential steps followed during the HVOF process. The as-sprayed coatings as well as the substrates are then characterized using various characterization techniques and the responses are studied and compiled. The details of the spraying and characterization parameters can be found somewhere else [15].

For HFFS process, mild steel is used as substrate and pure alumina is used as feedstock powder. The schematic diagram of HFFS process, the spraying parameters, and the comparative properties of HFFS coatings and PFS coatings can be seen in Figure 3. Authors have mentioned the details of HFFS coatings somewhere else [18].

Table 1: Coating feedstock powders nomenclature and their composition

Coating	Alumina(wt.%)	Ceria(wt.%)	rGO(wt.%)
S1	99.20	0.80	-
S2	99.15	0.80	0.05
S3	99.10	0.80	0.10
S4	99.00	0.80	0.20

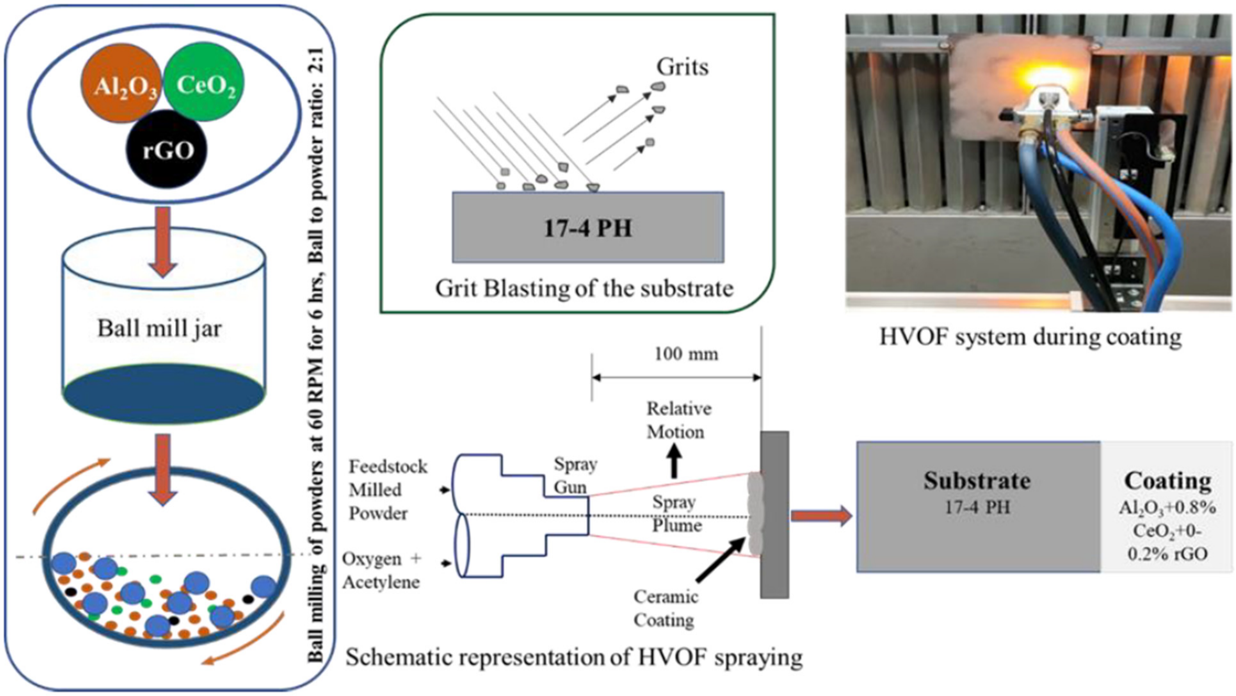
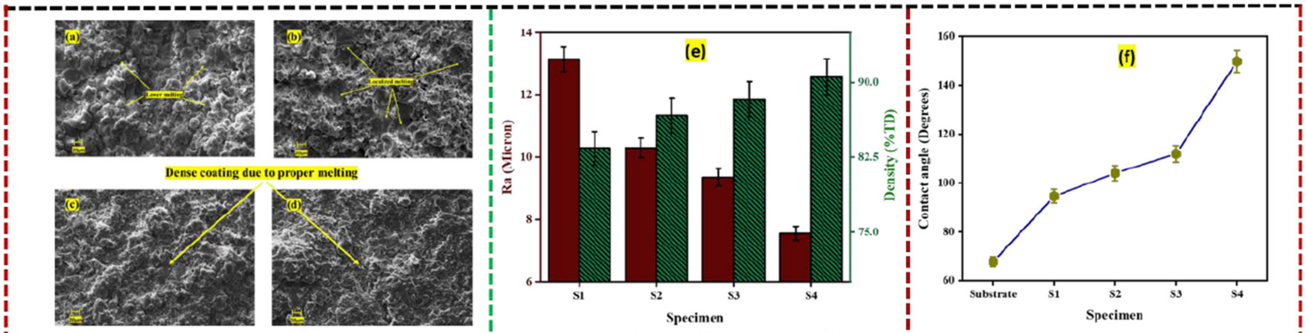


