Hot corrosion behaviour of plasma and d-gun sprayed coatings on t91 steel used in boiler applications

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Abstract: Material degradation by salt induced hot corrosion is a serious threat to Coal fired Boiler components. Corrosion resistant thermal spray coatings is a proven solution for this problem. This work compares the hot corrosion behaviour of a NiCoCrAlY coating on T91 boiler steel deposited using two different thermal spray methods namely Atmospheric Plasma Spray (APS) and Detonation Gun (D-Gun) spray. The coated samples were exposed to 650°C for 100 cycles (1 cycle being 1 hour holding plus 20 minutes cooling in air) in a thermal cycling furnace under a mixed deposit containing Na₂SO₄, K₂SO₄ and Fe₂O₃ to simulate the real time coal ash environment. The exposed coatings were examined using FESEM/EDS and XRD to analyze the extent and nature of corrosion attack. The results indicate that the D-Gun sprayed coatings provided superior corrosion resistance over their APS sprayed counterparts. NiO and Spinel oxide NiCr₂O₄ which offers corrosion resistance were formed in both the coatings with the APS sprayed coating being rich in the fast growing NiO which affected its corrosion performance. The enhanced corrosion resistance of the D-Gun sprayed coatings was attributed to its dense microstructure with minimal porosity and good intersplat bonding which minimized corrosion ingress.

1. INTRODUCTION

Steam temperature and pressure determines the efficiency of coal fired power plants to a greater extent. Accordingly, Super Critical and Ultra Super Critical power plants which operate at very high steam temperatures and pressure (>560°C and >220 Kg/cm²) relative to the critical point of water is being used for coal based power generation and Sub-critical power plants are already being phased out all around the world [1]. Higher temperatures and pressures enable greater operational efficiency and hence lower coal consumption per unit energy produced eventually leading to lower emission levels. However, the greatest challenge involves developing durable high temperature materials for many of the boiler parts. These include piping, headers, reheater and superheater tubes which are highly crucial. Apart from the high temperature creep and fatigue strength requirements, this application calls for a very crucial Hot corrosion/Fireside corrosion resistance [2].

High temperature corrosion induced by a thin film of fused salt deposit is termed as Hot corrosion [3]. Low quality coals having high amounts of sulphur, alkali metals like sodium, Potassium etc. produces very corrosive media during combustion near the superheater tubings. The resulting sulphate salts (Na₂SO₄, K₂SO₄) along with the fly ash particles (Fe₂O₃, SiO₂, Al₂O₃) stick to the boiler tubings. This in turn causes reduced heat transfer to the water/steam inside and very importantly tube damage by hot corrosion. The salt deposits react among themselves and with the protective oxide scales formed to produce low melting mixtures that accelerate corrosion. The salt deposits react with the protective
scale and render them unprotective by a mechanism called fluxing [4]. Corrosion resistant overlay coatings especially thermal spray coatings is a proven method to mitigate this problem. Thermal spray coatings protect the underlying substrate by forming a dense, adherent and slow growing Alumina/Chromia scales. A range of thermal spray processes which rely on high particle temperatures or high enthalpy (Plasma spray, Flame spray, etc.) and High particle velocities or Kinetic energy based (High velocity Oxy-fuel, Detonation spray, cold spray, etc.) are available for producing coatings [5].

Plasma spray coating relies on the immense heat produced by the plasma arc to heat and melt the powder particles which are taken by a stream of carrier gas towards the substrate. An inert gas mixture (Argon/Helium + Hydrogen/Nitrogen) is heated by a DC arc to produce the plasma arc. The process is very famous for coating ceramics and metallic bond coats. Due to the very high temperatures and comparatively low particle velocities involved, it suffers from increased particle oxidation and high coating porosity issues respectively but this could be overcome with optimised process parameters and advanced multi electrode plasma spray systems [6]. The D-Gun process uses a series of intermittent explosions to melt and accelerate the particles towards the substrate. A Detonation wave is produced inside a barrel by igniting an oxy-acetylene mixture and the powder particles are propelled and heated through it. Due to the high particle velocities involved, the coatings are denser with better intersplat bonding.

