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Corrosion Studies on HVOF Sprayed Ni-20Cr and Ni-50Cr Coatings on ASTM A213 TP347H Boiler Steel at 700^{0}C

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Abstract - **Ni-20Cr and Ni-50Cr coatings were deposited on ASTM A213 TP347H boiler tube steel by High Velocity Oxy Fuel (HVOF) thermal spray process. High temperature corrosion studies were conducted to investigate the comparative performance of the coatings. The tests were conducted in a simulated boiler environment (Na_2SO_4–60%V_2O_5) at 700^{0}C for 50 cycles. Each cycle consisted 1 hour of heating in the silicon carbide tube furnace followed by 20 min of cooling in air. The weight change measurements were recorded after each cycle to establish the kinetics of high temperature corrosion. The corroded samples were characterized by SEM/EDS analysis. It was observed that Ni-50Cr coated specimen was found to be more protective than Ni-20Cr coated specimen.**

Keywords: **High Temperature Corrosion, HVOF Thermal Spray, Boiler Steel.**

I. Introduction

Hot corrosion degradation of metals and alloys has been recognized as a serious problem for many high temperature aggressive environment applications, such as boilers, internal combustion engines, gas turbines, fluidized bed combustion and industrial waste incinerators [1-4]. Due to depletion of high grade fuels and for economic reasons, residual fuel oil along with coal is extensively used in the energy generation systems, which contains sodium, vanadium and sulphur as impurities [5]. In the combustion system, Na and S react with each other and form Na_2SO_4, Vanadium reacts with oxygen to form V_2O_5 and other complex vanadates. These compounds commonly known as ash, deposit on the surface of the materials and induce corrosion. The degradation of material occurs when these molten compounds destroy the protective oxide layers that naturally form on materials during boiler/ gas turbine operation [6-7]. Coating provides a way of extending the limits of use of materials at the upper end of their performance capabilities, by allowing the mechanical properties of substrate materials to be maintained while protecting them against wear or corrosion [5].

High temperature corrosion (hot corrosion) is a serious problem in power generation equipment, in gas turbines for ships and aircraft and in other energy conversion and chemical process systems e.g. in boilers, internal combustion engines, fluidized bed combustion and industrial waste incinerators [8]. The coating can add value t products up to 10 times of their cost [9]. Boiler steels are unable to meet requirement for both the high temperature strength and the high temperature corrosion [10]. The High Velocity Oxy Fuel (HVOF) process is reported to be a versatile technology and has been adopted by many industries due to its flexibility, cost effectiveness and the superior quality of coating produced. The hypersonic velocity of the flame shortens the time of interaction between the powder and flame, whereas low temperature of flame limits the grain growth and decomposition of coating. Due to the high impact velocity of particles the coatings show a high adhesive strength, high cohesive strength of individual splats, uniform microstructure, high density and low porosity [11-14].

The objective of this work is to explore the possibility of deposition of Ni-20Cr and Ni-50Cr coatings on ASTM A213 TP347H, by HVOF spray method and to study its high temperature performance in a simulated residual fuel fired boiler environment of molten salt (Na_2SO_4-60%V_2O_5) at 700^{0}C. The selected steel is used extensively for power plant boiler component, mainly in the super heater zone, where it has been observed that it suffers from high temperature erosion-corrosion by fly as particles. Moreover, the high-temperature boiler studies could provide an idea regarding the adhesion between the coatings and the substrate steels under thermal shocks [15]. The information arising out from the investigation will be useful to explore the possibility

of the use of HVOF spray coatings on the boiler tubes for increasing the life of the boiler tubes. The HVOF coatings are used in chemical industry, petroleum industry, glass mould industry and other industries [16].

II. Experimentation

A.Substrate Material

The boiler tube steel, ASTM A213 TP347H with the chemical composition as shown in Table I, have been used as substrate steel. This material is used as boiler tube material in some of power plants in northern India. The steel samples were cut to form approximately 20 x 15 x 5 mm^3 sized specimens. The specimens were polished and grit blasted with Al_2O_3 (grit 60) prior to application of HVOF spray coatings.

