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## Issue Highlights

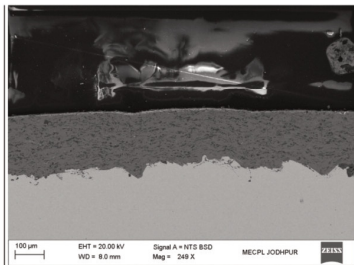
Featured Article: TS Powder Market Forecast 2021-2026

Technical Article: New trends of cold spraying process

Industry Research News: Dense ceramic coatings

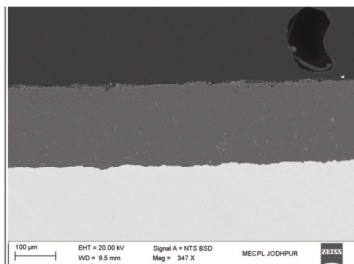
Research News from Academia

# INNOVATIVE CERAMIC COATING



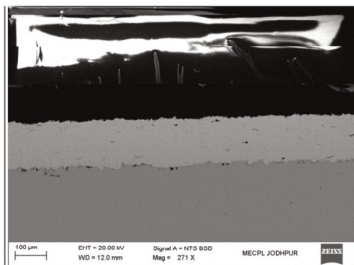
**Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>**

POROSITY % 1.0-2.0  
HARDNESS HV<sub>0.3</sub> 700-850  
ADHESION STRENGTH(MPa) 63.81  
AS-SPRAYED Ra (μm) 2.0-4.0



**Al<sub>2</sub>O<sub>3</sub>**

POROSITY % 2.0-3.0  
HARDNESS HV<sub>0.3</sub> 750-850  
ADHESION STRENGTH(MPa) 61.23  
AS-SPRAYED Ra (μm) 3.5-4.0



**YSZ**

POROSITY % 1.0-2.0  
HARDNESS HV<sub>0.3</sub> 550-700  
ADHESION STRENGTH(MPa) 39.29  
AS-SPRAYED Ra (μm) 2.0-4.0

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- LOW ROUGHNESS AS SPRAYED



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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.

**Editor**

Dr. Satish Tailor, Chief Scientist & GM-R&D, MECPL, India.

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# Thermal Spray Powder Market Forecast 2021-2026

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## The importance of global thermal spray material science trends in pandemic emergence supply arena

The continued material science additive manufacturing ingenuity development has become central to economic growth globally.

Recovery of the previous exponential growth before the pandemic effects slowed expansion has enabled collective research to develop sustainable, smart, and responsive materials that also offer improved physical properties. Novel formulations, including nanomaterials and biomaterials, impart new functionalities to existing materials while expanding the scope of innovation.

The supply demand for materials utilized in the versatility of component manufacturing is increasingly apparent in importance of economic recovery.

Demand for metal powder will in the near future outpace the available supply due to the interruption provided by the covid 19 epidemic.

Aerospace sector is expected to dominate the market demand. North America is expected to lead the regional market share.

## THERMAL SPRAY POWDER MARKET - GROWTH, TRENDS, COVID-19 IMPACT, AND FORECASTS (2021 - 2026)

The market is segmented by Powder Type (Tungsten Carbide, Molybdenum, Chrome Carbide, and Other Powder Types), End-user Industry (Aerospace, Automotive, Industrial Gas Turbines, Oil & Gas, Power, and Other End-user Industries), and Geography (Asia-Pacific, North America, Europe, South America, and Middle-East and Africa).

Fastest Growing Market: Asia Pacific

Largest Market: North America

CAGR: >7 %

## Market Overview

The market for thermal spray powder is anticipated to register a CAGR of over 7% during the forecast period. Some of the major factors driving the growth of the market studied are the increasing demand for higher performance customized alloy powders, increasing prominence for plasma spray coatings, and extensive consumption of thermal sprayed tungsten-cobalt (WC-Co) coatings.

Issues regarding process reliability and consistency and rising popularity of thermal spray ceramic coatings are expected to hinder the market's growth.

Industrial scale production of environmental barrier coatings (EBC) thermal spray powders are projected to act as an opportunity for the market in the future.

## Key Market Trends

Increasing Demand from the Aerospace Industry  
Ceramic powders, such as tungsten carbide and chrome carbide, are used as thermal barrier coatings in the aerospace and aviation sector, to protect components against intense heat and wear. In the aerospace sector, thermal spray powders are extensively used as the protective coatings of aircraft components and to repair the old ones. They are used in the protection of engine turbine blades and actuation systems, to provide high thermal resistance and longevity. Thermal spray powder coatings are largely employed for several purposes in jet engine components, such as crank shafts, piston rings, cylinders, valves, and so on. In addition, they are also applied in the coating of landing gear (bearings and axles inside the landing gear) to withstand the forces during landing and take-off.

