Evaluation of Thermocyclic Oxidation behavior of HVOF Sprayed WC-CrC-Ni Coatings

B. Somasundaram, Ravikiran Kadoli and M.R. Ramesh

Abstract—In the present study, the WC-Cr-C-Ni powder is HVOF sprayed on three different Fe-based steels namely SA213-T22, MDN-310 and SUPERFER 800H. Oxidation studies have been conducted on the coated as well as uncoated specimens at 700°C for 50 cycles in air under cyclic heating and cooling conditions. The weight change method was used to establish the kinetics of oxidation. WC-CrC-Ni coated steels showed slow oxidation kinetics and considerably lower weight gains than that of uncoated steels. The superior performance of WC-CrC-Ni coatings can be attributed due to the formation of a compact and protective oxide layer consisting of Cr2O3, NiO and their spinels like NiCr2O4 and NiWO4. The uncoated T22 steel suffered a catastrophic degradation in the form of intense spalling of the scale. The combined technique of X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray analysis (SEM.EDAX) and X-ray mapping were used to analyze the oxidized products of coated and bare substrate steels.

Keywords---Protective Coatings, WC-CrC-Ni, HVOF, High Temperature Oxidation

I. INTRODUCTION

POWER plants are one of the major industries suffering from severe oxidation, corrosion and erosion problems resulting in the substantial losses [1]. Oxidation and Corrosion from the firing of coal or oil is essentially related to specific impurities in the fuels which can lead to the formation of non protective scales or can disrupt normally protective oxide scales. There are three general areas where external oxidation and corrosion problems occur in the water wall or boiler tubes near the firing zone, the high temperature superheater and reheater tubes and ductwork that handles the combustion flue gases [2].

In search for cost-effective solutions for E-C problems, various coatings like thermal sprayed coatings have become attractive. The term thermal spray describes a family of processes that use chemical or electrical energy to melt (or soften) and accelerate particles of a material which is then deposited on a surface[3]. The quality of the coatings obtained by thermal spray techniques is related to the nature of the process and the processing parameters. On the other hand, thermal spray coatings are a good option to repair components and prevent excessive wear because during the deposition process no significant changes to the microstructure of substrates or excessive deformation are promoted [4].

The latest technology that completes the current family of thermal spray techniques is the high velocity oxy fuel process. This thermal spray technology uses the kinetic energy and the output of a supersonic flow of burned gases, to soften and to propel the spray powder onto the substrate. The ability to deposit coatings from a wide range of metals, cerments, and ceramics leads to the application of HVOF spraying in many different industries[5-7]. It is common knowledge today that the HVOF systems are capable of processing better carbide coatings than other thermal spray methods in terms of higher hardness and bond strength, lower oxides and porosity, combined with low residual stress in the coatings. The high kinetic energy of the powder particles with shorter residence time result in the deposition of dense coatings during HVOF process. This process is highly promising due to the benefits of lower cost, better performance, ability to deposit coatings whose thickness ranges from several micrometers to tenths of a millimeter, ability to deposit on a wide variety of shapes and sizes [8-10].

The development and use of WC-based coatings with metallic binders is now generally acceptable practice in fossil fuel energy processes. These coatings are selected primarily for applications requiring enhanced wear resistance and surface hardness and to a lesser extent, their oxidation and corrosion resistance. Numerous studies have been conducted on binary WC-Co based coatings and ternary WC-Co-Cr coatings, and to a lesser extent on WC-Ni and WC-CrC-Ni coatings [11].

Lutz-Michael Berger et al. [12] reported that WC-(W,Cr)2C-Ni coatings are having much superior oxidation and corrosion resistance to that of other commercial WC-based coatings and discussed that the composition WC-(W,Cr)2C-Ni can bridge the gap between WC-Co and Cr3C2-NiCr with regard to oxidation and corrosion resistance.

The objective of this work is to study the high temperature oxidation behaviour of HVOF sprayed WC-CrC-Ni coatings in air environment at an elevated temperature of 700°C. This coating combines the high wear resistance of WC and CrC and high temperature oxidation resistance of Cr2O3. There is no reported literature on the oxidation behaviour of HVOF spray deposited WC-CrC-Ni coating on the selected boiler steel substrates. Therefore, the current work has been focused to study the influence of HVOF sprayed WC-CrC-Ni coating on the oxidation behaviour of the boiler steels. The
The thermocyclic conditions used in the present study represent a more realistic approach towards solving the problem of oxidation and corrosion in real time applications, where conditions are more or less cyclic rather than isothermal. Furthermore, the high temperature boiler studies could provide an idea concerning the adhesion between the coatings and the substrate steels under thermal heat shocks.