Table I Chemical Composition Of Astm A213 TP347h Steel (In %Age)

C	0.04 - 0.1
Mn	2.0
P	0.04 max
S	0.03 max
Si	0.75
Cr	17 - 19
Ni	9 - 13
Fe	65.08

B.Development of Coatings

The Ni-20Cr and Ni-50Cr powders were coated on the steel samples using the commercially available HVOF spray process (HIPOJET-2700-M) at Metallurgical Equipment Corporation Pvt. Ltd Jodhpur (Rajasthan). Samples were grit-blasted before the HVOF spraying. All the process parameters, including the spray distance were kept constant throughout the coating process. The coating was deposited on all six sides of the specimen. The size of both the coatings was -45+15µm. (Grain size)

Table II Spray Parameters of HV of As-Sprayed N_i-20Cr and N_i-50 Cr.

Oxygen Flow rate	250 l/m
Air Flow rate	600
Spray distance	18 cm
Oxygen pressure	9 kg/cm^2

C.*Characterization of As-Sprayed coatings*

The as-sprayed coatings were examined visually. The Surface Roughness of the as sprayed coated samples was measured with the help of surface roughness tester. The each 3 fields on the surface of each coated specimens were used to obtain the value of surface roughness (µm). Porosity of the as-sprayed coatings was measured with the help of metallurgical microscope with image analyzer. The 3 field on the surface of each coated specimens were used to obtain the value of porosity. FE-SEM/EDS (FE-SEM, FEI, Quanta 200F) analysis was done to characterize the surface morphology of the HVOF sprayed Ni-20Cr and Ni-50Cr coated 347H steel before and after exposure to molten salt environment at 700^{0}C for 50 cycles.

D. Molten Salt Environment

Hot corrosion studies were performed in a molten salt environment (Na_2SO_4-60%V_2O_5) for 50 cycles under the cyclic conditions. Each cycle consisted of 1 hour heating at 700^{0}C in a silicon carbide tube furnace followed by 20 minutes of cooling at room temperature. This cyclic study provides the most severe conditions for testing and represents the actual industrial environment, where breakdown and shutdown occurs frequently. A cyclic study of 50 cycles had been performed as the study of 50 cycles is considered to be adequate for attaining the steady state oxidation for the material [17-18]. The studies were performed on coated specimens for the purpose of comparison. The specimens were mirror polished down with 1 mm alumina polishing on cloth wheel before the test. A coating of uniform thickness with 3 to 5 mg cm^{-2} of Na_2SO_4-60%V_2O_5 was applied with a camel hairbrush on the preheated sample (250^{0}C). The weight change measurements were taken at the end of each cycle with the help of an electronic balance having a sensitivity of 10^{-3} g. The mass change technique was used to formulate the kinetics of corrosion. Visual observations were also made after the end of each cycle with regards to colour, lustre, adherence/spallation tendency and other physical aspect of the oxide scale/coatings. After the hot corrosion studies, the corroded samples were analyzed by SEM/EDS analysis.

III. Results

A.Visual Observation and Thickness

The HVOF sprayed Ni-20Cr and Ni-50Cr was silver grey in colour. The thickness of the coating was found to be 200 - 250 µm. The thickness of the coating was found by (Elcometer) at Metallurgical Equipment Corporation Pvt. Ltd Jodhpur (Rajasthan).

B.Surface Roughness and Porosity

The surface roughness of as-sprayed Ni-20Cr and Ni-50Cr coatings were measured. The surface roughness of the as-sprayed Ni-20Cr coating was found to be 6.519µm whereas in case of Ni-50Cr was found to be 6.742**µm**. The surface roughness was measured with the help of surface roughness tester (Mitutoyo). The porosity value of as sprayed Ni-20Cr coating was found to be 0.40% whereas of Ni-50Cr coating was found to be 0.62%. The porosity of both Ni-20Cr and Ni-50Cr was measured with the help of Metallurgical microscope with image analyzer (Lietz Tooling system India Pvt. Ltd).

C.SEM/EDS analysis of As-Sprayed Coatings

The FE-SEM micrograph of as-sprayed Ni-20Cr coating is shown in Fig. 1a. The microstructure consists of spongy particles. The EDS analysis of the coating at two different points 1 and 2 indicated that the coating has a nearly uniform composition. As expected, Ni has been found as the main constituent. The marginal presence of O in the composition is also observed. The FE-SEM micrograph of as-sprayed Ni-50Cr showing elemental composition at some points is depicted in Fig 1b. A uniform microstructure is observed. Presence of Cr is more at both the selected points is more.

