Study Of Cyclic High Temperature Hot-Corrosion Behaviour of Bare And Ni-Cr Coating Over Mild Steel

Jitendra Kumar Pal[1], Shivam Trivedi[2]

M.Tech Scholar, Mechanical Engineering Department, Faculty of Engineering and Technology, Rama University,[1]
Assistant Professor, Mechanical Engineering Department, FET, Rama University,[2]
Kanpur, Uttar Pradesh, India
jpal3230@gmail.com[1] ,shivamtrivedi.psit@gmail.com[2]

Abstract— **Hot-Corrosion behaviour of mild steel at different Ni-Cr coatings thickness are studied, and also resistance offered by different coating thickness is also investigated. Hardness of mild steel was found to be increased from 202.25 to 341.75 VHN after the application of coatings. Parabolic rate constant (K_p) for high temperature oxidation of bare, 200-250µm, and 250-300µm thick Ni-Cr coated mild steel were calculated to be 1232.47, 3.98677, and 5.05509 ($\times 10^{-10} g^2 cm^{-4} s^{-1}$) respectively,**

Keywords: Hot-Corrosion; high temperature; thermal spray coatings; D-gun spray.

I. INTRODUCTION

Deterioration of a metal or its properties in the in the presence of water or an aqueous medium due to the reactions with its surrounding environment is known as corrosion. As a result of corrosion, metal gets converted into its compounds such as oxide, chloride, nitride, sulphide etc. depending on the metals exposed environment. Corrosion may be classified as dry corrosion, wet corrosion and hot corrosion. Dry corrosion or oxidation occurs when oxygen present in the air reacts with metal in the absence of liquid. Wet corrosion occurs in an aqueous medium in the presence of dissolved salts such as chlorides, sulphates or oxides and deposited onto the surface. Accelerated corrosion is experienced by metals and alloys when they are in contact with a thin film of fused salt in an oxidizing gas. This mode of attack is called hot-corrosion [1].Corrosion finds its place in many parts of our lives, rust holes in the body panels and outdoor rusting of steel household and garden appliances is a common sign of corrosion. Repairs made for the plumbing systems and the water and sewer utility lines, stains in the cooking utensil from hot foods are all effects caused by "corrosion". Hot corrosion of various parts used in gas turbine, rocket engines, furnaces, and high-temperature petro-chemical systems exposed to cyclic heating has been recognized as a severe problem, which results in the parts wall thinning and unwanted failures causing heavy losses. Hot corrosion often increases the corrosion loss of heat resisting alloys by over hundred times, in comparison to that caused by simple oxidation. Hot corrosion is generally dependent on temperature, the maximum effect lies in the

temperature range of 800-1000°C [2].Power plants are one of the major industries suffering from severe corrosion problems resulting in the enormous losses. For example, steam temperature of boilers is limited by corrosion and creep resistance of the components used in the boilers, which affects the thermal efficiency. Consequently, the thermal efficiency goes down and the electricity production is affected. Maintenance costs for replacing the broken pipes in these installations are also very high and to be estimated up to 54% of the total production costs. Other than the direct economic losses, indirect cost resulting from actual or possible effects of corrosion are more difficult to evaluate but are probably even greater. Some of them are (a) Plant downtime (b) Loss of product (c) Loss of efficiency (d) Contamination (e) Overdesign .Hot-corrosion issue can be resolved through number of preventive measures like controlling process parameters, fuel selection, design aspect, chemical additive, use of inhibitors, application of protective coatings etc. One of the economical, efficient and reliable ways to control or prevent the hot-corrosion problems is the application of a thin layer of corrosion resistant coating over the components exposed to corrosive environment. Coatings that have good thermal conductivity may enhance the service life of the components without affecting the thermal efficiency of the system. A key property of coating is their ability to adhere to surfaces contaminated with oxides, scales loose dirt, and organic matter, such as greases and oils. However, any coating system will perform better over a well-prepared surface with little or no foreign substances present. It has been said that a poor coating applied to a well-prepared surface is better than a good coating applied on a poorly prepared surface. Therefore, careful selection and quality control of surface-preparation processes are usually well worth the extra time and expense. Hence, D-gun spray coating is used to deposit coatings on heat facing components of the large units. Coating enhances the life-time of the material up to 10 times of coatings cost. The composition and structure of the coatings depend on exposed environments [2].Ni-Cr coatings have high temperature hot-corrosion resistance properties in corrosive environment [3]. During the service life of components, applied coatings are expected to form slow growing protective oxides on the exposed surface.