II. EXPERIMENTAL PROCEDURE

A. Development of Coatings

The Fe-based Super alloy designated as Superfer 800 (Midhani Grade), chrome moly steel designated as ASTM-SA213-T22 and austenitic steel designated as MDN 310 (Midhani Grade) were used as substrate materials. The chemical composition of the substrate steels is reported in Table 1. The specimens with close dimensions of 25mm × 25mm × 5mm were prepared for oxidation studies, ground with SiC papers down to 180 grit and were grit-blasted with Al₂O₃ powders previous to HVOF spraying for developing enhanced adhesion of the coating to the substrate.

HVOF spraying has been done using a HIPOJET 2700 equipment (M/S Metallizing Equipment Co.Pvt.Ltd, Jodhpur, India), which make use of the supersonic jet generated by the combustion of liquid petroleum gas and oxygen mixture. A commercially available (WC - 20CrC - 7Ni) powder of nominal composition [W - 19Cr – 7.25Ni - 6.8C] (wt %), was used as feedstock alloy. As evident from the micrographs of the coating powders shown in Fig.1a, the WC-CrC-Ni powder particles have spherical morphology. The particle size distribution of the powder as determined by the image analysis of the secondary electron micrographs are found to be in the range of 15 µm to 45 µm, consistent with the nominal size distribution as provided by the manufacturer. XRD peaks of the powder reveal that powder has crystalline phases of WC, Cr₇C₃ and Cr₃Ni₂, where as in the coatings, WC decompose to brittle W₂C.(Fig 1b). All the process parameters, including the spray distance, were kept constant throughout the coating process and they are given in Table 2. The optical image along the cross-section of as-sprayed coatings were obtained by using Zeiss Axiovert inverted optical microscope, interfaced with image analyzing software to find out the porosity content. Twenty fields of view per sample were taken at 250X magnification.

Table 1: Chemical Composition (Wt %) of Boiler Tube Steels

<table>
<thead>
<tr>
<th>Type of steel</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Ti</th>
<th>Al</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA213-T22</td>
<td>Bal.</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>1.1</td>
<td>0.5</td>
<td>0.4</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>MDN 310</td>
<td>Bal.</td>
<td>21</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>0.8</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Superfer 800</td>
<td>Bal.</td>
<td>32</td>
<td>21</td>
<td>0.3</td>
<td>0.3</td>
<td>-</td>
<td>1.5</td>
<td>1.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

B. High Temperature Oxidation Test

The uncoated and HVOF coated steels were subjected to thermocyclic oxidation tests at 700°C in silicon carbide tube furnace for 50 cycles. The furnace was calibrated to an accuracy of ±5°C using Platinum/Platinum-13% Rhodium thermocouple fitted with a temperature indicator. Physical dimensions of the specimens were then measured with the help of vernier caliper to evaluate their surface areas. Afterwards, the specimens were washed properly with acetone and dried in an oven to remove any moisture. The boat containing the specimen was introduced into hot zone of the furnace set at a temperature of 700°C. Holding time in the furnace was one hour in still air after which the boat with the specimen was taken out and cooled at the ambient temperature for 20 minutes. Following this, weight of the boat along with specimen was measured with the help of a Electronic Balance Model AY-120 with a sensitivity of 1mg and this constitutes one cycle of oxidation study. Any spalled scale in the boat was also taken into consideration for the weight change measurements. Visual observations were made after the end of each cycle with respect to color, luster or any other physical aspect of the oxide scales being formed. The samples after being subjected to oxidation were analysed using SEM/EDAX and XRD techniques. The reproducibility in the experiments was established by repeating the experiments for some samples.