Hot corrosion studies have been conducted in both real time Boiler environment and simulated conditions using Mixed salt deposits. In the former case, HVOF coated T91 samples were directly inserted in the Platen superheater zone of coal fired boilers and the corrosion performance was quantified based on the thickness loss and internal oxidation attack of coatings [7-9]. These works reported the superior performance of Chromium rich NiCr coatings over other coating compositions like Cr$_2$C$_2$-NiCr. In the simulated condition experiments, HVOF coated T91 samples were exposed to Thermal cycling furnaces in the presence of Na$_2$SO$_4$ + V$_2$O$_5$ salt mixture and again the Chromium rich coatings were found to perform better with oxides and spinel oxides of Ni and Cr making the positive difference [10,11]. T. Hussain et al. compared the hot corrosion performance of Plasma and HVOF sprayed candidate coatings on T91 steel with Na$_2$SO$_4$+K$_2$SO$_4$+Fe$_2$O$_3$ deposit and reported the Plasma sprayed NiCr coating as the best one owing to its higher Chromium content. Surprisingly, the HVOF coating couldnt get the better of plasma coating which was reported to be due to the recent technical advancements in plasma spray technology [12]. Esmaeil Sadeghi et al. compared the hot corrosion performance of HVAF coated Chromia and alumina forming coatings under chloride and sulphate environments and concluded that Alumina forming coatings were more susceptible in sulphate environments while Chromia forming coatings were more susceptible to chloride salts [13,14].

In this study, NiCoCrAlY coating was deposited on T91 boiler steel using APS and D-Gun spray techniques. Hot corrosion conditions were simulated using an aggressive mixed deposit of Na$_2$SO$_4$+K$_2$SO$_4$+Fe$_2$O$_3$ and the samples were thermal cycled for 100 cycles at 650°C. After exposure, the phases formed were studied using XRD analysis and the cross sectioned samples were analysed using FESEM with EDS elemental mapping to find out the extent of corrosion damage. There are very little to almost zero previous works studying the Hot corrosion performance of D-Gun sprayed NiCoCrAlY coatings. This study assumes importance since D-Gun coatings which produces denser coatings with exemplary intersplat bonding is a perfect choice for hot corrosion applications. Also by comparing a low density plasma spray coating with a D-Gun coating, we could understand the mechanism by which superior corrosion resistance is enabled in the latter.

2. EXPERIMENTAL WORK

2.1. Feedstock powder and substrate preparation
Commercially available gas atomized NiCoCrAlY powder (Amperit 410.1) was used for the study.
The particle size was 22-45 µm. The particle size was also confirmed with a Laser based particle size analyser and the D50 size was found to be 35.88 µm. The chemical composition of the powder was found to be 47Ni-23Co-17Cr-12.5Al-0.5Y (% weight) and was also confirmed with EDS analysis. The substrate material used was the T91 boiler steel. It is a ferritic-martensitic low carbon steel with the major constituents being 9Cr-1Mo-0.1C-0.1Nb-88Fe (% weight). Samples of 20mm x 20mm dimension was used for spraying. The samples were first cleaned with acetone and then grit blasted with grit 40 alumina to roughen the surface (R_a > 7µm) so that good mechanical interlock exists between the substrate and coating.

The SEM micrographs of the powder is given in figure 1. The gas atomization process has resulted in a spherical morphology and the particles are also dense.

