JMEPEG (2014) 23:493–505
DOI: 10.1007/s11665-013-0771-0

1059-9495/$19.00

Hot Corrosion Studies of HVOF-Sprayed Coating on T-91 Boiler Tube Steel at Different Operating Temperatures

Rakesh Bhatia, Hazoor Singh, and Buta Singh Sidhu

(Submitted May 5, 2012; in revised form August 5, 2013; published online November 6, 2013)

The aim of the present work is to investigate the usefulness of high velocity oxy fuel-sprayed 75% Cr_3C_2-25% (Ni-20Cr) coating to control hot corrosion of T-91 boiler tube steel at different operating temperatures viz 550, 700, and 850 °C. The deposited coatings on the substrates exhibit nearly uniform, adherent and dense microstructure with porosity less than 2%. Thermogravimetry technique is used to study the high temperature hot corrosion behavior of uncoated and coated samples. The corrosion products of the coating on the substrate are analyzed by using XRD, SEM, and FE-SEM/EDAX to reveal their microstructural and compositional features for the corrosion mechanisms. It is found that the coated specimens have shown minimum weight gain at all the operating temperatures when compared with uncoated T-91 samples. Hence, coating is effective in decreasing the corrosion rate in the given molten salt environment. Oxides and spinels of nickel-chromium may be the reason for successful resistance against hot corrosion.

Keywords corrosion resistance, 75% Cr_3C_2-25% (Ni-20Cr), hot corrosion, HVOF spray coating

1. Introduction

Hot corrosion is a serious problem in boilers, gas turbines, internal combustion engines, and industrial waste incinerators. It consumes the materials at an unpredictably rapid rate. As a consequence the load-carrying abilities of the components are reduced, leading eventually to their catastrophic failure (Ref 1). Due to depletion of high-grade fuels and for economic reasons, use of residual fuel oil in energy generation systems is well known. Residual fuel oil contains sodium, vanadium, and sulfur as impurities. These impurities react together to form low melting point compounds, which deposit on the surface of materials and induce accelerated oxidation (Ref 2).

Coatings provide a way of extending the limits of use of materials for higher temperature applications (Ref 3). The coatings used at higher temperatures must be dense enough that any residual voids can be filled by formation of protective oxides and be thick enough to postpone the diffusion of corrosive species to the substrate material until protective oxides form within the coating (Ref 4).

There are many techniques that can be used to deposit metallic coatings; however, thermal spray techniques such as flame spraying, arc spraying, plasma spraying, detonation gun, and high velocity oxy-fuel spraying are increasingly used for higher temperature application (Ref 5). Thermal spraying has emerged as an important tool of sophisticated surface engineering technology. High velocity oxy fuel (HVOF) process is a relatively new and rapidly developing technology, which can produce dense coatings with high hardness and adhesion values, and good erosion, corrosion, and wear resistance properties. This process has been widely adopted by many industries due to its flexibility and cost effectiveness (Ref 6). HVOF coatings are homogeneous and dense compared to the other types of thermal-sprayed coatings; nevertheless some residual oxides and porosity remain at splat boundaries (Ref 7). Cr_3C_2-NiCr based thermal spray coatings using high velocity oxygen fuel (HVOF) technique; appear to be the best alternative in most cases mainly when good wear or corrosion resistance is required (Ref 8-11).

Earlier studies performed by various authors have considered only one temperature for studying the corrosion problems. However, for better understanding of the corrosion behavior of Cr_3C_2-NiCr coating, the study needs to be done at a range of temperatures (550-850 °C) for application in boiler environment. The aim of the present work is to investigate the usefulness of HVOF sprayed commercially available 75% Cr_3C_2-25% (Ni-20Cr) powder on T-91 boiler steel and provide an insight to the corrosion behavior in molten salt environment of Na_2SO_4-V_2O_5 salt at different operating temperatures viz 550, 700, and 850 °C for 50 cycles. Na_2SO_4-60% V_2O_5 has been selected for the study due to the fact that the Vanadium, sulfur, and sodium are often present as impurities in low grade fuels (Ref 12). The cyclic oxidation conditions have been selected keeping in view that most of the actual industrial components work under cyclic conditions of operation. The information arising out from the investigation will be useful to explore the possibility of this coating for applications to the boiler tubes.

2. Experimental Details

T-91 boiler tube steel was used as substrate material. Specimens with dimensions of approximately 22 mm ×

Rakesh Bhatia and **Hazoor Singh**, Yadavindra College of Engineering, Punjabi University, G.K. Campus, Talwandi Sabo, Bathinda 151302 Punjab, India; and **Buta Singh Sidhu**, Punjab Technical University, Jalandhar-Kapurthala Highway, Kapurthala, Punjab, India. Contact e-mail: rakesh_lit@yahoo.co.in.

15 mm × 3 mm were prepared. The specimens were grit-blasted before development of the coatings by the HVOF process. Commercially available agglomerated sintered 75% Cr_3C_2-25% (Ni-20Cr) coating powder of size 45 ± 15 μm was used in the study. The coating was developed using commercial HVOF thermal spray system Hipojet 2100. All the process parameters were kept constant throughout the coating process. The spray parameters used for HVOF system were: oxygen flow rate of 250 LPM, a fuel (LPG) flow rate 60 LPM, an airflow rate of 900 LPM, a spray distance of about 200 mm, a fuel pressure of 8 kg/cm^2, an oxygen pressure of 9 kg/cm^2, and air pressure 5 kg/cm^2 and powder feed rate of 28 g/min.

2.1 Characterization of the Coatings

The coated samples were mirror polished and then subjected to XRD, SEM/EDAX analysis to characterize the surface and cross-sectional morphology of the coatings. The XRD analysis was carried out with a Diffraction patterns obtained with CuKα radiation. A field emission scanning electron microscope (FE-SEM) with an EDAX attachment was used for SEM/EDAX analysis. The porosity measurements were made with image analyzer software based on ASTM B276. To identify the cross-sectional details, the samples were cut across with a slow speed diamond cutter and subsequently hot mounted in transoptic powder and mirror polished. FE-SEM was used to obtain the back scattered electron (BSE) images to measure coating thickness. The microhardness of coatings was measured by the digital micro Vickers hardness tester. Surface roughness of the specimens was measured by surface roughness tester (Mitutoyo, Model SJ 201, Japan).

2.2 Molten Salt Corrosion Tests

Cyclic corrosion studies were performed in molten salt (Na_2SO_4-60 wt.% V_2O_5) for 50 cycles. Each cycle consisted of 1-h heating at given temperature, i.e., 550, 700, or 850 °C in a silicon carbide tube furnace followed by 20 min cooling at room temperature; the cyclic conditions have been chosen to create a more aggressive situation of corrosion attack. Ashes usually have high concentrations of compounds of vanadium, sodium and sulfur, mainly as Na_2SO_4-V_2O_5 complex and sodium-vanadates mixtures. Vanadium, sulfur, and sodium are often present as impurities in residual oils used as fuel (Ref 12, 13). Na_2SO_4-60% V_2O_5 has been selected for the study due to the fact that the vanadium and sodium are common impurities in low-grade fuels. The equilibrium diagram for varying composition of Na_2SO_4 was studied by Otero et al. (Ref 14) from which it was concluded that a mixture of Na_2SO_4-60% V_2O_5 is the lowest eutectic temperature mixture and this composition is extremely corrosive, as it has a low melting point at 500 °C. Tiwari (Ref 15) reported that the mixture of Na_2SO_4 and V_2O_5 in the ratio of 40:60 constitutes a eutectic with a low melting point of 550 °C and provides a very aggressive environment for hot corrosion to occur and they concluded that the corrosion increases with the increase in the temperature and V_2O_5 content in the mixture.

The studies were performed for uncoated as well as coated specimens for the purpose of comparison. Na_2SO_4-60% V_2O_5 mixture prepared in distilled water was applied uniformly on the warm specimens with the help of a camel-hair brush. The amount of the salt coating was kept in the range of 3.0-5.0 mg/cm^2. The salt-coated specimens as well as the alumina boats were then kept in the oven for 3-4 h at 100 °C. Then they were again weighed before exposing to hot corrosion tests in the tube furnace. The salt mixture was applied on the surface only once in the beginning of the test, and it was not replenished during the test. During hot corrosion runs, the weight of boats and specimens were measured together at the end of each cycle, with the help of electronic balance machine with a sensitivity of 1 mg. The spalled scale was also included at the time of measurements of weight change to determine total rate of corrosion. The surface of the corroded specimens was visually observed to record color, spalling, and peeling of scale during cyclic corrosion. Efforts were made to formulate the kinetics of corrosion. XRD, SEM/EDAX, and EPMA techniques were used to analyze the corrosion products.

3. Results

3.1 Thickness, Porosity, and Microhardness of the Coatings

The coating deposited is found to be uniform and dense in nature as shown in BSE image as shown in Fig. 1. The thickness of the coating was measured using BSE image taken along cross-section of the mounted sample. Average thickness of the coating was found to be 390 μm. The porosity of the coatings is a property, which has a significant role to play when high temperature corrosion resistant coatings are to be developed. Due to porosity the corrosion species can penetrate to the substrate for corrosion attack. The mean of five measurements performed is found to be $<2\%$.

The microhardness of the coatings is found to be variable with the distance from the coating-substrate interface. The microhardness of the substrate was found to be in the range of 242-393 Hv; whereas, the microhardness for 75% Cr_3C_2-25% (Ni-20Cr) coating was found to be in the range of 774-950 Hv. The mean of five values of surface roughness [R_a] of the coating was found to be 4.872 μm.

