

Dec. 2023 | Vol. 3 | Issue 3-4

# **SPRAYTODAY**<sup>TM</sup>



#### **Issue Highlights**

- Featured Article: Thermal Spray in India Opportunities and Challenges
- Technical Note: Process Gas and Its Influence on Cold Spray Process
- Academia Research: New Emerging Field: High Entropy Ceramics for Next-Generation Thermal Barrier Coatings
- Highlights of Asian Thermal Spray Conference & Expo 2023 (ATSC2023)

www.inscience.in/spraytoday



## SPRAY COLD® (COLD SPRAY SYSTEM)

**MSC-500** 

panel)

MEC cold spray system with trolley, powder

feeder and PLC controlled

Introducing a metal deposition process that eliminates the need for blast cleaning and oxy-fuel gases. It operates solely with air, providing a coating with high bond strength and density. This process is versatile, allowing the application of almost any metal powder, including brass, copper, Ni, Al, Zn, Sn, bronze, Ta, Nb, Pb, stainless steel, Ti, AlSiC, AlCuZn, NiZn, CuSnPb, NiCr, polymers, and many more.

#### **Application of Low Pressure Cold Spray**

- ▲ Repair bearing seats
- ▲ Repair forms & patterns for casting
- Powder for spraying
- ▲ Hermetically seal radiators and air conditioner
- ▲ Add electrical conductive layers to materials
- ▲ Additive manufacturing and many more.





#### Engine Crank Case

e Durable, Eco-Friendly Brake Innovation



MSC-500

MEC

MCS-23 Cold spray gun with heater installed

#### **COATING FEATURES**

- ▲ High adhesion (30-80 MPa)
- ▲ High cohesion (30-80 Mpa)
- ▲ Homogeneity of the surface
- ▲ High electrical conductivity between the coating and the substrate
- ▲ Any coating thickness (20 microns to 10 cm)
- Roughness of the surface coating is Rz = 20-40
- Processing coatings can be produced by conventional machining methods
- The coating may be applied to any metal, glass, and ceramics



#### Manufacturing Inductive Cookware



Prevent & Repair Damage



#### www.mecpl.com

#### SYSTEM FEATURES

- ▲ Touch screen operation
- Pressure Range: Upto 10 Bar
- ▲ Heating Range: 100-500° C
- Wide Range of Spray material Spectrum
- Working Gas: Air Only
- ▲ Single-Phase Electrical Supply Requirement

Technical Specification of set of equipment SPRAYCOLD®

- ▲ Mass flow controlled powder feeder
- Detachable type control screen

#### SPRAYCOLD® IN ACTION

reclinical specification of set of equipment of NATEOLD			
Maximum compressed air input pressure	10 bar ( 150 psi)		
Compressed air consumption	0.3-0.4 m /min		
Compressed air purity	free of water and oil		
Compressed air operating pressure (inside spraying gun MCS - 23)	Upto 8 bar (120 psi)		
Compressed air operating temperature (in the input of the nozzle)	100 - 500° C		
Power supply	One-phase alternate current of $50\pm1\text{Hz}$ and $220\text{V}$ ( $\pm10\%$ )		
Maximum power consumption	3.3 kW		
Time required for reaching an operating condition	no more than 30 seconds		
Powder consumption	10-60 gm/min (Compatible Powder will be supplied by MEC)		
Capacity of Powder Feeder	3350 CC (3.3 Liter)		
Dimensions of the equipment: -Control panel with powder feeder	800(W)x500(L)x1600(H)		
Total mass of the equipment	106 kg (approx)		

#### UTILITIES TO BE ARRANGED BY THE USER

- ▲ Spray booth with dust collector for clean working.
- Oil & Moisture free compressed air, air supply pressure: 05-08 bar (70-120 psi)
- ▲ Powder for spraying
- ▲ Electric input power supply 190 VAC to 240 VAC, 50/60 Hz single phase.
- ▲ All wiring and conduit from customer's main power source to machine's power unit and earthling wherever required.

#### METALLIZING EQUIPMENT CO. PVT. LTD. SO 9001:2015 SO 17025:2017 A \$9100, CE Email : marketing@mecpl.com / sales@mecpl.com

#### www.indo-mim.com

4



## **GAS ATOMIZED METAL POWDER FOR**

Thermal Spray Coating, Hard-facing and Additive Manufacturing Applications



Tel: +91 80 61418636 Email: infopowders@indo-mim.com

Bangalore, India- 562 114

Manufacturing Plant: San Antonio, TX - 78226

Tel: +1-210-467-5229 Email: infous@indo-mim.com Sales & Engineering Office:

Stuttgart, Germany - 70565 Tel: +49 711 6550 0242 Email: infoeu@indo-mim.com

#### Quality Certifications:



## **SPRAYTODAY**<sup>TM</sup>

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

#### **CHIEF EDITOR**

Dr. Satish Tailor, MECPL Jodhpur

#### INDIAN THERMAL SPRAY ASSOCIATION EXECUTIVE COMMITTEE & Editorial Board

Prof. Harpreet Singh, *President* Prof. S Bakshi, *VP (Academia)* Dr. RM Mohanty, *VP (Industry & Lab)* Dr. Satish Tailor, *General Secretary* Prof. Anup Kumar Keshri, *Joint Secretary* Prof. Kamaraj M, *Senior Executive Member* Prof. Jyotsna Dutta Majumdar, *Executive Member* Dr. Sisir Mantry, *Executive Member* Prof. Shashi Bhushan Arya, *Executive Member* 

**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.

SPRAYTODAY<sup>™</sup> is a quarterly publication of the INSCIENCEIN Publishing, affiliated to the Indian Thermal Spray Association<sup>®</sup> [iTSA] as its official newsletter. Published and distributed digitally INSCIENCEIN Publishing. Copyright<sup>®</sup> 2022

The Indian Thermal Spray Association is a standing committee of the "ITSA Association for Thermal Spray Technology and Research®", India.

