

Hot Corrosion Study of High Velocity Oxy-Fuel (HVOF) Sprayed Coatings on Boiler Tube Steel in Actual Coal Fired Boiler

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Abstract. The present study was focused on the effect of high velocity oxy-fuel (HVOF) sprayed 93(WC-Cr₃C₂)-7Ni and 86WC-10CO-4C coatings on boiler steel alloys ASME SA213 T22 and ASME SA213 T91 in coal fired boiler environment. To assess the performance of the coatings in actual conditions the coated as well as the uncoated steels were subjected to cyclic exposures, in the superheater zone of a coal fired boiler for 10 cycles at 900 °C. Both the coatings used were observed to be uniform and dense having thickness between 200-250 µm. Each cycle consists of 100 h heating followed by 1 h cooling at ambient conditions. The thermogravimetric technique was used to establish the kinetics of corrosion. X-ray diffraction (XRD), Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) techniques were used to analyse corrosion products. The hot corrosion resistance of 86WC-10CO-4C coating was found better on ASME SA213 T22 whereas 93(WC-Cr₃C₂)-7Ni coating was better on ASME SA213 T22.

Keywords: corrosion, boiler steel, degradation, HVOF, coal fired boilers

Introduction

Hot corrosion has been recognised as a severe problem in boiler tubes of super heater and reheater zone, which may result in premature failure of the tubes. One method to overcome this major problem is the use of thermal spray protective coatings. In past few years, high velocity Oxy-fuel (HVOF) spraying has shown a dramatic influence on the field of thermal sprays. The coating produced is less porous and has higher bond strength than that produced by other methods which is due to the high velocity and high impact of the sprayed powder (Tan *et al.*, 1999). The cost corrosion of metals may rises over \$300 billion per year (4.2% GNP) in United States. It is estimated that every year about 40% of total US steel production goes to replace the corroded parts and products. Although these problems of corrosion can not be wholly remedied but corrosion-related costs can be diminished by more than 30% with the development and use of better corrosion resistant coatings (Priyantha *et al.*, 2003). Thermal spraying has been considered successful to apply the protective coatings, without disturbing any other properties of the component (Bala *et al.*, 2009; Tillmann *et al.*, 2000). Mostly all the thermally sprayed coatings include splats and splat boundaries. Due to the porosity present at splat boundaries, the coatings are prone to corrosive attack (Usitalo *et al.*, 2004). HVOF coatings provide low

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porosity, homogeneous, compact and hard structures with sufficient thickness to stop the advancing of electrolytes (Guilemany *et al.*, 2008). Kawakita *et al.* (2005) studied that with the addition of molybdenum, a considerable improvement was noticed against corrosion and was most effective on 8% mass molybdenum. Sidhu *et al.* (2006) studied the role of high velocity oxyfuel (HVOF) coatings in improving hot corrosion resistance of boiler tube steel (ASTM-SA210 GrA1) and investigated that among Cr₂C₃-NiCr, NiCr, Wc-Co and stellite-6 coatings, NiCr showed maximum whereas Wc-Co showed minimum resistance to corrosion. Sidhu *et al.* (2006a) devised Ni-20Cr wire coating proved effective than Cr₂C₃-NiCr using Ni-based superalloy in environment of molten salt Na₂SO₄-V₂O₅ at 900 °C. Sidhu *et al.* (2006b) successfully applied Ni-20%Cr wire coatings onto Ni- and Fe- based superalloys by high velocity oxyfuel process (HVOF) for hot corrosion studies with purpose to characterise the surface and cross-section morphology and confirmed the presence of Ni as main constituent of Ni-20%Cr coating. Sidhu (2006) and Prakash (2006) experimentally investigated that plasma sprayed stellite-6 have higher resistance to erosion-corrosion and T11 coated steel showed the maximum degradation resistance. Sidhu *et al.* (2006c) investigated that NiCrBSi coatings were beneficial in lowering the corrosion rate in given environment. Sidhu *et al.* (2006d) used HVOF (high

