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Current Status of Prevention of Hot Corrosion of Boiler Steels with Thermal Spray Coating

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***Abstract* - In the thermal power plant, various conventional steels are used to manufacture boiler components. Due to high operating temperature of these boilers, these conventional steels are unable to resist hot corrosion. In recent years researchers have used various techniques to resist hot corrosion out of these techniques, thermal spray coating process have gained lot of interest due to the ease of coating, low operating cost, and various other advantages. With these coating processes a thin layer of coating material is developed over steel alloys surface which creates hindrance to penetration of corroding element and hereby reduce corrosion. This paper is an attempt to present a comprehension the study related to hot corrosion of thermal spray coating on boiler steels at high temperatures.**
***Keywords:* Thermal Spray, Microstructure, Corrosion, Porosity, Mechanical Properties**

I. INTRODUCTION

At elevated temperature, accelerated oxidation is experienced by metal and alloys when they are exposed to corrosive environment which leads to deposition of thin film of fused salt on the surface of metal leading to the formation of porous non protective oxide layer on the surface and sulphides inside the substrate as described by the Singh H *et al.*,[1]. In boiler steel and turbine occurs due to presence of sulphur in coals and oil fuels which produces SO2 and further partially oxidize to SO3.[2] Element causing corrosion enter into boiler tube with the air and with fuel. Sulphur impurity react with NaCl to formNa2SO4 with in the boiler tube as proposed by DeCrescente and Bornstein [3,4].

$$2NaCl + SO_3 + 1/2O_2 \rightarrow Na_2SO_4 + Cl_2$$

As the higher grade fuel are depleted at a faster pace, therefore residual fuels are beings used for production of energy. Impurities such as Na, K, S and V are present in the residual fuel which forms the compound having a low melting point. Corrosion is initiated by these low melting compounds as they get deposited on the surface of the material. These melting compounds react with oxygen to form Na_2SO_4 and V_2O_5. These compounds are known as ash. Protective oxide layer is deteriorated by these molten compounds during the boiler/gas turbine operations [5,6]. Shut down of plant is due to the hot corrosion of boiler steels tubes at elevated temperature. Besides the shutdown of plants there is loss of thermal efficiency and wastage of material which causes the expenditure of billions of dollars on the machine, equipments and corroded structure. Also human injury or loss of life can happens due to the premature failure of component. The inability to completely eliminate the problem of hot corrosion results in finding the different ways to minimize its effects on metal and alloy steel at elevated temperatures [7, 8].

Inability of conventional steels to resist hot corrosion at elevated temperature in thermal power plants provides a pathway for researchers to research on different coating materials and methods to resist erosion and corrosion of boiler steel tubes. From the different methods thermal spray coating techniques has significant effect on reducing the hot corrosion and increasing the life of components. In recent past this techniques has increased its importance. As a thermal spray process is flexible, cost effective and super quality of microstructure is produced its is widely used in the industries [9]. Coating produced by thermal spray method doesn't have any specific limitation with respect to the base composition. With a few millimeter thickness, coating of high hardness can be produced [10]. For protection of boiler components HVOF, plasma, arc and flame method are mostly used. Due to relatively higher in cost plasma method is preferred less and also due to remelting flame method is rarely used [11]. To increase the corrosion resistance researchers used HVOF technique, thermal spray technique and D-gun spray technique to produce hard faced coating. This following part of paper explained the work done by researcher on thermal spray coatings.

II. STUDIES ON THERMAL SPRAY COATING

Kamal *et al*. [12] studied the performance of NiCrAlY+0.4wt. %CeO2 coating on super alloys. They used Detonation-Gun spray method for coating on superni 75 superni 718 and superf 800h. They incorporate the rare earth metal such as CeO2 in coating to enhance the corrosion protection. Coating composition Ni-22Cr-10Al-1Y is used on the substrate.the result was examined using weight change, X ray diffraction, SEM/EDAX X-ray mapping, Cross sectional technique. The bare specimen show more weight gain as compared to the coated specimen. XRD analysis detected the major and minor phase as CrS, NiO, Cr2O3 and Al2O3. It was identified that CeO2 was uniformly distributed on the substrate which help in increase in corrosion protection. Bare specimen

undergoes higher corrosion where as coating specimen least. Coated superf 800H showed higher corrosion resistance than the three superalloy.