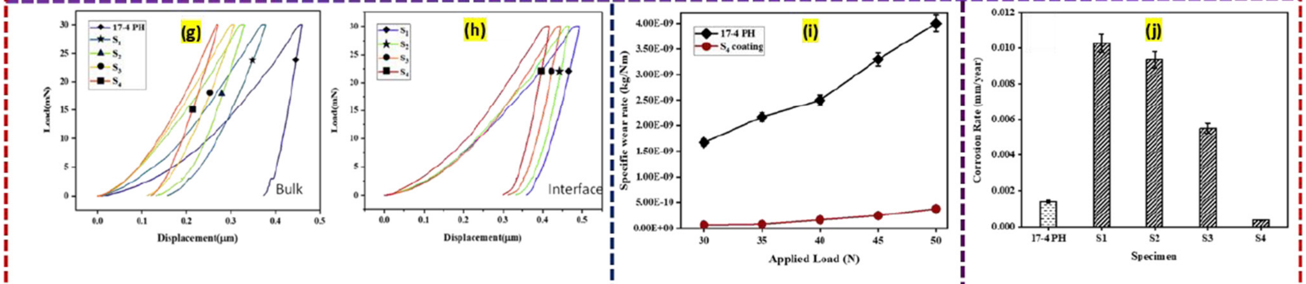
Figure 1: Sequential steps followed during the coating development through HVOF process



SEM micrographs of as-sprayed coatings (a) S_1, (b) S_2, (c) S_3 and (d) S_4.

Average surface roughness and density variations in the as-sprayed coatings.

Contact angle of the substrate and different coatings.

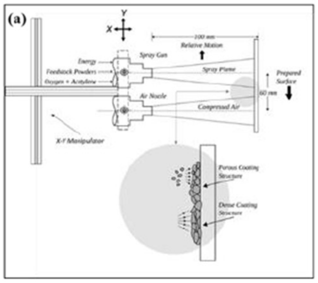


P-h curves recorded during nanoindentation for different specimens.

Specific wear rate vs applied load data for the specimens at various loads.

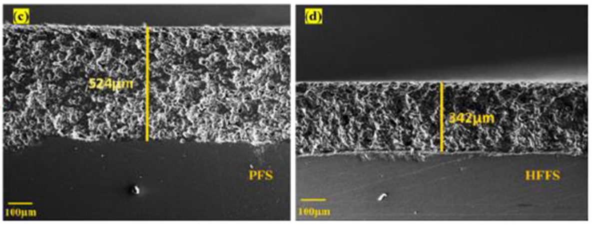
The corrosion rate of all the specimens.

