# PLASMA SPRAYED CARBON NANOTUBES COMPOSITE COATINGS FOR HIGH TEMPERATURE CORROSION PROTECTION: A REVIEW

Rakesh Goyal[1*], Vikas Chawla[2], Buta Singh Sidhu[3]
*[1]Research Scholar, Deptt. Of Mechanical Engineering, I.K.G. Punjab Technical University, Jalandhar, India*
*[2]Principal, Ferozepur College of Engineering and Technology, Ferozepur*
*[3]Dean, MRSSTU, Bathinda*

***Abstract***—Thermal spraying coating methods are most effective surface protection methods to apply protective coatings for corrosion protection in high temperature applications. These coatings are important means to develop various types of coatings to increase the corrosion resistance to enhance the performance and life of components. Plasma spraying is versatile and well established technique to apply coatings for improved corrosion resistance on boiler components. Plasma sprayed coatings of various ceramic materials such as Alumina ($Al_2O_3$), calcia (Ca)-stabilized zirconia ($ZrO_2$) and other refractory materials have been developed for various high temperature applications. Due to excellent properties of Carbon nanotubes, CNTs are a potential applications for composite coatings for corrosion resistance. It is observed that composite coatings consisting of Carbon nanotubes as reinforced particles have been successfully deposited by thermal spray techniques. This paper reviews the performance of plasma spray coatings, plasma sprayed alumina coatings and plasma sprayed carbon nanotubes composite coatings developed by various researches in recent past.

***Keywords***—*Thermal Spray, Plasma Spray, Carbon Nanotubes, Corrosion, Reinforcement, Mechanical properties*

## I. INTRODUCTION

The material conservation has become an important concern due to ever increasing global competition [1]. Corrosion is defined as the deterioration of materials by reaction with the environment. Corrosion affects properties that are to be preserved. This mode of degradation of metals at high temperature is known as oxidation or dry corrosion. At elevated temperature, the surfaces of metals and alloys are covered with thin film of fused salt, and this is known as hot corrosion [2]. Advancements in development of materials and cooling technologies have led to increase in operating temperature of gas turbines, boilers and industrial waste incinerators [3]. The use of low grade fuels along with high temperature requires special attention to the phenomenon of hot corrosion [4-6]. The problem of hot corrosion was taken as serious problem first time with the degradation of boiler tubes in steam generating plants and degradation of gas turbine air-foil materials in 1940's [7, 8]. A case study revealed that out of 89 failures of boiler tube, which occurred in one year, 50 failures were due to hot corrosion by ash [9]. The sudden failure of components can result in human injury and loss of life. It is estimated that the direct cost due to hot corrosion in United States is 3-5% of the Gross Domestic Product [10].

No material is immune to hot corrosion attack for a long time. In the past, superalloys have been developed and used in high temperature applications to reduce the corrosion, but these superalloys are also not be able to resist high temperature corrosion for long [2]. Therefore, thermal spray coatings have been developed to provide protection against hot corrosion [11, 12]. Thermal spray process has important characteristics such as flexibility in coating material choice, low substrate thermal input and virtually no substrate dissolution [13]. The invention of first thermal spray process is attributed to M.U. Schoop of Switzerland. The technique of thermal spraying has developed at a fast pace due to progress in the advancement of materials and modern coating technology. Pawlowski [14] has summarized the thermal spray processes that have been considered to deposit the coatings as: (1) Flame spraying with a powder or wire, (2) Electric arc wire spraying, (3) Plasma spraying, (4) Spray and fuse , (5) High Velocity Oxy-fuel (HVOF) spraying, (6) Detonation Gun. Plasma spraying is versatile and well established technique to apply coatings for improved corrosion resistance on boiler components [15]. Plasma spray technique has advantage of depositing ceramics, metals and a combination of these and generates homogenous coatings with desired microstructure on a vide rage of substrate materials [16]. Plasma sprayed coatings of various ceramic materials such as Alumina ($Al_2O_3$), calcia (Ca)-stabilized zirconia ($ZrO_2$) and other refractory materials have been developed for various high temperature applications [12, 16-20]. Alumina is an exceptionally important ceramic material which has many technological applications. It has high hardness, chemical inertness and high melting point. It can retain upto 90% of its strength even at 1100 $^0$C [21]. It is reported that the corrosion resistance of alumina coatings are higher than that of cermet and metallic coatings [22]. There is an increasing demand on these coatings with increased thermal characteristics [23].