3.2 Corrosion Kinetics

The weight gain plot for the uncoated and coated T-91 boiler tube steel in the presence of molten salt of Na_2SO_4-60% V_2O_5 at 550°, 700°, and 850 °C for 50 cycles have been shown in Fig. 2. Uncoated boiler tube steel indicated higher weight gain with respect to coated samples at all the operating temperatures and with maximum weight gain at 850 °C. On the other hand, 75% Cr_3C_2-25% (Ni-20Cr) coated sample showed lesser weight gain throughout the entire range up to 50 cycles in the given molten salt environment. The weight gain during corrosion testing for coatings was found to be lowest at 550 °C, whereas maximum weight gain for the coating has been reported at 850 °C. The weight gain data of the coated samples is 8.3, 4, and 1.3 times lower than uncoated steel at 550, 700, and 850 °C operating temperatures, respectively.

The uncoated steel has shown irregular scale, cracks, and spalling right from 1st cycle, peeling of the scale from 10th cycle and also gave some metallic sound during cooling for some cycles. The uncoated T-91 sample subjected to hot corrosion at 850 °C was totally consumed by the end of 47th cycle. However, the coated samples completed 50 cycles at all the temperatures under study. The weight gain square (mg^2/cm^4) verses time (number of cycles) plots are shown in Fig. 2 to establish the rate law for the hot corrosion. Uncoated sample at 550 °C and coated samples at 550° and 700 °C follows parabolic rate law, whereas a deviation from the parabolic rate law has been observed for coated sample at 850 °C and uncoated samples at 700 and 850 °C. The parabolic rate constants, Kp for uncoated and 75% Cr_3C_2-25% (Ni-20Cr) coated T-91 boiler tube steel at different operating temperatures viz. 550, 700 and 850 °C are shown in Table 1.

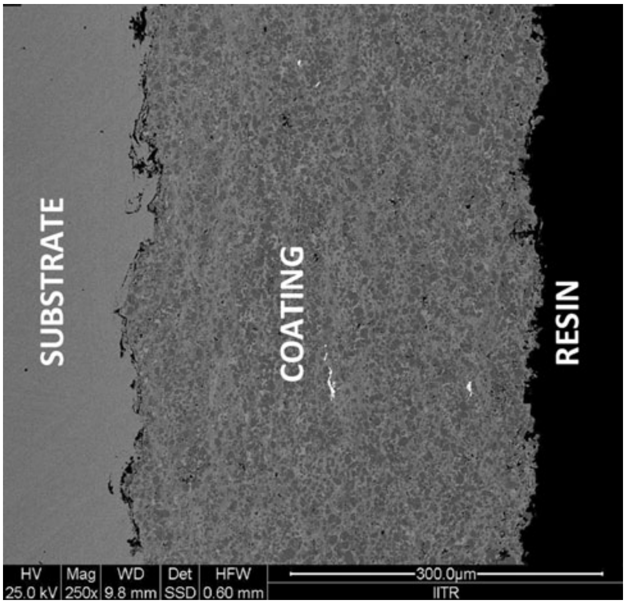

Fig. 1 Cross-sectional microstructure of 75% Cr_3 C_2-25% (Ni-20Cr) sample

3.3 XRD Analysis

The surface XRD analysis for T-91 boiler tube steel after exposure to the hot corrosion at different given temperatures is shown in Fig. 3(a-c). As obvious from the analysis, the uncoated steel has indicated the formation of mainly iron oxide (Fe_2O_3) in the scale along with Cr_2O_3. At 550 °C temperature phases of Na and V in the form of Na_2SO_4 and V_2C has also been observed. At 700 °C along with iron oxide (Fe_2O_3) and Cr_2O_3, salt compound of V has also been found.

The surface XRD analysis for coated T-91 boiler tube steel after exposure to the hot corrosion at different operating temperatures viz. 550, 700, and 850 °C for 50 cycles is presented in Fig. 4(a-c), respectively. Coated T-91 boiler tube steel has indicated the formation of Cr_2O_3 and $NiCrO_3$ in the oxide scales. At 550 °C temperature phases of Na and V in form of Na_2SO_4 and Ni_3 $(VO_4)_2$ has also been observed. At 700 °C the formation of oxides of Cr and Ni can be seen. Small peaks of $NiCrO_3$ and Ni_3 $(VO_4)_2$ has also been observed. At 850 °C the main phases analyzed are Fe_2O_3 and $NiFe_2O_4$ along with some weak peaks of Cr_2O_3.

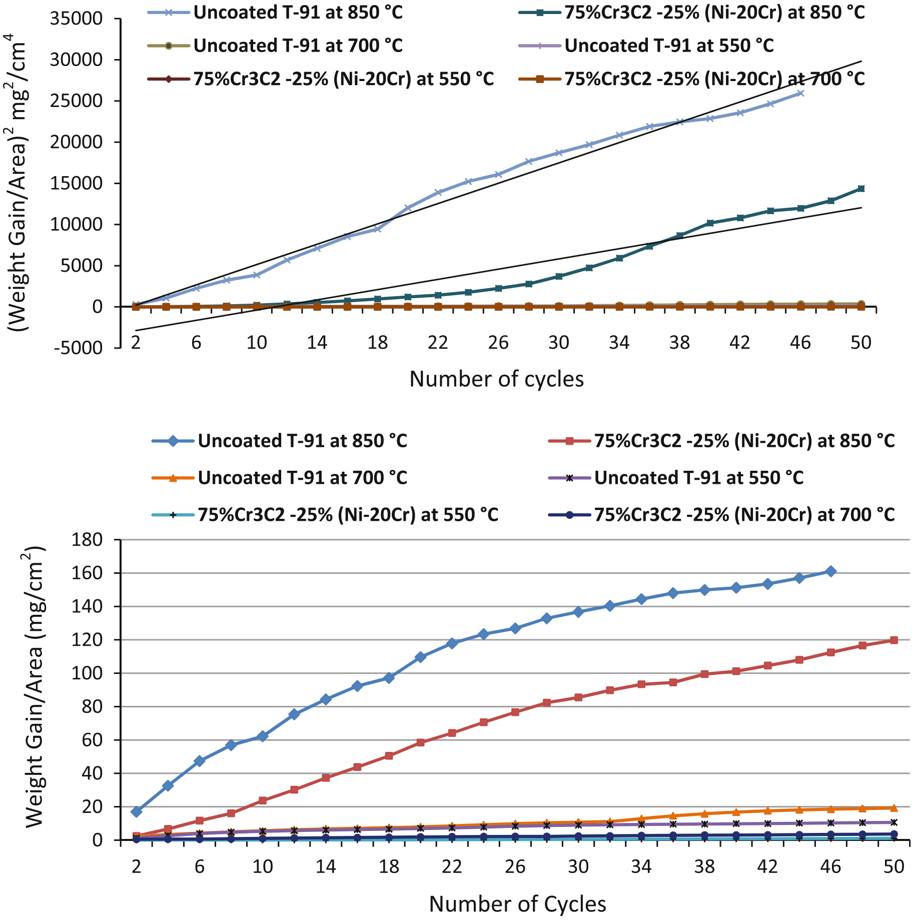

Fig. 2 The weight gain plots for the Uncoated and 75%Cr_3C_2-25% (Ni-20Cr) coated T-91at different temperatures subjected to cyclic oxidation for 50 cycles in Na_2SO_4-60% V_2O_5

Table 1 The parabolic rate constants (K_p) for uncoated and 75% Cr_3C_2-25% (Ni-20Cr) coated T-91 boiler tube steel at 550, 700 and 850 °C

Sample	Temperature, °C	Parabolic rate law constant (K_p) 10^{-10}, $g^2/cm^4/s^1$
Uncoated T-91	550	12.952
75% Cr_3C_2-25% (Ni-20Cr) coated T-91		0.0833
Uncoated T-91	700	46.944
75% Cr_3C_2-25% (Ni-20Cr) coated T-91		1.2388
Uncoated T-91	850	3427.7
75% Cr_3C_2-25% (Ni-20Cr) coated T-91		840.27

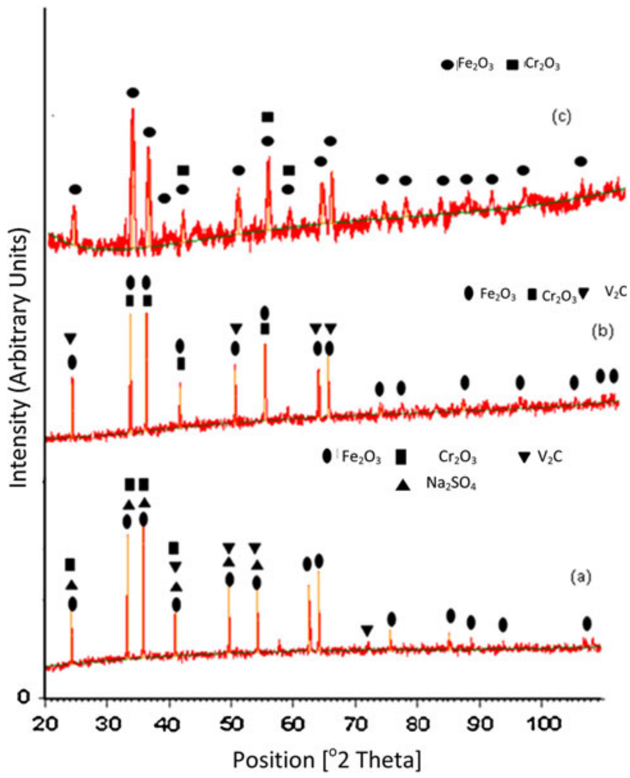

Fig. 3 X-ray diffraction profiles of the uncoated T-91 boiler steel subjected to corrosion in molten salt (Na_2SO_4-60%V_2O_5) environment at (a) 550 °C (b) 700 °C and (c) 850 °C for 50 cycles