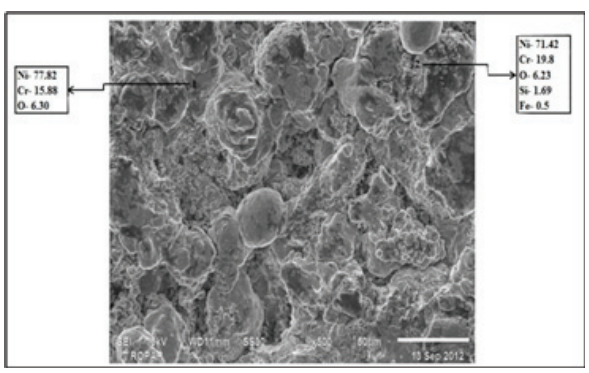

Fig. 1a FE-SEM/EDS analysis of HVOF sprayed Ni-20Cr coated 347H steel

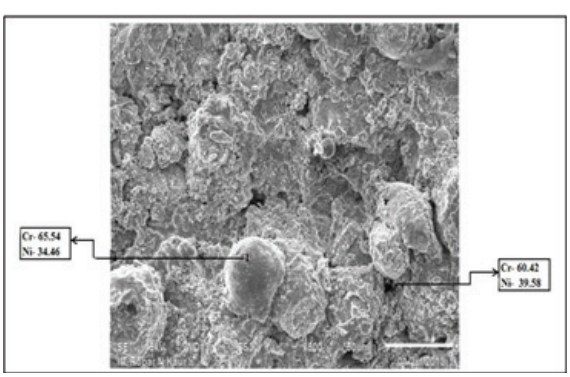

Fig. 1b FE-SEM/EDS analysis of HVOF sprayed Ni-50Cr coated 347H steel.

D. High Temperature Corrosion Behaviour

The weight change plot for the HVOF sprayed Ni-20Cr and Ni-50Cr coated substrate subjected to the cyclic studies for 50 cycles at 700^0C have been shown in Fig 2. During the high temperature corrosion testing in the aggressive molten salt environment, the HVOF sprayed Ni-20Cr showed higher weight loss upto 10 cycles, thereafter upto the end of 28th cycle it shows very small appreciable change apart from the occurrence of very fine powder in the boat. It is worth mentioning that there was no crack formation of the oxide scales for this coating during the whole 50h exposure. In case of HVOF sprayed Ni-50Cr substrate comparatively lesser weight loss was observed in the initial cycles of study cycle and it almost remain consistent upto 32nd cycle. Slight weight change was observed after that, however the trend showed that weight loss of Ni-50Cr coated steel was less as compared to that of Ni-20Cr coated steel.

E. SEM/EDS Analysis

The SEM/EDS analysis for the HVOF sprayed Ni-20Cr coated 347H steel after exposure to the molten salt environment for 50 cycles has been shown in Fig. 3a. The oxide scale is found to have distinct micro-structural features. Although it appears to have a crystalline microstructure, in general, yet the crystal size and shape distribution vary in different zone of the scale. From the EDS analysis it concludes that Ni, Cr and O are the main elements. The SEM/EDS analysis for the HVOF sprayed Ni-50Cr coated 347H steel after exposure to the molten salt environment for 50 cycles has been shown in Fig. 3b. From EDS analysis it concludes that Cr and o as main elements. The oxide scale is found to have distinct microstructural features in different areas.

IV. Discussion

The HVOF spray process provides the possibility of the deposition of Ni-20Cr and Ni-50Cr coatings on the 347H steel. A coating of about 200 - 250 µm was obtained. The surface roughness of HVOF sprayed Ni-20Cr coated 347H was found to be 6.519**µm.** The surface roughness of HVOF sprayed Ni-50Cr coated 347H was found to be 6.742 **µm.** The porosity of HVOF sprayed Ni-20Cr coated 347H was found to be 0.4% whereas for HVOF sprayed Ni-50Cr coating was found to be 0.62%. The coatings should have minimum possible porosity because high values can do harm