With the invention of Carbon nanotubes (CNTs) in 1991, a new era of interest in the field of nanotechnology began [24, 25]. Iijima discovered microtubules of graphite carbon which are arranged in the form of a cylinder known as carbon nanotubes [26]. Carbon nanotubes possess exceptionally enhanced mechanical, thermal and electrical properties as compared to carbon steels [27, 28]. Carbon nanotubes are

100's of times stronger than the high grade carbon steels and have many times higher tensile modulus than steel [29-31]. These properties of CNTs make them potential reinforcement for the composite materials [32]. In this review paper, recent work on Plasma sprayed coatings and CNTs reinforced Alumina coatings has been discussed.

## II. SOME STUDIES ON PLASMA SPRAYED COATINGS

Sidhu, et al. [16] sprayed Ni–20Cr and Stellite-6 powders on boiler tube steels ASTM-SA210-grade A1, ASTM-SA213-T-11 and ASTM-SA213-T-22 through shrouded plasma spray process. NiCrAlY was sprayed as a bond coat of before applying these coatings. Metallography, XRD and SEM/EDAX techniques have been used to analyse plasma sprayed coatings. The XRD analysis St-6 coatings showed the presence of Co, Cr, Ni, CrCo and FeNi for as-sprayed and after laser remelting. Ni3Al phase was also observed in addition to the above phases.

Singh, et al. [33] deposited NiCrAlY, Ni–20Cr, Ni3Al and Stellite-6 metallic coatings on a Fe-based Superalloy (32Ni–21Cr–0.3Al–0.3Ti–1.5Mn–1.0Si–0.1C–Bal Fe) by plasma spray method. NiCrAlY was used as bond coat. Hot corrosion studies were conducted after exposure to molten salt at 9000C under cyclic conditions. The coatings showed better corrosion resistance as compared to that of uncoated superalloy. It was observed that NiCrAlY coating was most protective followed by Ni–20Cr coating. Ni3Al coating effectively decreased the weight gain to about one-third as compared to uncoated superalloy. Stellite-6 coating decreased the weight gain to around 60% of that of the bare superalloy. It was concluded that the formation of oxides and spinels of nickel, aluminium, chromium or cobalt contributed to development of hot corrosion resistance in the coatings.

Ananthapadmanabhan, et al. [23] developed plasma sprayed composite coatings of calcia stabilized zirconia and alumina by pre mixing different weight percentages of CaSZ and Al2O3 powders. The researchers studied the effect of annealing and powder composition on the properties of coatings. After experimentations, it was observed that the as sprayed specimens consist of stabilized zirconia and alumina. Anealing led to destablization of CaSZ which resulted in generation of free zirconia. It was concluded that the extent of destabilization depended on the powder composition, annealing temperature and time of annealing. The developed coatings were found to have good thermal shock resistance in high temperature applications.

Racek, et al. [34] deposited nanostructured yttria stabilized zirconia and conventional YSZ coatings using plasma spray techniques. It was observed that a wide range of micrstructers and porosities were produced by combining different deposition techniques and varying feedstock materials.

Vaidya, et al. [35] deposited commercial grade spherical molybdenum powder by plasma spray method and the spray stream was characterized for resulting particle state. A splat map was deposited through a spray stream guillotine to capture the fingerprint of the plume cross-section. It was observed that flattening and fragmentation were affected by particle condition before impact in plasma spray. Higher velocities and temperateures resulted in fragmented splates and in greater bonding to substrate surface due to partial melting at contact between splat and substrate. It was also observed that plasma sprayed molybdenum coatings undergo oxidation in the in-flight stage and after deposition. The oxidation resulted in change in coating properties.

Khan and Lu [18] deposited coating comprised of 93 wt.% ZrO2 and 7 wt.% Y2O3 (YSZ); CoNiCrAlY bond coat; and AISI 316L stainless steels substrate by an air plasma spraying technique and determined thermal cyclic lives of the coatings a function of bond coat surface roughness, thickness of the coating and the final deposition temperature. It was observed that with increase of TBC's thickness the thermal shock life of the specimens significantly decreased. It was also noted that with decrease in bond coat roughness, the thermal shock life decreased slightly.

