Experimental Evaluation of High Temperature Corrosion Performance of 75Ni25Cr Coated and Bare 347H SS in Air and Simulated Husk Fired Boiler Environment

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Abstract. Corrosion occurring at elevated temperatures is a serious problem in areas such as gas turbine applications and power plants that use high temperature boilers. In this paper, we carry out experimental investigation for reducing corrosion rate so as to enhance the corrosion and wear characteristics of 347HSS and quantify the effect of 75Ni25Cr on 347HSS in terms of improved corrosion resistance. A coating of 75Ni25Cr was deposited on 347HSS boiler tube by the process of Detonation Gun. Corrosion studies were conducted on bare as well as D-Gun coated 347H stainless steel specimens in air and simulated husk fired boiler atmosphere at 800 °C under cyclic conditions. Each cycle consisted one hour of heating in the tubular furnace and 20 min of cooling at room temperature. Fifty such cycles were completed to observe performance of these specimens. The weight change measurements were performed after each cycle to establish the kinetics of corrosion using weighing balance. Scanning Electron Microscopy, X-ray diffraction and X-ray mapping analysis techniques were used to analyse the corrosion products formed on the surface of these substrates.

Keywords: D-gun, 75Ni25Cr, High temperature corrosion

1. Introduction
In thermal power plants the efficiency of the boilers may be increased by rising the pressure and temperature of boiler [2]. In past the temperature of boiler was between 400 °C to 600 °C but nowadays the temperature has been increased to 700 °C to 900 °C. However, at such high temperature oxidation of superheater tubes in boiler occurs at very fast rate [1]. These components are made up of austenitic stainless steel. To reduce oxidation rate and sustain longer life of components, austenitic steels having higher chromium content is used such as 347HSS and 304SS [3]. The presence of high amount of chromium can help in development of protective oxide scale that tend to reduce oxidation of parent material for longer hours [4]. These alloys undergo very intense oxidation at an elevated temperature, which reduces the life of components significantly [2, 3, 4]. Hence it is important to provide some kind of external protection to increase the life of the components. There are wide varieties of applications where thermal sprayed coatings have been employed. Among these applications surface treatment of mechanical parts has been used so as to prevent oxidation. [6].
The objective of thermal sprayed coating is to improve surface properties like low porosity, resistance to corrosion and high bond strength which are desired for the current study and are best achieved by D-gun process [7]. D-gun spraying process converts the consumable material into molten droplets and then deposits these molten droplets on parent material at supersonic speed to form dense layered coating. This technique is capable of depositing wider range of metallic cermet and ceramic powder on various alloys [7]. The present study focuses on high temperature corrosion behavior of bare 347H SS sample and 347H SS sample coated with 75Ni25Cr by D-Gun process in air and simulated boiler environment at 800 °C under cyclic condition.

2. Experimentation

2.1. Substrate and Coating deposition

347HSS having composition 17−19%Cr, 9−13%Ni, 0.08%C, 2%Mn, 0.75%Si, 0.045%P, 0.030%, S was procured from Cheema Boilers located at Ropar Punjab in the form of sheet. The samples were cut down from the 347HSS sheet into 15 mm x 20 mm. Thickness of both the samples have been reduced to 5 mm. Bare and Ni − 25Cr coated 347HSS were used for oxidation studies. D-gun surface coating technique was used for coating steel substrate. Before coating deposition, the substrate were polished using emery papers of 220, 400 and 600 grit size followed by cloth polishing. After that substrates were cleaned with the distilled water and acetone. The samples were coated with Ni25Cr coating powder by using D-Gun technique. D-gun technique was available at SVX Powder M Surface, Greater Noida, Uttar Pradesh, India.

2.2. Oxidation Test

Alumina boats were used in the experiment to hold the samples. They were heated repeatedly at 1000 °C for two hours cycles until the weight of boat became constant. To monitor the physical dimensions and weight change of the sample, vernier caliper and digital weighing balance were used respectively. To carryout oxidation study, the specimens were subjected to 800 °C in a tubular furnace for 50 cycles. Every cycle was composed of 1 hour of heating and 20 mins of cooling in furnace and air respectively. After each cycle samples were weighted using digital weighing balance and the weight of these samples were recorded.

2.3. High Temperature Corrosion Test

At the beginning of high temperature corrosion test the salt solution was made by mixing distilled water with 10%KCl, 10%NaCl, 40%Na2SO4 and K2SO4 in china dish. This solution was applied on all six surfaces of the substrate and approximately about 3-4 mg was deposited per cm² surface area of the sample. These substrates were then heated at 80 °C for two hours in tubular furnace in order to evaporate the moisture from the salt that was applied on sample. After that samples were kept in the alumina boats and where subjected to 50 cycles of heating and cooling as was done in oxidation test.

3. Results

3.1. Visual Analysis for Oxidation Test

Visually every sample was observed after each cycle. This type of inspection helps in determining the various changes in colour, luster and amount of spallation that occur during different cycles. It also tends to better understanding of development of cracks if any that have occurred during experimentation.