Chatha *et al*. [13] observed the behavior of NiCr coating on T-91 boiler steel in Platen Superheater of coal fired boiler. High velocity oxygen fuel method is used for coating the substrate. The substrate are placed for 15 cycle where each cycle consist of 100 h cycle and 1 hr of cooling at ambient temperature. The results were studied by using weight change technique, XRD technique, SEM/EDS and cross sectional analysis. Using these techniques it was observed that bare T-91 steel form porous oxide scale, higher weight gain as compared to coated steel. XRD analysis showed that bare steel had higher content of Ferrous oxide whereas coated steel had higher content of chromium oxide which protect the steel from corrosion. Cross sectional analysis shows that bare steel had cracked, porous, thick loosely bounded scale where as coated steel has continuous, dense coating without any degradation.

Chatha *et al*. [14] investigated the coating resistance behavior of NiCr and Cr3C2–NiCr coating on T-91 boiler steel at 750°C. For coating High velocity oxy fuel method is employed. The substrate was place inside the molten salt environment (Na2SO4–60%V2O5) at 750°C for 50 cycle each cycle consist of ihr of heating and 20 min of cooling in air. The results were observed using the weight change measurement, cross sectional analysis, SEM/EDAX analysis, X-ray diffraction, XRD analysis technique. It was seen that uncoated specimen was experienced higher weight gain due to the formation of unprotective iron oxide as the major phase. It was found that NiCr reduced the weight gain more than the Cr3C2–NiCr. Hence it reveals that NiCr coating on T-91 steel is better than Cr_3C_2–NiCr with HVOF method. Thus both the coating help in controlling the hot corrosion Jagadeeswaran *et al*. [15] investigated the hot corrosion of Al2O3+CoCrAlTaY coating on Ti-31 alloy in salt environment. High velocity oxygen fuel method is used for coating the substrate. Experiment is performed under the salt environment condition of 50%V2O5 and 50% Na2SO4 at 800°C. Results were obtained using the XRD, SEM/EDS and weight change measurement technique. It was found that uncoated substrate showed a high gain in weight change measurement and high content of oxides whereas coated substrate had low change in weight measurement and high content of chromium oxide layer which protect the substrate from the further oxidation.

Bhatia *et al*. [16] observed the performance of 75%Cr3C2-25%NiCr coating on T-91 steel at different operating temperature. Coating was performed using High velocity oxy fuel method. The coating produced on the specimen was uniform, dense and adherent with less than 2% porosity. The specimens were placed in the corrosive environment of Na_2SO_4 - 60%V_2O_5 for 50 cycle, each cycle consist if 1hr heating at given temperature i.e 550, 700, 800 in furnace and 20 minute of cooling at ambient temperature. The result were obtained using the visual analysis, thermo gravimetric technique, XRD, SEM/EDS, and cross sectional analysis techniques. The uncoated specimen show the higher weight gain as compared with the coated specimens at all the operating temperatures. It was also noted that uncoated specimen has irregular scale, cracks and spallings whereas coating specimen has uniform and less or negligible cracks. Reason behind the coating resistance was oxides and spinels of nickel-chromium. Hence it was found coating provides better corrosion resistance than the uncoated T-91 sample.

Singh, Singh [17] studied to find out the effect of erosion and corrosion of Al2O3 coating on T-91 steel at elevated temperature in actual boiler environment. Detonation gun sprayed method is used for coating the substrate. The coated and uncoated specimen was placed in boiler for 10 cycles and results were examined using thermo gravimetric technique and SEM/EDAX. After the analysis it was found that weight change in uncoated specimen was more than that of coated specimen, however change in weight is less. SEM/EDAX show that coated specimen shows presence of Al, O, Zr , Si whereas Fe was only found in uncoated specimen.