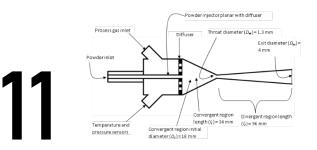
**ITSA** and **INSCIENCEIN Publishing** are not responsible for the accuracy of information in the editorial, articles, and advertising sections of this publication. Readers should independently evaluate the accuracy of any statement in the editorial, articles, and advertising sections of this publication that are important to him/her and rely on his/her independent evaluation.

A subscription to **SPRAYTODAY<sup>IM</sup>** is free for individuals interested in the thermal spray and coatings industry. http://www.inscience.in/spraytoday.html Write us spraytoday@inscience.in

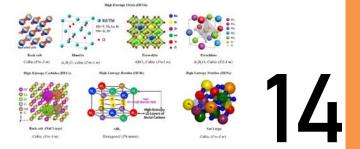
## **Contents**



### Featured Article: Thermal Spray in India -Opportunities and Challenges



#### Technical Note: Process Gas and Its Influence on Cold Spray Process



Academic Research: New Emerging Field: High Entropy Ceramics for Next-Generation Thermal Barrier Coatings

Dec. 2023 | Vol. 3 | Issue 3-4



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

	tintiat
Highlights of Asian Thermal Spray	
Conference & Expo 2023 (ATSC 2023)	18
Indian Thermal Spray Asso. Membership	21
Official Journal Publication of the iTSA	21

To contribute an article, advertisement, subscription request, back issue copies, and changes of address should be sent to: spraytoday@inscience.in

#### **ABOUT THE COVER**

Arc Spray in action by MECPL Jodhpur

## METALLIZATION WIRES

## World Leaders In: - Zinc Wire/Rods - Zn-Al alloy Wire - Aluminium Wires - Tin-Zinc Wires - Tin Babbit Spray Wire - Other Spray metallization Wires

## OTHARI METSOL PVT. LTD.

Formely Khosla Engineering Pvt. Ltd.

An ISO 9001 : 2015 & 14001:2015 Certified Company

Gat No. 130, Village Dhanore Off Alandi Markal Road,

Tal - Khed, Dist- Pune 412105

www.khoslaengineering.com

sales@khoslaengineering.com

+91 2135 6578403/412

Editorial

#### SPRAYTODAY<sup>™</sup>| **≪itsa**

## **Editor's Note**



Dear Readers,

We are thrilled to share highlights of the recently organized Asian Thermal Spray Conference and Expo 2023 (ATSC2023) hosted at the Indian Institute of Technology (IIT) Madras; jointly organized by The Indian Thermal Spray Association (iTSA), Asian Thermal Spray Society (ATSS) and Indian Institute of Technology Madras on 2-4 Nov 2023. The conference served as a vibrant hub for experts, researchers, and industry professionals, fostering a rich exchange of ideas and experiences.

Attendees were immersed in a diverse array of presentations, ranging from the latest breakthroughs in thermal spray materials to novel applications across sectors. The event provided a unique platform for networking, facilitating collaborations that promise to shape the trajectory of thermal spray technology not only in India but across the Asian continent.

As we delve into the latest edition of our **SPRAYTODAY** Magazine, we are excited to explore the dynamic landscape of thermal spray technology and its transformative impact on various industries in India. This issue encapsulates a myriad of developments, showcasing the prowess of thermal spray applications and the innovative strides taken by Indian researchers, engineers, and industry leaders.

I am particularly pleased to be allowed to recommend to you the latest issue of the **SPRAYTODAY**. This issue includes invited innovative featured articles from industry and academia experts on Thermal Spray in India – Opportunities and Challenges; Process Gas and Its Influence on Cold Spray Process; and New Emerging Field: High Entropy Ceramics for Next-Generation Thermal Barrier Coatings, that illustrate current research trends in thermal spray development.

As we navigate the pages of this magazine, let's collectively embrace the spirit of innovation and collaboration. The thermal spray community in India is not just witnessing change; it is driving it. We hope this edition sparks inspiration, fosters knowledge exchange, and fuels the passion for pushing the boundaries of thermal spray technology.

Thank you for being part of our journey. Be healthy, active, and curious! Merry Christmas & Happy New Year 2024!

Best Regards,

(Dr. Satish Tailor)

7

# dichto

capillary sealer Gas and Liquid-tight impregnation of thermal spray coatings

**Seals Porosity in Thermal Spray Coatings** 

**Temperature and Chemical Resistant** 

**Deepest Capillary Penetration** 

**Over 25+ Sealer Grades** 

#### **Increase Service Life of Coatings**

Dichtol HTR HS #2530	<ul> <li>High Solid Content Sealer temperature</li></ul>
1-component system	Resistant up to +500°C (+932°F) <li>Ideal For Insulation Application</li>
Dichtol HTR HS #2505	• High temperature resistance upto +700°C
1-component system	• Good Solvent Resistant
Dichtol HM #2407 2-component impregnationsystem	<ul> <li>Epoxy Based Sealerfor Anilox rolls</li> <li>High Chemical Resistance</li> <li>Temperature Resistance to 120°C</li> </ul>











Made in Germany

+91-080-48519779 www.diamanttriumph.com +91-080-41280766

65/6, A.P Complex 2nd Floor, Marathahalli info@triumphiz.in Sarjapur Rd,Agara Village,Juction,Bengaluru, Karnataka 560102

## Thermal Spray in India - Opportunities and Challenges

#### By **Subramaniam Rangaswamy, PhD, TSS-HOF, USA.** Email: <u>bullu@aol.com</u>

Thermal Spray (TS) is a widely used coating process in many industrial applications around the world. Some estimates put the market size at more than US\$7.5 billion. On a relative basis, growth of this technology in India has been somewhat sluggish until the early 2000's. Thermal Spray probably started in India around the 1950's and for nearly 3 decades it was mostly focused on Wire Arc and Flamespray metallizing. The first few Air Plasma Spray systems came to India in the late 1970's and early 1980's. Plasma spray activities began to grow in military aviation and commercial job shops between 1980 to 2000. HVOF activities began to pick up from the early to mid-1990's. Since then, there has been a moderate growth of Thermal Spray activities in power generation and several other industrial applications.