Gell, et al. [36] discussed nanostructured alumina and titania based coatings sprayed by plasma spraying technique and used Taguchi design of experiments to define the optimum plasma spray conditions to produce nanostructured alumina–titania coatings. It was observed that the microstructure and properties of these coatings were related to a critical process spray parameter, defined as the gun power divided by the primary gas flow rate. Optimum properties were determined at intermediate values of the parameter. It was observed that the nanostructured alumina–titania coatings exhibited superior wear resistance, adhesion, toughness and spallation resistance. The nanostructured Al2O3–13 wt.% TiO2 coatings developed by the researchers were approved by the U.S. Navy for shipboard and submarine applications.

Chen, et al. [37] depsoted Yttria partially stabilized nanostructured zirconia coatings deposited by atmospherical plasma spraying (APS). The Scanning electronic microscopy (SEM), Transmission electron microscopy (TEM), X -ray diffraction (XRD) and Raman spectrum (RS) were used to characterize the coatings. The results obtained showed that the plasma-sprayed zirconia coating possessed nanostructure with average grain size of 73 nm. It was found that the average thermal expansion coefficients of the coating at the first and second thermal cycle from room temperature to 12000C were 11.0 and 11.6 x10-6 0C-1, respectively. The thermal diffusivity of the nanostructured zirconia coating was found to be 1.80–2.54 x10-3 cm2/s between 200 and 12000C. The microhardness of the nanostructured zirconia coating was observed as 8.6 GPa, which was 1.6 times of microhardness of traditional zirconia coating.

Lima, et al. [38] deposited the nanostructured PSZ (ZrO2-7wt.%Y2O3) experimental feedstock was plasma sprayed under different parameters in air on low carbon steel substrates. It was observed that the microhardness of the nanostructured PSZ feedstock was low due to the weak agglomeration and relatively high porosity of the nanostructured agglomerates. It was observed that the nanostructured coatings presented a bimodal distribution in their Weibull plots which indicated the presence of two phases which were described as molten and non-molten. The presence of the bimodal distribution in the mechanical properties allowed the prediction of microhardness values of these nanostructured coatings.

Sampath, et al. [39] studied the substrate temperature effects on splat formation, microstructure development and properties of plasma sprayed coatings for partially stabilized zirconia. The deposits have been formed nominally at these two different temperatures and their microstructures and properties have been analyzed. The results showed that threshold transition temperature existed for the substrate surface beyond which the splat morphology changed from a fragmented to a more contiguous morphology. In the case of zirconia that temperature appeared to be in the range of about 250–300°C, which was roughly 10% of the melting temperature of zirconia. It was observed that the splat–substrate and inter-splat contact was significantly improved at higher temperatures leading to reduced porosity, increased thermal conductivity and strength.

Sidhu and Prakash [40] evaluated the hot corrosion behaviour of plasma-sprayed Ni3Al coatings on steel in oxidation and molten salt environments at 9000C. Ni3Al coatings were applied on boiler tube steels through a plasma spray process. Ni–Cr–Al–Y was used as a bond coat. Coatings were exposed to air and molten salt at 9000C under cyclic conditions. It was observed that Ni3Al coating was very effective in decreasing the corrosion rate in air and molten salt at 9000C in the case of ASTM-SA210 grade A1 and ASTM-SA213-T-11 types of steel. It was also noted that ASTM-SA213-T-22 steel showed very poor resistance to hot corrosion in molten salt environment, with spalling of the oxide scale. The substrate steel oxidised in air showed the formation of Fe2O3, whereas the oxidised coated steels showed a major phase of NiO and included Al2O3 and Fe2O3.