The aircraft production industry is booming in the Asia-Pacific and South American regions. Countries, such as China and India, are witnessing

growth in the aircraft passenger travel rate, owing to the rising consumer incomes and increasing airport infrastructure network. The air travel passenger fleet in the Asia-Pacific region is expected to rise by 5.7%, while the aircraft fleet is expected to increase at a rate of 4.8% during the forecast period. The total aircraft fleet is expected to reach to a number of 17,520 by 2036. Similarly, the Latin American and Middle Eastern regions are also expected to witness significant growth rates of 4.4% and 5.1%, respectively, between 2017 and 2036. With increasing aircraft fleet, the repair and maintenance of aircraft also increases YoY.

All the aforementioned factors are expected to drive the market during the emergence from pandemic slowdown.

The thermal spray powder market is fragmented, with many of the major players currently dominate the market. Key players in the thermal spray powder market include Hoganas AB, Linde plc, TreibacherIndustrie AG, HC Starck GmbH, and Plasma Powders & Systems Inc., among others.

Thermal spray diversity appears to have gained traction in multiple industries.

The most commonly used thermal spray dielectric materials are polymers and oxide ceramics. It has been found that ceramics exhibit greater durability and resistance to wear than polymers. Additionally, ceramics also exhibit better dielectric strengths. Although oxides of titanium (titania) and aluminum (alumina) are the most commonly used, some other oxides are also employed in dielectric coatings.

India is the largest producer of sheet mica. India's metal and mining industry was estimated to be \$106.4 billion in 2010.

Rise in infrastructure development and automotive production are driving growth in the metals and mining sector in India. India has a vast mineral potential with mining lease granted for longer durations of 20 to 30 years. India produces 95 minerals - 4 fuel-related minerals, 10 metallic minerals, 23 non-metallic minerals, 3 atomic minerals and 55 minor minerals (including building and other minerals). India is expected to overtake Australia and the US in early 2020 to be the world's second-largest coal producer.

India holds a fair advantage in cost of production and conversion cost of steel and alumina. The country is the second largest crude steel producer with production of 111.2 million tonnes (MT) of crude steel in 2019. Crude steel production and finished steel production stood at 108.5 MT and 101.03 MT, respectively, in FY20. India is the largest producer of sheet mica in the world and has the seventh largest bauxite reserves at around 2,908.85 MT in FY19. Iron ore production in the country increased to 206.45 million tonnes (MT) in FY20. In FY20, India's iron and steel export were valued at US\$ 9.28 billion. During FY16-FY20, India's export of iron and steel grew at a CAGR of 14%.

Production of aluminium stood at 3.65 MT in FY20. Aluminium export from the country reached 1.50 MT in FY19 and 0.52 MT in FY20. In value terms, aluminium export from the country stood at US\$ 20.18 million in FY20.

Coal production in the country stood at 729.10 million tonnes (MT) in FY20 and reached 304.88 MT in FY21 (as of October 2020).

The index of mineral production was 132.7 in March 2020. Mining group under Index of Industrial Production (IIP) stood at 109.7 for FY20, witnessing a growth of 1.7% y-o-y. Mineral production in India reached Rs. 68,577.09 crore (US\$ 9.73 billion) in FY20E (till February 2020). National Mineral Policy 2019 was launched for transparency, better regulation and enforcement, and balanced social and economic growth into the sector.

In November 2020, the Union Coal Minister, Mr. Pralhad Joshi, stated that 19 mines have successfully been auctioned; this is the highest number of successfully auctioned mines in any tranche of coal auctions. The country's first-ever commercial mining auction will garner a total revenue of Rs. 6,656 crore (US\$ 900.59 million) annually from mines spread over the following five states—Madhya Pradesh, Chhattisgarh, Odisha, Jharkhand and Maharashtra.

The Government of India has allowed 100% Foreign Direct Investment (FDI) in the mining sector and exploration of metal and non-metal ores under the automatic route, which will propel growth in the sector. Power and cement industries also aiding growth in the metals and

mining sector. Given the strong growth expectations from residential and commercial building industry, demand for iron and steel is set to grow.

From April 2000 to June 2020, FDI inflows in metallurgical industries stood at US\$ 14,227.21 million. In the same period, FDI inflows in mining, diamond and gold ornaments and coal production sectors stood at US\$ 2,786.32 million, US\$ 1,179.40 million and US\$ 27.73 million, respectively.

India is positioned positively to gain momentum in recovery due to its established resource deposits.

The new map of technology advances lets scientists combine elements faster than ever before and is helping them create all sorts of novel elements. And an array of new fabrication tools are further amplifying this process, allowing us to work at altogether new scales and sizes, including the atomic scale, where we're now building materials one atom at a time.

As the capability to create the metamaterials used in carbon fiber composites for lighter-weight vehicles, advanced alloys for more durable jet

engines, and biomaterials to replace human joints advances We're seeing breakthroughs in energy storage and quantum computing.