There are a few critical reasons for the slow growth of TS in India compared to elsewhere in Europe and North America. First, there was a widespread lack of 'awareness' about this technology and its benefits for many applications. Second, there was a lack of locally manufactured feedstock powders and advanced spray equipment which affected coating costs significantly. Finally, there has been very limited aero MRO activity in India which could otherwise have helped move this technology forward.

#### What are some of the growth opportunities now?

India is a complex country; the huge population, GDP growth, rising household income, infrastructure development.... All present some good growth opportunities for thermal spray now. Significant among these opportunities are in the sectors of Electric Power generation (both Thermal and Hydro); Steel industry and Aviation MRO work. These opportunities come with challenges as well.

#### Hydroelectric and Thermal Power Generation

Many of the rivers used for Hydropower generation in the Himalayan region of India contain a high amount of Silt (fine dust like mineral sediments). These minerals cause havoc on the turbine runners during operation and can degrade the runners by solid particle erosion and cavitation erosion. To minimize the erosion and extend the life of the runners, several types of hard coatings were tested on the runners. TS coatings of WC-Co-Cr materials applied by High Velocity Thermal Spray processes offer some level of protection for these applications. Coatings with low porosity (less than 0.5%); hardness in the range of HV 1100- 1300 and coating thickness up to 300 microns are the industry standard. Notwithstanding the success of the HVOF applied WC-CoCr coatings, there are some technical challenges to be overcome. In many instances, transportation/logistics to remote areas for onsite work pose their own challenges. When the turbines are very large (for e.g.: 80T or 100T or 150 T), they will need very sophisticated handling systems to apply uniform coatings on the profiles of large runners.

When it comes to Thermal Power Generation, a typical boiler has various components such as water wall tubes, super heater tubes and others that require protection from corrosion and erosion. For HT corrosion resistance, powders or wires of Nickel based, high Chrome containing alloys are used. Coatings up to a thickness of 250 microns with a hardness HV 600 to 700 are employed.

#### SPRAYTODAY<sup>™</sup>| **≪** itsa

These types of coatings are generally used in the incinerator areas (superheater, screen tubes and water wall), BLRB (superheater, Water walls) and Crude Oil (Water wall) areas. In areas where high erosion is anticipated, harder Chrome Carbide-Nichrome composite powders are applied using HVOF processes. These Chrome Carbide coatings typically have hardness's of around HV 800 – 900 and are applied to a thickness of about 200 microns.

Thermal Power Plants in India see wide variations in the types of hot corrosion and erosion at various locations inside the boilers. Also, onsite application of these coatings is not trivial. Finally, the variability in the quality and ash content of Indian sourced coal will be a factor to predict the success of these coatings.

#### Steel Industry Applications for Thermal Spray

Steel sector in India is on a significant growth pattern due to projected increase in per capita consumption; liberalized policies and significant investments by the government of India. There are a vast number of applications for thermal spray in the steel industry from Furnace areas (Hoods, Ducting, Tuyeres and Nozzles) to the Continuous Casting and Processing rolls (including Caster rolls, Wrapper and Process rolls, Bridle rolls, Deflector rolls), Annealing line rolls and Galvanizing Line rolls.

Many of the transport rolls are spray-fused with NiCrBSiC based alloys sometimes blended with WC -Co powders for increased wear resistance. Continuous Annealing Line (CAL) rolls (also known as Hearth Rolls) are coated with specialized MCrAlY-Oxide strengthened composites by HVOF. Galvanizing Line rolls (also sometimes known as Sink Rolls) are coated with WC Cermet type coatings.

There are a number of opportunities to expand thermal spray in the steel industry such as a) development of replacements for Hard Chrome Plating b) Improved TBC's for furnace hardware c) Development of High Entropy alloys (HEA) d) New non skid coatings and e) multilayer coatings for Galvanizing Line hardware. Among the challenges is the ability to develop fusing techniques for large size transport rolls when applying self-fluxing alloys. Another challenge is to develop coatings and application technology to meet the needs of CAL and CGL rolls. This technology is still in the early stages in India.

#### **Aviation Sector in India**

**FEATURE** 

Civil Aviation - Opportunities and Challenges

In the Civil Aviation sector, consumer demand is constantly increasing resulting in increased fleet size. Several Government policies such as the MRO Policy of 2021; National Civil Aviation Policy of 2016; Rationalization of GST and removal of GTO are incentives for the growth of MRO in the civil sector.

While there is potential upside to the growth of MRO activity and Engine maintenance work within India, there are also many significant challenges. The ability to break into value chains cannot be trivial. Significant barriers will be present from OEM's, International MRO's, and many airline operators. Additionally, dealing with offset clauses, credit availability, Licensing/certifications, IPO controls and many other factors will not be easy.

#### Military Aviation - Opportunities

More recently, there are several published reports about the French Indian collaboration for the supply of Rafale fighter jets and engines to the Indian Navy and Airforce. Government of India plans to invest roughly \$1 Trillion of funding in the next 25 years.

#### Summary

In a nutshell, there are significant opportunities for the growth of Thermal Spray in India. In addition to the above sectors (Power Generation, Steel Industry and MRO in the Aviation sector), Government of India through the Department of Science and Technology has identified Surface Engineering as a thrust area and making funds available for R&D. Indian Government is also investing huge amounts in infrastructure developments (USD 500 Billion plus). Liberalized government policies are attracting FDI (Foreign Direct Investments). Finally, it is a very positive sign that the TS community in India (comprising of many academic institutions and industrial partners) is coming together under the new iTSA. This bodes well for TS growth in India for the next several years.