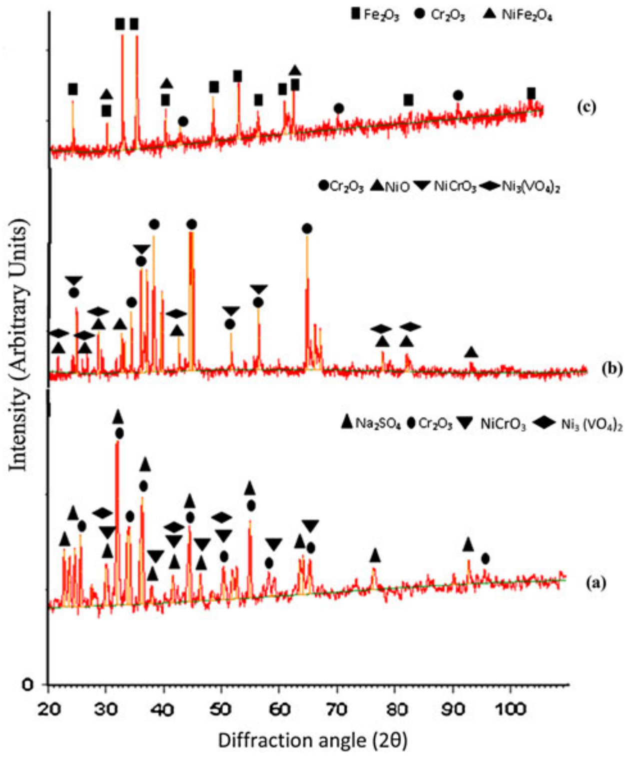

Fig. 4 X-ray diffraction profiles of the 75% Cr_3C_2-25% (Ni-20Cr) coated T-91 boiler tube steel subjected to corrosion in molten salt (Na_2SO_4-60%V_2O_5) environment at (a) 550 °C (b) 700 °C and (c) 850 °C for 50 cycles

3.4 SEM/EDAX of the Surface of Corroded Samples

SEM/EDAX micrographs with EDS spectrum of the uncoated T-91 boiler tube steel samples showing surface morphology after cyclic hot corrosion in Na_2SO_4-60%V_2O_5 environment for 50 cycles at 550, 700, and 850 °C are shown in Fig. 5(a-c), respectively.

In general, the EDS analysis of samples corroded at all temperatures reveals the scale rich in Fe and O, which indicates the possibility of formation of Fe_2O_3. Small amount of Cr and marginal amount of Ni are also indicated at the points of analysis, thereby predicting the possibility of formation of Cr_2O_3 and NiO. Significant amounts of Mo and Nb at the points of investigation indicating the diffusion of these elements from substrate into the top scale region.

After exposure at 550 °C the top surface of substrate seems to be consisting of flakes of scale and sharp whiskers. Overall the exposed areas of the scale seem to be adherent. The scale has an amorphous appearance after 50 cycles at 700 °C. The scale consists of sharp whiskers and a mixture of clusters of scale. Overall the exposed areas of the scale seem to be adherent, but at some places spalling of scale can also be seen. After 47 cycles of hot corrosion at 850 °C, large clusters of scale is observed at the surface of the steel at some places and the scale seems to grow in the adjoining areas where small clusters are observed to be formulating.

SEM/EDAX micrographs with EDAX spectrum of the 75%Cr_3C_2-25% (Ni-20Cr) coated T-91 boiler tube steel samples showing surface morphology after cyclic hot corrosion in Na_2SO_4-60%V_2O_5 environment for 50 cycles at 550, 700, and 850 °C are shown in Fig. 6(a-c), respectively.

Micrograph in Fig. 6(a) for the coated and corroded steel at 550 °C shows the top surface consisting of corrosive species even after completion of 50 cycles in form of Na (26.8 and 12.39%), S (32.61 and 4.8%), and V (3.30 and 18.35). Sufficient amount of O can also be observed on the top surface. EDAX analysis also shows sufficient amount of Cr and Ni to form protective spinels. Percentage of Fe is very marginal,

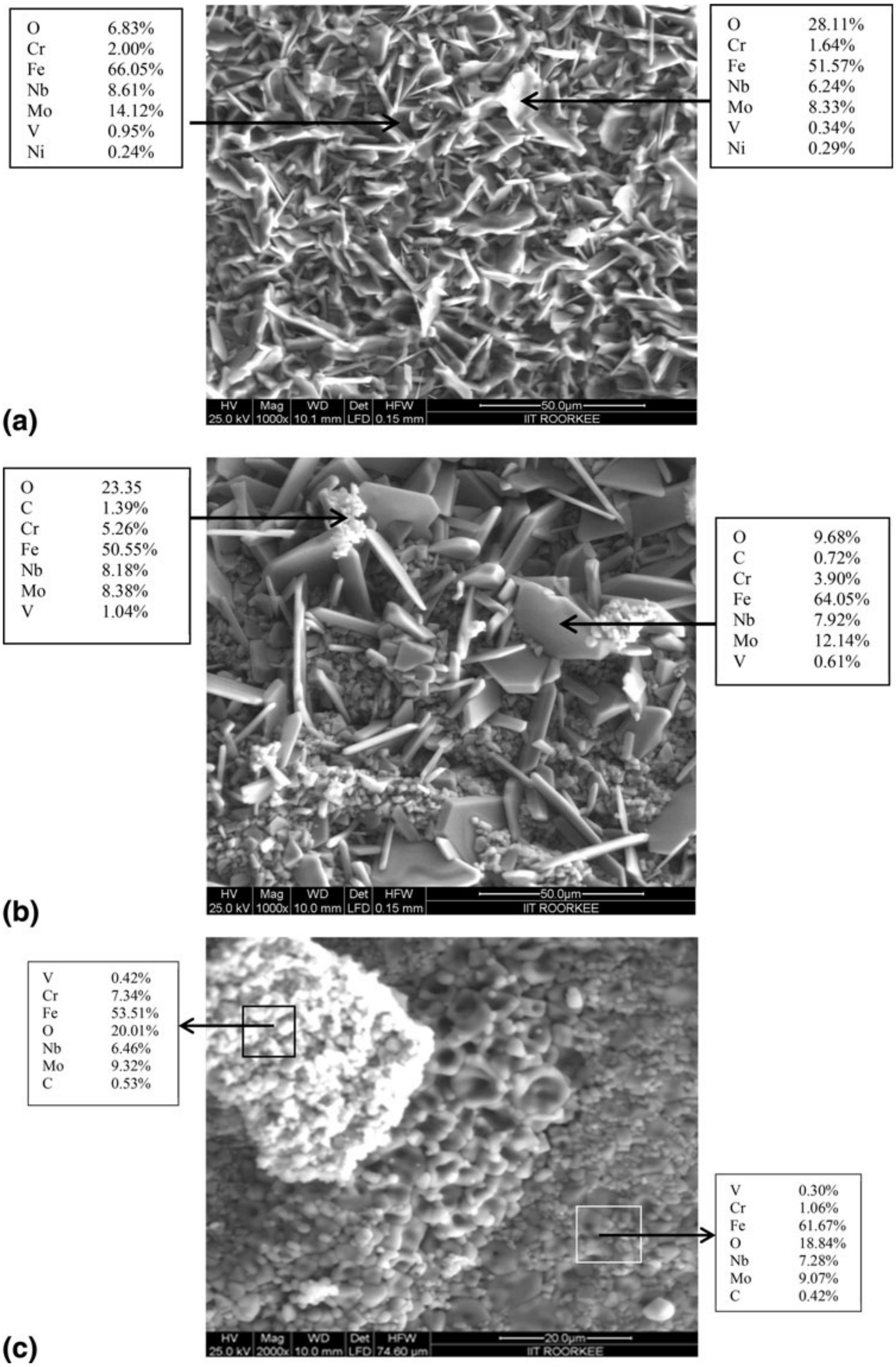

Fig. 5 (a) SEM/EDAX micrographs with EDS spectrum of the uncoated T-91 boiler tube steel samples showing surface morphology after cyclic hot corrosion in Na_2SO_4-60%V_2O_5 environment for 50 cycles at 550 °C (b) SEM/EDAX micrographs with EDS spectrum of the uncoated T-91 boiler tube steel samples showing surface morphology after cyclic hot corrosion in Na_2SO_4-60%V_2O_5 environment for 50 cycles at 700 °C (c) SEM/EDAX micrographs with EDS spectrum of the uncoated T-91 boiler tube steel samples showing surface morphology after cyclic hot corrosion in Na_2SO_4-60%V_2O_5 environment for 50 cycles at 850 °C

indicating start of formation of non protective oxide of iron (Fe_2O_3).