Figure 2: (a-d) SEM micrographs, (e-f) physical properties, (g-h) mechanical properties, (i) wear performance and (j) corrosion response of the coatings developed by HVOF

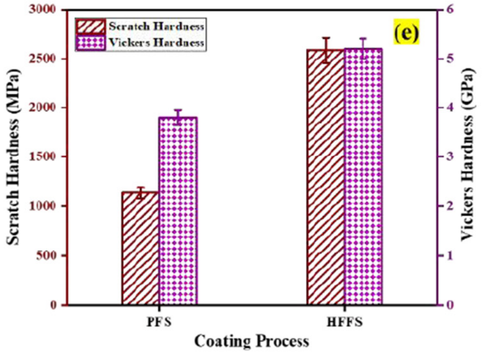


(b)			
HFFS	Oxygen	Pressure	2.5 Bar
		Flow	45 Lit/min
	Acetylene	Pressure	1.1 Bar
		Flow	55 Lit/min
	Air	Pressure	6 Bar
		Flow	500 Lit/Min
	Spray Distance		4 Inches
	Nitrogen(Carrier Gas)	Flow	10 Lit/min
	Powder Feed Rate		25g/min

Schematic representation of (a) HFFS apparatus and (b) spraying parameters.



Cross-sectional micrographs of coatings developed by (c) PFS and (d) HFFS process.



Scratch and Vickers hardness of coatings developed by PFS and HFFS process.

Figure 3: (a)HFFS apparatus, (b) spraying parameters of HFFS and (c-e) comparison between PFS and HFFS coating properties

Results and Discussion

The properties of Al2O3-0.8CeO2-rGO based coatings developed through the HVOF process are shown in Figure 2. Clearly, from Figure 2(a-d), it can be observed that the density of the coatings gradually increased with increase in rGO content in the coatings. The degree of melting also improved with localized melting and larger splat size as shown in Figure 2(b-d). Since surface roughness of a coating is a function of degree of melting of particles, number of unmelted and semi melted particles in the coatings, the surface roughness of the coatings gradually decreased with increase in the rGO concentration (Figure 2(e)). The density of the chipped off coatings (Figure 2(e)) revealed that the density of the coatings increased from 83 % theoretical density (TD) to 90% TD with addition of rGO from 0-0.2 wt.% which validates the observation made in Figure 2(a-d). The reason of all these observations may be attributed to the heat carrying capacity of rGO. RGO, being thermally conductive, carries more heat compared to its surroundings thereby promoting localized melting (Figure 2(b)) and enhancing the density of the coatings. Further, due to absence of oxygen containing functional groups (OFGs) in rGO, it possesses hydrophobic nature in general. The addition of rGO into the Al2O3-0.8CeO2 matrix enhanced the hydrophobicity nature of the coatings too (Figure 2(f)). The enhanced density with refined microstructures of the coatings helped in enhancing the hardness of the coatings at the surface as well as the interface (Figure 2(g-h)). Localized melting of the coatings helped in better adhesion and mechanical interlocking of the splats at the coating-substrate interface which can be quantified in terms of hardness at the interface (from P-h curve, Figure 2(h)). The enhanced density and super hydrophobicity nature of the S4 coating attributed to better corrosion resistance compared to the substrate (the substrate shows excellent corrosion resistance owing to the high chromium content (17 wt.%)). The wear response of the best performed coating i.e. S4 and the substrate at various loads (30-50 N) against EN31 steel as counterpart revealed that the wear rate of the substrate as well as coating increased with increase in load. Also, at a particular load, the harder material (in the present case the coating) showed minimum wear. These observations are in agreement with the conventional Archard's law of wear [4]. The details discussions about the other aspects of the coatings are mentioned by the authors elsewhere [15].

However, if observed closely, the enhancement of the density is not proportional to the quantity of rGO in the coatings (Figure 2(e)). Rather, the density reaches to a saturation level, and it might be possible that addition of further rGO in the coatings will not improve the density of the coatings significantly. Hence a novel and modified flame spray process i.e. HFFS is proposed to develop dense ceramic coatings in a single step.