#### SPRAYTODAY<sup>™</sup>| **≪**itsa

11

## Process Gas and its Influence on Cold Spray Process

#### By Eklavya Calla, PhD

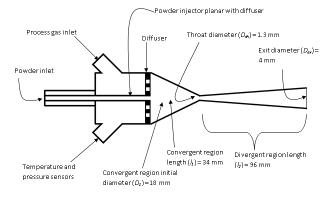
Principal Engineer, GE Vernova, Bangaluru, India. Email: <u>eklavya.calla@ge.com</u>

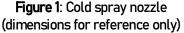
Cold spraying as a deposition technique with niche applications in repair and additive manufacturing has become very popular in recent times. Cold spray process uses a converging-diverging (CD) nozzle to accelerate process gas to supersonic velocities. The process gas accelerates feedstock particles due to its drag force and the subsequent impact of these particles on substrate creates the bonding between substrate and feedstock particles due to rapid deformation and adiabatic shear instability at the site of impact. Helium and nitrogen are the commonly used process gases in cold spray. Cold spray can deposit materials that are metallurgically bonded to the substrate, have negligible in-flight oxidation or phase change with ~99% density (1-4).

Cold spray process can be well understood using compressible fluid flow equations under the following assumptions (5):

- 1. The flow is one dimensional
- 2. The gas flow is isentropic (adiabatic and frictionless)
- 3. The gas is approximated as a perfect gas with constant specific heats
- 4. The gas flow is calculated without considering the influence of the powder flux

Above assumptions largely hold true as bulk of the flow occurs in the middle of the nozzle and its interactions with the nozzle wall can be ignored. Similarly, heat transfer through the nozzle walls and effect of feedstock powder flux can be ignored as gases are moving rapidly through the nozzle with little time for heat exchange and powder flux is maintained at a level where efficient deposition takes place. A schematic of the cold spray nozzle can be seen in Figure 1 (2).





Compressibility effects are important when the gas velocity is >0.3 Mach (6). A counter intuitive phenomenon for compressible fluid flows would be increase in velocity with increase in area whereas, for sub-sonic noncompressible flows constriction of area increases pressure and increases flow velocity e.g. a water hose. For compressible fluid flow, a nozzle where the throat has velocity of Mach 1 is considered to be running in choked condition. Any further increase in gas mass flow in this nozzle will not increase the velocity at the throat but will result in higher density of gas. Supersonic flow is achieved in CD nozzle after the throat as cross-section area increase results in expansion of the compressed gases and their acceleration. Cross-section area of throat of a cold spray CD nozzle is important because this area determines the gas mass flow required for choked nozzle and subsequent expansion of nozzle to generate supersonic flow (5), (7).

#### SPRAYTODAY<sup>™</sup>| **≪** itsa

#### **FEATURE – Technical Note**

12

The exit Mach number (M) in a CD nozzle that is running in choked condition (i.e. Mach 1 velocity at throat) is given by the following equation (5):

$$\frac{A}{A^*} = \frac{1}{M} \left[ \frac{2}{\gamma + 1} \right] \left[ 1 + (\frac{\gamma - 1}{2}) M^2 \right]^{\frac{\gamma + 1}{2(\gamma - 1)}}$$
(1)

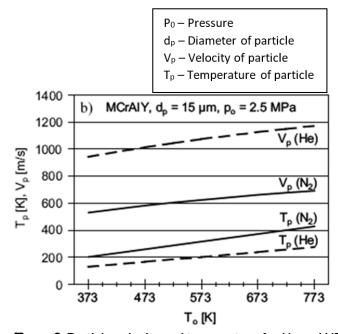
A is area of exit, A\* is area of throat, g is Cp/Cv of the gas used. A choked nozzle achieves supersonic flow at exit where a normal shock occurs and turns the flow to subsonic.

The nozzle in above example (Figure 1) will have an exit Mach number of 4.9 for helium gas as per equation 1 and if sufficient gas mass flow is maintained, the normal shock can be extended beyond the nozzle exit and a supersonic flow can be obtained throughout the nozzle and at the exit (2). As can be seen in equation 1, the exit Mach for a choked nozzle is influenced only by the area ratio (A/A\*) and the g value of gas. g for helium is 1.66 while for nitrogen it is 1.41. The velocity of sound at room temperature itself is dependent on the type of gas; ~1000 m/s in helium and ~330 m/s in nitrogen. There is another influence on the sonic velocity (a), and that is absolute temperature (T) of the gas. The relation between T and sonic velocity is given by the relationship (5):

Where, R is the specific gas constant and m; m is the molecular weight of the gas. Increasing process gas temperature increases sonic velocity and helps with higher exit gas velocities in CD nozzles.

Thus, helium is a very effective gas to achieve high velocities in cold spray. Typical cold spray nozzles can accelerate process gas to 4-6 Mach (2). The higher g of Helium aids in achieving higher Mach number for the same nozzle expansion ratio while lower molecular mass of helium results in higher  $\overline{R}$ , thus higher sonic velocity.

Due to its ability to achieve higher velocities helium gas can very easily accelerate feedstock particles above the critical velocity and makes parameter improvement relatively simpler. Nitrogen on the other hand does not achieve such high velocities in the nozzle and thus parameters to get good quality deposits can be a challenge. Methods to improve deposition with nitrogen have primarily focused on increasing gas temperature to achieve higher sonic velocities.



**Figure 2**: Particle velocity and temperature for He and N2 at different process gas temperatures

Figure 2 (8) shows the particle velocity and temperature versus different process gas temperatures for helium and nitrogen.