Surface EDAX for coated and corroded steel at 700 °C reveals relatively lesser weight percentages of Na, V, and S at the top surface than the sample corroded at 550 °C indicating the diffusion of these in to substrate to form aggressive environment and starting the corrosive attack. Even at this temperature the presence of Fe is marginal; however, sufficient

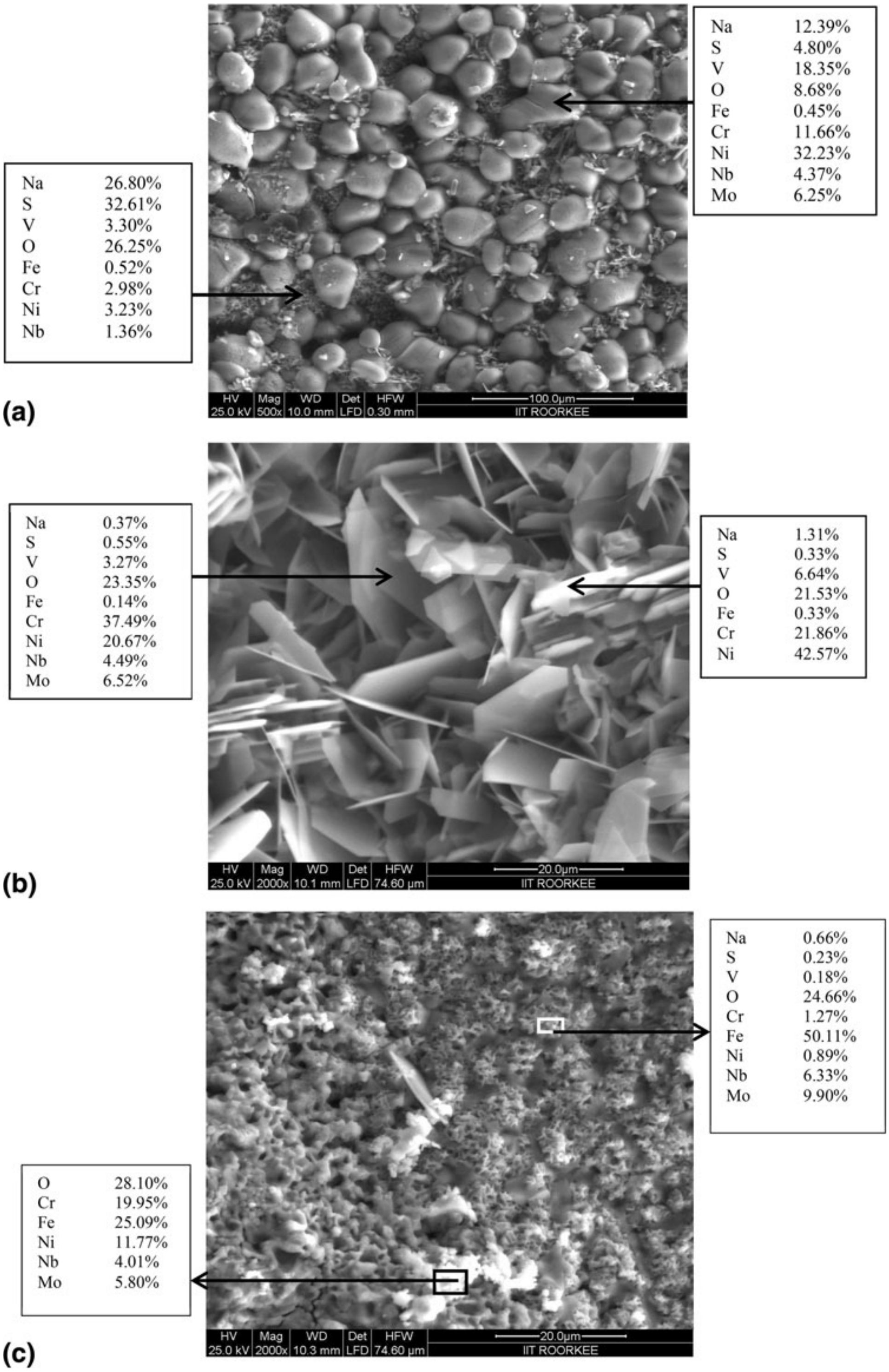

Fig. 6 (a) SEM/EDAX micrographs with EDS spectrum of the 75%Cr_3C_2-25% (Ni-20Cr) coated T-91 boiler tube steel samples showing surface morphology after cyclic hot corrosion in Na_2SO_4-60%V_2O_5 environment for 50 cycles at 550 °C (b) SEM/EDAX micrographs with EDS spectrum of the 75%Cr_3C_2-25% (Ni-20Cr) coated T-91 boiler tube steel samples showing surface morphology after cyclic hot corrosion in Na_2SO_4-60%V_2O_5 environment for 50 cycles at 700 °C (c) SEM/EDAX micrographs with EDS spectrum of the 75%Cr_3C_2-25% (Ni-20Cr) coated T-91 boiler tube steel samples showing surface morphology after cyclic hot corrosion in Na_2SO_4-60%V_2O_5 environment for 50 cycles at 850 °C

percentage of Cr and Ni can be observed at the points of investigations. The top surface of scale consists of sharp whiskers leading to spalling of scale in form of flakes (Fig. 6b).

After cyclic hot corrosion at 850 °C amorphous growth of scale can be observed at the surface of the steel as shown in Fig. 6(c). The flakes of scale can also be observed at some places. The EDAX analysis reveals traces of Na, V, and S at some places. The scale in general is found to be rich in Fe (50.11%) and O (24.66%) which indicates the possibility of formation of Fe_2O_3. However, at the other location Cr (19.95%) and Ni (11.77%) are available along with O (28.10%), thus indicating possible formation of protective oxides. Significant amounts of Mo and Nb are also seen at the points of investigation indicating the diffusion of these elements from substrate into the coating.

3.5 Cross-Sectional Analysis of the Oxide Scales

FE-SEM/EDAX analysis was carried out at different points of interest along the cross-section of the hot corroded uncoated and HVOF-sprayed Cr_3C_2-NiCr coated T-91 boiler tube steel and the results are shown in Fig. 7 and 8.

At all the temperatures diffusion of Mo and Nb from substrate towards outer layer of scale is observed. The SEM micrograph (Fig. 7a) of sample after exposure at 550 °C shows that there is a thick layer of scale on the top surface. Points 1 and 2 on the substrate are found to be rich in Fe. Thereafter, Fe content can be seen declining. However, the EDAX analysis of outer layer of scale shows high percentage of Fe and O, thereby indicating the formation of oxide of iron.

The EDAX analysis (Fig. 7b) of the sample after hot corrosion at 700 °C shows that the weight percentage of Fe starts declining from point 1 to point 3 and again starts increasing substantially; whereas, O is continuously increasing from point 1 to point 6 indicating the formation of non-protective oxide of iron. Significant percentage of V, Nb, and Mo can also be seen in the EDAX analysis.

Figure 8(a) shows hot corroded coated T-91 boiler tube steel sample at 700 °C. EDAX analysis at points 1, 2, and 3 shows rich percentage of Fe. EDAX analysis also shows a sharp decrease in percentage of Fe and steep rise in percentage of Cr thereafter. This clearly indicates presence of high percentage of Cr to form protective oxides to save substrate against corrosive attack. Top layer of the scale at point 7 shows significant amount of O and Cr indicating the formation of Cr_2O_3.

The micrograph shown in Fig. 8(b) shows a thick oxide layer (Fe_2O_3) on sample corroded at 850 °C. The weight percentage of Cr can be seen decreasing from point 2 onwards. Presence of significant amount of Fe and O can also be seen at different points indicating the existence of non protective oxide

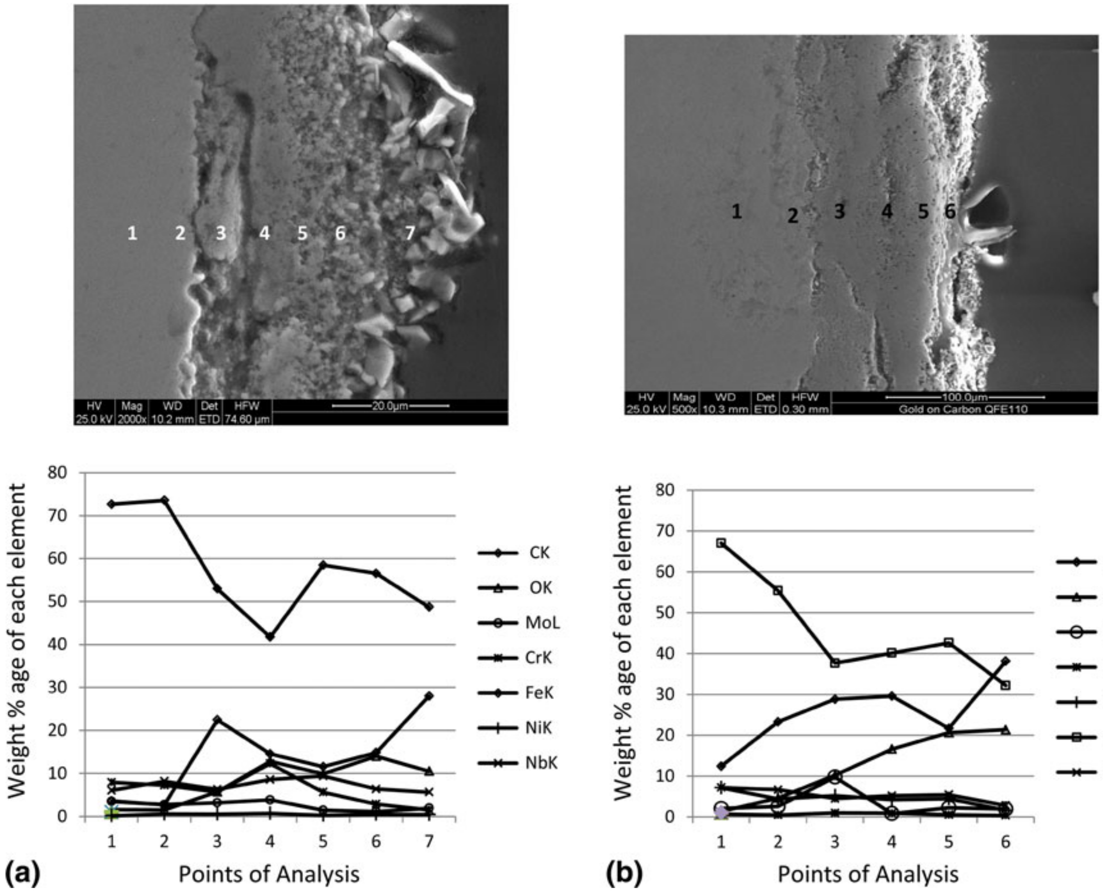

Fig. 7 (a) shows the cross-sectional analysis of uncoated T-91 boiler tube steel samples after cyclic hot corrosion in Na_2SO_4-60%V_2O_5 environment for 50 cycles at 550 °C (b) shows the cross-sectional analysis of uncoated T-91 boiler tube steel samples after cyclic hot corrosion in Na_2SO_4-60%V_2O_5 environment for 50 cycles at 700 °C