Sidhu and Prakash [41] successfully deposited Ni–22Cr–10Al–1Y (NiCrAlY), Ni–20Cr, Ni3Al and Stellite-6 (St-6) coatings by a plasma spray process on boiler tube steels. The NiCrAlY was sprayed as a bond coat of approximately 150μm thickness in each case before the final coating. The cyclic hot corrosion behaviour of these coatings was studied in molten salt (Na2SO4–60% V2O5) at 900°C. The internal oxidation and cracking of scale was observed during the testing. The plasma sprayed coatings were found to be beneficial in increasing the hot corrosion resistance of specimen. The maximum protection was observed in case of St-6 coating and was a minimum in case of Ni3Al coating.

Sidhu and Prakash [19] investigated the behaviour of stellite-6 as plasma sprayed and laser remelted coatings in molten salt environment at 900 ◦C under cyclic conditions. Stellite-6 coated GrA1 steel was proved to be the most effective among other bare and coated. Slightly higher weight gain values for coated steels might be attributed to the presence of vertical cracks through which the oxidising environment could have attacked the substrate steels. The authors concluded that the cracks might have been formed due to oxide inclusions introduced at the time of formation of coatings and the stresses developed during cooling of coated samples.

Sidhu and Prakash [42] investigated the erosion-corrosion (E-C) behaviour of plasma as sprayed and laser remelted Stellite-6 (St-6) coatings on boiler tube steels in the actual coal fired boiler environment. The experiment was performed in the superheater zone of a coal fired boiler where the temperature was around 7550C. The plasma sprayed coating was found to be very effective in the boiler environment and has shown much less degradation due to E-C even after 1000 h of exposure in the coal fired boiler environment under cyclic conditions.

Singh, et al. [3] investigated the hot corrosion performance of plasma sprayed coatings on a Fe based superalloy. NiCrAlY, Ni–20Cr, Ni3Al and Stellite-6 metallic coatings were deposited on a Fe-based Superalloy (32Ni–21Cr–0.3Al–0.3Ti–1.5Mn–1.0Si–0.1C–Bal Fe). NiCrAlY was used as bond coat. Hot corrosion experiments were conducted on uncoated as well as plasma spray coated superalloy specimens after exposure to molten salt at 9000C under cyclic conditions. It was observed that the plasma spray coated specimens have shown better performance as compared to the uncoated specimens.

## III. SOME STUDIES ON ALUMINA (AL2O3) BASED COATINGS

Turunen, et al. [43] developed nanocrystalline Al2O3- and Al2O3–Ni-coatings by HVOF process. Ten percent of nickel was added in order to toughen the coating. Pure nanostructured alumina powders were manufactured from boehmite, which was agglomerated by spray drying, heat treated to alumina and finally sintered. The comparison between pure Nano alumina coating (n-Al2O3) and the reference coating showed that the hardness was higher for n-Al2O3 coatings. This was attributed to the use of nanocrystalline feedstock, which resulted in the refinement of the coating microstructure. The alpha alumina content of the resulting coating was relatively low in all spray conditions. The introduction of nickel into the coating resulted in more variations in the coating structure at different spray conditions.

Lin, et al. [44] deposited nanostructured and conventional Al2O3–3 wt.% TiO2 coatings were by atmosphere plasma spraying. The tribological properties of both coatings against a silicon nitride ball were examined in the temperature range from room temperature to 6000C. It was observed that the friction coefficients of both coatings were ranged from 0.85 to 0.10. A protective layer consisting of silicon oxide existed on the worn surface of both coatings at room temperature which led to the lower wear rate. At higher temperature, brittle fracture was observed on the worn surfaces of both the coatings, which was enhanced with the increase in temperature. It was found that the wear resistance of the nanostructured coating was superior to that of the conventional coating except at high temperatures.

Sobiecki, et al. [45] fabricated alumina oxide coatings on 1045 steel and examined the structure and properties of the coating. The material used in the experiments was alumina powder added with titanium dioxide (13 wt.%) with a grain size of 22–45 micrometer. It was observed that oatings produced on the substrates by polishing with sand papers of various grades appeared to have no satisfactory adhesion. It was shown that the best adherence to the substrate is achieved with the Al2O3 coating produced on a sand pre-blasted substrate which was having a high microhardness, low porosity and good frictional wear resistance. There were no microcracks observed in the coatings.