![Figure 1: (a) Scanning Electron Micrograph of WC-CrC-Ni Powder; (b) X-ray Diffraction Patterns for Powder and as-Sprayed Coating](image-url)
Table 2: Spray Parameters Employed for HVOF Spray Process

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Oxygen flow rate</td>
<td>250 l/min</td>
</tr>
<tr>
<td>Fuel (LPG) flow rate</td>
<td>65-70 l/min</td>
</tr>
<tr>
<td>Air-flow rate</td>
<td>550 l/min</td>
</tr>
<tr>
<td>Spray distance</td>
<td>178 mm</td>
</tr>
<tr>
<td>Powder feed rate</td>
<td>23 g/min</td>
</tr>
<tr>
<td>Fuel pressure</td>
<td>681 kPa</td>
</tr>
<tr>
<td>Oxygen pressure</td>
<td>981 kPa</td>
</tr>
<tr>
<td>Air pressure</td>
<td>588 kPa</td>
</tr>
</tbody>
</table>

III. RESULTS

A. Coating Structure and Properties

The HVOF coatings have been deposited on a stationary substrate and the necessary thickness has been achieved by varying the required number of passes. The thickness of the coatings has been found to be in the range of 270-300 µm. The average porosity value of the coatings was found to be less than 2.5%. The average microhardness value found to be 1093 Hv with a standard deviation of 76. The bond strength of the coating was measured as 73.13 MPa whereas the HTK Ultra Bond epoxy glue used in the present study had a characteristic tensile strength of 80 N/mm². This indicates that the coating cohesive strength is superior to the adhesive strength.

The optical cross-sectional micrograph of the coating before oxidation is illustrated in Fig. 2, which shows the deposition and build up of melted particles in a layered fashion and then solidifies in the form of fine spalt during impact. The micrograph mainly consists of Cr₃C₂ or Ni phase and WC phases. The dark spots distributed in the optical image are the porosity and porosity are mainly produced at grain boundary between Cr₃C₂ and WC phase or between Ni and WC phase. Contrast dark areas close to coating substrate interface are inclusions.

B. Thermogravimetric Studies

The macrographs of the uncoated and HVOF sprayed coated steels subjected to cyclic oxidation in air for 50 cycles are shown in Fig. 3. All the uncoated alloys developed a dark grey coloured oxide scale. During the cyclic oxidation, the minimum spallation of scale was observed for the Mdn steel as compared to the other steels. The scale formed on the T22 steel was found to be fragile and cracked from centre of the sample. The color of the oxide scale on the surface of all the three coated steels is greenish grey. The oxide scale was found to be compact and strongly adherent to the substrate, with no tendency for spalling.

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The plots of cumulative weight gain (mg/cm²) as a function of time expressed in number of cycles are shown for uncoated and coated steels in Figs. 4(a) and 4(b). The weight gain for the T22, MDN and Superfer steels at the end of 50 cycles are found to be 16.89, 0.67 and 0.63 mg/cm² respectively. Clearly, the T22 steel showed a maximum weight gain during the cyclic oxidation studies as compared to MDN and Superfer steels. The total weight gain values for the coated T22, MDN and Superfer steels at the end of 50 cycles of oxidation studies are found to be 0.79, 0.34 and 0.50 mg/cm² respectively. The variation in weight change values is due to Sputtering of thin oxide layer formed on the surface of the coatings. Though a small difference exists in weight gain for different coated substrates, the net weight gain for all coated materials is less compared to weight gain for uncoated substrates.

Therefore it can be inferred from the thermogravimetric data that the required protection against cyclic oxidation has been provided by WC-CrC-Ni coatings.
Figure 4: Plot of Weight Gain/area vs. Number of Cycles. (a) Uncoated Steels, (b) Coated Steels subjected to Oxidation for 50 cycles at 700°C

The plot of weight gain square versus time (Fig. 5a) for uncoated steels shows the observable deviation from the parabolic rate law for T22 steel, which indicate that the oxide films were poorly protective at 700°C. It is evident from the plot that the MDN and Superfer steels followed parabolic behaviour. The parabolic rate constant $K_p$ was calculated by a linear least-square algorithm function in the form of $(\Delta W/A)^2 = K_p \times t$, where $\Delta W/A$ is the weight gain per unit area, and $t$ is the oxidation time in seconds. The $K_p$ for the T22, MDN and Superfer steels are $16.92 \times 10^{-10}$, $0.0143 \times 10^{-10}$, $0.000246 \times 10^{-10}$ g$^2$ cm$^{-4}$ s$^{-1}$ respectively. All the coated steels show parabolic behaviour (Fig. 5b) and the $K_p$ for the coated T22, MDN and Superfer steels are found to be $3.4694 \times 10^{-12}$, $5.6388 \times 10^{-13}$ and $1.2666 \times 10^{-12}$ g$^2$ cm$^{-4}$ s$^{-1}$ respectively.