velocity oxy-fuel) process for deposition of NiCrBSi, Cr₂C₃-NiCr, Ni-20Cr and stellite-6 coatings on Fe-based superalloy to study the performance of coatings under cyclic conditions in Na₂SO₄-60%V₂O₅ at 900 °C and noticed that Ni-20Cr coating showed maximum resistance to corrosion. Goyal *et al.* (2008) studied that ZrO₂ was capable of reducing high temperature corrosion in all alloys and was most useful in Superni 75 followed by Superco 605 and slightly in Superfer 800H. Rajasekaran *et al.* (2004) explained that D-gun spraying minimizes the degradation of the feedstock powder due to lower heat and shorter duration involved in the deposition process. Kamal *et al.* (2009) investigated that hot-corrosion resistance was better for Cr₃C₂-NiCr-coated superalloys as compared to the uncoated superalloys in the presence of 75 wt.% Na₂SO₄+ 25 wt.% K₂SO₄ film due to the formation of protective oxides of chromium and nickel. Kaushal *et al.* (2011) revealed that coating had potential to lower the high temperature corrosion using detonation gun spray method to deposit Ni-20Cr onto ASTM A213 TP347H boiler steel. Manpreet (2011) proved Cr₃C₂-NiCr coating to be highly protective against corrosion. Using detonation-gun spray process in which very high particle velocities approaching 4-5 times the speed of sound are achieved. Mishra *et al.* (2013) reported that aluminium, chromium and yttrium were acting as protective oxides for boiler environmental conditions when the performance of plasma sprayed Ni-22Cr-10Al-1Y coating on different super alloys such as Superni 75, Superni 600, Superni 718 and Superfer 800H was investigated. Kaushal *et al.* (2014) found Detonation sprayed coating to be most protective among all HVOF, detonation gun and cold sprayed Ni-20Cr coatings on T22 boiler steel tube, he also demonstrated that all three techniques were

beneficial in decreasing the corrosion rate of steel. Kumar *et al.* (2014) noticed that oxidation resistance had been increased by addition of CeO₂ in small amount and also found that Cr₃C₂-NiCr coated and Cr₃C₂-NiCr+0.4wt.%CeO₂ coated Superni 600 had less parabolic rate constant than that of bare Superni 600.

Current study was planned to compare the behaviour and effect of 93(WC-Cr₃C₂)-7Ni and 86WC-10Co-4Cr coatings on ASME SA213 T22 and ASME SA213 T91 materials by assessing its surface and sub surface on heating it at 900 °C under cyclic conditions.

Materials and Methods

Substrate materials. For the present study, two Steel based alloys namely ASME SA213 T22 and ASME SA213 T91 were selected as the substrate materials. These steel alloys were obtained from Guru Nanak Dev Thermal Power Plant, Bathinda, Punjab (India). The samples of both alloy steels were cut with the dimensions of 20 mm × 15 mm × 5 mm. Then emery papers of grit sizes 100, 150, 220, 320, 600, 800 and 1000 were used to polish the samples. Alumina powder was used for grit blasting of samples. Following two illustrates the chemical composition for ASME SA213 T22 and ASME SA213 T91 boiler tube steels are illustrated in Table 1-2, respectively.

Coating materials. Coatings selected were of two types namely 93(WC-Cr₃C₂)-7Ni and 86WC-10Co-4Cr. Further, these coatings were deposited onto two steel based alloys using HVOF spray process. Table 3 shows composition and particle size of coating powder.

HVOF spraying. High velocity oxy-fuel thermal spray method was selected for deposition of coatings on two steel alloys at Metallizing Equipment Co. Pvt. Ltd,

Table 1. Chemical composition for ASME SA213 T22 boiler tube steel

T22	C	Si	Mn	S	P	Cr	Mo	Fe
Nominal (%)	0.05-0.15	0.5	0.30-0.60	0.025	0.025	1.90-2.60	0.87-1.13	Balance
Actual (%)	0.09	0.5	0.43	0.025	0.025	2.24	0.98	Balance