Jegadeeswaran, et al. [46] investigated High Velocity Oxy-Fuel coating of Ti-31 alloy using fused, blended powder, Al2O3+CoCrAlTaY for hot corrosion. The studies were done on the coated and uncoated Ti-31 under a salt environment of 50% Na2SO4 and 50%V2O5 at 800°C. The samples were characterized using XRD and SEM/EDS. It was observed that the coated sample had more corrosion resistance than uncoated sample. XRD and SEM analysis indicated that the surface was rich in oxides. The sample weight gain was following a parabolic relationship with time. It was concluded that the presence of high level of chromium in HVOF sprayed coating imparts improved hot corrosion resistance at 800°C, in a molten salt environment of Na2SO4 + V2O5.

Singh and Singh [47] studied high temperature Erosion-Corrosion of Detonation Gun Sprayed Al2O3 Coated and Uncoated T-91 Boiler steel in Actual Environment of Boiler. The coated and uncoated samples were subjected to cyclic erosion-corrosion in actual environment i.e. in boiler for 10 cycles. It was observed that coated T-91 experienced 2.96 % weight loss due to the erosion of the scale formed on the sample whereas uncoated T-91 did not show weight loss inferring that less erosion was experienced by the uncoated sample.

Katiki, et al. [48] compared hot corrosion behavior of Al2O3-TiO2 plasma spray coatings on Inconel 625 in air oxidation and molten salt environment K2SO4–60%NaCl environment at 800°C under cyclic conditions for 50 cycles. Al2O3-TiO2 coatings were deposited on Inconel 625 superalloy with plasma spray process. The Al2O3-TiO2 coated Inconel 625 showed less weight gain in both air oxidation and molten salt environment as compared to the uncoated alloy indicating the protective behaviour of the coatings. The SEM image indicated that the uncoated samples showed a rough irregular surface as well as spalling behavior of the scale after exposure to molten salt environment. The scale formed on Al2O3-TiO2 coated Inconel 625 was almost consistent and continuous when exposed in air oxidation. It was concluded that better hot corrosion resistance of plasma sprayed Al2O3-TiO2 was due to the formation of some Ni-Cr spinels oxides.

Zirconium dioxide and Aluminium oxide–40% Titanium dioxide thermal barrier coatings (TBCs) were deposited on Nickel based Inconel 625 superalloy with plasma spray process by Katiki, et al. [49]. Hot corrosion behaviour of ZrO2 and Al2O3-TiO2 plasma sprayed thermal barrier coatings on Nickel based Inconel 625 superalloy was compared in air oxidation and in molten salt environment i.e K2SO4–60% NaCl environment at 800°C under cyclic conditions for 50 cycles. A 40-50 μm thick coating of Ni-Cr powder bond coat was deposited on all the samples. It was found that ZrO2 coating provided better corrosion resistance than Al2O3-TiO2 coating. The Al2O3-TiO2 coating protected the substrate with the formation of Cr2O3 scale at the top and Al2O3 scale beneath in K2SO4–60%NaCl molten salt environment at 800°C for 50 cycles. Hot corrosion resistance of Al2O3-TiO2 coating was due to the formation of some Ni-Cr spinels oxides.

Shaw, et al. [50] deposited Al2O3-13 wt.% TiO2 coatings with plasma spray method using reconstituted nanosized Al2O3 and TiO2 powder feeds and evaluated effects of various plasma spray conditions on the microstructure, grain size, phase content and microhardness of the coatings. It is found that phase transformation of nanosized Al2O3 and TiO2 during heat treating, sintering and thermal spraying was identical to that of micrometer-sized coatings. The hardness and density of the coating increased with the spray temperature. The phase content and grain size of the coating exhibited a strong dependency on the spray temperature. The coating sprayed using nanopowder feed displayed a better wear resistance than the coating sprayed using commercial coarse-grained powder feed.

Yılmaz, et al. [51] coated Al2O3 and Al2O3–13wt% TiO2 by plasma sprayon AISI 316L stainless-steel substrate with and without Ni–5wt% Al as bond coat layer. It was observed that the dominant phase was Al2O3 for both coatings. It was also found that the hardness of coating with bond coat was higher than that of coating without bond coat. The hardness of pure alumina coating with and without bond coat was higher than the hardness of Al2O3–13 wt% TiO2 coatings with and without bond. It was seen that percentage of cohesion strength was higher than that of adhesion strength.