Although increasing process gas temperature can increase gas velocity, it comes at the cost of lower gas density in nozzle. The area in the nozzle is constant and since dimensions of the nozzle used are constant and there is a limit to the pressure that a cold spray equipment can achieve, increase in temperature is associated with decreasing mass flow to maintain the gas pressure thus lower gas flow results in lower gas density which has an adverse impact on the ability of the gas to accelerate feedstock particles which in turn influences the amount of feedstock which the gas can effectively carry. There have been studies to show that cold spray gas flow can manage ~20-25% of the total gas mass as feed stock feed rate and any higher feed rate will come at the cost of lower deposition rates. Feedstock powder typically comes as a particle size distribution and in

#### **FEATURE – Technical Note**

absence of reaction/oxidation during flight, the most important criteria for deposition in cold spray is for feedstock particles to achieve or exceed critical velocity. A larger particle will accelerate less while a smaller particle will experience bow shock near the substrate and deflect away. Thus, there will be an optimum particle size distribution for cold spray nozzle that can form a deposit and when parameters are optimized to achieve the critical velocity for a particle size distribution, very high deposition efficiencies (>90%) can be achieved (9).

Cold spray feedstock when accelerated above critical velocity experiences high strain rate deformation upon impact on substrate. strain rates up to  $0.5 \times 109$  s-1 and strains up to 4 are observed in cold spray deposition. Such rapid deformation at the nodes of maximum strain and the short time does not allow heat of deformation to escape thus raising the local temperature at nodes to above the melting point of the material. The bonding of impacting particle takes place by the following phenomena (4) (10) (3):

- 1. High velocity impact ruptures the surface oxide film on substrate and impacting particles
- 2. High strain rates and localization of heat raises the temperature to above melting point at the nodes.
- 3. Close contact of clean surfaces at high temperatures creates incipient bonding at the substrate-particle interface.

The purpose of process gas is to accelerate feedstock particles sufficiently aiming to ensure participation of larger surface areas of impacting particles in the above process, larger surface participation results in better bonding.

Helium gas due to higher velocity is more effective in achieving the above phenomenon. Studies have demonstrated that deposition efficiency of above 90% can be achieved with helium gas. A major drawback of helium is that it is scarce and expensive. Most helium used commercially is obtained from some oil and gas wells where it is a byproduct. Thus, attention in cold spray is focused on improving parameters with nitrogen while reserving the use of helium for some niche applications. Bibliography

- Alkhimov, A.P., A.N. Papyrin, N.I. Nesterovich, and M.M. Shuspanov. 5302414 United States of America, 1994.
- Eklavya, Calla. Cold Gas Dynamic Spray of Tin and Copper. Nottingham: University of Nottingham, 2005.
- Particle-substrate interactions in cold gas dynamic spraying. Zhang, D., P.H. Shipway, and D.G. McCartney. Ohio, USA: ASM International, 2003. Thermal Spray 2003: Advancing the Science and Applying the Technology. pp. 45-52.
- Bonding mechanism in cold gas spraying. Assadi, H., F. Gartner, T. Stoltenhoff, and H. Kreye. 15, 2003, Acta Materialia, Vol. 51, pp. 4379-4394.
- 5. Oosthuizen, P.H. and Carscallen, E. Compressible fluid flow. New York : McGraw Hill, 1998.
- Mbuyamba, Jean-Baptiste Mulumba. Calculation and design of supersonic nozzles for cold gas dynamic spraying using Matlab and Fluent. Johannesburg: University of the Witwatersrand, 2013.
- Gas dynamic principles of cold spray. Dykhuizen, R.C. and M.F. Smith. 2, 1998, Journal of thermal spray technology, Vol. 7, pp. 205–212.
- Development of cold gas sprayed coatings. Voyer, J., T. Stoltenhoff, and H. Kreye. s.l.: ASM International, 2003. Advancing the Science and Applying the Technology. pp. 71–78.
- Deposition of copper by cold gas dynamic spraying: an investigation of dependence of microstructure and properties of the deposits on the spraying conditions. Calla, E, D. McCartney, and P. Shipway. Osaka : s.n., 2004. Thermal Spray 2004: Advances in Technology and Application: Proceedings of the International Thermal Spray Conference.
- Cold spray nozzle Mach number limitation. Jodoin, B. 4, 2002, Journal of thermal spray technology, Vol. 11, pp. 496-507.

To contribute an article, advertisement, subscription request, back issue copies, and changes of address should be sent to: <u>spraytoday@inscience.in</u>

#### SPRAYTODAY<sup>™</sup>| **€itsa**

## New Emerging Field: High Entropy Ceramics for Next-Generation Thermal Barrier Coatings

#### By Kunal Bhalchandra Bhole, Rahul Kumar, Shashi Bhushan Arya

Department of Metallurgical and Materials Engineering, National Institute of Technology, Karnataka, Surathkal, Mangalore, 575025, India. Email: <u>sbarya@nitk.edu.in</u>

#### Abstract

High Entropy materials including the Alloy (HEAs) and Ceramics (H-ECs) namely high entropy oxides, nitrides, carbides, and borides, have evolved as a promising group of engineering materials with diverse applications, prominently featuring their pivotal role in thermal barrier coatings (TBCs). It is still a new concept of high entropy materials which offers a broad spectrum of research potential. H-ECs, represent equimolar or near equimolar ratios of cations or anions with a high configurational disorder. The configurational entropy for high entropy materials must be greater than or equal to 1.5 times the universal gas constant ( $\Delta$ Sconfig  $\geq$  1.5R). The synergy of H-ECs allows the opportunities for tailoring the material properties to particularly satisfy the specific requirements for thermal insulation and protection against harsh conditions to enhance the TBC performance. H-ECs display exceptional features like low thermal conductivity, high thermal expansion coefficient, high hardness, and higher thermal stability than conventional ceramics, hence making them the best choice for TBCs in high-temperature applications. The utilization of H-ECs plays a crucial role in mitigating issues related to both CMAS (Calcium-Magnesium-Alumino-Silicates) penetration and hot corrosion in TBCs. The synthesis route, elemental composition, crystal structure, type of coating and performance of H-ECbased TBCs have been reported.