Figure 5: Plot of $(\text{Weight gain/area})^2$ vs. Number of Cycles. (a) Uncoated Steels, (b) Coated Steels subjected to Oxidation for 50 cycles at 700°C

C. X-ray Diffraction Analysis

The X-ray Diffraction patterns of the oxide scale formed on the surface of oxidized WC-CrC-Ni coated steels after cyclic oxidation in air at 700°C are shown in Fig.6. The XRD results reveal the presence of the phases like Cr$_2$O$_3$, NiO, WO$_3$, WC and mixed spinel-type oxides of NiWO$_4$ and NiCr$_2$O$_4$. The Cr$_3$C$_2$ phase in the as-sprayed coating has been transformed into Cr$_2$O$_3$ after oxidation. All the three coated steels have been found to have identical oxides on the surface.

Figure 6: X-ray Diffraction patterns for Coated Steels Subjected to Cyclic Oxidation in Air

D. SEM/EDAX Analysis

The surface morphology (Fig. 7) of the oxide scale formed on the surface of WC-CrC-Ni coated steels is thick, continuous and non uniformly consisting of voids. Fig. 7a shows the surface morphology of oxide scale formed on the oxidised WC-CrC-Ni coated T22 steel. Oxide scale consists of spherical globules dispersed in the non uniform matrix. The EDAX analysis on the spherical globules revealed the possibility of formation of oxides and carbides of tungsten and chromium (35.73%W, 10.04%Cr, 28.64%C and 16.46%O) as the main constituent along with NiO (8.03%Ni) and the EDAX analysis on the matrix showed similar morphology composed of oxides and carbides of tungsten and chromium (37.44%W, 17.08%Cr, 21.57%C and 19%O) as principal phases along with a minor amount of NiO (4.87%Ni).
Similar observations have been noticed for the WC-CrC-Ni coated MDN and superfer steel (Fig. 7b and Fig. 7c). The dominating presence of W, Cr and Ni peaks supports the possibility of formation of spinels of mixed oxide of W, Cr and Ni on the surface of the oxidized coating.

E. Cross-Sectional Analysis

The BSE image and EDAX point analysis across the crosssection of the oxidized WC-CrC-Ni coated T22 steel at 700°C are shown in Fig. 8. A continuous, crack free and thick oxide scale is formed on the coated T22 steel which has retained the lamellar structure during the course of study. The topmost part of the scale (point 1), containing mainly Cr, W and Ni (26.94 Wt% of Cr, 29 Wt% of W, 5.07 Wt% of Ni) with about 21.04 Wt% of O and 17.01 Wt% C is rich in oxides and carbides of Cr and W. The EPMA analysis has detected 34.92 Wt% of Cr, 16.79 Wt% of W, 6.23 Wt% of Ni with 20.27 Wt% of O and 20.88 Wt% of C at point 2. Thus it can be inferred that the subscale (Point 2) is also rich in oxides and carbides similar to the topmost part of the scale. The light grey area (points 4 and 6) across the crosssection is detected as nickel rich splats (44.66 Wt% Ni at point 4 and 39.1 Wt% Ni at point 6 respectively), mostly in an un-oxidised state, as relatively lesser amount of oxygen is present at these points. The dark grey phase at the boundaries of these splats (points 3 and 5) consists mainly of tungsten rich splats (50.63 Wt% W at point 3 and 47.38 Wt% W at point 4 respectively). The coating region below the oxide scale shows a negligible amount of oxygen which infers that this region remained unoxidised. The dominating presence of Ni at the point 7 indicates the interdiffusion of nickel from the coating into the substrate.

F. EPMA Analysis

Elemental X-ray mapping for the WC-CrC-Ni coated T22 steel subjected to cyclic oxidation for 50 cycles shows a continuous and adherent thick oxide layer formed on the external surface of the coating as shown in Fig. 9. The coating is oxidized partially which is restricted to few microns on the surface. The x-ray mapping revealed that this adherent topmost layer is rich in Ni, Cr and W which corroborates the formation of oxides and spinel oxides of Ni, Cr and W on the external surface. Mapping for W and C reveals the formation of WC on the external surface of the coating. The absence of O below the topmost scale reveals that the nickel and tungsten rich splats are not oxidized at the end of 50 cycles of oxidation studies. The thick oxide scale formed on the surface acts as a
barrier to the inward diffusion of oxygen and other oxidizing species into the coating.