These protective oxides should not allow the corrosive species to diffuse into the coating and to reach the substrate material, which results in the failure of the system [4].

II. EXPERIMENTAL PROCEDURE

Mild steel was procured in the form of rectangular sheet. Chemical compositions of substrate materials was determined using Spark spectroscopy and represented in Table 1, respectively.

TABLE 1. CHEMICAL COMPOSITION OF MILD STEEL.

ELEMENTS	C	Mn	Si	S	P	Fe
Wt. %	0.18	0.89	0.21	0.017	0.018	balance

Specimens were cut in the dimensions of 15 x 15 x 5mm, followed by polishing using 320, 600, 1000, 1200 and 1500 grit size polishing papers. Before application of coatings, the specimens were degreased with the help of acetone. D-gun spray technique was used to deposit the NiCr coating over the specimens. Coatings were deposited on the specimens in the thickness ranging of 200-250 μm and 250-300 μm on the six faces of the mild steel specimens at SVX Powder M Surface Pvt. Ltd., Greater Noida. Mechanical interlocking is the main mechanism of thermal spray coating adhesion/adherence.

High temperature hot-corrosion study of bare and Ni-Cr coated mild steel specimens were conducted in a laboratory muffle furnace at a temperature of 750±10°C for 50 cycles with holding time 1 h. Specimens were kept in alumina boats during the experiments. The boats used for the study were preheated at a constant temperature of 1000°C for 10 h, with the assumption that the weight of the boat would remain constant during the course of high temperature study. Specimens were weighing after each cycle with the help of electronics weighing machine (DAB 220). Hardness were performed on bare and Ni-Cr coated specimens at 5 kg load and with dwell time 10 s with the help of Vickers hardness testing machine (VM-50). Scanning electron microscope (Carl Zeiss EVO 50) was used to study images, EDS and elemental mapping of the specimens.

III. RESULTS AND DISCUSSION

3.1. Mild steel

Splat-like layered morphologies was present in the coatings due to the deposition and re-solidification of molten or semi molten powder particles. There were no indications of micro cracks in the microstructures. The dark spots in the coating/coating substrate interface were mostly inclusions (Fig. 1). The circular jet-black dark dots were expected to be porosity. Some micro-pores were present and randomly distributed in the coatings. Further all the coatings irrespective of coating powder composition

were found to be free from any visible surface cracks. The coatings in general had smooth surfaces. Energy dispersive x-ray spectroscopy (EDS) and elemental mapping of as-sprayed 250-300 μm thick Ni-Cr coated mild steel specimen is shown in the fig. 1. Value of average hardness of bare mild steel specimen was 202 VHN. Hardness increased rapidly with application of coatings from 202.25 VHN to 341.75 VHN.
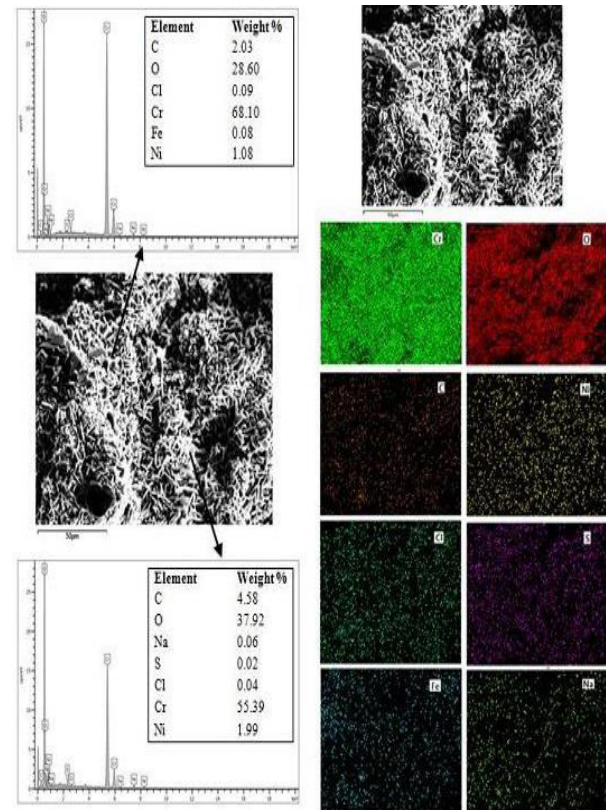

Figure 1. EDS (area analysis) and elemental mapping of as sprayed 250-300 μm thick Ni-Cr coating on mild steel.