Singh *et al*. [18] studied the coating resistance of Cr3C2-NiCr coating, Stellites-6 and Stellites-21 on grade A-1 steel boiler. Coating was performed using detonation gun sprayed method on three substrate one by one. The experiment is performed for 10 cycles each cycle consist of 100hr of heating at 900°C and 1 hr of cooling at ambient temperature. The result were examined using the thermo gravemetric technique, SEM/EDS, weight change measurement and cross sectional analysis. It was found that bare substrate undergoes more corrosion as it had high percentage of iron oxide whereas coated substrate had higher percentage of chromium oxide, nickel oxide, cobalt oxide which prevent the substrate from corrosion.

Singh *et al*. [19] studied the coating effect of Ni3Al and TiO2 coating on T91 boiler tube steel in simulated boiler environment at 900°C. HVOF method is used for coating on the substrate T-91 steel. Specimen was placed in molten salt environment for 50 cycle. The oxide scale of T-91 steel tubes is examined using XRD Technique. It was found that uncoated specimen has Fe2O3, Fe3O4, Cr2O3 as a main phase where as coated specimen has NiO, Al2O3 as a major phase while Fe2O3, Fe3O4 as a minor phase. TiO2 was found to be most protective then NiAlO3 as NiO had loose structure thus leads to more pores result in increase in corrosion. Hence the coating provides the protection from the corrosion environment.

Singh *et al*. [20] investigated the thermal spray coating of NiCrAlY coating on T-91 steel . High velocity oxygen fuel method is used for coating the substrate. Coated and uncoated specimen are placed in SiC furnace for 50 cycle each cycle consist of one hour heating and 20 minute cooling. The results were analyzed using weight change technique, SEM, EDS and X ray diffraction technique. It

was found that uncoated substrate exhibit weight gain during oxygen study, intense spalling and peeling off scale. Fe2O3 is formed on the uncoated substrate and EDS analysis reveals Fe and O as major element which forms Fe2O3. On the other hand coated substrate showed negligible weight gain and formation of Cr2o3 which reveals Chromium oxide as the major phase which prevent corrosion. Cr, Al, Ni was main element where as Fe was minor element in coated substrate. Hence NiCrAlY coating showed significant role in controlling the hot corrosion.

Chatha *et al*. [21] studied the coating performance of 75 Cr3C2-25NiCr coating on T-91 boiler tube steel in coal fired boiler at 900°C. High velocity oxy-fuel method is used for coating the T-91 substrate. Coated and uncoated substrate were place inside the steel boiler for 15 cycles each cycle consist of 100 hr of heating and 1 hr of cooling at ambient temperature. The results were examined using X-ray mapping, SEM/EDS, cross sectional analysis technique. It was seen that internal oxidation attack at inside the substrate and corrosion scale formation result in metal loss in uncoated T-91 steel substrate. The coated substrate on other side finds no internal crack and no corrosion formation and showed well adherence property to boiler tube steel. Hence it reveals that coating helps in preventing the hot corrosion.

Sidhu *et al*. [22] investigated the corrosion resistance of 93(WC-Cr3C2)-7Ni, 75Cr3C2-25NiCr, 83WC-17Co and 86WC-10Co-4Cr coating , on T-91 steel. Coating was employed using the High velocity oxy-fuel method. The uncoated and coated substrate were placed inside the coal fired boiler for 10 cycle, each cycle consist of 100hr of heating at 900°C and 1hr of cooling at ambient temperature. The result was obtained using the visual examination, SEM/EDS, weight measurement technique, X-ray diffraction. It was found using SEM/EDS that uncoated T91 mainly consisted of iron oxide and chromium oxide which did not prevent the corrosion as iron oxide moves inside the substrate and cause corrosion where as coated specimen were having major phase as chromium, nickel, cobalt, tungsten as major phase and absent of iron oxide thus it reveals that it prevent the corrosion. Hence it is found that coating helps in preventing the hot corrosion and coating shows the order of resistance as 93(WC-Cr3C2)-7Ni>86WC-10Co-4Cr>83WC-17Co>75Cr3C2-25NiCr.