Table 2. Chemical composition for ASME SA213 T91 boiler tube steel

T91	C	Si	Mn	S	P	Cr	Mo	Ni	V	Al	Fe
Nominal (%)	0.07-0.14	0.20-0.50	0.30-0.60	0.02	0.02	8.0-9.5	0.85-1.05	0.4	0.18-0.25	0.015	Balance
Actual (%)	0.11	0.33	0.41	0.02	0.02	8.8	0.93	0.4	0.21	0.015	Balance

Jodhpur, Rajasthan (India). Commercial HVOF (HIPOJET-2100) apparatus functioning with oxygen and liquid petroleum gas (LPG) as input gases, was used. Table 4 shows spray parameters.

The coatings have been designated as follows: C1 T22: 93(WC-Cr₃C₂)-7Ni coated T22 specimen, C1 T91: 93(WC-Cr₃C₂)-7Ni coated T91 specimen, C2 T22: 86WC-10Co-4Cr coated T22 specimen, C2 T91: 86WC-10Co-4Cr coated T91 specimen.

Table 3. Composition and particle size of coating powder (supplied by MEC Jodhpur)

Coating powder	Composition (wt%)	Particle size (µm)
93(WC-Cr ₃ C ₂)-7Ni	WC(73), Cr ₃ C ₂ (20), Ni(7)	-45+15
86WC-10Co-4Cr	WC(86), Co(10), Cr(4)	-45+15

93(WC-Cr₃C₂)-7Ni coated T91 specimen, C2 T22: 86WC-10Co-4Cr coated T22 specimen, C2 T91: 86WC-10Co-4Cr coated T91 specimen.

Table 4. Spray parameters employed during HVOF spray process

Parameters	Values
Oxygen flow rate	250 LPM
Fuel (LPG) flow rate	60 LPM
Air flow rate	900 LPM
Spray distance	200 mm
Fuel pressure	6 kg/cm ²
Oxygen pressure	8 kg/cm ²
Air pressure	6 kg/cm ²