Keywords: High Entropy Ceramics, CMAS (Calcium-Magnesium-Alumino-Silicates), Hot Corrosion.

Thermal barrier coatings often termed thermal protection coatings are usually applied on metallic surfaces as thermal insulation for high-temperature components such as gas turbine engines for protection against the harshest environments (Hot corrosion, Oxidation, CMAS penetration, and Cyclic thermal effects) [1]. The conventional ceramic material yttria-stabilized zirconia (YSZ) is a commercial TBC material that is extensively used because of its beneficial thermal and mechanical properties. Despite this, its practical application has been restricted due to phase transformation above 1200°C as it fails to maintain its phase stability and causes volumetric expansion on the coating thus leading to premature failure of the TBC system [2]. Hence, a need to explore novel candidates for innovative TBCs that exhibit exceptional thermo-physical and mechanical properties arises as the demand for greater operating temperatures within the turbine is increasing for new-generation turbines.

Over the past few years, there has been a remarkable development in utilizing the idea of high entropy materials in the crafting of ceramic materials for hightemperature applications. H-ECs attain a significant level of compositional disorder through the incorporation of five or more atomic species within their lattice structure. This increases entropy and improves thermodynamic stability, particularly at higher temperatures [3].

Fig. (1) illustrates the yearly publication trends for key high-entropy ceramics, including HEOs, HENs, HECs, HEBs, and HEHs. This data was retrieved from Scopus on

#### **FEATURE - Academic Research**

#### SPRAYTODAY<sup>™</sup>| **≪itsa**

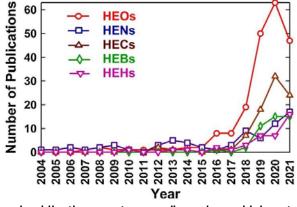


Figure 1: The annual publication counts regarding primary high-entropy ceramics [4]

High-Entropy Oxide (HEOs) RE/TM RE= Y, Yb, Lu, Er RE. TM= Zr, Hf RE. Zr Rock-salt Fluorite Perovskite Pyrochlore Cubic (Fm-3 m) A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> Cubic (Fd-3 m)  $A_2B_2O_7$  cubic (Fm-3 m) ABO3 Cubic (Pm3 m) High-Entropy Carbides (HECs) High-Entropy Borides (HEBs) High-Entropy Nitrides (HENs) 🔵 Hf O Ta Zr D Boron Net 0 Ti High-Entropy 2D Layers of Metal Cations Rock-salt (NaCl-type) AlB<sub>2</sub> NaCl-type Cubic (Fm-3 m) Hexagonal (P6/mmm) Cubic (Fm-3 m)



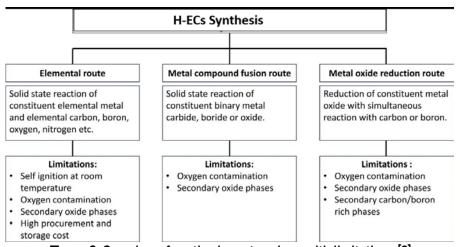


Figure 3: Overview of synthesis routes along with limitations [3]

#### SPRAYTODAY<sup>™</sup>| **≪**iTSA

August 12, 2021, and encompasses a total of 477 publications. Presently, HEOs with a significant number of publications highlight their relevance in the field of H-ECs due to their specific properties and show potential for TBC applications. Consequently, the emphasis of the article is predominantly directed towards HEOs.

The properties of high-entropy ceramics are shaped by the crystal structures they enact. The Fig. (2) shows the typical crystal structures of H-ECs.

Various synthesis methods can be employed to produce these ceramics which are shown in Fig. (3) along with limitations.

The high-entropy oxide (La0.2Nd0.2Sm0.2Eu0.2Gd0.2)Ce207 (HECO) has been successfully synthesized. In comparison to conventional La2Ce2O7 (LCO), HECO demonstrates a smaller corrosion depth. The sluggish diffusion effect observed in HECO significantly hampers the nucleation of corrosion products, contributing to its enhanced resistance against corrosion [5]. The reported highentropy zirconate ceramic (HEZ) (Gd0.2Y0.2Er0.2Tm0.2Yb0.2)2Zr207 was synthesized through solid-state reaction and sintering at elevated temperature which exhibits a fluorite structure. Key attributes include ultra-low thermal conductivity (0.82 W × m-1 × K-1 at 1200 °C), thermal expansion coefficients comparable to YSZ (10.61 × 10-6 K-1 at 1300-1400 °C), superior mechanical properties comprising high hardness, elastic modulus, and fracture toughness are exhibited by the material. Additionally, it demonstrates notable resistance to CMAS corrosion. This positions HEZ as a promising material for applications in hightemperature and corrosive environments [6].

It's important to note that research in this area is ongoing, H-ECs encounter challenges from hot corrosion and CMAS, and the understanding of how H-ECs specifically interact with the mechanisms of hot corrosion in TBCs is evolving. Their unique combination of thermal stability, resistance to thermal shock, oxidation resistance, mechanical strength, and tunable properties positions H-ECs as promising candidates for the next generation of TBCs, contributing to improved efficiency and longevity in aerospace and other high-temperature applications, further investigation is needed to optimize their compositions and assess their performance in practical applications. In conclusion, the advent of high-entropy ceramics represents a paradigm shift in material science, offering a diverse range of compositions with unparalleled properties and opens new frontiers for innovation across various industries, paving the way for advanced applications in high-temperature environments.