Jiang *et al.*, [23] discussed corrosion resistance behavior of Fe based amorphous coating. Coating method used is Plasma spray jet method. The coated and uncoated substrate was placed in salt environment of 70%Na2SO4-30K2SO4 at 700°C for 84 hr in coal fired boiler. The results were obtained using the weight change measurement, SEM/EDS, cross sectional analysis techniques. It was noted that bare substrate undergoes corrosion at early stage of cycle as analyzed by weight change measurement but coated substrate show little gain in weigh but at later there was negligible weight gain and corrosion was negligible as compared to bare substrate. It was also noted that if the coating thickness lies between the range of 270-380µm there was effective protection to the coated substrate. In this no cracks, spallation was found on the substrate which protects the interior of substrate from the corrosive medium.

Chatha *et al.*, [24] investigated application and performance of thermal spray coating of Cr3C2-NiCr under various environments for erosion and corrosion. Mechanical and microstructure properties of carbide coating are discussed. With plasma spray, HVOF and detonation gun method carbide coating is deposited successfully. At elevated temperature, coating resistance of carbide coating is very high. With thermal sprayed coating, at splat boundaries voids are formed through which coating were attacked as concluded by author.

Niranatlumpong *et al.*, [25] studied about failure occurred formation of oxides by plasma spray method on Ni Cr alloys overlay coatings. They have observed that if the coating procedure is done on 1100 degree C and with maximum required time more than 100 Hours then coating failures may result a sub parabolic behavior develops in coating, an Initial spallation occurs by de-lamination within layers during cooling. With relatively plasma sprayed coating the internal oxidation also arises and may lead to the aluminum depletion in aluminum alloys. As oxidation tests are performed in thermal gravimetric assembly .results shows that oxidation rate was more until alumina layer is developed at intermediate exposure periods the results are better for coating as they withstand with high temperature and pressure. Testing is done by XRD technique.

Singh *et al.*, [26] experimented on corrosion behavior of plasma sprayed Ni_3Al coating on Steel in oxidation and molten salt environment at 900ºC. They considered three types of material GrAl, Low Carbon steel T-11 and medium carbon steel T-22 specimens from boiler tubes. Specimens are polished with Al_2O_3 (60 µm Grit) before coating is done by nickel and aluminum of 3:1 of quantity of grits and applied with plasma spray method in this argon was used as shielding gas and powder carrying gas Ni-20Cr-10Al powder (150 µm) is used. Tested with XRD, SEM and hardness is tested by micro hardness tester. Results tells us that pre coating of aluminum done at 250º C prevents the inter formation of oxide layer at elevated temperature. In molten salt testing environment (Na2So4) at 900ºC the weight gain by T-11 material was less as compared to T-22 material. It was 2/3 of T-22.GrAl gains 1/7 of T-22 material in 50 Cycles. On GrAl found formation of Fe_3O_4 on its peaks and on *t-22 it was not formed observed in XRD. As NiO and Al2O3 formed on all steel components. GrAl are corroded in molten salt environment and and On T-22 the substrate material forms the oxidized film below coating. It is observed as the nickel and aluminum are dissolves in surface of material as Chromium withstands and prevents material from corrosion and erosion.

Singh *et al.*, [27] Studied microstructure and mechanical properties of HVOF sprayed Cr_3C_2 coating on the boiler

tube tubes by using LPG gas as fuel gas. In this various coatings are used and tested such as carbide coating but due to high impact of velocity of flowing gases and fluid it causes failure to these coatings instead of this nickel chromium coating used which with stand with high IMAPCT and high velocity fluids using HVOF process (high velocity oxy fuel) and its structural testing is done by X ray diffraction techniques such as SEM and XRD techniques .Results are obtained as resistance of corrosion. The critical hardness values of the steels were found to be in the range of 200–280 Hv. This coating range is found to be desire able and durable.

Bala *et al.,* [28] Studied about accelerated hot corrosion of cold spray Ni-50Cr Coating on Boiler steels. Experiment is performed under the aggressive environment of Na_2So4-60% under cyclic conditions. Boiler Steel Specimen is coated with Ni-50Cr of 60 grit particles 45 +- 15 um with high velocity Cold spray process of coating and testing methods were XRD Techniques material was mainly used was T-22 Mostly used in boilers and steam turbines these coatings prevents from formation of Fe_2O_3 on the surface of T-22 material. Testing techniques are used X ray technique as average thickness was 339 micro meter with hardness range of 282-419 Hv. Is performed about 50 cycles at 900 deg C. as this is observed that bare specimen has very less life span as it get corroded and eroded than coated one