![SEM micrographs of NiCoCrAlY powder.](image)

2.2. Coating generation and characterization

Optimized process parameters were used for both APS and D-Gun coatings. A Sulzer Metco 9MB gun with ABB robotic arm was used for plasma spraying while a custom designed D-Gun system was used for detonation spraying. Coating was produced only on one surface of the substrate. A minimum coating thickness of at least 250µm was desired and accordingly the number of passes was decided. The back side of the substrates were cooled with air jets during plasma coating to avoid thermal degradation of the samples due to very high temperatures involved with plasma spray. Tables 1 and 2 shows the spraying parameters used for the APS and D-Gun coatings respectively.

| Parameter                        | Values                                      |
|----------------------------------|---------------------------------------------|
| Primary gas (Argon) flow rate, scfh\(^a\) | 90                                          |
| Secondary gas (Hydrogen) flow rate, scfh | 11                                          |
| Input current, Amperes           | 500                                         |
| Voltage generated, Volts         | 62-65                                       |
| Powder feed rate                 | As preferred in Sulzer metco catalogue      |
| Standoff distance, mm            | 100                                         |

\(^a\) standard cubic feet per hour

In general, a monoatomic gas is used as a primary one and a diatomic one as a secondary one. The diatomic gas has an additional energy of dissociation associated with it and hence can be used to control the enthalpy of the plasma plume. In our case, the voltage generated can be varied based on the flow rate of hydrogen gas.
Table 2. Spraying parameters for D-Gun coatings.

| Parameter                              | Values |
|----------------------------------------|--------|
| Acetylene gas flow rate, slph \(^a\)    | 1900   |
| Oxygen gas flow rate, slph              | 2300   |
| Carrier gas (Nitrogen) pressure, bar    | 1      |
| Standoff distance, mm                   | 165    |
| Frequency (Shots per second)            | 3      |

\(^a\) standard litres per hour

Following the coating process, each coated 20 x 20 mm sample was cut into four 10 x 10 mm samples using wire EDM process and they were used for characterization and further hot corrosion studies. The 10 x 10 mm coated samples were further cut using Isomet precision cutter and were mounted in acrylic cold mount before polishing them for SEM cross sectional imaging. Besides, the surface of the coated samples was subjected to XRD analysis using Cu K\(_{\alpha}\) radiation for finding out the phases formed after coating. The cross sectional hardness of the coatings was found out using Vickers micro hardness test. The test was performed at a load of 200 grams and the average of 10 indentations was taken as the hardness value. The surface roughness of the coatings was measured using a Mitutoyo surface roughness tester. The porosity of the coatings was measured from the SEM cross sectional images using an image analysis software.

2.3 Hot Corrosion tests
The salt deposit used for the test composed of 37.5% Na\(_2\)SO\(_4\), 37.5 K\(_2\)SO\(_4\) and 25 Fe\(_2\)O\(_3\) (mol. %). This mixture represents a composition of Alkali iron tri-sulphates that is a principle contributor of fireside corrosion in coal fired boilers. All the three salts are part of the coal and fly ash environment also. The salts were mixed in stoichiometric ratio and the mixture was made into a slurry by adding water. This slurry was then pasted onto the preheated coated samples at their centre using an artist’s fine hairbrush. Preheating of the samples (upto 150°C) is necessary for better adhesion of the salt mixture. Also the salt coated samples were post heated to 150°C for 1 hour for the same reason. The amount of mixed salt deposit applied onto each sample was approximately 10 mg/cm\(^2\). The samples were loaded onto Alumina crucibles and kept in a thermal cycling furnace for 100 cycles. Each cycle consisted of a ramp up segment where 650°C is reached followed by soaking at that temperature for 1 hour followed by 20 minutes of cooling in ambient air. The purpose of this imposed cyclic loading is to simulate the extreme fluctuations that may happen during a power plant running. The hot corroded samples after 100 cycles were studied using XRD analysis and FESEM/EDS analysis of the cut cross-sections to analyse the extent of corrosion. figure 2. shows the salt applied coated samples placed in an alumina crucible.

![Salt loaded samples in Aluminacrucible.](image)

3. RESULTS AND DISCUSSIONS

3.1 As-sprayed Coating Microstructure
Figure 3(a) and figure 3(b) show the cross sectional SEM micrographs of the Plasma and D-Gun
coated NiCoCrAlY coatings respectively.