Amara Raja Batteries Ltd, India's second-biggest traditional battery maker by value, will build a lithium-ion assembly plant as it seeks to grab a slice of the market for electric vehicle power packs that are set to grow to \$300 billion by 2030.

The battery maker is in the process of building a 100 megawatt-hour assembly plant in the southern state of Andhra Pradesh and the company is working closely with the Indian Institute of Technology in Chennai, Chief Executive Officer S. Vijayanand said in an interview in New Delhi.

"There's incubation work going on because we are at a beginning stage both from the market-demand and product-development perspective," Vijayanand said. "We are very focused on building solutions for the early stage of electrification of vehicles and work with the OEM programs at the same time"

The manufacturing sector recovery is dependent on the security of material supply acquisition.





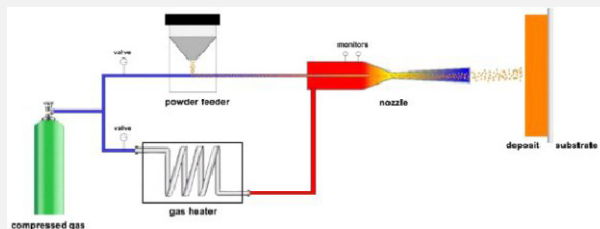
# New trends of cold spraying process

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**C**old spraying (CS) is known as an unique thermal spraying method due to low process temperature [1,2]. In contrast to other methods CS utilizes high kinetic energy resulting in extensive plastic deformation of sprayed material. Powder particles are accelerated by working gas that flows through convergent-divergent nozzle and gain supersonic velocity. Process temperature do not exceed the melting point of applied powder material and thus particles form the coating in solid state. Therefore CS shows many advantages, including: (i) high efficiency of the spraying process resulting in thick coatings and can be acknowledged as additive manufacturing technology, (ii) high coating quality, e.g. low porosity or oxidation level [3,4], (iii) uniform microstructure without phase transformation or grain growth [5-8], (iv) possibility to form a coating on thermally sensitive substrate due to controlled thermal energy [4], and (v) usually compressive residual stresses resulting from peening effect of impinging solid particles [3]. Initially CS was dedicated to ductile materials due to the necessity of deformation upon particles impact on the substrate. Therefore, mostly metals and mixtures of metals and ceramics were applied as feedstock powders [3,9]. Nowadays, more and more nontypical materials, such as ceramics, are proposed, increasing possible applications of the CS method.

## Metal vs. ceramic particles deposition

In CS the coating deposition is dependent on the velocity of the particles. Therefore coating formation is possible due to a nozzle with a special converging-diverging shape, which is known as de Laval nozzle. In the nozzle working gas (air, nitrogen, helium or their mixtures) gains supersonic velocity and accelerates the powder particles due to the drag force [2,10,12-14]. Finally, particles are projected by supersonic gas towards the substrate and impact with high kinetic energy



on the material surface. Preheating of the propellant gas increases the temperature and velocity of the powder [15,16]. When so called critical velocity is exceeded, particles embed on the substrate. It should be emphasise that the velocity of a single particle will be determined by the size, shape and density of the particle, the temperature and pressure of the gas, the type of working gas (molecular weight and the adiabatic exponent) and the geometry of the nozzle [17]. Furthermore, all of these parameters have a crucial impact on the formation and properties of the coating, and the efficiency of spraying [1,2,12]. In the CS process the deposition of the coating begins with formation of a first layer due to the particle-substrate interactions. Powder particles are caved in the substrate and the adhesion base on jet formation of both materials. Afterwards a proper coating is deposited with the particle-coating interactions, which are responsible for the cohesive bonding.

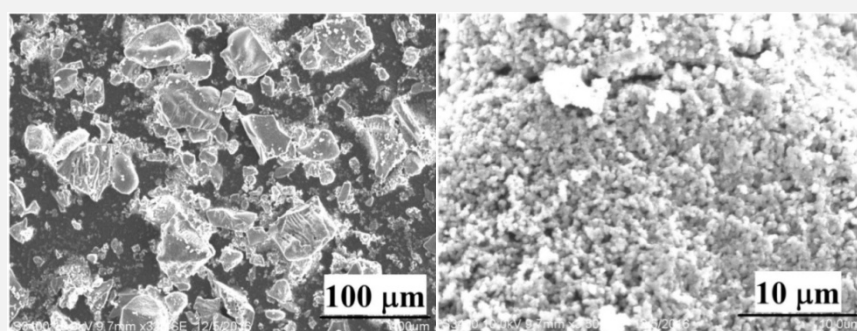
In the case of metallic particles the bonding is prescribed to formation of adiabatic shear instabilities during impact which occur as a result of high strain rate deformation processes and create a metal jet consisting of the particle and substrate material [18].