Macrophotos of bare 347H SS and 75Ni25Cr coated 347H SS after 1st cycle 5th cycle and 50th cycle of oxidation at 800°C has been shown in Figure 1. In case of bare 347H SS, it was observed that reddish brown scale was formed just after 1st cycle of oxidation. After 5th cycle
Figure 1. Visual macro-photos of (a) Polished Bare 347H SS and after undergoing to oxidation at 800°C in furnace for (b) 1st cycle formation of reddish brown oxide layer, (c) 15th cycle formation of grey oxide layer (d) 50th cycles formation of dark grey oxide layer

Figure 2. Visual macrophotos of (a) 75Ni25Cr coated 347H SS and after undergoing to oxidation at 800°C in furnace for (b) 1st cycle (c) 15th cycle (d) 50th cycles formation of green oxide layer of oxidation, reddish oxide layer disappeared and pitch grey oxide appeared on the surface of sample. No further changes were seen upto 50th cycles. On the other hand light greenish oxide layer appeared on the surface of Ni-25Cr coated 347H SS just after 1st cycle of oxidation and remained till 5th cycle. After 6th cycle, it was noticed that green coloured layer appeared on the surface of sample and remained till 50th cycle has been shown in Figure 2.

3.2. Visual Analysis of Hot Corrosion Test
The substrates during high temperature corrosion study reviled change in colour as there was formation of oxide scale at the surface of specimens. Macro-photos of bare 347HSS and 75Ni25Cr coated 347HSS after 1st cycle, 15th cycle and 50th cycle of hot corrosion test at
800 °C has been shown in Figure 3 and Figure 4 respectively. Orange colour oxide scale was

![Figure 3. Visual macro-photos of (a) Polished Bare 347HSS and after ungoing to hot corrosion test in salt atmosphere at 800 °C for (b) 1st cycle formation of orange coloured oxide layer , (c) 15th cycle (d) 50th cycles excessive spallation occurs.](image)

formed on bare 347H stainless steel after the completion of 1st cycle. After 15th cycle noticeable spallation was observed and the colour of oxide layer changed to light blue with light orange patches on it. Subsequently after 50th cycle high amount of sputtering of bare 347HSS was observed. In case of 75Ni25Cr coated sample showed better resistance to corrosion as there was negligible amount of spallation. From Figure 4 it can be clearly seen that colour of sample changed to greenish blue after 1st cycle. No colour change after 1st cycle was observed.

![Figure 4. Visual macro-photos of (a) Ni25Cr coated 347HSS and after undergoing to hot corrosion test in salt atmosphere at 800 °C for (b) 1st cycle, (c) 15th cycle formation of blue coloured oxide layer (d) 50th cycles.](image)

3.3. Weight Change Analysis

Weight change data in (mg/mm²)² versus number of cycles for uncoated and coated 347HSS specimens subjected to oxidation and high temperature corrosion in simulated environment at 800 °C for fifty cycles were plotted and shown in Figure 5 and Figure 6 respectively. It can
Table 1. $k_p$ values of bare 347HSS and 75Ni25Cr coated stainless steel

| Substrate                              | Parabolic rate constant $k_p$ ($10^{-8}g^2cm^{-4}s^{-1}$) |
|----------------------------------------|------------------------------------------------------------|
| Bare 347HSS Under oxidation test       | 0.011                                                      |
| 75Ni25Cr coated 347HSS under oxidation test | 0.0005                                                   |
| Bare 347HSS under hot corrosion test   | 2                                                          |
| 75Ni25Cr coated 347HSS under hot corrosion test | 0.1                                                       |

Figure 5. $(Weight gain/area)^2$ vs number of cycles plot for bare 347HSS and coated 347HSS undergone oxidation test.

Figure 6. $(Weight gain/area)^2$ vs number of cycles plot for bare 347HSS and coated 347HSS undergone hot corrosion test.

be seen from the graph that both coated sample and bare sample followed parabolic behaviour. Parabolic rate constant $K_p$ was also calculated for both the samples (bare as well as 75Ni25Cr coated 347HSS). Values of $K_p$ are shown in table 1

3.4. Surface analysis
Surface morphology of bare and coated samples after subjected to 50 cycles of oxidation at 800 °C has been shown in Figure 7(a). From figure it can be seen dense porous grey oxide layer
Figure 7. SEM/EDS analysis of oxidized (a) bare 347HSS, (b) 75Ni25Cr coated 347HSS, after 50 cycles.

Figure 8. SEM/EDS analysis of hot corroded (a) Bare 347HSS, (b) 75Ni25Cr coated 347HSS, under simulated boiler environment after 50 cycles.
appeared on the bare 347HSS specimen. High Cr content was shown by EDS which may be due to the presence of Cr oxide layer which may be protecting the metal form further oxidation. In case of Ni25Cr coated sample dense clusters of oxide was formed on the surface of the coating as shown in Figure 7(b) For high temperature corrosion test oxide scale formed on the surface of bare 347H stainless steel and 75Ni25Cr coated 347H stainless steel after cyclic oxidation has been shown in Figure 8. Irregular structure and porous oxide scale was found in case of bare347HSS and in case of Ni – 25Cr coated 347HSS, platelets like structure was formed. Occurrence of O2 and Cr at the surface of both the specimens in extensive quantities was found by EDS analysis, this might be due to the presence of high quantity of Cr2O3. The presence of Cr2O3 was also detected by XRD analysis which proves its occurrence.