Ni-Cr coated specimens showed minor weight gain up to 50th cycle, whereas high weight gains were observed in case of bare mild steel starting from 1st cycle and continued till 50th cycle. During oxidation of bare mild steel, scale formation was noticed at the end of 1st cycle and swelling of the scale was observed at the end of 8th cycle. Hot-corroded bare mild steel had irregular scales with cracks at the edges. The fragile scale formed over the surface of the bare mild steel that could not sustained, and started peeling off from the surface. Minor spalling of scale started at the end of 19th cycle for bare specimens. However, the scale formation continued till 50th cycle. Also some metallic sound was observed during cooling. Coated mild steel showed a continuous and defect free interfacial contact with the substrate steel. The colour of oxide formed just after 1st cycle over the bare and coated mild steel specimens was dark gray which remained till the completion of 50th cycle.

Fig. 2 shows the surface morphology (EDS and elemental mapping) of the bare and D-gun sprayed NiCr coated mild steel specimens of different coating thickness after 50 cycles at 750±10°C. Elemental mapping analysis of hot-corroded bare specimen shows scale rich in Fe and O as shown in fig. 2(a). This indicates the formation of iron

oxides ($Fe/FeO/Fe_3O_4/Fe_2O_3$). Small content of Fe was observed at the top layer of the coated specimen probably due to diffusion as shown in fig. 2(b) and 2(c). Scale formed over the bare specimen after 50 cycles was amorphous in appearance, and composed of peeled off particles. EDS results of coated specimens reported large amount of Cr and O and marginal amount of Ni at the points of analysis. This represents that the exposed areas of the scale seemed to be adherent in the case of coated specimens. Thus, the coated specimens were good corrosion resistance as no scaling was observed till the completion of 50th cycle, while the bare specimens were totally consumed.