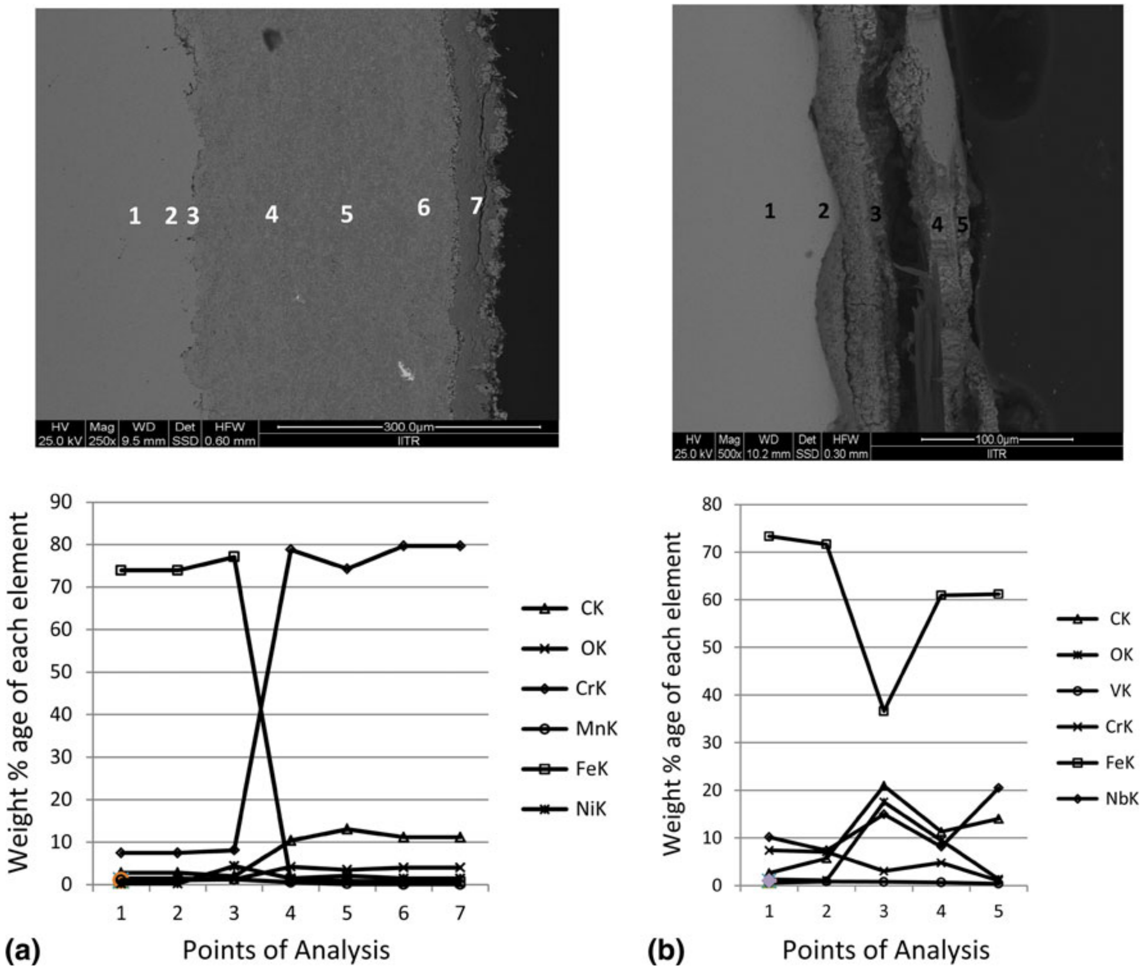

Fig. 8 (a) Cross-sectional analysis of 75%Cr_3C_2-25% (Ni-20Cr) coated T-91 boiler tube steel samples after cyclic hot corrosion in Na_2SO_4-60%V_2O_5 environment for 50 cycles at 700 °C. (b) Cross-sectional analysis of 75%Cr_3C_2-25% (Ni-20Cr) coated T-91 boiler tube steel samples after cyclic hot corrosion in Na_2SO_4-60%V_2O_5 environment for 50 cycles at 850 °C

layer of Fe_2O_3. Significant percentage of Nb can also be seen in the EDAX analysis at all points of investigation showing the diffusion of elements from substrate towards the top surface.

3.6 X-ray Mapping Analysis

X-ray mapping analysis of the scale formed on uncoated and coated T-91 boiler tube steel samples after hot corrosion at different operating temperatures for 50 cycles are shown in Fig. 9-11.

For uncoated T-91 boiler tube steel movement of Mo from substrate towards the outer scale has been observed in mapping. The upper scale is found to be rich in Fe and O as shown in Fig. 9 for sample corroded at 850 °C for 50 cycles. Presence of Cr-rich areas from where Fe is depleted indicates the possibility of formation of chromium oxide (Cr_2O_3).

X-ray mappings for the oxide scale of coated T-91 boiler tube steel samples after cyclic hot corrosion in Na_2SO_4-60%V_2O_5 environment for 50 cycles at 550 °C is shown in Fig. 10. It can be clearly analyzed from the mappings that Fe is restricted to substrate and a thick layer of Cr and Ni throughout coating is also present. A thick layer of V at the top of scale can also be seen. In the mappings diffusion of Mo from substrate towards coating can also be seen.

After cyclic hot corrosion at 850 °C the x-ray mappings for the oxide scale of sample (Fig. 11) shows a thick oxide layer with disintegrated scale at the top surface rich in Fe, O, Cr, and Ni. This indicates existence of protective oxides of Cr and Ni along with non protective oxides of Fe. Movement of Mo towards outer surface can also be visualized in the mapping.

4. Discussion

HVOF-sprayed on T91 boiler tube steel exhibits a dense, adherent and uniform coating. The coating thickness was measured along the cross-sections of some randomly selected samples, which was found to be 390 µm thereby ensuring integrity of the coatings. Higher thickness may lead to disintegration of the coatings as reported by Singh et al. (Ref 16), Roy et al. (Ref 17), and Espallargas et al. (Ref 18) in their studies for Cr_3C_2-NiCr coatings.

Dense coatings usually provide better corrosion resistance than the porous coatings. The coatings should have minimum possible porosities because they can do harm to the persistent corrosion resistance of thermal spray coatings (Ref 19, 20). Low value of porosity in case of HVOF-sprayed coatings might

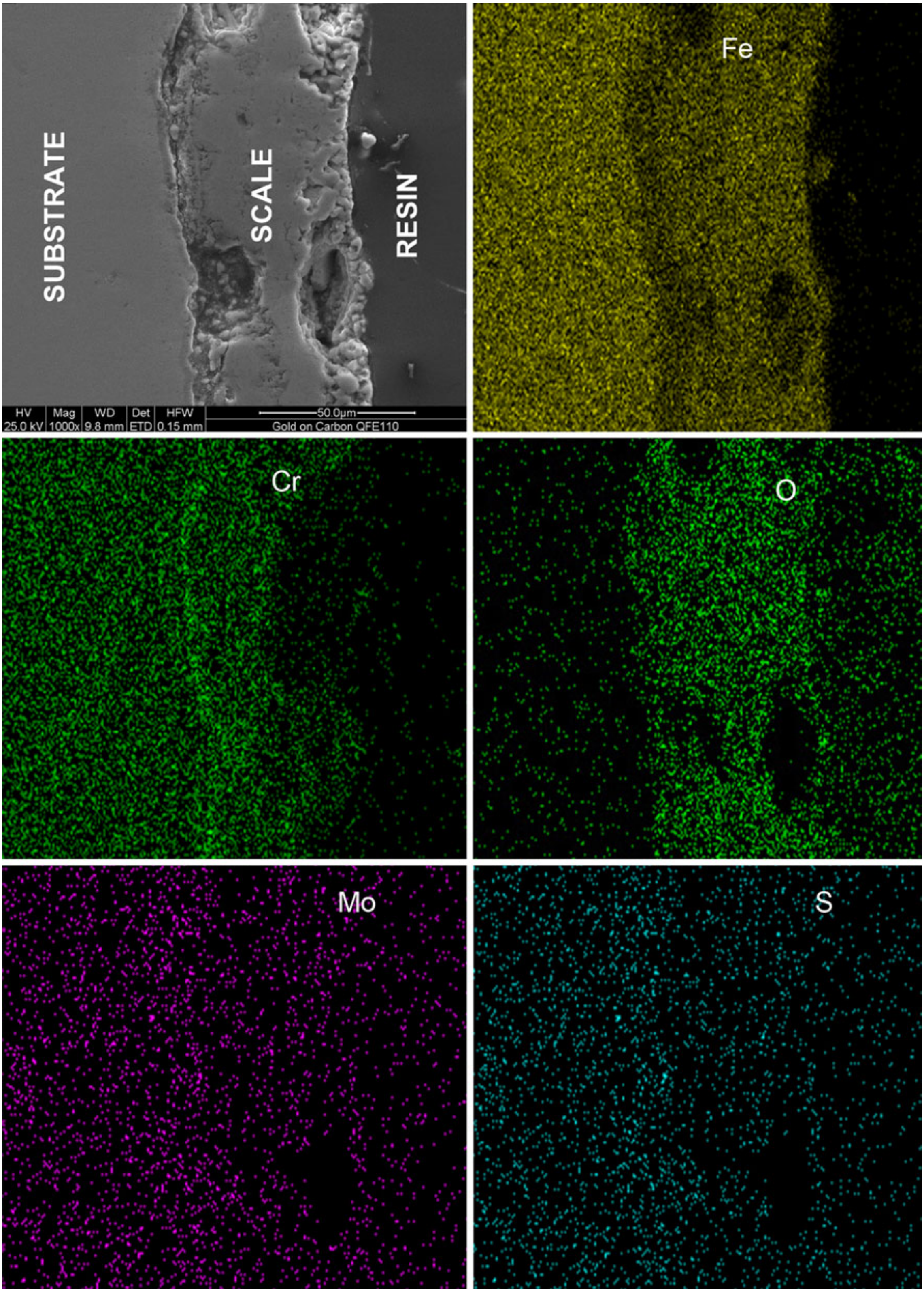

Fig. 9 Composition image (SE) and x-ray mapping of the cross-section of the uncoated T-91 boiler tube steel subjected to cyclic oxidation at 850 °C in Na_2SO_4-60% V_2O_5 corrosive environment for 50 cycles