Another contributing mechanism including: mechanical interlocking [18] and intermixing of substrate and powder material [19,20]. This type of mechanism implies difficulties in bonding ceramic particles owing to material brittleness [21]. Up to now composite coatings have been very popular,

in which metal acts as a binder for ceramic particles [22–24]. Such coatings are usually sprayed using mixtures of various ceramics and metals. When the amount of binder is insufficient ceramic particles hit each other, crush and rebound from the substrate or deposited coating. In consequence they are not evenly distributed in the coating and their amount is lower than in initial feedstock powder. In the worst case process can take a form of grit-blasting, in which ceramic particles erode the substrate instead of form a coating. Some research showed that the fraction of ceramics in the as-sprayed coating was significantly lower compared to the initial amount in the powder [25,26]. Reduction of ceramic content and problems with its distribution makes difficult production of i.e. catalytic coatings with cold spray method. The research on ceramic particles coated with a thin metal layer has been undertaken. The thin layer absorbs energy during impact, deforms plastically and in consequence enables formation of composite coating. The ceramic is much more evenly distributed and its amount is higher [27–29].

The next step was aimed to obtain pure ceramic coatings and to explore bonding mechanism during the deposition process. First attempts proved that deposition of ceramic coatings is possible through substrate deformation and mechanical interlocking of ceramic particles in substrate material. The subsequent layers were

deposited owing to metal particles, which were detached from the substrate and acted as a binder in the coating. This bonding mechanism implies that thickness of the coating is limited owing to difficulties with provision of metal particles from the substrate [30]. The impossibility of pure ceramic coating formation was related to the morphology and large size of the powder particles. Salim et al. proved that the key feature in formation of ceramic coatings is the use of agglomerated submicron powder [31]. TiO<sub>2</sub> was synthesized in a simple hydrolysis method of titanyl sulfate in distilled water with a small addition of inorganic salt. The powder formed agglomerates with one nanoparticles and was then post-treated with annealing and hydrothermal treatment. Cold spray coating was not obtained by the as-synthesized powder, instead only particle embedment was observed. On the contrary, the annealed powders formed thin coatings. When deposited using the same cold spray parameters, the hydrothermal treated TiO<sub>2</sub> formed a thicker coating of about 150 µm. This was explained by the synergistic effect of the hydrothermal process enabling formation of oriented TiO<sub>2</sub> agglomerates. Ceramic nano-sized powder limits drag force and it is impossible to achieve critical velocity by single particles. As a result coating formation will not succeed. Therefore, application of nano-particles agglomerates or aggregates is the only solution (Fig. 1).



**Figure 1:** Morphology(SEM) of amorphous TiO<sub>2</sub> powder after the sol-gel synthesis [32]

## Bonding mechanism of ceramic particles

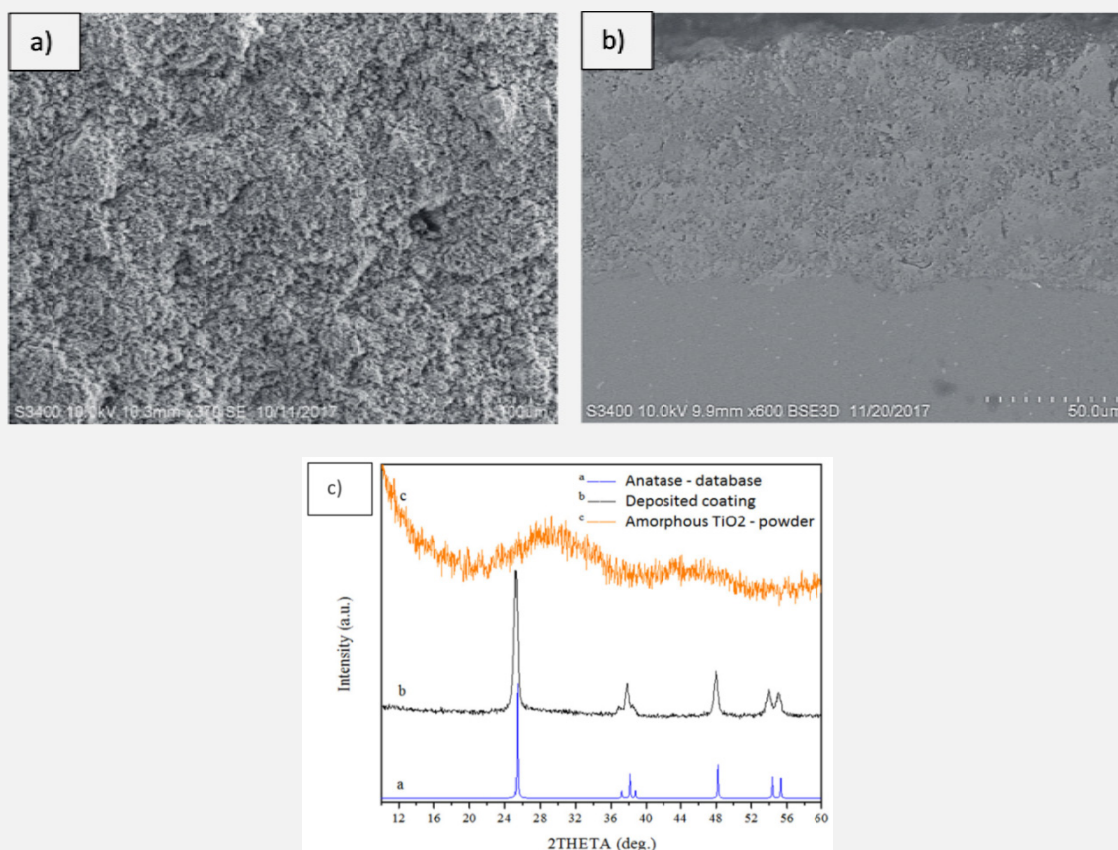
It is commonly believed that during impact of agglomerated particles fragmentation and packing of the particles occurs [32]. The fractured nanoparticles stick together with few bonding sites. Subsequent agglomerates strike the coating providing shock compaction of the nanoparticles. The nanoparticles are consolidated at high heat