Sidhu *et al.,*[29] studied about hot corrosion HVOF sprayed Cr_3C_2 –Ni Cr and Ni -20Cr. Coating on nickel based super alloy in the molten salt environment of Na_2So_4 60% at 900 deg C" of temp the 45 micro meter grit was used for coating at 50 cycles as each cycles about of 1 hour. The amount of salt coating was kept in the range of 3.0- 5.0 mg/cm^2. And kept it in oven for 3 – 4 Hours and thermo gravimetric method is used to study the kinetics of corrosion after that testing is done by XRD and SEM techniques. The results are obtained is Ni-20Cr coating was better then Cr_3C_2-NiCr coating. The formation of oxides of nickel and chromium blokes the pores os the surface of workpiece so that oxygen could not react even at high temperature when Moisture of environment is present in it.

Kamal *et al.,* [30] at al studied about hot corrosion behavior of detonation gun sprayed Ni Cr coatings on fe (Iron) based Super alloys in Na_2So_4 Environment at 900 Degree C. The coatings are done with the porosity less than 0.8%. This coating helps in prevention of fusion of gases at very high temperature such as 900* C and above by making a layer on the surface of material. The thermo gravimetry technique is used in molten salt Na_2So_4 at 900 environments with 100 cycles in silicon carbide furnace with 20 min cooling time. They used XRD tests to study the microstructure of grains of materials after putting it in to corrosive environment, as Results are obtained as bare element gets corroded in very less time as compared to coated one in high temperatures.

Kumar *et al.,* [31] Studied about hot corrosion of micro structurally different sections of 2.25Cr-1Mo (T-22) boiler tube welding. this study explains that even welded portions gets oxidized under molten salt Na2So4 – 60% V_2O_5 environment in boiler at 900%.the welding base metal is tungsten which gets easily oxidized under this environments at very higher rates can be studied by X ray techniques of various phase change and oxide formations. For testing the T-22 material is placed in thermal power plant environment. As tubes of this materials are with TIG Welding as weld metal shows the ferrite, pearlite and bainite formation on slow cooling. In the region of molten salt the spallation of oxide layer is found to formed on the boundaries as cycles and temperature increases simultaneously. XRD inspection shows that formation of Fe_2O_3 on the weld portions at heat affected zones as chromium should be added with electrode to minimize the weight gain due to corrosive environment and to stop corrosion and erosion.

Jayanathan *et al.,* [32] has been studied about hot corrosion studies of detonation gun sprayed coating Ni Cr Al Alloy + 0.4 wt.% CeO_2 coated super alloys in environment of molten salt they have taken three super alloys namely Superni 75 , superni 718 and superfer 800 H are coated with M Cr Al materials as m are mainly Nickel/cobalt or combination of both these are coated in the molten salt environment of Na_2So_4 with 0.4 % of cerium oxide CeO_2.Coating is done with D Gun Spray Process. As previously done experiments showed that use of cerium improves the efficiency of aluminide coating and prevents the dry sand erosion and corrosion in dilute H_2So_4 and Nacl Solution. It reduce the rate of hot corrosion attack at elevated temperatures around 1000º C. as it forms the $CeVo_4$ on the material surface. These micro structural characteristics are studied from FE-SEM / EDAX , X ray mapping and XRD techniques to study corrosion mechanism. Results shows that during testing that the bare superfer 800H shown maximum weight gain followed by superni 71 and superni 718 super alloys.and after coating the superifer 800H showed minimum weight gain. Which indicates that it is prevented from oxidation of surface.

Singh *et al.,* [33] has observed the status of Cr3C2-25 (Ni-20Cr) and Ni-20Cr coatings on T-22 boiler steel tube material in boiler. In boiler the temperature goes around 900º C and above to save material of boiler tubes they have tested two types of specimen coated with High Velocity Oxy Fuel (HVOF) process in the environment of molten salt (Na_2So_4-V_2O_5) for 50 Cycles at 900ºC, 30µ thick coating is applied. The experimentation is done in boiler of silicon tube furnace. Analysis was done by using XRD techniques shows that formation of NiO and Cr2O3 on the surface of specimen. Uncoated specimen T-22 tested gives the result as Fe2O3 forms at minor peaks of the surface and Cr_2O_3 major peaks. The coating prevents this oxidation which erodes the material even at elevated temperatures of 900º C and above.