#### References

- Kailun WANG, Jinpeng ZHU, Hailong WANG, Kaijun YANG, Yameng ZHU, Yubin QING, Zhuang MA, Lihong GAO, Yanbo LIU, Sihao WEI, Yongchun SHU, Yanchun ZHOU, and Jilin HE, "Air plasma-sprayed highentropy (Y0.2Yb0.2Lu0.2Eu0.2Er0.2)3AI5012 coating with high thermal protection performance", Journal of Advanced Ceramics 2022, 11(10): 1571–1582.
- Yun XUE, Xiaoqin ZHAO, Yulong AN, Yijing WANG, Meizhen GAO, Huidi ZHOU, Jianmin CHEN, "Highentropy (La0.2Nd0.2Sm0.2Eu0.2Gd0.2)2Ce207: A potential thermal barrier material with improved thermo-physical properties", Journal of Advanced Ceramics 2022, 11(4): 615–628.
- 3. Tejesh C. Dube and Jing Zhang, "Underpinning the relationship between synthesis and properties of high entropy ceramics: A comprehensive review on borides, carbides and oxides", Journal of the European Ceramic Society 44 (2024) 1335-1350.
- 4. Saeid Akrami, Parisa Edalati, Masayoshi Fuji, and Kaveh Edalati, "High-entropy ceramics: Review of principles, production and applications", Materials Science & Engineering R 146 (2021) 100644.
- Yun Xue, Xiaoqin Zhao, Yulong An, Hengchang Nie, Meizhen Gao, Huidi Zhou, and Jianmin Chen, "Corrosion behavior of high-entropy (La0.2Nd0.2Sm0.2Eu0.2Gd0.2)Ce207 in different aggressive molten salt", Corrosion Science 204 (2022) 110414.
- Rongxue Yan, Wenping Liang, Qiang Miao, Hui Zhao, Ruixiang Liu, Jingli Li, Kai Zang, Meijing Dong, Xiping He, Xiguang Gao, and Yindong Song, "Mechanical, thermal and CMAS resistance properties of highentropy (Gd0.2Y0.2Er0.2Tm0.2Yb0.2)2Zr207 ceramics", Ceramics International 49 (2023) 20729– 20741.

To contribute an article, advertisement, subscription request, back issue copies, and changes of address should be sent to: spraytoday@inscience.in





### Materials for Thermal Spray Coating



- Aluminum Oxide (A99)
- Titanium Oxide (T99)
- Alumina Titania (AT1, AT3, AT13, AT40)
- Mullite (Aluminum Silicate)
- Yttria Stabilized Zirconia
- Calcia Stabilized Zirconia
- Magnesia Stabilized Zirconia

For, Wear Resistance, Corrosion Resistance, Thermal Barrier Coating, Environmental Barrier Coating, Chemical Inertness etc., applications

Customized precision chemistry & consistent particle size distributions.

Homogenous grains with good flow characteristics, and optimal grain morphology.

#### CONTACT US

Carborundum Universal Limited Electro Minerals Division, Kochi 683109 - India

Mail: salesemd@cumi.murugappa.com Web: www.cumi-minerals.com

#### SPRAYTODAY<sup>™</sup>| **≪itsa**

## Highlights of Asian Thermal Spray Conference & Expo 2023 (ATSC 2023)

The 12th International Conference and Expo on Asian Thermal Spray (ATSC 2023) was successfully organized by Indian Institute of Technology (IIT) Madras in association with the Asian Thermal Spray Society (ATSS) and The Indian Thermal Spray Association (iTSA), during Nov. 2-3, 2023 at the IC&SR building, IIT Madras, Chennai, India. The event witnessed an overwhelming response from across the world, and had 6 Plenary Talks, 11 Keynote Talks, 34 Invited Talks, 50 Contributory Talks, and 22 Technical Poster Presentations with more than 200 delegates participating from various Industries, Academic Institutes, and Research Organizations.

The Conference and Expo was inaugurated on 2nd Nov. 2023 by the Chief Guest Prof. V. Kamakoti, Director, Indian Institute of Technology Madras along with the Head of the department of Metallurgical & Materials Engineering, IIT Madras, Prof. N. V. Ravikumar. The convenor, Prof. M. Kamaraj welcomed the gathering and Prof. Srinivasa Rao Bakshi, co-convenor presented the details of the Asian Thermal Spray conference & Expo 2023. In the plenary talks, all 6 speakers were inducted into the hall of fame of thermal spray. Prof. V. Kamakoti delivered the presidential address and welcomed everyone to the vibrant campus of IIT Madras. He also mentioned the importance of collaboration between the industries and academia and was overwhelmed with the response for the conference from different parts of the world.

The participants belonged to more than 35 universities and were from 13 countries namely, Sweden, UK, Germany, France, USA, Canada, Australia, New Zealand, Japan, Singapore, Thailand, Korea and India, making it truly international. There were more than 80 delegates from the Indian industries catering to the fields of automotive, aerospace, thermal and hydro-power, oil and gas, general manufacturing, defence, nuclear, space and semiconductor sectors.

The generous support of industrial sponsors like Pratt & Whitney, Metallizing Equipment Company Pvt. Ltd., Carborundum Universal Limited- Electro Minerals Division, SJVN limited, Applied Materials Inc. and Indo-MIM Pvt. Ltd. made a significant impact on the event. Government agencies, including the Office of Global Engagement, IIT Madras, Defence Research and Development Organisation (DRDO), Indian Space Research Organisation (ISRO), Science and Engineering Research Board (SERB), and the Board of Research in Nuclear Sciences (BRNS), also played a crucial role in ensuring the success of this conference through their contributions.