Figure 2.EDS spectrum and elemental mapping of (a) bare, (b) 200-250 µm, and (c) 250-300 µm, thick Ni-Cr coated mild steel after high temperature hot-corrosion of 50 cycles.
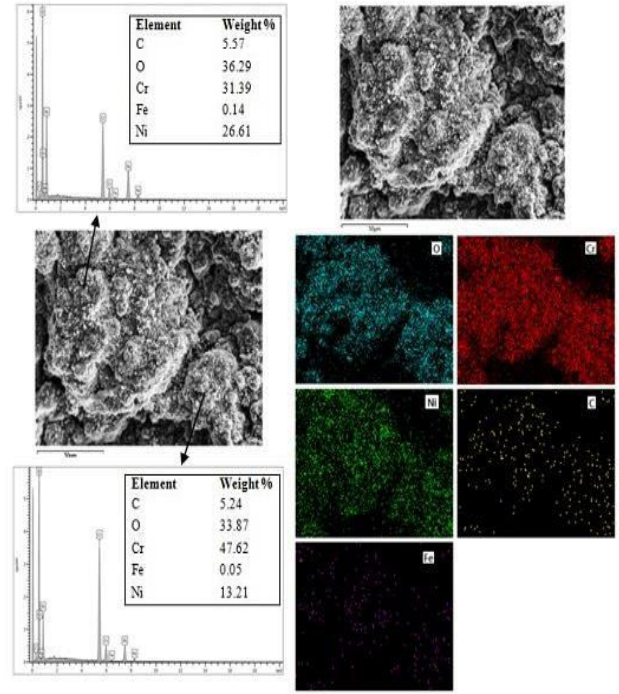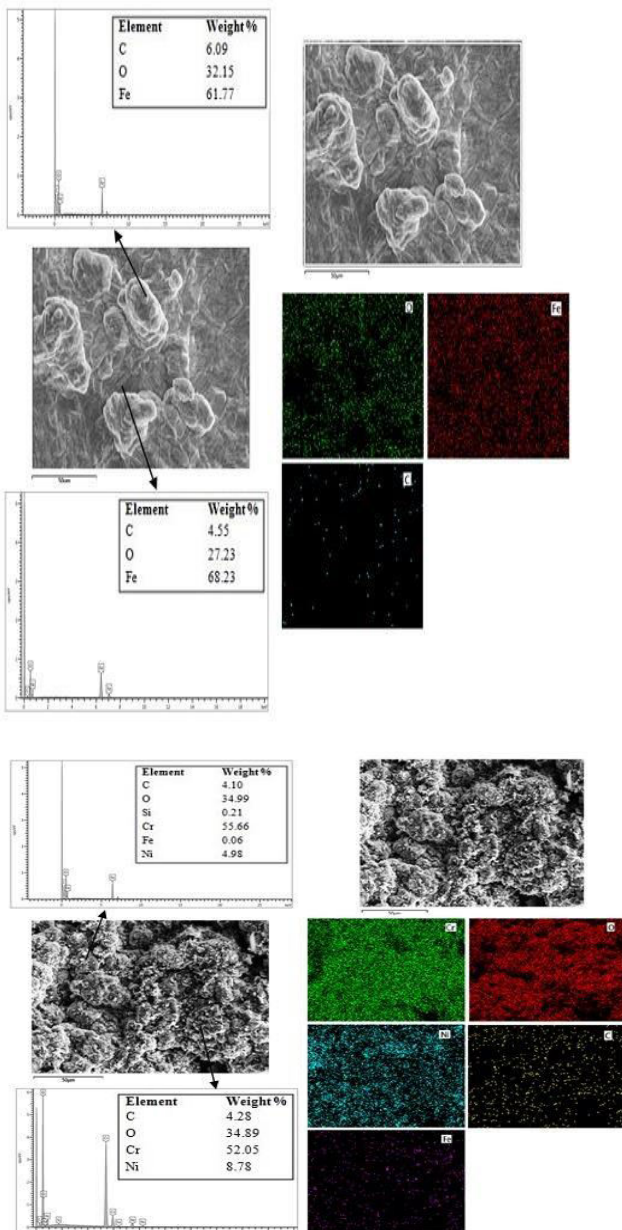
3.1.1. Evaluation of corrosion rate

Fig. 3 shows the graph between cumulative weight gains per unit surface area (mg/cm^2) vs. number of cycles for the mild steel specimens subjected to high temperature hot-corrosin at 750±10°C.Graph indicates that Ni-Cr coated mild steel specimens attained marginal weight gain till 50th cycle, whereas high weight gain was observed bare mild steel specimen. Overall weight gain after 50 cycles of high temperature hot-corrosion for the bare, 200-250 µm, and 250-300 µm thick Ni-Cr coated mild steel specimens were calculated to be 114.92829, 5.60327, and 14.1813 mg/cm^2, respectively. Overall weight gain in 250-300 µm thick NiCr coated was higher as compared to 200-250 µm thick Ni-Cr coated specimens because bond strength decreased with increase in coating thickness results corrosive media penetrates easily in higher thickness. Therefore 250-250 µm thick Ni-Cr coated specimens showed better resistance against high temperature oxidation in comparison to 200-250 µm thick Ni-Cr coated mild steel. Further, square of weight gain (mg^2/cm^4) vs. number of cycles graph was plotted for the mild steel specimens as shown in fig. 4.Parabolic rate constant (K_p) values were calculated by fitting the plotted curves with the linear regression.
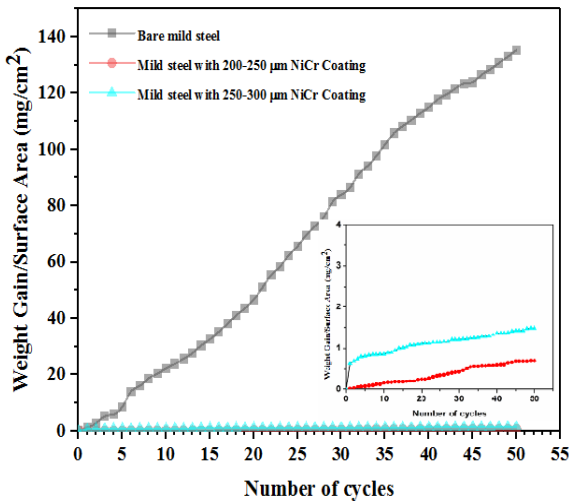
Figure 3. Weight change/surface area (mg/cm^2) vs number of cycles graph of mild steel subjected to high temperature hot-corrosion after 50 cycles.