energy and pressure [32].The bonding mechanism can be prescribed to the slipping or sliding of particles over other particles [33], which is much easier for ceramic materials composed of nanoparticles [34]. Additionally, it was concluded that tightly agglomerated particles resulted in less number of porosity. Striking agglomerated large



particles with high drug force promote better adhesion between the particles and the substrate. Non-agglomerated particles gain lower velocity and, what is more, tend to collide more easily than in agglomerated form [33]. Therefore, the impact of a single particle is weak and exhibits low inertial levels to penetrate the stagnation layer on the substrate [35]. The application of ceramic powder used for CS was analyzed by Cinca et al. [36] who claimed that the deposition of the sintered HA powders was observed to proceed through pore collapse, fragmentation and densification as well as grain refinement [37]. On the other hand the agglomerated structure deposition takes place through the compaction of the nanocrystalline grains within the particle upon impact [36]. Therefore, in case of aggregates constructed from the crystalline particles, bonding mechanism takes place mostly by fragmentation and slipping or sliding of particles over particles [36,37]. Another factor influencing coating formation is material phase. Application of

soft agglomerates consisting of amorphous particles enables effective powder deposition and coating production due to an exotic for ceramic materials plastic deformation. According to the free volume theory and larger atomic mobility formation and propagation of shear bands is known as a common mechanism inducing plasticity in varieties of materials, e.g. metallic, polymeric glasses and amorphous oxides as well [38,39]. Yang et al. [38] states that a key parameter responsible for plastic deformation is metastable degree of ceramic material. Nevertheless, amorphous ceramic provides one more advantage, which is the possibility of crystallization. The crystallization induced through cold spraying of amorphous  $\text{TiO}_2$  powder significantly improved coating structure quality and mechanical properties as well [32,40,41]. Pure anatase [40] or mixture of anatase-amorphous phases coating [42], is of great interest due to its potential high photocatalytic activity.



**Figure 2:** Micrographs (SEM, BSE) of amorphous powder sprayed with the use of air preheated to 600 °C, (a) coating surface, (b) cross section and (c) XRD spectra [32]

The further investigation of ceramic coatings formation with CS method opens totally new manufacturing routes of ceramics. It will allow to obtain ceramic coatings which will maintain initial properties of feedstock with low energetic method. The applications include thermally sensitive substrates and endangered with phase transition ceramic powders, e.g. TiO<sub>2</sub>.

### Summary

Cold spraying basically was assigned to deposit metal or metal-ceramic composite coatings. Nevertheless, a series of research determined the crucial properties responsible for pure ceramic deposition. Bonding mechanism depends strongly on the morphology of the powder and material phase as well. Application of agglomerates or aggregates is mandatory. In the case of crystalline aggregates, bonding mechanism takes place by slipping or sliding of nanosized particles over particles with simultaneous pore collapse, aggregate fragmentation and structure densification. Soft agglomerates consisting of amorphous particles enable coating formation due to large atomic mobility and local free volume, which are beneficial to the formation of shear bands and further plastic deformation. Additional factor seems to be crystallization of amorphous powder while particles impact onto the substrate with high kinetic energy. Summarizing, the CS process is full of unpredictable phenomena resulting in outstanding coating properties and new applications are just a matter of time.

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**“We welcome Industrial Partners to utilize this Unique National Facility at IIT Ropar”**

**Call for Research and Industrial Collaborations**

The center would welcome any type of collaborations with industry or research and development organizations or educational institutions. This collaboration could include new product design and development by cold spraying, consultancy assignments, industrial problem solution, fundamental and applied research. We can also explore joint funding for carrying out these activities from some governmental and non-governmental agencies, and international research organizations.