The conference also included 6 stalls from the exhibitors-Metallizing Equipment Company Pvt. Ltd., C&M Technologies GmbH, Germany, INDO-MIM Pvt. Ltd., Kinetic Surface technologies, Kothari Metsol Pvt. Ltd. and Keepsake Engineering Consultancy Pvt. Ltd. who demonstrated state of the art technologies and services in the areas of thermal spray. It is also important to thank the advertisers, Uniquecoat Technologies LLC., HVAF Systems, Virginia, USA, Shreenath Engineering Industries, Nagpur, ATS Techno Pvt. Ltd., India, International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI) and Murti Udyog Limited, Rajasthan. The conference, a dynamic gathering of intellectual prowess, featured an ensemble of distinguished speakers whose expertise ignited the room with thought-provoking insights. The event served as a vibrant platform, where brilliant minds converged to share and cultivate innovative concepts, forging new frontiers in the realm of knowledge. Among the multifaceted topics that took center stage were the domains of wear and corrosion, thermal barrier coatings, processing and applications, characterization advanced techniques, and the fascinating world of cold spray held in parallel sessions. The conference had the vibrant panel discussion moderated by Prof. Vikram Jayaram, Honorary professor, Indian Institute of Science, Bengaluru. It was a panel consisting of experts from various fields to present their view on thermal spray technologies from an industrial perspective. Shri Abhijit Vaidya, Cummins India Ltd., Pune, Shri Srivenkata Subramaniam, Ather Energy, Bangalore, Shri Rahul Sood, Industrial processors and metallizers, Delhi, Shri Ankur Modi, Metallizing equipment company Pvt. Ltd., Jodhpur, Shri Malay Choudhury, Tata steel Ltd., Jamshedpur, Shri Nilesh Patil, Kothari Metsol Pvt. Ltd., Dhanore and Shri Harish Kumar Sharma, SJVN Limited, India participated in the panel discussion. The discussion on the implementation of thermal spray technology in their respective fields resulted in various criteria that need to be addressed. The effect of thermal spray on the market, return on investment, defining the problem statement for the thermal spray technology to

#### FEATURE - ATSC2023 Highlights

#### SPRAYTODAY<sup>™</sup>| **≪itsa**



Welcome Address by Convener ATSC 2023, Prof. M. Kamaraj



Plenary Speaker Prof. Christopher Berndt



About ATSC by Co-Convener ATSC 2023, Prof. S Rao Bakshi



Plenary Speaker Prof. Armelle Vardelle



Souvenir Release by Prof. V. Kamakoti, Director, IIT Madras



Plenary Speaker Prof. Robert Vaßen



Plenary Speaker Prof. Kazuhiro OGAWA



Plenary Speaker Prof. Sanjay Sampath



Keynote Talk Dr. Sunghun Lee



Felicitation of Sponsors



Keynote Talk Dr. Rogerio S. Lima



Awarding Best Oral Presentation



Plenary Speaker Prof. Shrikant Joshi



Keynote Talk Prof. Tanvir Hussain



Felicitation of Chief Guest Dr. Kamachi Mudali, Vicechancellor, HBNI, Mumbai

#### SPRAYTODAY<sup>™</sup>| **≪itsa**

#### FEATURE – ATSC2023 Highlights

hold its ground in the sector etc. The discussion also addressed the importance of collaboration between the industries and the academia subsequently, large-scale industries and the small-scale industries. The refurbishment field is a huge area where thermal spray technology can have a greater advantage than the conventional routes.

The valedictory session featured Dr. Kamachi Mudali, Vice-Chancellor of the Homi Bhabha National Institute, Mumbai, as the presiding dignitary. The welcome address was eloquently delivered by Prof. M. Kamaraj, the convenor of the event. Prof. Srinivasa Rao Bakshi, coconvenor of ATSC 2023, presented a comprehensive summary of the conference. Dr. Sisir Mantry, the jointsecretary of ATSC 2023, introduced the esteemed chief guest. During his address, Dr. Kamachi Mudali underscored the significance of thermal spray technologies and the evolving global landscape in various sectors. He emphasized the pivotal role of thermal spray technologies in India, particularly in the aviation, automotive, energy, and healthcare industries.

The event also featured a special segment where industrial and government sponsors, as well as exhibitors, were honored for their valuable contributions. Additionally, outstanding posters and oral presentations were recognized and celebrated as an integral part of the conference.

Dr. Satish Tailor, the secretary of ATSC 2023, expressed heartfelt thanks to all participants and officially concluded the conference with a vote of thanks.



Join iTSA

#### SPRAYTODAY<sup>™</sup>| **≪**itsa

## 21

## We invite you to join iTSA!



Why become a member of iTSA?

The iTSA provides the useful information to all colleagues interested in thermal spraying in the large industries, societies, job shops, university and laboratories. The iTSA members have access to the additional services such as job proposition, information about services related to thermal spraying in different states of India,

forum of users which enables research of missing information related to thermal spraying and much more. The iTSA membership enables also a reduction in the fees of the events organized by the Society.

Become a member today! https://www.indtsa.org/join-itsa

For more information, please visit <a href="https://www.indtsa.org/">https://www.indtsa.org/</a> or write us <a href="https://www.indtsa.org/">info@indtsa.org/</a>

### **Our Journal Publication**

Journal of Thermal Spray and Engineering (JTSE) ISSN: 2582-1474



JTSE is an international archival journal publishing scientific papers on thermal spray technology; Journal provides a platform for researchers to share their original and innovative findings, in addition to identifying methods of production and application that include, but are not limited to, HOVF, plasma spray, flame spray, wire arc spray, and cold spray, Powder technology, Gas flow, particle motion, and heat transfer, Stress and strain analysis, Coating deposition mechanism, Single particle deposition and solidification upon impact, Coating mechanical and thermal properties, Coating microstructures and phase transformation, Functional coatings, Torch design and optimization, New thermal spray technology, Robotic programming

and kinematic analysis, Torch trajectory definition and optimization, Novel applications of thermal spray coating, Mathematical and theoretical analysis on related subjects, Finite Element Analysis on related subjects. JTSE Covers Review Articles, Research Articles, Letter To Editor, Conference & Book Review, Notes and Short Communications. All the published articles are available for Download for Free.

DOI: https://doi.org/10.52687/2582-1474/

Journal website http://www.inscience.in/JTSE.html

Manuscript Submission http://www.inscience.in/manuscript-submission.html

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



#### https://www.indtsa.org/





http://www.inscience.in/