![Coating SEM micrographs](image1)

**Figure 3.** As coated SEM micrographs of (a) APS and (b) D-Gun coatings.

Through image analysis it was found that the thickness of the APS and D-Gun coatings were 264 µm and 356 µm respectively. The lamellar structure of the splats can be seen in both the coatings. It is evident that the oxide stringers are more in the APS microstructure due to the high temperatures involved during coating. Also more splat boundaries are visible in the APS microstructure which indicates comparatively poor bonding between adjacent splats. These splat boundaries could prove detrimental during corrosion tests as they provide a pathway for ingress of corrosive species. Al$_2$O$_3$ grits can be found embedded at the coating substrate interface for both the coatings. Also these are found inside coating for D-Gun samples. These grits came in during the substrate grit blasting and have remained there even after air jet cleaning. Also these are found inside coating for D-Gun samples which could have come during the fine polishing process which use Alumina suspension. Overall, the D-Gun microstructure looks much denser with fewer oxide inclusions.

### 3.2 Roughness, Micro hardness and Porosity of the coatings

|                      | APS coating | D-Gun Coating |
|----------------------|-------------|---------------|
| Roughness (R$_a$), µm| 7           | 10            |
| Micro hardness (HV$_{0.2}$) | µ = 335 with σ = 57 | 421 with σ = 54 |
| Porosity (%)        | 2.1         | 0.9           |

The D-Gun coatings were slightly rougher than the APS coatings as shown in table 3. As expected the D-Gun coatings had higher micro hardness values owing to the better intersplat bonding which in turn is due to the higher particle velocities involved during coating. Also the D-Gun coatings were denser with a total porosity of 0.9% compared to the 2.1% obtained in APS coating. This could be due to the large fraction of unmelted particles in APS coatings which promotes poor splat bonding and results in porosity.
3.3 Post Hot corrosion coating microstructure

Figure 4. BSE image and elemental mapping of the APS sprayed coating after hot corrosion.
Figure 4(a) shows the cross sectional BSE image of the hot corroded APS coated NiCoCrAlY sample. It is evident that the coating has undergone damage due to hot corrosion and the corrosion products
have seeped in through the coating. Around 90 µm thickness of the coating has been affected by the corrosion process and only some 120 µm of the coating is unaffected. Figure 4(b) shows the oxygen ingress into the coating which is of a considerable amount. Figure 4(d) clearly shows the adherent Fe on the coating (Fe$_2$O$_3$) salt. Also the presence of Sulphur, Sodium and Potassium can be seen from the elemental mapping. The top scale is enriched in Cobalt and chromium which indicates the possible formation of oxides or spinel oxides of cobalt and chromium which can be verified by XRD analysis.

Figure 5(a) shows the cross sectional BSE image of the hot corroded D-Gun coated sample. It is clearly evident that it has undergone very little corrosion damage in comparison to its APS counterpart. Only 20 µm of the coating has been affected by the corrosion products and almost 330 µm coating thickness is left unaffected. The oxygen ingress into the coating is also very less. Also from seeing the presence of Fe, Na, K and S only on the topmost layer of the coating, it can be inferred that these species have not been able to destroy the protective layer of coating. No particular enrichment of elements has been found unlike the ones found in APS coatings.

Thus from the FESEM and EDS elemental mapping analysis of the corroded samples, it is conclusive that D-Gun sprayed NiCoCrAlY coatings have exhibited far superior corrosion resistance. This can be attributed to their dense microstructure with minimal porosity and good bonding of individual splats. Porosity and Splat boundaries are the two major short circuit diffusion paths for corrosive species. Since the APS coatings had more of these paths, the corrosive species have been able penetrate to penetrate through the coating easily.

3.4. Post Hot corrosion XRD Analysis

Figure 6 shows the XRD analysis of as coated versus corroded samples of the APS coating. The major peaks in the as coated samples are those of Ni(Cr,Al) followed by Co(Cr,Al). Minor peaks of Co$_3$O$_4$ was also detected which indicated the oxidation of cobalt during coating formation. The corroded samples retained the Ni(Cr,Al) peaks while substantial amounts of NiO peaks were found which indicates the oxidation of the coating. Also a good amount of Spinel oxide NiCr$_2$O$_4$ peaks were found which is generally very protective against oxidation. Also the intensity of Co$_3$O$_4$ peaks increased which indicate more amount of oxidation of cobalt compared to the as coated condition.