(a) Photograph of Cold-sprayed copper coating on SS316L steel (b) SEM image

**About IIT Ropar**

IIT Ropar is the highest-ranked Indian newcomer in Times Higher Education (THE) World University Rankings 2020 table, enroled in the 301-350 band with its very high score for citation impact and its reasonably strong showing on the Industry Income measure. IIT Ropar has also ranked 63rd in latest THE Emerging Economies University Rankings 2020. The Institute is spread over 500 acres of land on the bank of river Satluj.


CSAM Copper Rings  
M. Ahn, S. I. Yoo, G. Kozhiko, Seoul, Japan (2011)

**Harpreet Singh Ph.D.**  
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**National Facility for High-Pressure Cold-Spray**

The Next Generation Coating Technology  
- A Sustainable Way to Surface Engineering and Additive Manufacturing



**What is Cold Spray?**

Cold Spray is a technology for forming surface coatings by spraying particles on substrate materials at high velocity in a supersonic gas flow. Particles that properly exceed their critical velocity will plastically deform, adhering to the substrate and to one another to create a dense coating.

The term “Cold Spray” derives from the fact that the particles are not heated to their melting point. That is to say that the particles form a dense coating by plastically deforming on the substrate while still in solid state.

**What is Unique about Cold Spray System at IIT Ropar?**

The established cold spray system works at extreme N<sub>2</sub> gas pressures (Up to 70 bar), and the gas could be heated up to 1000°C. This makes it state-of-the-art cold spray equipment, which can even be used for additive manufacturing, in addition to surface engineering. Several difficult to coat materials can be deposited as surface coatings or even as standalone 3D products. This is the second of its kind facility in India, which is a fully-automated industrial scale set-up.

**Existing and Potential User Industries**

- ✓ Aeronautical / Aerospace
- ✓ Bio-medical
- ✓ Thermal Power Plants
- ✓ Hydro Power Plants
- ✓ Gas Turbines
- ✓ Automobile
- ✓ Chemical Processing
- ✓ Textile
- ✓ Cookware
- ✓ Defence

**Specialised Industries:**  
Sputtering Targets

**BENEFITS FOR INDUSTRY**

- High production rates and reliable feed rates of up to 500 g/min and unbeatable irreversibility due to integration of feeder and gun in one unit and robotic arm
- Rapid prototyping and additive manufacturing for product development
- High-level skill development for new businesses in surface engineering

**BENEFITS FOR RESEARCH**

- Unmatched range of unexplored materials and feedstock powders combinations
- Several gaps in scientific understanding of the process
- Many un-answered questions!!

**Materials which can be deposited?**

Gold (Au)	Nickel (Ni)	Nickel-Chromium (NiCr)
Silver (Ag)	Titanium (Ti)	Composites/Ceramics
Aluminium (Al)	Superalloys	Selected ceramics
Zinc (Zn)	Stainless Steel	Many more to be explored
Tin (Sn)	Ti-6Al-4V	
Copper (Cu)	Aluminium Bronze	



# Dense Ceramic Coatings

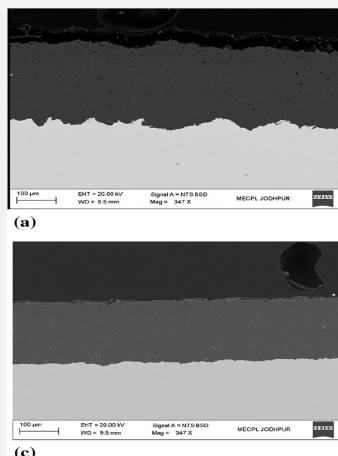
**M**etallizing Equipment Company Pvt. Ltd. Jodhpur is pleased to launch a new product "CERAJET-2021", It is a new generation thermal spray process named "**Hybrid low-velocity Oxy-fuel**" (HLVOF). The ceramic coatings obtained by HLVOF process competes well with that of obtained by Atmospheric Plasma process. Yet the capital and operating costs are much lower. The patent application is filed.

It is particularly suitable for thin as 15 micron minimum upto 250 microns and dense coatings of alumina, alumina-titania, chromium oxide, YSZ and combinations thereof. The whole process of the coating is fully automatic.