Yılmaz, et al. [51] estimated the influence of plasma spray conditions on the structure of Al2O3 coatings. It was observed from the microstructures of copper electroplated Al2O3 coatings that a ceramic coating is deposited with flattened ceramic particles. It was observed that pores at the interfaces of flattened particles had size of same order as that of diameter of flattened particle along the direction of flattening although pore channel may be curved with it comes to encounter the bounded area. It was found that vertical cracks occur in all alumina coatings with vertical crack density over 1 per 10 micrometer. The higher mean bonding rate gave higher vertical crack due to rapid cooling of flattened particles after solidification.

## IV. SOME STUDIES ON CARBON NANOTUBES REINFORCED COATINGS

Kaewsai, et al. [52] developed stainless steel/carbon nanotube (SS/CNT) composite coating by thermal spray from the feedstock powder synthesized by chemical vapour deposition at a synthesis temperature and time of 800 °C and 120 min under ethanol atmosphere. It was observed that grown CNTs covering the surface of stainless steel particles were multi-walled type with an average diameter of about 44 nm and had splat characteristic and lamellar structure. The CNTs were clearly observed in the composite coating. The hardness of composite coating was higher than that of pure steel coating, whereas the coefficient of friction was almost 3 times lower than that of stainless steel coating. It was concluded that CNT reinforced coatings gave better wear resistive performance as compared to stainless steel coatings.

Singhal, et al. [53] have fabricated Al-matrix composites reinforced with amino-functionalized multiwalled carbon nanotubes (fCNTs) using the powder metallurgy process. fCNTs (1.5 wt.%) were dispersed in Al powder by high energy ball milling. Al–fCNTs composites (1.5 wt.%) were fabricated by the consolidation of powders at 550 MPa followed by sintering at 620 °C under a vacuum of 10−2 Torr for 2 h. It was observed that the dispersion of fCNTs in Al-matrix was much higher than those of non-functionalized MWCNTs. Microhardness was observed to be 400 kg/mm2 for Al-matrix composites loaded with 1.5 wt.% fCNTs. It was found that the sintered composites had a good dispersion of fCNTs in Al matrix and they did not agglomerate with each other. It was concluded that the formation of a thin transition layer of $Al_4C_3$ between fCNTs and Al matrix was responsible for load transfer from Al matrix to fCNTs.

Alumina–carbon nanotube (CNT) composites with different quantities of CNTs were fabricated to investigate the effect of the distribution of CNT in the ceramic matrix on the tribological behavior [54]. The composites with CNT content up to 12 wt.% were fabricated by tape casting, followed by lamination and hot pressing. The wear behavior of the CNT reinforced composites was investigated using a ball-on-reciprocating wear tester under an unlubricated condition at room temperature. It was observed that the wear rate of hot-pressed samples decreased with increasing up to 4 wt.%, but the wear rate increased with further addition of CNT. The wear rate of the tape casted composites decreased uniformly with increasing CNT addition up to 12 wt.%.

Kwok, et al. [55] Deposied CNT reinforced HA coatings on Ti6Al4V followed by vacuum sintering at 8000C. Submicron HA powders with different morphologies including spherical, needle-shaped and flake-shaped were used in the EDP process to produce dense coatings. Electrochemical corrosion behavior of the HA coatings in Hanks' solution was investigated by means of open-circuit potential measurement and cyclic potentiodynamic polarization tests. Surface hardness, adhesion strength and bone bioactivity of the coatings were also studied. It was found that the HA coated specimens had a thickness of about 10 mm with corrosion resistance higher than that of the substrate and adhesion strength higher than that of plasma sprayed coating. It was found that the CNT-reinforced HA coating markedly increased the coating hardness without compromising the corrosion resistance or adhesion strength.