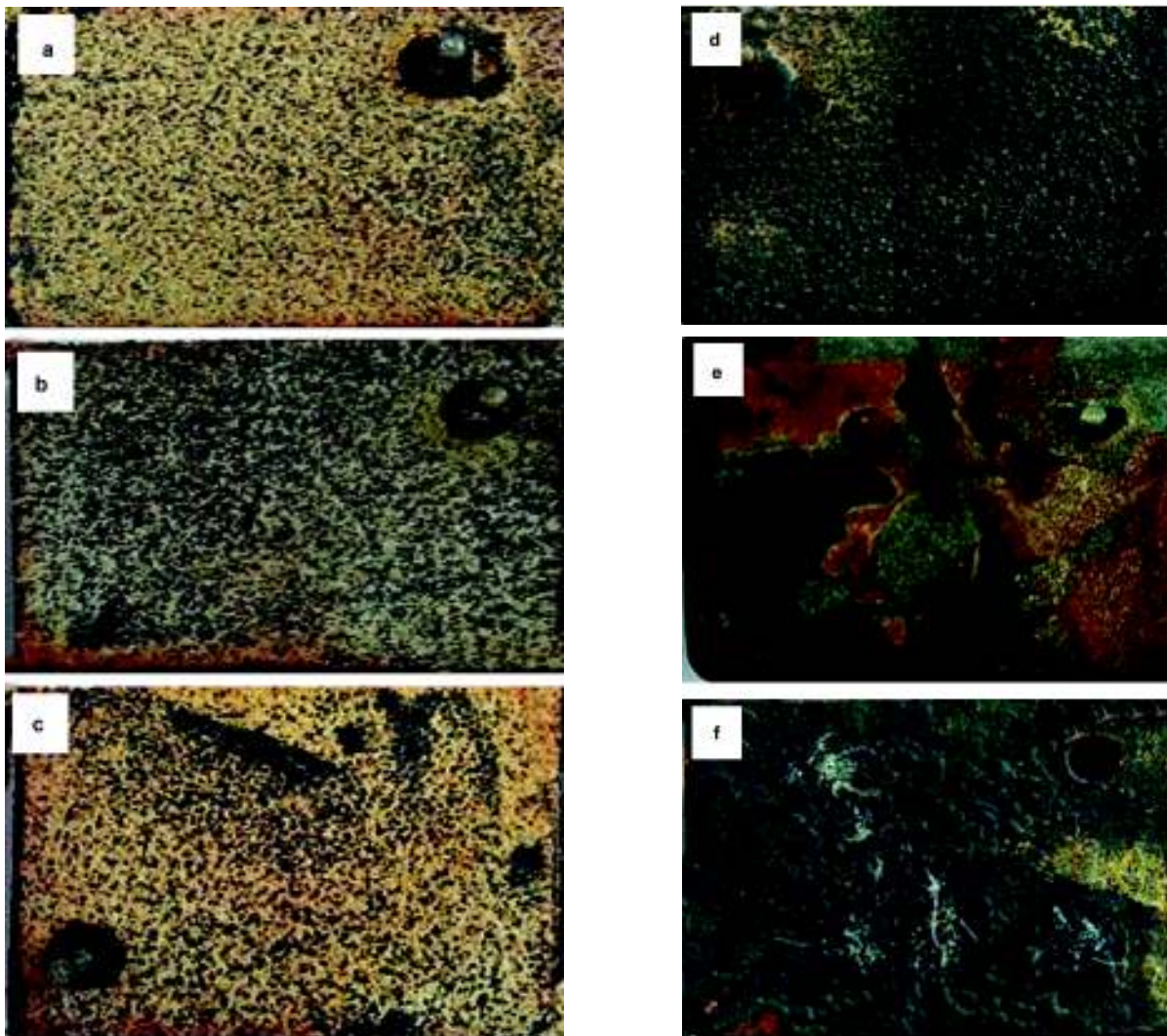


Fig. 1(a-f). Macrographs of the HVOF sprayed T22 and T91 specimen (a) C1 T22 (b) C1 T91, (c) C2 T22, (d) C2 T91, (e) T22 uncoated and (f) T91 uncoated.

Studies in coal fired boilers. The uncoated as well as HVOF coated steel alloy specimens were examined in an actual boiler environment in the middle zone of platen superheater of the Stage-II boiler of Guru Nanak Dev Thermal Plant, Bathinda, Punjab (India). Nichrome wire was passed through a predrilled hole of 1 mm among all the samples, then these samples were inserted through the soot blower dummy points at 34.5-m height from the base of the boiler and these specimens were exposed for 10 cycles to combustion environment. Each cycle consisted of 100 h heating, followed by 1 h cooling at ambient conditions. The temperature was measured at regular intervals and the average temperature during the study was observed to be about 900 °C with variation of ± 10 °C. The specimens were visually observed for any change on surface and weight of specimens was measured subsequently at the end of each cycle.

The samples were examined by X-ray diffraction (XRD), Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) after the cyclic studies. The hot corrosion behaviour of bare and HVOF coated ASME SA213 T22 and ASME SA213 T91 in the given environment was assessed by measuring the thermogravimetric data, metal thickness loss corresponding to the corrosion scale development and the depth of internal corrosion attack after 1000 h exposure under cyclic conditions.

Results and Discussion

Visual examination of uncoated and HVOF coated T22 and T91. The macrographs for uncoated steel based alloy and HVOF sprayed 93(WC-Cr₃C₂)-7Ni and 86WC-10Co-4Cr coatings on T22 and T91 after 1000 h exposure to the superheater zone of the coal fired boiler are depicted in Fig. 1.

Weight change measurements. Weight change measurements of bare, 93(WC-Cr₃C₂)-7Ni coated and 86WC-10Co-4Cr coated of both ASME SA213 T22 and ASME SA213 T91 subjected to cyclic oxidation for 10 cycles at 900 °C are noticed. Weight gained by 86WC-10Co-4Cr coated T22 was minimum and weight gained by bare T22 steel alloys was maximum. Figure 2 shows the graph between weight change per unit area and number of cycles for both the uncoated and HVOF coated (T22, T91) samples subjected to 1000 h cyclic exposure to low temperature superheater zone of coal fired boiler at 900 °C. Figure 3 shows the column graph for weight gained per unit area of uncoated and coated

samples (where C1= 93(WC-Cr₃C₂)-7Ni, C2= 86WC-10Co-4Cr).