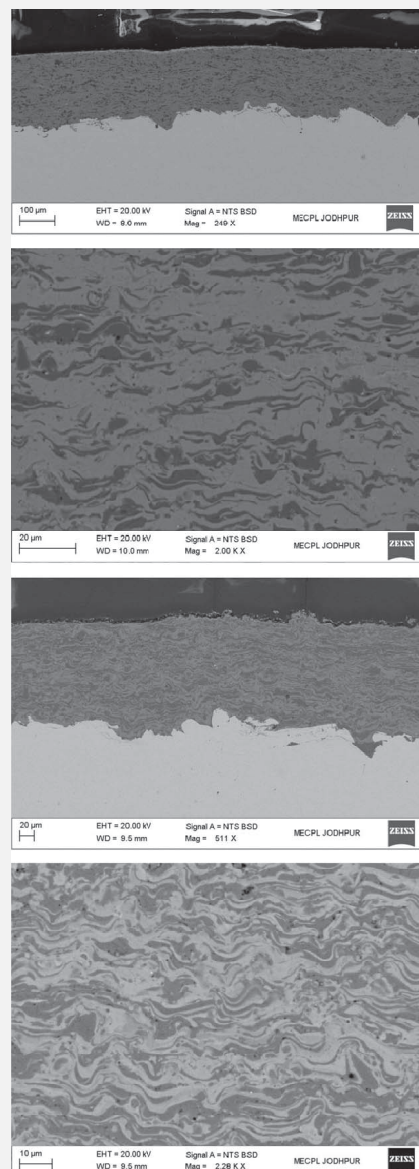
Customer can see live demonstration or get sample & commercial offer on request.

For comparison with APS and for more information please see our research publications based on our new technology

1. "Microstructure evolution and mechanical properties of Al<sub>2</sub>O<sub>3</sub>-40%TiO<sub>2</sub> coating by Hybrid-Low Velocity OxyFuel process" published in "Physica Scripta".  
<https://iopscience.iop.org/article/10.1088/1402-4896/abce37/meta>
2. "High-Performance Al<sub>2</sub>O<sub>3</sub> Coating by Hybrid-LVOF (Low-Velocity Oxyfuel) Process" published in "Journal of Thermal Spray Technology".  
<https://link.springer.com/article/10.1007/s11666-020-01033-6>



Al<sub>2</sub>O<sub>3</sub>



Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>

The coatings are dense and uniform



If you have any further questions, please write to [dgm\\_rnd@mecpl.com](mailto:dgm_rnd@mecpl.com)

# Interfacial bonding and chemistry effect on TBC

**Fredy James J and SB Arya\***

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Thermal barrier coatings (TBC) are coatings employed in high temperature turbine engine components with the aim of protecting the underlying components from high temperature interactions of oxidation, corrosion along with environmental deposits, such as calcium-magnesium-alumino-silicate (CMAS) and foreign object damage. The turbine component materials are superalloys (nickel based), as they offer comparatively better performance at elevated temperature. However, a typical constituent in a TBC system include a top coat (mostly ceramic), bond coat and a metallic substrate. The top coat enables thermal insulation, oxidation and corrosion resistance to the component, while bond coat bridges the properties between ceramic top coat and metallic bond coat.

The chemistry of the substrate is highly significant, as elements diffusion at elevated temperature can have detrimental effects on stability of the TBC system. In many cases, traces of substrate elements have been detected to migrate to bond coat and bond coat-top-coat interface, forming oxides at interface on oxygen ingress. An undesirable compound at interface such as Mn-Cr spinels so formed shortens the component life from stress development and expansion mismatches.

The interfacial mechanism is more dependent on the bond coat and top coat chemistry, as the oxidation reactions takes place at the interface forming thermally grown oxide (TGO) layer. Although, it is well established fact that high enriched (~100%)  $\text{Al}_2\text{O}_3$  is the preferred TGO composition, other oxides and spinels may form at interface upon oxidation.

The most established commercial grade material for top coat is yttrium stabilized zirconia (YSZ) offering superior performance up to  $1200^\circ\text{C}$ . However, this YSZ tends to destabilize above  $1200^\circ\text{C}$ , from a volume expansion suffered by transformation from tetragonal to monoclinic zirconia phase. The top coat microstructure also

determines the oxygen permeability and the oxidation interactions, which leads to interface TGO. Other than permeability, oxygen diffusion may occur by ionic movement along the grain boundaries.

The TGO growth at interface follows a parabolic trend and brings about a stress gradient along top coat thickness and may further lead to cracking failure. The aluminium enriched bond coat system leads to an initial higher kinetics of alumina formation which slows down on aluminium depletion. As oxidation time increases, spinels forms with a higher kinetics increasing TGO thickness while purity decreases and finally TGO may consist of sub layers with alumina layer and mixed oxide ( $\text{NiO}$ ,  $\text{CoO}$ ,  $\text{Cr}_2\text{O}_3$ , Ni-Cr spinels) layers as constituents. This higher kinetics and spinel formation aids a stress development at the interface. Thus, it is evident that the bond coat chemistry significantly influences the interface TGO growth kinetics.

In case of any intrusions near interface, the stress difference between top coat and TGO will not be the same on either side of intrusion, which is attributed to a stress level readjustment by intrusion morphology at non uniform interface through decohesion and microcracking. Also, on continuous high temperature exposure, the stable  $\text{Al}_2\text{O}_3$  phase of TGO, grows between topcoat micro cracks, which accumulates interfacial stress often liberated on threshold as microcracks. The interface being rough and non-uniform, TGO will be wavy in geometry creating stress variations within through thickness of TGO.