The hybridized flow in HFFS process is developed due to the flow of high pressurized air coming out of an additional nozzle placed beside the PFS gun (Figure 3(a)) whose movement is synchronised with the primary gun. This pressurized air helps in providing additional velocity to the splats, spreading the splats, and increasing the splats interaction thereby enhancing the density of HFFS coating to ~98 %TD [18]. The enhancement in density resulted in the increment of the scratch and Vickers hardness of the HFFS coatings compared to the PFS coating (Figure 3(e)). Also, the morphological images of the cross sections of the coatings PFS and HFFS coating reveals that the coatings developed through HFFS is dense and compact compared to PFS coatings developed in a single step. Hence, post fusion or any kind of post treatment is eliminated through HFFS process to develop dense ceramic coatings on steels.

Conclusion

The present investigation reveals that,

1. It is possible to develop wear and corrosion resistant alumina based ceramic coatings on steel using HVOF thermal spray process.
2. Addition of rGO in the Al2O3-0.8CeO2 matrix helps in enhancing the physical, mechanical, tribological and electrochemical (corrosion) properties of the coatings.
3. HFFS process, a modified version of PFS process, can be deployed/ applied instead of PFS/HVOF to develop dense ceramic coatings.

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Metallurgically Formed Niobium Carbide Composites for Corrosion, Erosion and Wear Protection

*By **Leo Antony**, Kymera International-SCM Metal Products Division, RTP, NC.*
Email: Leo.Antony@kymerainternational.com

New cored wire materials have been developed, bringing a new dimension to the thermal spray coatings of Niobium Carbide Composites. Niobium Carbide (NbC) Composites can now be metallurgically formed and deposited using this cored wire material during the wire arc spray process. The resultant coating has already proved to be an excellent candidate for corrosion, erosion, wear, and anti-slip protection.

Recognition of the potential of NbC Composites has brought with it new approaches and the development of novel feedstock materials. Increased demand of coated and non-coated component longevity, more cost-effective coating solutions, health and safety considerations during coating processes and post coating machining operations, proved a strong motivation to produce a new cored wire for wire arc processing.

Using HSC 10 Chemistry software package, thermodynamic models were generated as a first step in the coating design process, to determine the optimum cored wire feed stock composition. HSC 10 utilized the Gibbs Free energy minimization method to determine the ideal stoichiometries of the cored wire to achieve the desired metal matrix NbC composite coating. An example of a thermodynamic model is shown below in Figure 1. In this case, a Nickel-Chromium metal matrix with NbC composite was generated.

With the options of changing the metal matrix between Iron, Nickel, and Aluminum, this NbC composite coating system is versatile, cost efficient and high performing in various lab/field validation test conditions. In the case of Fe based NbC composite coating, the resultant material offered.

1. 6X better than uncoated carbon steel under severe sulfidizing environment and are comparable to other Ni base coatings.
2. 20% better in erosion testing (ASTM-G76) than other competing products shown in Figure 2.
3. Less fume generation because of the metallurgical reaction during spraying
4. Less toxicity considering the coating contains less Chromium, Nickel, and no Tungsten Carbide or Cobalt.
5. Broad functionality of applications – Wire Arc, Laser Cladding/Laser – Direct Energy Deposition (DED), Plasma Transferred Arc etc.
6. Excellent ductility – The coating can be bent 25 degrees without cracking, which is ~ 25% better than other competing products in this segment.
7. The coating can be machined to 80Ra - 160Ra, and ground to 6Ra - 25 Ra (shown in Figure 3) for various industrial applications. Ra equals Roughness Average in microinches.

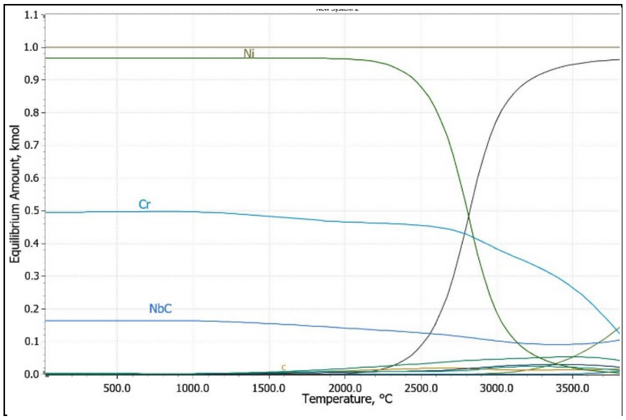

Figure 1: Gibbs free energy minimization plot for the Nickel base NbC Composite coating system

An example of an Aluminum base NbC Composite coating microstructure, XRD results and post bend test pictures are shown in Figure 4, 5 and 6.