be due to high kinetic energy of the powder particles propelled out of the gun nozzle toward the substrate leading to an excellent joining of flat disk particles with the substrate and with an interlayer, and thus the coatings produced by HVOF spraying process are very dense (Ref 16, 21). Porosity measurements of the coating has been found to be less than

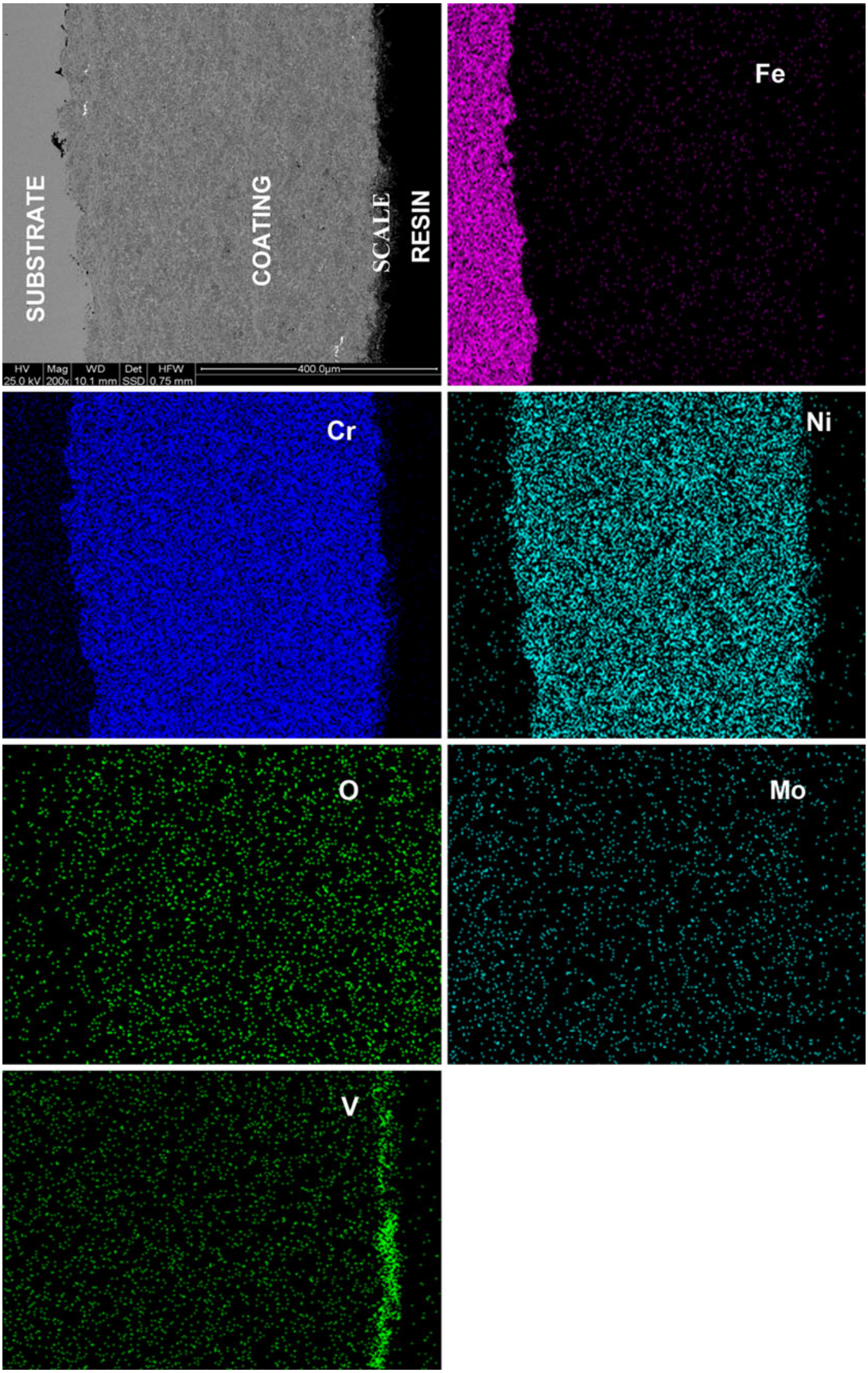

Fig. 10 Composition image (SE) and x-ray mapping of the cross-section of the 75%Cr_3C_2-25% (Ni-20Cr) coated T-91 boiler tube steel subjected to cyclic oxidation at 550 °C in Na_2SO_4-60% V_2O_5 corrosive environment for 50 cycles

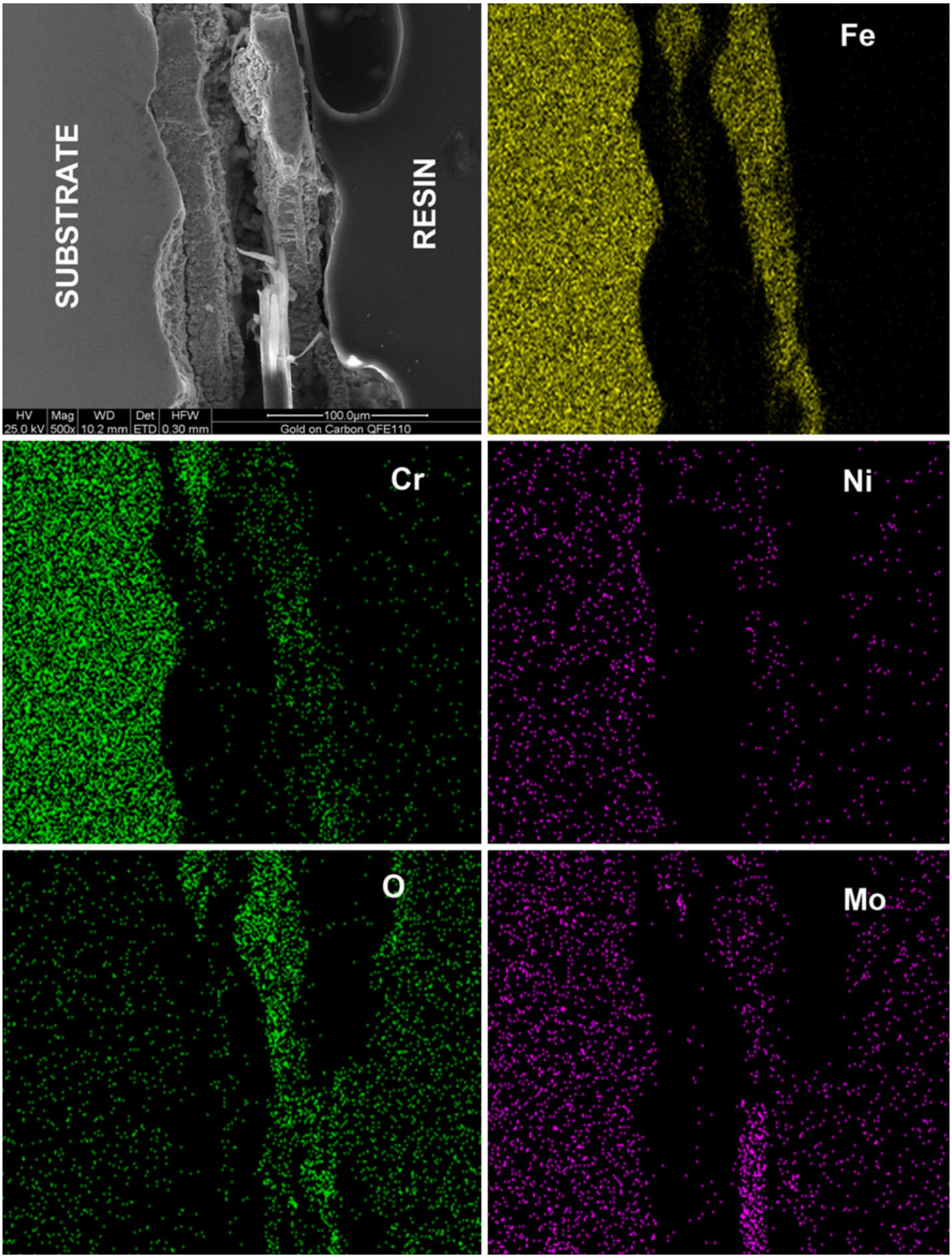

Fig. 11 Composition image (SE) and x-ray mapping of the cross-section of the 75%Cr_3C_2-25% (Ni-20Cr) coated T-91 boiler tube steel subjected to cyclic oxidation at 850 °C in Na_2SO_4-60% V_2O_5 corrosive environment for 50 cycles

2% and are identical to the values of porosity for HVOF coated Cr_3C_2-NiCr coatings reported by Singh et al. (Ref 16), Murthy et al. (Ref 22), and Fedrizzi et al. (Ref 23) in their studies.