Tribological behavior of plasma sprayed carbon nanotube reinforced aluminum oxide ($Al_2O_3$) composite coatings was investigated at room temperature, 573 K and 873 K using tungsten carbide by Keshri, et al. [56]. It was found that the weight loss due to wear of Al2O3 coating was increasing with the temperature while $Al_2O_3$-CNT coating showed a decreasing weight loss with the temperature. Increase in wear resistance of $Al_2O_3$-CNT coating compared to $Al_2O_3$ coating was 12% at room temperature which gradually increased to 56% at 573 K and 82% at 873 K. It was concluded that the improvement in the wear resistance of $Al_2O_3$-CNT coating was due to higher hardness at the elevated temperature as compared to $Al_2O_3$ coating, and CNTs bridging between splats. The coefficient of friction of $Al_2O_3$ coating was nearly constant at room and 873 K whereas that for $Al_2O_3$-CNT coating decreased at 873 K.

Keshri, et al. [56] investigated the effect of carbon nanotube (CNT) addition on the splat formation in plasma sprayed aluminum oxide (Al2O3) composite coating with 0, 4 and 8 wt.% CNTs in Al2O3 matrix. It was observed that with an increasing CNT content, splat morphology became more circular and disk-shaped. The average diameter of disk-shaped splats increased with increase in CNT content. The addition of CNTs increased thermal capacity and increased viscosity of the melt. Increase in thermal capacity delayed the localized solidification which resulted in higher splat diameter while agglomeration of CNTs at the periphery of the splat resulted in higher viscosity of the melt which suppressed the splat fragmentation.

Mazaheri, et al. [57] developed multi-walled carbon nanotube nanostructured zirconia composites with a homogenous distribution of different MWCNT quantities (ranging within 0.5–5 wt.%). An increase in indentation fracture toughness and a slight hardness improvement were observed with the addition of 5 wt.% (12.5 vol.%) MWCNTs. This was attributed to the extent of interfacial bonding between MWCNTs and zirconia grains. High temperature mechanical tests of zirconia/MWCNTs nanostructured composites showed a significant reduction of plastic strain in the presence of MWCNTs while monolithic zirconia exhibited superplastic deformation.

Ahmad, et al. [58] fabricated multi-walled carbon nanotubes (CNTs) reinforced Al2O3 nanocomposites hot-pressing resulted in inprovements in fracture toughness, by 94% and 65% with 2 and 5 wt.% CNTs addition respectively, compared with monolithic $Al_2O_3$. The increase in mechanical properties was attributed to the good dispersion of CNTs within the matrix, crack-bridging by CNTs and strong interfacial connections between the CNTs and the matrix. It was observed that a possible aluminium oxy-carbide interfacial phase was produced via a localized carbothermal reduction process which had good chemical compatibility and strong connections with both CNTs.

Keshri, et al. [59] used chemical vapour deposition method to achieve a homogeneous dispersion of carbon nanotubes

(CNTs) on aluminum oxide ($Al_2O_3$) powder deposited by plasma spray method on a steel substrate to produce a 96% dense $Al_2O_3$ coating with CNT reinforcement. It was observed that with the addition of 1.5 wt.% CNTs there was 24% increase in the relative fracture toughness of the composite coating. The improvement was due to uniform dispersion of CNTs and toughening mechanism such as CNT bridging, crack deflection and strong interaction between CNT/$Al_2O_3$ interfaces. The wear tests were performed by ball on disk tribometer. It was observed that with the increase in normal loads from 10 to 50 N, the wear volume loss and coefficient of friction of the coating was increased. It was also found that wear resistance of the $Al_2O_3$–CNT composite coating improved by 27% at 50 N.

Li, et al. [60] developed Zirconia/graphene nanosheets (ZrO2/GNs) composite coatings using a plasma spraying technique. It was observed that the graphene nanosheets additives (1 wt%) were homogeneously distributed in the ZrO2 matrix and most of them were anchored at the splat interface. The results of wear test showed that the ZrO2/ graphene nanosheets composite coating exhibited good wear resistance and low friction with the addition of graphene nanosheets. The wear rate of composite coating was reduced to $1.17\times10^{-6}$ mm3/N m at 100 N, which corresponded to a 50% decrease compared with the pure ZrO2 coating.