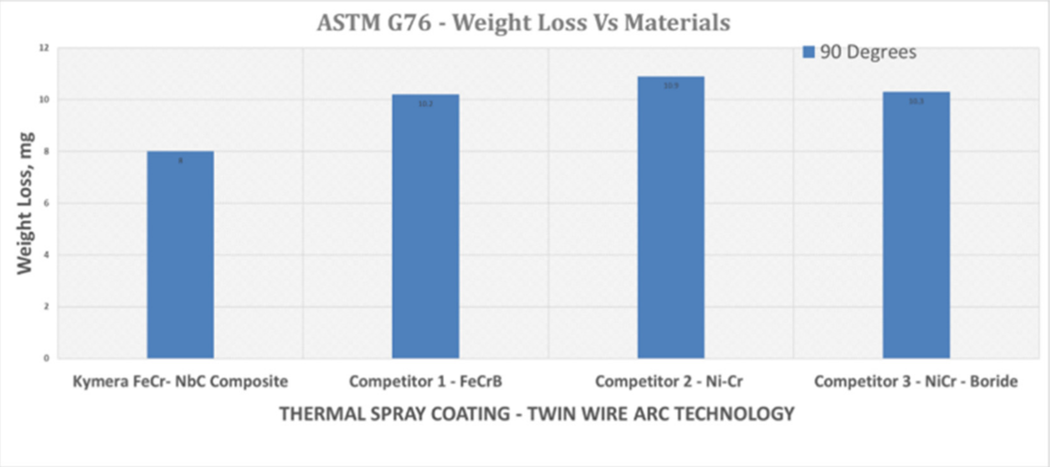

Figure 2: Relative erosion performance of tested thermal spray materials

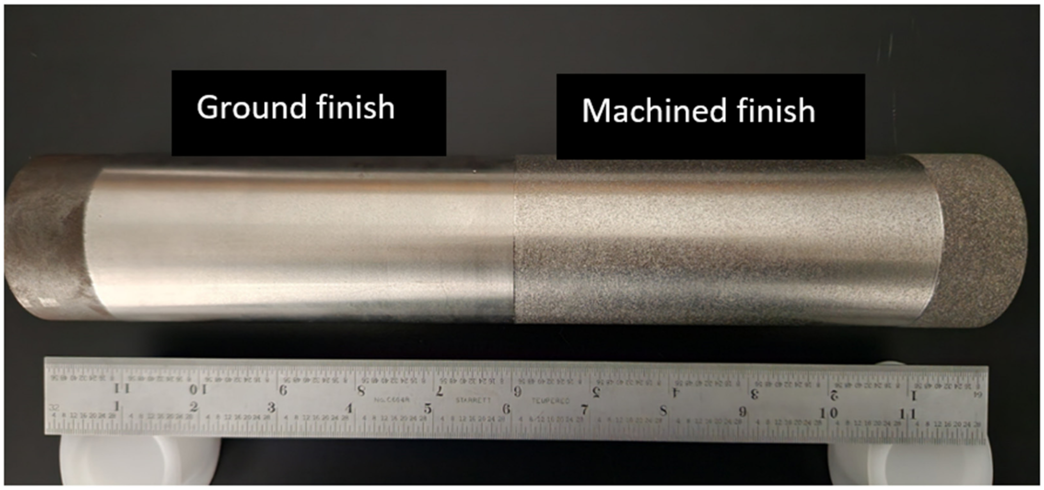

Figure 3: Fe base NbC composite coating surface finish

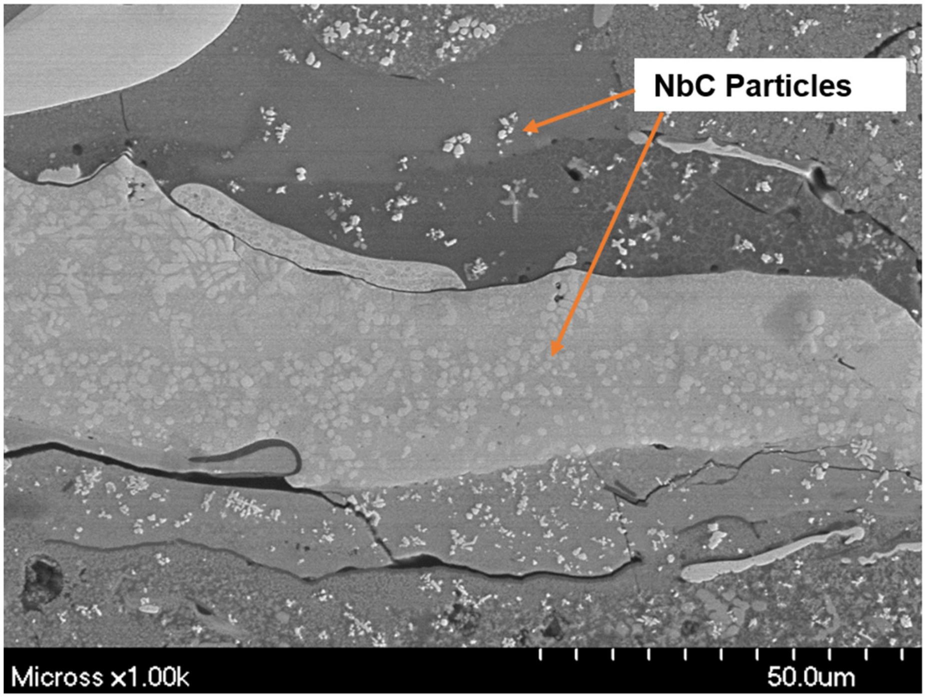

Figure 4: Metallurgically formed NbC particles homogeneously spread within the Aluminum base metal matrix splats