Figure 9: BSEI and Elemental X-ray Mapping at the Cross-Section of the WC-CrC-Ni Coated T22 Steels Subjected to Oxidation

IV. DISCUSSION

The HVOF coatings on the substrate alloys have been successfully deposited and the thickness of the coatings is in the desirable range of 270–300 µm. The decreased porosity value of the coatings is linked to the melting behaviour of the powder particles during HVOF spraying and to the higher kinetic energies of powder particles during HVOF spraying. The partially melted particles form an almost porosity-free coating when they reach the substrate at high velocity. The porosity obtained in the sprayed coatings are in good accordance with the findings of Sahraoui et al. [13] for the HVOF sprayed coatings. The coatings showed nearly similar peaks as compared to that of the powder representing no change in their phase composition after HVOF spraying.

The WC-CrC-Ni coated steels show lower weight gain in comparison to the uncoated steels as reported in section III(B). Weight gain after 50 cycles of oxidation of WC-CrC-Ni coated T22, MDN and Superfer steels are found to be 0.79, 0.34 and 0.50 mg/cm² respectively. The parabolic rate constant (Kₚ) are lower for all the coated steels in comparison to the uncoated steels, thereby further indicating lower oxidation rates for the coated steels. The oxidation behavior of the coated steels is parabolic in nature upto 50 cycles and hence the oxide scales formed have shown the tendency to act as diffusion barriers. The minor deviation from the parabolic rate law can be attributed to the Sputtering of thin oxide layer formed on the surface of the coatings. Hence, it can be inferred that WC-CrC-Ni coatings are successful in protecting the substrate steels from the accelerated oxidation to a considerable extent.

Coatings developed a thick oxide scale after subjecting to 50 cycles of oxidation in air environment. The XRD analysis of the surface of the oxidized scale revealed the existence of Cr₂O₃, NiO, WO₃, WC and mixed spinal-type oxides of NiWO₄ and NiCr₂O₄. Cr₃C₂ has been predominantly oxidized to form Cr species. These species are thermodynamically unstable under accelerated oxidation conditions and straight away oxidized to Cr₂O₃[14-16]. The formation of Cr₂O₃ and NiO during the early stages of oxidation lowers the oxygen potential, preventing preferential oxidation of tungsten as WO₃. The refractory tungsten carbide and chromium carbide in the coating retains the properties of the coating by acting as a strengthener. After completion of the Cr₂O₃ external scale, the solid state reaction between initially grown stable binary oxides replaces ternary oxides such as NiWO₄ and NiCr₂O₄ during the intermediate stages of oxidation. The non protective spinel oxide NiWO₄ induce formation of a friable and porous scale which was responsible for the increase in oxidation rate. Since NiWO₄ is a compound of NiO and WO₃, NiWO₄ would have poor oxidation resistance in the given oxidation environment. Similar observations have been reported by Peters et al. [17] and Lee et al. [18]. The spinel NiCr₂O₄ have much smaller diffusion coefficients of the cations and anions than those in their parent oxides, hence helps to develop oxidation resistance [19].

EPMA and EDAX analysis along the cross section of the oxidized coating reveal that oxidation has been restricted only to the external surface upto few microns to form a thick and continuous oxide scale and rest of the coating below the protective oxide layer formed remains unoxidised. Oxygen has not penetrated into the substrate steel, which further indicates that the protective oxides of Cr, Ni and their spinel oxides acts as diffusion barrier to the transportation of oxidizing species into the inside of coating. Hence coating provides necessary protection to the substrate steel.

V. CONCLUSION

The following points are concluded based on experimental results:

1. HVOF spray process has been successfully used to deposit WC-CrC-Ni coating on SA213-T22, MDN-310 and Superfer 800 H substrates in the range of 270–300 µm thickness. The microhardness and bond strength recorded was 1093 Hv and 73.13 Mpa respectively with porosity less than 2%.

2. The coatings exhibit almost similar peaks as compared to that of the powder indicating no change in their phase composition after spraying. The powder and as-sprayed coating have major phases of WC, Cr₃C₁ and Cr₃Ni₂.
3. The protective oxide scale formed on the outermost surface mainly composed of oxides of Ni, Cr, and mixed spinel oxide NiCr$_2$O$_4$. These oxides might have acted as diffusion barrier to the inward diffusion of oxidizing species and hence rest of the coating remains unoxidised. The carbides of tungsten and chromium retain the mechanical properties of the coating.

4. The parabolic rate constant ($K_p$) are lower for all the coated steels in comparison to the uncoated steels and hence the WC-CrC-Ni coating is successful in protecting the substrate steels against the accelerated oxidation.

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