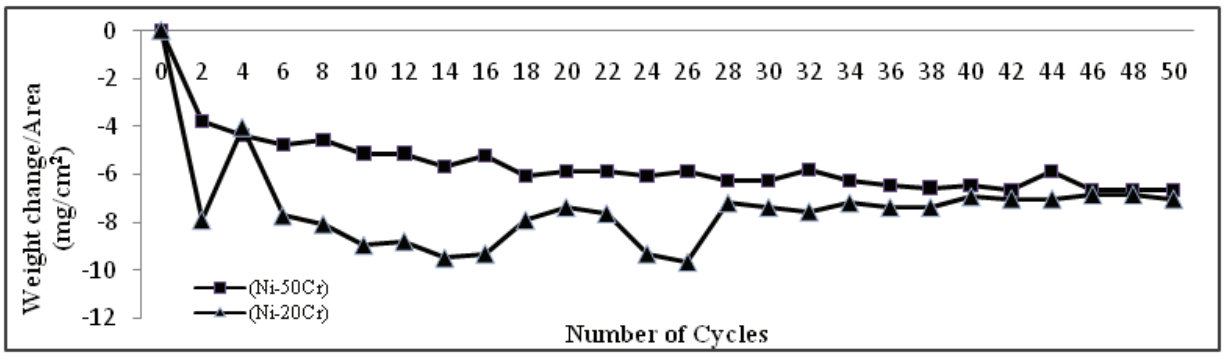

Fig. 2 Weight change/area vs. number of cycles for HVOF sprayed Ni-20Cr and Ni-50Cr coated 347H steel

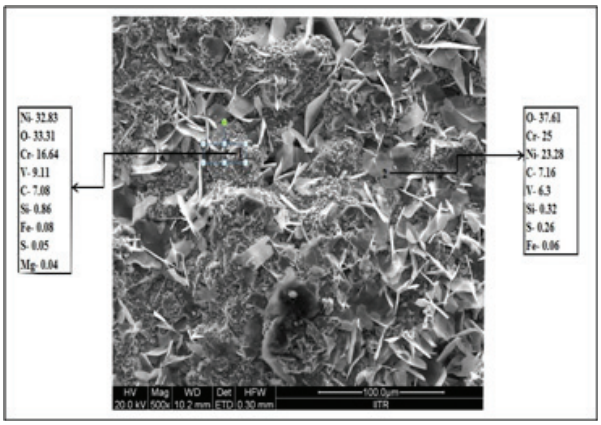

Fig. 3a FE-SEM/EDS analysis of HVOF sprayed Ni-20Cr coated 347H steel subjected to simulated boiler environment (Na_2SO_4-60%V_2O_5) at 700^{0}C for 50 cycles.

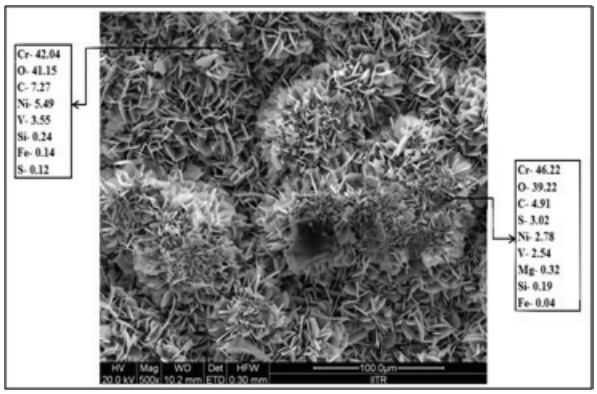

Fig. 3b FE-SEM/EDS analysis of HVOF sprayed Ni-50Cr coated 347H steel subjected to simulated boiler environment (Na_2SO_4-60%V_2O_5) at 700^{0}C for 50 cycles.

to the persistent erosion- corrosion resistance of thermal spray coatings. The average porosity of the HVOF coating has been found to be marginal with a porosity value of less than 1%.The measured value of porosity is in good agreement with the earlier studies. Sidhu et al. [19] also observed the similar features of HVOF sprayed coatings. The Ni-50Cr coating was successful in decreasing the corrosion rate of the boiler steel significantly as compared to Ni-20Cr coating as shown in Fig. 2. The SEM/EDS analysis of HVOF sprayed Ni-20Cr and Ni-50Cr coated 347H have been shown in Fig. 3a and Fig. 3b. The major constituents elements of HVOF sprayed Ni-20Cr coated steel was Ni, Cr and O. The major constituents elements of HVOF sprayed Ni-50Cr coated steel was Cr and O.

V. Conclusion

The HVOF process provides the possibility of developing Ni-20Cr and Ni-50Cr coatings on the 347H steel. The value of surface roughness in case of HVOF sprayed Ni-20Cr coated substrate was found to be better than HVOF sprayed Ni-50Cr coated substrate. The value of porosity in case of HVOF sprayed Ni-20Cr coated substrate was founds to be better than HVOF sprayed Ni-50Cr coated substrate. The HVOF sprayed Ni-50Cr coated substrate was found to be successful in reducing the corrosion rate of the 347H boiler steel, although the diffusion of Fe from the substrate to the coating was observed.

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