In 1993, Wanger showed that ideal ionic diffusion-controlled hot-corrosion of pure metals should follow a parabolic corrosive rate law as represented by equation (1) [6].

where W is the weight gain per unit area, t is time, k_p is the parabolic rate constant, and C is a constant.

Metals demonstrating a parabolic corrosive rate yield a straight line when the data are plotted as W^2 versus time. It can be concluded from fig. 4 that Ni-Cr coated specimens follow nearly a parabolic rate law. The parabolic rate constants (K_p) for bare, 200-250 µm, and 250-300 µm thick Ni-Cr coated mild steel specimens are shown in Table 3. Parabolic rate constant of coatings was found to be very small in comparison to that of bare mild steel specimen, indicating the protective nature of the coatings against high temperature hot-corrosion. Since, lower the value of K_p, better the corrosive resistance.

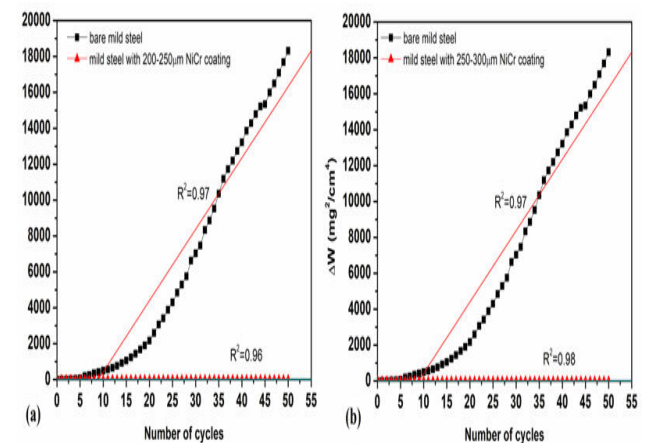Table 3. Parabolic rate constant (K_p) of corroded mild steel.

Specimen	K_p(10^{-10} g^4/cm^4/s)
Bare mild steel	736.003
200-250 µm thick Ni-Cr coated mild steel specimens	1.22216
250-300 µm thick Ni-Cr coated mild steel specimens	10.1276

The correlation coefficients for bare, 200-250 µm, and 250-300 µm thick NiCr coated mild steel specimens were 0.97, 0.96, and 0.98 respectively, as shown in the fig. 4.

Figure 4. Weight gain square (mg^2/cm^4) vs number of cycles graph of (a) bare and 200-250 µm thick, and (b) bare and 250-

300 µm thick, Ni-Cr coated mild steel subjected to high temperature hot-corrosion.

It was observed that coated specimens followed parabolic rate law and show constant weight gain, thereby slowing down the further corrosion process. Initially higher weight gain was observed probably due to accelerated interfacial reaction. This weight gain may be due the corrosion of entrapped air in the coating [3]. Elemental mapping of corroded mild steel specimen show Fe and O element, that confirms the formation of iron oxides. Presence of Cr and O were confirmed by the needle/platelet type of oxides. Surface morphology of the coated specimen indicates higher amount of Ni, Cr and O which may be attributed to the formation nickel oxide and chromium oxide. Chromia provide resistance against corrosion at elevated temperatures, as it preferentially reacts with O_2 to form the chromate and stabilizes the melt chemistry [10]. The presence of thick continuous band of protective oxides in the scales of coated specimens does not allow the corrosive species and the metallic ions to travel into the substrate and acts as a barrier to diffusion, results prevention of further hot-corrosion processes.

IV. CONCLUSIONS

1. Hardness of mild steel was increased from 202.25 to 341.75 VHN after the application of coatings.

2. Parabolic rate constant (K_p) for high temperature hot-corrosion of bare, 200-250 µm, and 250-300 µm thick Ni-Cr coated mild steel were be 736.003, 1.22216, and 10.1276 (×10^{-10}g^2 cm^{-4} s^{-1}) respectively, The parabolic rate constant of coatings was found to be very small as compared to that of bare mild steel, indicating the protective nature of the coatings against high temperature hot-corrosion .