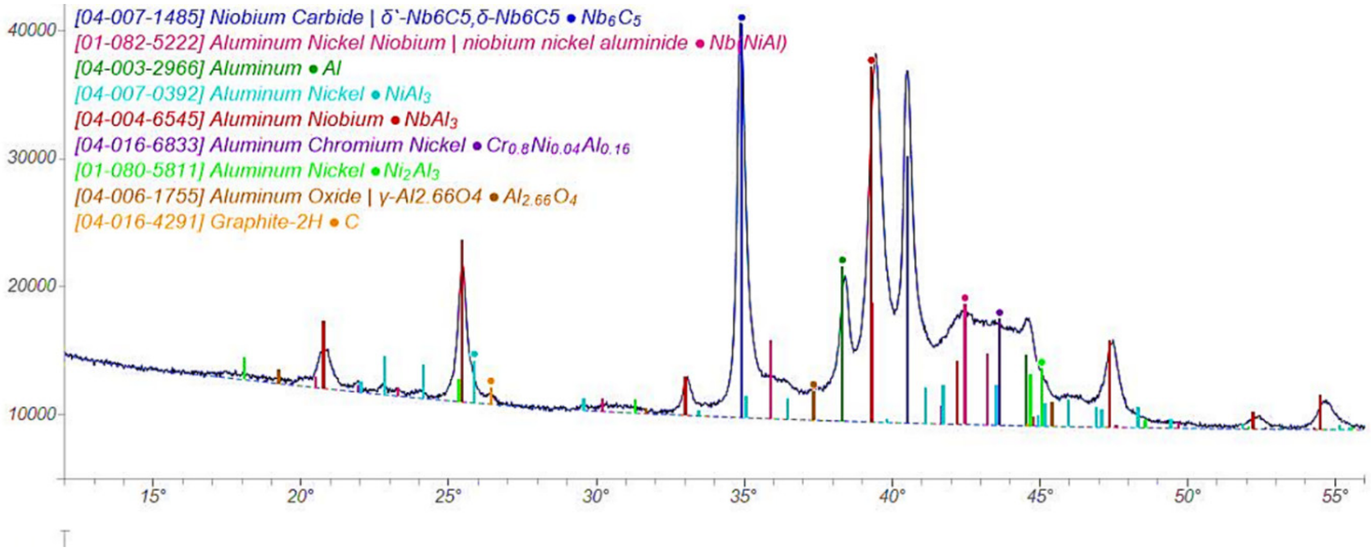

Figure 5: XRD results of the Al base NbC Composite Coating

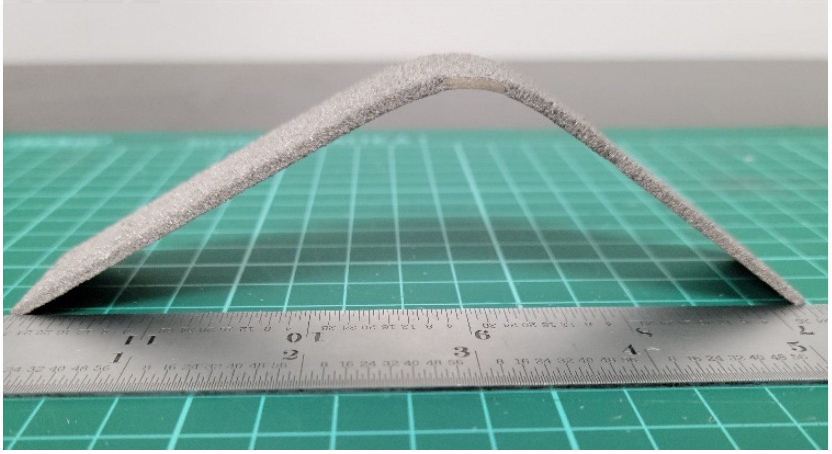

Figure 6: Post bend testing of Al base NbC composite coating

XRD results clearly showed a distinct NbC peak in Figure 5. Niobium carbide was primarily observed as the major phase along with some amounts of intermetallics containing niobium, nickel and aluminum, and aluminum.

The Aluminum base NbC composite (Microstructure shown in Figure 4) offers excellent ductility, and it can be bent in excess of 65 degrees without any cracking (shown in Figure 6). The average hardness of this composite was ~ 750HV (61 HRC), which is approximately 4X greater than Stainless Steel 304 material. This coating protects any steel substrate against saltwater corrosion, which was confirmed at the Kymera lab.