A dispersion process for producing carbon nanotube (CNT)-reinforced magnesium alloy (CNT/AZ31) composites was developed by Han, et al. [61] . The process includeed the preparation of a CNT/fMg precursor with uniformly dispersed CNTs followed by the synthesis of CNT/AZ31 composites by subsequent melting and hot extrusion. It was observed that the CNTs uniformly dispersed in the molten AZ31 without agglomeration because of the use of the CNT/Mg precursor. The structure of the CNTs was remained intact and was not destroyed, and good interfacial bonding existed between the CNTs and the AZ31 matrix. The tensile yield strength of the CNT composite was 22.7% greater than that of AZ31 alloy. It was due to the heterogeneous nucleation effect of the CNTs and the good interfacial bonding between the CNTs and the matrix.

Bakshi, et al. [62] developed multiwalled carbon nanotube (CNT) reinforced aluminum nanocomposite coatings using cold gas kinetic spraying. A good dispersion of the nanotubes in micron-sized gas atomized Al–Si eutectic powders was obtained by using spray drying. 5 wt.% CNT were blended with pure aluminum powder to give overall nominal CNT compositions of 0.5 wt.% and 1 wt.% respectively. It was observed that the cold spraying resulted in coatings of the order of 500 μm in thickness. CNTs were found to be shortened in length due to fracture that occurred due to impact and shearing between Al–Si eutectic particles and the aluminum matrix. It was found that the elastic modulus values were from 40–229 GPa which was attributed to microstructural heterogeneity of the coatings that comprised pure Al, Al–Si eutectic, porosity and CNTs.

## V. CONCLUSIONS

1. The problem of hot corrosion is a serious problem in high temperature applications
2. It is clear from the literature review that to increase the corrosion resistance of metals, Researchers developed coatings by thermal spray techniques viz. HVOF techniques, Plasma spray, D-gun spray techniques to increase the corrosion resistance.
3. Plasma sprayed coatings of various ceramic materials such as Alumina (Al2O3), calcia (Ca)-stabilized zirconia (ZrO2) and other refractory materials have been developed for various high temperature applications. It is reported that the corrosion resistance of alumina coatings are higher than that of cermet and metallic coatings. There is an increasing demand on these coatings with increased thermal characteristics.
4. It is not possible to produce defect free plasma spray coatings. The thermal spray coatings consist of cracks or voids. These voids originate from the spraying process and are found at the splat boundaries. In the corrosive environment, these coatings are attacked through these voids. Therefore, despite success of thermal spray coatings in recent past, there has still a great interest among researchers to develop new coating materials for enhanced corrosion resistance at high temperature.

5. The properties of CNTs make them potential reinforcement for the composite materials. CNTs act as inert physical barriers to the initiation and development of corrosion, modifying the microstructure of the coating layer and hence improving the corrosion resistance of the coating. It is revealed in the literature that very few investigations have been made on the corrosion behavior of CNTs–metal composite coatings. Some researchers have developed different wt.% CNTs-Al2O3 composite coatings and studied their tribological behavior. But no studies on CNTs-Al2O3 composite coatings for high temperature corrosion are available. Therefore, there is scope of investigation of developing new composite coatings by mixing different wt. percent of carbon nanotubes with alumina, and subsequently depositing and investigating hot corrosion behavior of these newly developed coating on different grades of commercially available boiler steels.

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Rakesh Goyal is doing his Ph.D. as a Research Scholar of Mechanical Engineering Deaprtment with IKGPTU, Kapurthala, Jalandhar, Punjab, India and is working as an Associate Professor in Mechanical Engineering department at Chitkara University, Punjab. He has been the reviewer of many International Journals. He has been the member of various national and international technical Societies. He has more than 20 Publications in various national/International Conferences & Journals.
Work Experience: 13 years

Dr.Vikas Chawla; Principal & Professor (Mech.Engg.);Young Scientist, Bharat Vidya Shiromani and Best Engg. College Teacher Awardee; Ph.D.:I.I.T. Roorkee,India; Supervised numerous B.E. & M.E. research projects and supervising PhD dissertations; Publication: 63 Publications in International Referred Journals and Conferences & filed 4 Patents.
Teaching Experience: 18 years

Dr. Buta Singh Sidhu is presently working as Dean c at MRSSTU, Bathinda (Pb.) India has 25 years experience in teaching and research. Supervised number of Ph. D. and M. Tech. Thesis and has 66 publications in international journal and conferences. Working on number of sponsored research project in the concerned area.