X-ray diffraction. X-ray diffraction analysis patterns for both corroded uncoated and HVOF coated samples are shown in Fig. 4. Uncoated specimen after introduction to boiler temperature for 10 cycles indicated the presence of Fe₂O₃. The 93(WC-Cr₃C₂)-7Ni coated T22 and T91 steel alloys show the existence of α -WC, γ -NiCr and β -Cr₃C₂ on their surface. In case of 86WC-10Co-4Cr coated T22 and T91 specimen, the surface scale indicated the occurrence of α -WC, β -W₂C.

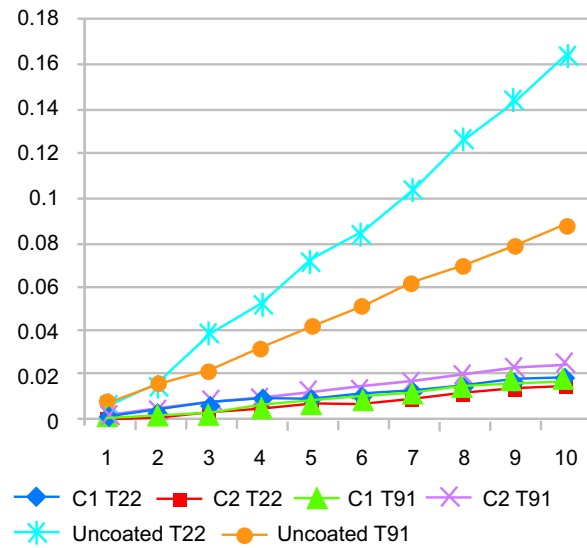


Fig. 2. Weight change vs cycles plots for the uncoated and HVOF coated (T22, T91) samples subjected to 1000 h cyclic exposure to low temperature superheater zone of coal fired boiler at 900 °C.

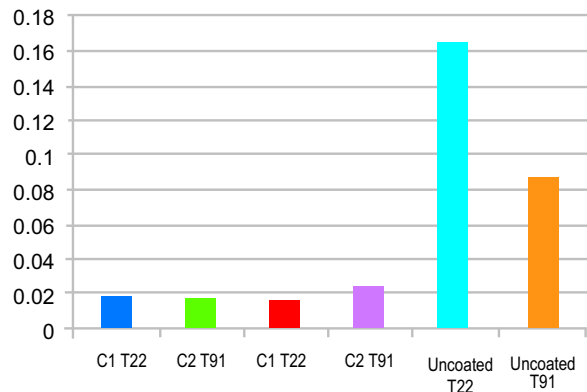


Fig. 3. Column chart of weight gain per unit area for uncoated and HVOF coated samples.