Uncoated carbon steel substrate corroded 5.5 mils/day where as the Al base NbC composite coating protected the carbon steel substrate and no salt corrosion was observed after 90 days of testing. All these coating features make this material an excellent candidate for marine, offshore, and Navy flight deck applications against corrosion, wear and anti-slip issues.

Though this material was tested and validated for specific component applications, this NbC composite could extend its application in broader Industrial, Metals and Mining, Pulp and Paper, Oil and Gas, Power, Wind, Hydro, and other Government agencies like DOD, DOE etc. uses.

Twin-arc and cored wire products have been in the market for many years and continuous innovations like this newly developed NbC composite coatings system can revive components making them longer lasting and more sustainable, while maintaining cost effectiveness, environmental friendliness and excellent use properties.

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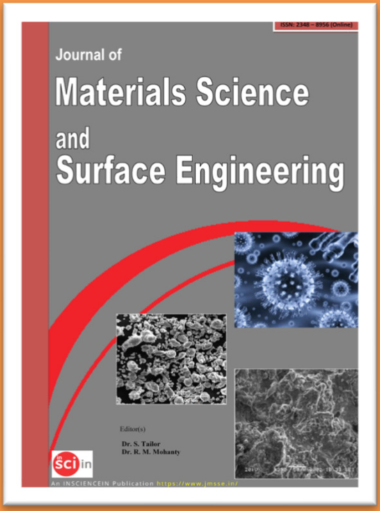

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