Kumar *et al.,* [34] examined oxidation studies on base metals, weld metals and HAZ regions of TIG weld ments in 2.25Cr-1Mo (T-22) boiler tube under different conditions.

TIG welding is mostly used to weld two tubes in boiler or turbine blades used of T-22 materials gets corroded in elevated molten salt environments mostly at HAZ. This experiment is studied the formation of layers of oxides in heat affected zones by XRD methods , the HAZ showed more weight gain as due to formation of chromium oxide on the boundaries of HAZ . as to confirmed it cyclic testing is done by 50 repetive cycles followed by cooling process side by side the physical measurements are tested with Digital vernier caliper . In experiment the material is kept in alumina boat at 1200 ºC for 6 to 8 hours. Then this boat is kept in furnace of 900ºC for 1 hour , and then it is taken out and cooled in ambient temperature. For 20 min. then the weight of boat with specimen is measured after each cycle and found that weight is increasing with each repetition of cycle. And changed microstructure after each cycle is observed by XRD method. The colour of oxide layer formed on it was of blackish grey and small spalling was started just after fourth cycle. The cracks are started appearing after 30th cycle. Mostly these cracks were on HAZ.

Singh *et al.*,[35] studied about behaviour of Ni_3Al and TiO_2 coatings on T-91 material used in boiler tube steel in boiler environment at 900ºC.They have used boiler tube material mostly used ASTM SA 213 its another common name is T-91.The two specimen were taken and coated with HVOF process thickness of 250-300µm , one with Ni_3Al and other with TiO3 . after coating the material are kept in the atmosphere of molten salt Na_2So_4 with 60% of V_2O_5 at 900ºC with reparative cycles about 50 at 1 hour of heating and after each cycle the material is kept under 20 ,minutes of cooling at Room temperature. It is found that Ni3Al coating was very useful as it decreases the corrosion rate at 900ºC temperature in molten salt atmosphere and protective than TiO_3 coating. X ray Diffraction XRD, Scanning spectroscopic analysis SEM techniques are used to study the behavior of coatings and rate of corrosion during experiment. The results shows that 80Ni-20Cr results better than $75Cr_3C_2$-25(Ni-20Cr) coating. This experiment is performed in thermal plant. The process of Weight change is observed through thermo grevimetric process.

Mangla *et al.*, [36] Studied about behavior of HVOF and plasma sprayed Ni-20Cr coated T-22 steel in actual coal boiler environment. They tested the T-22 material or steel with two different methods one with HVOF and Other is plasma spray method to coating of t-22 with Ni-20Cr. The testing is performed in the actual boiler burned with coal field. The uncoated material makes spelled oxide layer formation and by both coating techniques this spelled layer is not formed at boiler coal field environment at high temperatures of 900ºC. Coating of Ni-20Cr makes the layers of NiO , Cr_2O_3 on the surfaces as shown by XRD and EDS testing. This is confirmed as the HVOF process resulted better corrosion resistance than plasma spray method of coating and weight was less of deposition of material by 77.8% to 65 % as compared to deposition in plasma coated material

III. CONCLUSION

In this paper, detailed literature review has been done for corrosion behavior of thermal spray coating on boiler steels at elevated temperatures and the following conclusions are made; For high temperature environment applications corrosion has been found as a serious problem in the degradation of boiler steel tubes. In the recent past , various coatings techniques are used on the surface of steel by the structure to resist the corrosion at elevated temperatures as studied in the literature survey. D gun spray technique, HVOF technique and thermal spray technique has produced hard faced coatings to increase the corrosion resistance. By using this techniques and sophisticated coating system 100 % defect free steels are not possible to achieve as the coating techniques produced the micro pores on the layer of coating and this acts as a path way for the corrosion species to attack on the substrate resulting in spallation and many local micro cracks on the steel, hence there is a scope to enhance over improve these coatings by decreasing the defect and reducing the porosity. There is a future scope for further research work in this area to minimize these defects.

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