Figure 7 shows the XRD analysis of D-Gun sprayed coatings. Like APS as sprayed coatings, this too had Ni(Cr,Al) and Co(Cr,Al) peaks in the as coated condition. But there were no Co$_3$O$_4$ peaks which indicates absence of cobalt oxidation during spraying. Compared to the APS Corroded coatings, there was lesser intensity NiO peaks which suggests the lesser degree of oxidation of the coating. Also since NiO is a fast growing oxide, higher amounts of it in APS coating could have caused the spalling of the oxide scale which is visible in the BSE image. Protective spinel oxide NiCr$_2$O$_4$ was also found in the D-Gun coated corroded samples.

In both the APS and D-Gun corroded samples, KNaSO$_4$ peaks were found in major amounts. Fe$_2$O$_3$ and Na$_2$SO$_4$ peaks were also found in minor amounts. While the Fe$_2$O$_3$ in the applied salt deposit doesn’t react with other two salts, the Na$_2$SO$_4$ and K$_2$SO$_4$ react with each other to form KNaSO$_4$ which could have been the principle species breaking the protective oxide films formed on the coating.
4. CONCLUSION

The hot corrosion performance of Plasma and D-Gun sprayed NiCoCrAlY coating on T91 boiler steel was studied under Alkali iron trisulphate salt deposits at 650°C and the results were reported based on the XRD and Cross sectional FESEM/Elemental mapping analysis of the corroded samples. It was found that the D-Gun sprayed coating showed superior corrosion resistance compared to the APS coating. The better performance was attributed to the dense microstructure and lack of short circuit diffusion paths in the D-Gun coating microstructure. Both the coatings formed Protective NiCr$_2$O$_4$ spinel oxides. But the APS coating formed comparatively more amount of the fast growing NiO scale which resulted in spalling of its oxide layer that further accelerated the corrosion attack. This study also demonstrates the excellent corrosion resistance of D-Gun coatings which could be considered for Hot corrosion applications as a parallel option alongside other high velocity thermal spray processes.
REFERENCES

[1]. Chetal S C, Jayakumar T and Bhaduri A K 2015 Proc. Indian Natn. Sci. Acad.81 739-54
[2]. Viswanathan R and Bakker W 2001 J. Mater. Eng. Perform.10 81-95
[3]. Santosh Kumar, Manoj Kumar and Amit Handa 2018 Eng. Fail. Anal.94 379-95
[4]. Khanna A S 2002 High Temperature Oxidation and Corrosion (Materials park, OH: ASM International)
[5]. Davis J R 2004 Handbook of Thermal Spray Technology (Materials park, OH: TSS/ASM International)
[6]. Lech Pawlowski 2008 The Science and Engineering of Thermal Spray Coatings (Wiley)
[7]. Chatha S S, Hazoor S Sidhu and Buta S Sidhu 2013 J. Therm. Spray Techn.22(5)838-47
[8]. Rakesh Bhatia, Hazoor S Sidhu and Buta S Sidhu 2015 Metall. Mater. Trans. E2(1)70-86
[9]. Chatha S S, Hazoor S Sidhu and Buta S Sidhu 2016 Adv. Mater. Res.1137 88-100
[10]. Chatha S S, Hazoor S Sidhu and Buta S Sidhu 2012 Surf. Coat. Technol.206 4212-24
[11]. Chatha S S, Hazoor S Sidhu and Buta S Sidhu 2012 Surf. Coat. Technol.206 3839-50
[12]. Hussain T, Dudziak T, Simms N J and Nicholls J R 2013 J. Therm. Spray Techn.22(5) 797-807
[13]. Reza Jafari and Esmaeil Sadeghi 2019 Corros. Sci.160 108066
[14]. Sadeghimeresht E, Markocsan N and Nylen P 2016 J. Therm. Spray Techn.25 1604-16