3. 200-250 µm thick Ni-Cr coated mild steel showed better resistance against high temperature hot-corrosion as compared to 250-300 µm thick Ni-Cr coated mild steel specimens, because bond strength decreases with increase in coating thickness thereby corrosive media penetrates higher coating thicknesses easily as compared to lower coating thicknesses.

V. ACKNOWLEDGEMENT

REFERENCES

[1] Paul B, Prakash J, Sarkar PS, Formation and characterization of aluminide coating over grade 91 steel using D-Gun spray coating technique, Surface & Coat Tech. 2012;282:61–67.

[2] Chatha S.S., Sidhua H.S and Sidhu B.S., "High temperature hot corrosion behaviour of $75Cr_3C_2$– $25(Ni–20Cr)$, NiCr and Cr_3C_2-NiCr Coatings on T91 Boiler Steel in an Aggressive Environment at 750°C," Surface and Coating Technology, (2014), Vol. 206(19), pp. 3839-3850.

[3] Mudgal D., Singh S. and Prakash S. "High Temperature Cyclic Oxidation Behaviour of Al and Fe Based Super alloys," Journal of Minerals and Materials Characterization and Engineering, (2014), Vol. 11, No. 3, pp. 211-219

[4] Sidhu T.S., Prakash S. and Agrawal R.D., "Evaluation of hot corrosion resistance of HVOF coatings on a Fe3Al based super alloy in molten salt environment," Material Science and Engineering: (2015A), A, Vol. 430(1), pp. 64-78.

[5] Singh L., Chawla V. and Grewal J. S., "A Review on Detonation Gun Sprayed Coatings," JMMCE, (2016), Vol. 11, pp. 243-256.

[6] Das D., Balasubramaniam R. and Mungole M. N., "Hot corrosion of carbon alloyed Fe_3Al-based iron aluminides", Material Science and Engineering: A,(2002), Vol. 338(1), pp. 24-32.

[7] Pawolowski L., (2016), "The science and engineering of thermal spray coatings", John Wiley & sons, New York

[8] Sundararajan G., Sen D. and Sivakumar G., (2016), "The Tribological Behaviour of Detonation Sprayed Coatings: The Importance of Coating Process Parameters," Wear, Vol. 258(1), pp. 377-391

[9] Tan J.C., Looney L. and Hashmi M. S. J., (2016), "Component Repair using HVOF Thermal Spraying," Journal of Materials Processing Technology, Vol. 92, pp. 203-208.

[10] Fontana M.G., (2017), "Oxidation rate laws, Corrosion Engineering," 3rd ed., Tata McGraw-Hill, Delhi, pp. 514.

[11] Johnson D.M., Whittle D.P. and Stringer J., (2017), "Mechanisms of Na2SO4-induced accelerated oxidation," Corrosion Science, Vol. 15(6-12), pp 721-739.

[12] Khanna A.S., (2002), "Introduction to High Temperature Oxidation and Corrosion," ASM International, Materials Park, Ohio.

[13] Uusitalo M.A., Vuoristo P.M.J. and Mantyla T.A., (2017), "High Temperature Corrosion of Coatings and Boiler Steels in Oxidizing Chlorine-containing Atmosphere," Material Science and Engineering: A, Vol. 346(1), pp. 168-177.

[14] Hancock P., (1987), "Vanadic and chloride attack of superalloys," Materials Science and Technology, Vol. 3(7), pp. 536-544.

[15] Eliaz N., Shemesh G., Latanision R.M., (2002), "Hot corrosion in gas turbine components," Engineering Failure Analysis, Vol. 9(1), pp. 31-43.

[16] Hocking M.G., (1993), "Coatings Resistant to Erosive/Corrosive and Severe Environments," Surface and Coating Technology, Vol. 62(1-3), pp. 460-466.

[17] Heath G. R., Heimgartner P., Irons G., Miller R. D. and Gustafsson S., (1997), "An Assessment of Thermal Spray Coating Technologies for High Temperature Corrosion Protection," Material Science Forum, Trans Tech Publications, Vol. 251, pp. 809-816.