The microhardness of the HVOF-sprayed coating was found to be higher than their corresponding substrate. High microhardness value is believed to be due to the high kinetic energy acquired by the powder particle, which ensures a good cohesion, denser, and more homogeneous structure, deformation reinforcement and oxides free spray process, as suggested by Mingxi et al. (Ref 24). The measured values of microhardness of HVOF coating under study is found to be in good agreement with the findings reported by Murthy et al. (Ref 22), Yin et al. (Ref 25), Żórawski et al. (Ref 26), and Sidhu et al. (Ref 27).

The uncoated T-91 steel after cyclic hot corrosion in given salt mixture have shown parabolic behavior in general, except for some deviations shown at 700 and 850 °C, which may be attributed to cyclic and rapid growth of inhomogeneous oxides as suggested by Sidhu et al. (Ref 28), Singh et al. (Ref 29), Kamal et al. (Ref 30), and Bala et al. (Ref 31). The formation and spalling of scale was lesser at 550 °C temperature. The reason for this might be attributed to the melting temperatures of salt mixture constituents, which melt in the temperature range of 500-550 °C (Ref 14, 15). However, the uncoated T-91 steel showed rapid formation of scale and intense spalling after exposure to the molten salt induced corrosion for 50 cycles at 700 and 850 °C.

The weight change graph (Fig. 2) showed that the weight gain of samples increased continuously from the initial cycles and continued till the end of studies. The higher corrosion rate during initial hours of study might be attributed to the direct application of salt layer on the metallic surface which allow rapid oxygen pick up by a diffusion of oxygen through molten salt layer, resulting in earlier corrosive attack and the diffusion of corrosive species in the substrate (Ref 32). So, in the earlier stages of hot corrosion there is a rapid increase in the mass of the uncoated specimen during initial cycles is due to rapid oxidation. After a period it has been observed that the rate of corrosion tends to become almost uniform with the further progress of study (Ref 32). Higher initial period weight gain results are in good agreement with the earlier studies by Singh et al. (Ref 33), Tiwari and Prakash (Ref 34), Hamid et al. (Ref 35), and Singh et al. (Ref 36) for their studies on boiler steels in the same molten salt environment.

According to Sachs (Ref 37) poor corrosion resistance of the uncoated sample is due to intense spalling and sputtering which can be attributed to the severe strain developed as a result of Fe_2O_3 precipitation from the liquid phase and the interdiffusion of intermediate layer of iron oxide. Also presence of Fe and Mo in a thin layer might have imposed severe strain on the scale, because Mo oxides causes an alloy induced acidic flux which might have resulted in spallation, cracking, and exfoliation of the oxide scale. These cracks might have allowed the corrosive molten salt contents to reach the metal substrate (Ref 21, 28). Fe_2O_3 phase is indicated in XRD analysis shown in Fig. 5(a-c). The outward diffusion of Mo from substrate towards top scale can be seen in x-ray mapping shown in Fig. 9. Similar diffusion process has been reported in the studies conducted by Kamal et al. (Ref 30), Sidhu et al. (Ref 38), Mahesh et al. (Ref 39), and Singh et al. (Ref 33).

In the given molten salt environment, the coated T-91 boiler tube steel at 550 and 700 °C gets oxidized from the top surface and the remaining portion was found similar to the as sprayed coating. The EPMA analysis (Fig. 10) and EDAX analysis (Fig. 8a) also confirm absence of O and other corrosive species in the substrate and near coating substrate interface at 550 and 700 °C temperatures. At 850 °C, the coating was completely consumed in saving the substrate from the corrosive attack as shown in Fig. 11.

The surface XRD/EDAX analysis indicated the formation of non protective oxide of Fe_2O_3 as the main constituent of the top scale in the uncoated steel after the hot corrosion in Na_2SO_4-60% V_2O_5 environment at all the three temperatures selected for study. The formation of Fe_2O_3 has also been reported by Singh et al. (Ref 33), Bala et al. (Ref 40), Das et al. (Ref 41), and Kaur et al. (Ref 42) during their studies on hot corrosion in Na_2SO_4-60%V_2O_5 environment at high temperatures.

XRD analysis as shown in Fig. 6(a) and (b) indicated formation of Cr_2O_3, $Ni_3(VO_4)_2$and $NiCrO_3$ phases at 550 °C and Cr_2O_3, NiO, $NiCrO_3$ and $Ni_3(VO_4)_2$ phases at 700 °C. NiO, Cr_2O_3, and $NiCrO_3$ has been reported as protective oxides and also acts as diffusion barriers for oxidizing species by Seierstein and Kofstad (Ref 43), Stroosnijder et al. (Ref 44). Formation of similar phases have been reported by Kamal et al. (Ref 30), Singh et al. (Ref 33), Hamid (Ref 35), Singh et al. (Ref 36), Sidhu et al. (Ref 45), and Kaur et al. (Ref 42) in their studies. The presence of these elements at the surface of the corroded samples after 50 cycles in the given environment of molten salt has been validated by EDAX analysis (Fig. 8a).

The scale formed on the surface of the coating when the sample is subjected to cyclic corrosion for 50 cycles in given molten salt environment at 850 °C is observed to be thick and having multiple layers. The EDAX analysis along cross section of the sample shows that the Weight percentage of Fe is very high at all points of observation. The XRD analysis also confirms the phases of Fe_2O_3, $NiFe_2O_4$. The x-ray mapping shown in Fig. 11 also validated the formation of non protective oxides of Fe.

5. Conclusions

- The 75%Cr_3C_2-25% (Ni-20Cr) coating has been successfully deposited by HVOF process. The coating has 390-μm thickness, less than 2% porosity, 4.872 μm roughness, uniform and dense microstructure.
- The coating was found useful in providing necessary corrosion resistance to T-91 boiler steel against molten salt (Na_2SO_4-60%V_2O_5) environment under cyclic conditions.
- The coated steel followed the parabolic law of oxidation at 550 and 700 °C and its parabolic rate constants were small when compared with that of bare steel at all the temperatures under study.
- Formation of the protective oxides of chromium and nickel, and their spinels like Cr_2O_3, NiO, and $NiCr_2O_4$ at 550 and 700 °C might have contributed in blocking the transport of degrading corrosive species through the coating and thus contributed to hot corrosion resistance.
- Fe_2O_3 was identified as the major phase by XRD, EDAX, and EPMA analysis in the scale of uncoated T-91 boiler tube steel. The bare steel underwent intense spalling of scale.
- Some elements of the substrate such as Mo and Nb showed a tendency of outward diffusion from the substrate to the coating.

Acknowledgment

Rakesh Bhatia et al, thankfully acknowledge the research grant from Department of Science and Technology (SERC Division), New Delhi (SR/S3/ME0049/2009 dated 18-7-11) for carrying out the R&D work on “Development of Corrosion Resistant HVOF

Sprayed Cr_3C_2-NiCr Coatings for Boiler Tube Steels Operating at Elevated Temperatures."