3.5. XRD
X-ray diffraction revealed formation of Cr2O3 and NiCr2O4 for both coated as well as bare sample which were subjected to oxidation test as shown in Figure 9. Cr2O3 was discovered as major phase. Peaks of Na2CrO4, Fe2O3, and MnO2 were also identified.

XRD diffractograms for coated and uncoated 347H stainless steel subjected to high temperature corrosion in (40% Na2SO4, 10% NaCl, 40% K2SO4, 10 % KCl) environment at 800°C for 50 cycles are depicted in Figure 10. To identify various phases present in the bare and coated 347HSS which have been run under hot corrosion test, XRD analysis was done. XRD of bare sample shows the existence of corrosion protective oxides of, Cr2O3, NiCr2O4, NiO, K2CrO4 etc. Presence of non-protective oxides i.e Fe2O3 was majorly present in bare 347HSS sample. On the other hand major peaks on coated sample were those that help in reducing rate of corrosion like Cr2O3, NiCr2O4, NiO, K2CrO4.

![XRD diagram](image_url)

**Figure 9.** XRD analysis of bare 347HSS0 and 75Ni25Cr coated 347HSS under oxidation for 50 cycles.
Figure 10. XRD analysis of bare 347HSS and 75Ni25Cr coated 347HSS under high temperature corrosion for 50 cycles.

4. Discussion
From visual macrophotos it can be clearly observed that both bare and 75Ni25Cr coated 347H stainless steel showed good corrosion resistance after oxidation in air at 800°C. No spallation or sputtering was observed throughout the 50th cycle. Occurrence of reddish orange oxide just after the 1st cycle may be due to formation of iron oxide ($Fe_3O_4$) [10]. Weight gain analysis depicted that both the samples have good oxidation resistance which may be due to presence of Cr and Ni which forms the protective oxide when combines with oxygen [11]. Weight gain graph of bare 347HSS showed a little increase in weight during first few cycles which can be attributed to the initial development of oxide scale at 800°C. SEM/EDS study depicted presence of rhombohedral oxide layer on the exterior surface of bare 347HSS. Cr and O$_2$ where major phases present in this layer. On the other hand in case of Ni – 25Cr coated 347HSS presence of thick and dense oxide layer was observed which was composed of chromium, nickel and oxygen. In the literature it was reported that $Cr_2O_3$ scale has rhombohedral structure [8, 9]. Therefore it could be inferred that the $Cr_2O_3$ oxide scale was present in both of the specimens. XRD analysis also revealed that the both specimens consist of $Cr_2O_3$ as protective oxide layer. The substrates during High temperature corrosion study reviled change in colouration as there was development of oxide scale on the crest of the surface of specimens at a temperature of 800°C. Orange coloured oxide scale was formed of bare 347H stainless steel after the completion of 1st cycle which can be due to the occurrence of iron oxide layer. After 15th cycle noticeable spallation was observed and the colour of oxide layer changed to light blue with light orange patches on it. Subsequently after 50th cycle high amount of sputtering of bare 347HSS was observed. In case of 75Ni25Cr coated sample showed better resistance to corrosion as there was negligible amount of spallation. From Figure 4 it could be simply seen that colour of sample changed to greenish blue after 1st cycle. No colour change after 1st cycle was observed. Weight gain analysis showed that 75Ni25Cr coated samples provided better protection towards corrosion than bare 347HSS sample as $K_p$ value of coated sample was far less than latter one. Also XRD analysis revealed formation of major peaks on coated sample were those that help in reducing rate of corrosion like $Cr_2O_3$, 

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NiCr₂O₄, NiO, K₂CrO₄.

5. Conclusions

• Both bare and Ni₂₅Cr coated 347HSS showed good resistance to corrosion in air, whereas in simulated bio-fuel fired boiler environment bare 347HSS underwent excessive spallation.
• During hot corrosion test, higher weight gain of samples was experienced in the present study in the given environments for both the samples which may be due to the fact that molten salt species may have penetrated into the coating to cause fast corrosion. Nevertheless after formation of oxide scale around the specimens the rate of weight gain decreased.
• Porous irregular shaped oxide layer was formed on the bare 347HSS sample. SEM/EDS analysis showed presence Fe, O and Ni where present in major quantities. XRD analysis revealed Fe₂O₃ as major peaks present in substrate which explains the reason for excessive spallation.
• However the study conducted in simulated husk fired boiler environment revealed that 75Ni₂₅Cr coated 347HSS sample exhibited superior corrosion performance which is due to the formation of protective Cr₂O₃ and NiCr₂O₄ oxide layer as compared to excessive formation of unprotective Fe₂O₃ oxide layer on bare 347HSS sample.

6. References

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