The bond coat chemistry also has significant effect on rumpling behaviour of TGO, failure location of spallation interface and stress concentration at interface. Although rumpling is not a preferred event, there are reports showing that TGO rumpling reduces the accumulated residual stress in case of Pt-Al bond coat. In case of Pt-Al bond coat, the aluminium depletion causes a transformation from single phase  $\beta$ -(Pt,



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Ni)Al to a mixture of  $\beta$ -(Pt, Ni)Al and  $\gamma'$ -(Pt, Ni)<sub>3</sub>Al inducing non uniform volume change at TGO interface. This mechanism of rumpling is dominated over by the ability of bond coat microstructure to resist plastic deformation. The two phase microstructure evolved may have a strengthening effect, by precipitation of fine dispersed phase. A bond coat composition with superior aluminium rich beta phase can provide a sound TGO. Diffusing an alumina layer between top coat and bond coat also leads to a thin sound TGO. The presence of alumina will decrease the oxygen ingress via reduced porosity and prevents TGO thickening and subsequent failure. Under same exposure time, the stress development will vary depending on the phase transformations and martensitic formation in the system. The martensitic structure induces molar volume shrinkage on cooling, causing additional TGO stress. Aluminium depletion and rise in Ni further content leads to martensitic phase formation on cooling, a very low Al leading to coarse martensitic structure. Also, Ti and Ni from

substrate tend to segregate at aluminium depleted regions, which accelerates kinetics of further oxidation. Similarly, interface toughness is highly dependent on the interface science. The intrusions or impurity segregation will tend to reduce the toughness, which is undesirable.

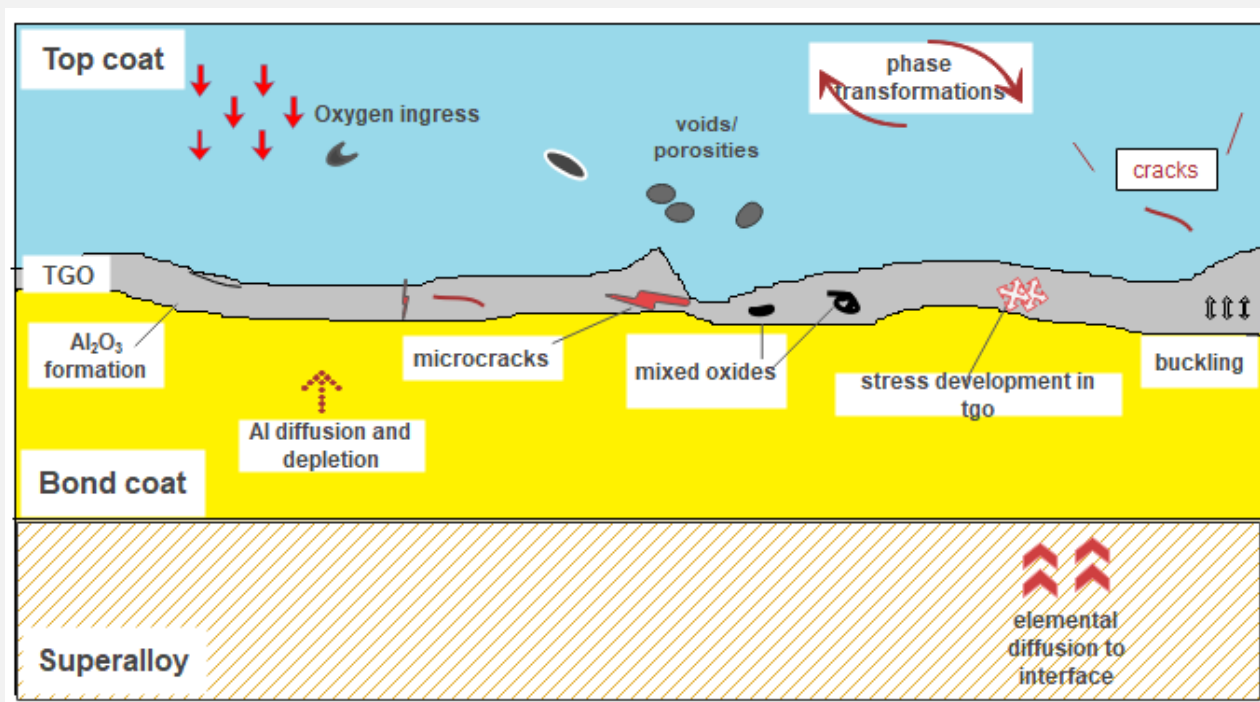
Thus, it is evident that the chemistry of the system has a dominant factor on developing a sound thermally grown oxide (TGO), thermal stability and on TBC performance at elevated temperature over other factors. More researches are to be performed in optimising the chemistry for an enhanced lifetime.

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India's 1<sup>st</sup> thermal spray magazine

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