References

1. N. Eliaz, G. Shemesh, and R.M. Latanision, Hot Corrosion in Gas Turbine Components, *Eng. Failure Anal.*, 2002, **9**, p 31–43
2. T.S. Sidhu, A. Malik, S. Prakash, and R.D. Agrawal, Oxidation and Hot Corrosion Resistance of HVOF WC-NiCrFeSiB Coating on Ni- and Fe-Based Superalloys at 800 °C, *J. Therm Spray Technol.*, 2007, **16**, p 844–849
3. W.M. Zhao, Y. Wang, L.X. Dong, K.Y. Wu, and J. Xue, Corrosion Mechanism of NiCrBSi Coatings Deposited by HVOF, *Surf. Coat. Technol.*, 2005, **190**(2-3), p 293–298
4. T.S. Sidhu, S. Prakash, and R.D. Agrawal, Studies on the Properties of High-Velocity Oxy-Fuel Thermal Spray Coatings for Higher Temperature Applications, *Mater. Sci.*, 2005, **41**(6), p 805–823
5. G.R. Heath, P. Hiemgartner, G. Irons, R. Miller, and S. Gustafsson, An Assessment of Thermal Spray Coating Technologies for High Temperature Corrosion Protection, *Mater. Sci. Forum*, 1997, **251-254**, p 809–816
6. T.S. Sidhu, S. Prakash, and R.D. Agrawal, State of the Art of HVOF Coating Investigation—A Review, *Mar. Technol. Soc. J.*, 2005, **39**(2), p 55–66
7. M.A. Uusitalo, P.M.J. Vuoristo, and T.A. Mantyla, High Temperature Corrosion of Coatings and Boiler Steels in Reducing Chlorine-Containing Atmosphere, *Surf. Coat. Technol.*, 2002, **161**(2-3), p 275–285
8. U. Erning and M. Nestler, *Proceedings of United Thermal Spray Conference (UTSC 99)*. Düsseldorf, 1999, p 462
9. A.C. Savarimuthu, I. Megat, H.F. Taber, J.R. Shadley, E.F. Rybicki, W.A. Emery, J.D. Nuse and D.A. Somerville, *Proceedings of 1st International Thermal Spray Conference (ITSC 2000)*, Canada, 2000, p 1095
10. P.L. Ko and M.F. Robertson, Wear Characteristics of Electrolytic Hard Chrome and Thermal Sprayed WC-10 Co-4 Cr Coatings Sliding Against Al-Ni-Bronze in Air at 21 °C and at −40 °C, *Wear*, 2002, **252**, p 880–893
11. T. Sahraoui, N.E. Fenineche, G. Montavon, C. Coddet, *Proceedings of International Thermal Spray Conference (ITSC 2004)*, Japan, 2004, p 488
12. Y. Harada and T. Kawamura, Control of Gas Side Corrosion in Oil Fired Boiler, *Mitsubishi Heavy Ind. Tech. Rev.*, 1980, **17**, p 139
13. Y. Harada, S. Naito, T. Tsuchiya, and Y. Nakajima, Problems of Low Grade Oil Firing Boilers and Their Solutions, *Mitsubishi Heavy Ind. Tech. Rev.*, 1981, **18**(2), p 85–95
14. E. Otero, A. Pardo, J. Hernaez, and F.J. Perez, The Corrosion of Some Superalloys (At 1000 K) in Molten Eutectic Mixture 60% V_2O_5-40% Na_2SO_4: The Influence of the Oxygen and Carbon Residues, *Corros. Sci*, 1992, **34**, p 1747–1757
15. S.N. Tiwari, Investigations on Hot Corrosion of Some Fe-, Ni- and Co-Base Superalloy in Na_2SO_4-V_2O_5 Environment Under Cyclic Conditions, Ph. D. Thesis, University of Roorkee, India, 1997
16. H. Singh, B.S. Sidhu, and S. Prakash, Mechanical and Microstructural Properties of HVOF Sprayed WC-Co and Cr_3C_2-NiCr Coatings on the Boiler Tube Steels Using LPG as the Fuel Gas, *J. Mater. Process. Technol.*, 2006, **171**, p 77–82
17. M. Roy, A. Pauschitz, R. Polak, and F. Franek, Comparative Evaluation of Ambient Temperature Friction Behaviour of Thermal Sprayed Cr_3C_2-25(Ni20Cr) Coatings with Conventional and Nano-Crystalline Grains, *Tribol. Int.*, 2006, **39**, p 29–38
18. N. Espallargas, J. Berget, J.M. Guilemany, A.V. Benedetti, and P.H. Suegama, Cr_3C_2-NiCr and WC-Ni Thermal Spray Coatings as Alternatives to Hard Chromium for Erosion-Corrosion Resistance, *Surf. Coat Technol.*, 2008, **202**, p 1405–1417
19. L. Zhao, J. Zwick, and E. Lugscheider, HVOF Spraying of Al_2O_3-Dispersion-Strengthened NiCr Powders, *Surf. Coat. Technol.*, 2004, **182**(1), p 72–77
20. W.M. Zhao, Y. Wang, L.X. Dong, K.Y. Wu, and J. Xue, Corrosion Mechanism of NiCrBSi Coatings Deposited by HVOF, *Surf. Coat. Technol.*, 2005, **190**, p 293–298
21. T.S. Sidhu, S. Prakash, and R.D. Agrawal, Performance of a High Velocity Oxy-Fuel Sprayed Coatings on a Fe-Based Superalloy in Na_2SO_4-60%V_2O_5 Environment at 900 °C, Part I: Characterisation of the Coatings, *J. Mater. Eng. Perform.*, 2006, **15**(1), p 122–129
22. J.K.N. Murthy, S. Bysakh, K. Gopinath, and B. Venkataraman, Microstructure Dependent Erosion in Cr_3C_2-20(NiCr) Coating Deposited by a Detonation Gun, *Surf. Coat. Technol.*, 2007, **204**, p 3975–3985
23. L. Fedrizzi, L. Valentinelli, S. Rossi, and S. Segna, Tribo Corrosion Behavior of HVOF Cermet Coatings, *Corros. Sci.*, 2007, **49**, p 2781–2799
24. L. Mingxi, H. Yizhu, and S. Guoxiong, Microstructure and Wear Resistance of Laser Clad Cobalt-Based Alloy Multi-layer Coatings, *App. Surf. Sci.*, 2004, **230**(1-4), p 201–206
25. B. Yin, G. Liu, H. Zhou, J. Chen, and F. Yan, Sliding Wear Behavior of HVOF Sprayed Cr_3C_2-NiCr/CeO_2 Composite Coatings at Elevated Temperature Upto 800 °C, *Tribol. Lett.*, 2010, **37**, p 463–475
26. W. Żórawski and S. Kozerski, Scuffing Resistance of Plasma and HVOF Sprayed WC12Co and Cr_3C_2-25(Ni20Cr) Coatings, *Surf. Coat. Technol.*, 2008, **202**, p 4453–4457
27. H.S. Sidhu, B.S. Sidhu, and S. Prakash, Wear Characteristics of Cr_3C_2-NiCr and WC-Co Coatings Deposited by LPG Fueled HVOF, *Tribol. Int.*, 2010, **43**, p 887–890
28. T.S. Sidhu, S. Prakash, and R.D. Agrawal, Characterizations and Hot Corrosion Resistance of Cr_3C_2-NiCr Coating on Ni-Base Superalloys in an Aggressive Environment, *J. Therm. Spray Technol.*, 2006, **15**(4), p 811–816
29. H. Singh, Gitanjaly, S. Singh, and S. Prakash, High Temperature Corrosion Behaviour of Some Fe-, Co- and Ni-Base Superalloys in the Presence of Y_2O_3 as Inhibitor, *Appl. Surf. Sci.*, 2009, **255**(15), p 7062–7069
30. S. Kamal, R. Jayaganthan, S. Prakash, and S. Kumar, Hot Corrosion Behavior of Detonation Gun Sprayed Cr_3C_2-NiCr Coatings on Ni and Fe-Based Superalloys in Na_2SO_4-60%V_2O_5 Environment at 900 °C, *J. Alloys Compd.*, 2008, **463**(1-2), p 358–372
31. N. Bala, Investigations on the Hot Corrosion Behaviour of Cold Spray and HVOF Spray Coatings on T22 and SA 516 Steels, Ph.D. Thesis, Punjab Technical University, India, 2010
32. H.S. Sidhu, B.S. Sidhu, and S. Prakash, The Role of HVOF Coatings in Improving Hot Corrosion Resistance of ASTM-SA210 GrA1 Steel in the Presence of Na_2SO_4-V_2O_5 Salt Deposits, *Surf. Coat. Technol.*, 2006, **200**(18-19), p 5386–5394
33. S. Singh, H.S. Sidhu, and B.S. Sidhu, High Temperature Hot Corrosion Behaviour of NiCr and Cr_3 C_2-NiCr coatings on T91 Boiler Steel in an Aggressive Environment at 750 °C, *Surf. Coat. Technol.*, 2012, **206**, p 3839–3850
34. S.N. Tiwari and S. Prakash, Studies on the Hot Corrosion Behaviour of Some Superalloys in Na_2SO_4-V_2O_5, Proc. of SOLCEC, Kalpakkam, India, 22-24th Jan., 1997, Paper C33
35. A. Ul-Hamid, Diverse Scaling Behavior of the Ni-20Cr Alloy, *Mater. Chem. Phys.*, 2003, **80**, p 135–142
36. H. Singh, D. Puri, and S. Prakash, Some Studies on Hot Corrosion Performance of Plasma Sprayed Coatings on a Fe-Based Superalloy, *Surf. Coat. Technol.*, 2005, **192**(1), p 27–38
37. K. Sachs, Accelerated High Temperature Oxidation Due to Vanadium Pentoxide, *Metallurgia*, Apr., 1958, p 167-173
38. T.S. Sidhu, S. Prakash, and R.D. Agrawal, Studies of the Metallurgical and Mechanical Properties of High Velocity Oxy-Fuel Sprayed Stellite-6 Coatings on Ni- and Fe-Based Superalloys, *Surf. Coat. Technol.*, 2006, **201**, p 273–281
39. R.A. Mahesh, R. Jayaganthan, and S. Prakash, Microstructural Characterization and Hardness Evaluation of HVOF Sprayed Ni-5Al Coatings on Ni- and Fe-Based Superalloys, *J. Mater. Process. Technol.*, 2009, **209**, p 3501–3510
40. N. Bala, H. Singh, and S. Prakash, High Temperature Corrosion Behavior of Cold Spray Ni-20Cr Coating on Boiler Steel in Molten Salt Environment at 900 °C, *J. Therm. Spray Technol.*, 2009, **19**, p 110–118
41. D. Das, R. Balasubramaniam, and M.N. Mungole, Hot Corrosion of Fe_3Al, *J. Mater. Sci.*, 2002, **37**(6), p 1135–1142
42. M. Kaur, H. Singh, and S. Prakash, High Temperature Corrosion Studies of HVOF Sprayed Cr_3C_2-NiCr Coating on SAE-347H Boiler Steel, *J. Therm. Spray Technol.*, 2009, **18**(4), p 619–632
43. M. Seiersten and P. Kofstad, The Effect of SO_3 on Vanadate-Induced Hot Corrosion, *High Temp. Technol.*, 1987, **5**(3), p 115–122
44. M.F. Stroosnijder, R. Mevrel, and M.J. Bennet, The Interaction of Surface Engineering and High Temperature Corrosion Protection, *Mater. High Temp.*, 1994, **12**(1), p 53–66
45. T.S. Sidhu, S. Prakash, and R.D. Agrawal, Hot Corrosion Studies of HVOF Sprayed Cr_3C_2-NiCr and Ni-20Cr Coatings on a Nickel Based Superalloy at 900 °C, *Surf. Coat. Technol.*, 2006, **201**, p 792–800