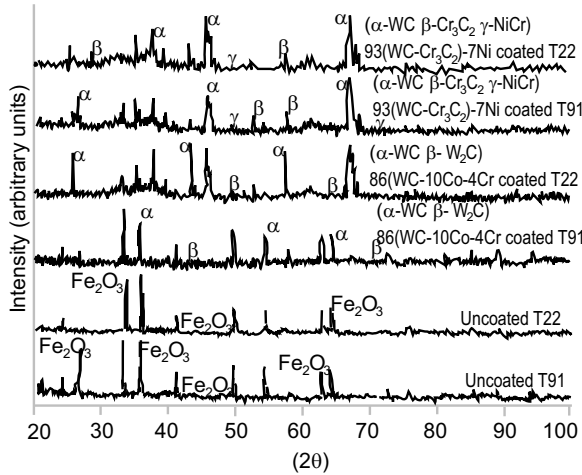
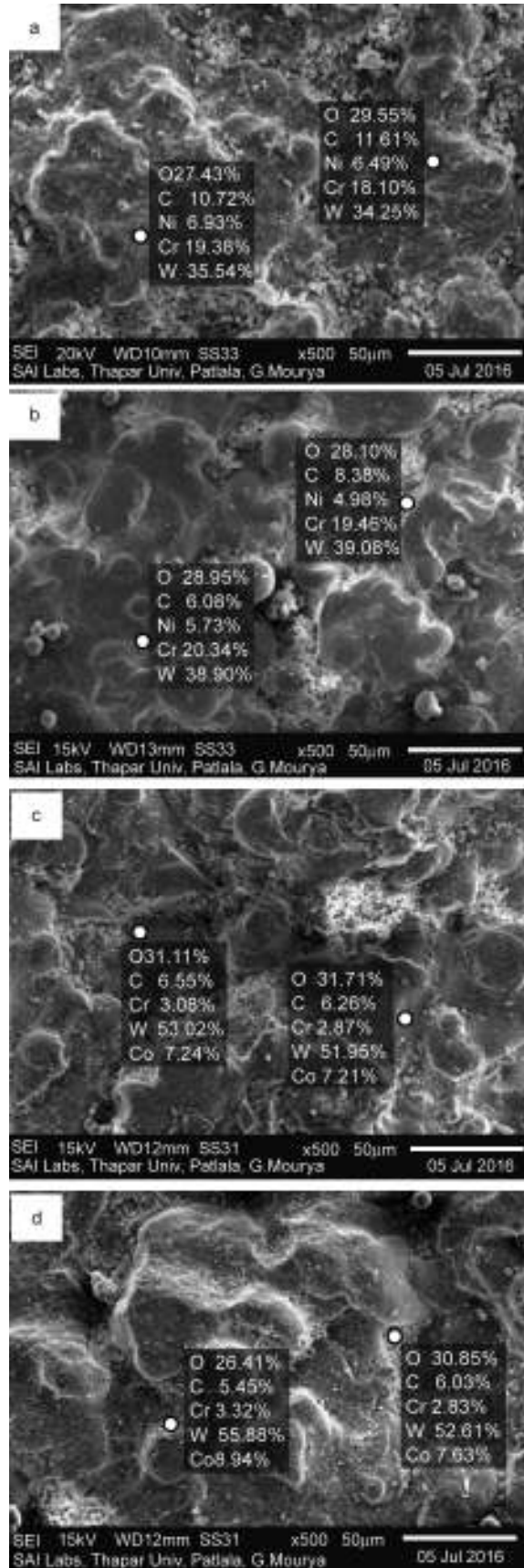


Fig. 4. X-ray diffraction of T22 and T91 of uncoated and HVOF coated specimens.

SEM/EDS. In scanning electron microscopy the pictures show the existence of carbides and oxides. Additionally it has been proved by energy dispersive spectroscopy (EDS) by identifying the carbon and oxygen and also proved by X-ray diffraction (XRD). Scanning electron microscopy (SEM) images of both uncoated as well as coated ASME SA213 T22 and ASME SA213 T91 alloy steel specimens are shown in Fig. 5.

Conclusion

- All the coatings on both the steel alloys were uniform and dense with thickness of coatings was between 200–250 μm.
- HVOF spraying process has been effectively employed for depositing 93(WC-Cr₃C₂)-7Ni and 86WC-10CO-4Cr coatings on steel alloys namely ASME SA213 T22 and ASME SA213 T91.
- All the coatings on both steel alloys namely ASME SA213 T22 and ASME SA213 T91 used in present studies have provided resistance to corrosion in coal fired boiler environment in superheater zone when exposed for 10 cycles at 900 °C and have shown the following order of resistance to corrosion.
86WC-10CO-4Cr coated T22 > 93(WC-Cr₃C₂)-7Ni coated T91 > 93(WC-Cr₃C₂)-7Ni coated T22 > 86WC-10CO-4Cr coated T91.
- Among all uncoated and coated samples, the uncoated samples have shown least resistance to corrosion. But ASME SA213 T22 has shown minimum resistance to corrosion.



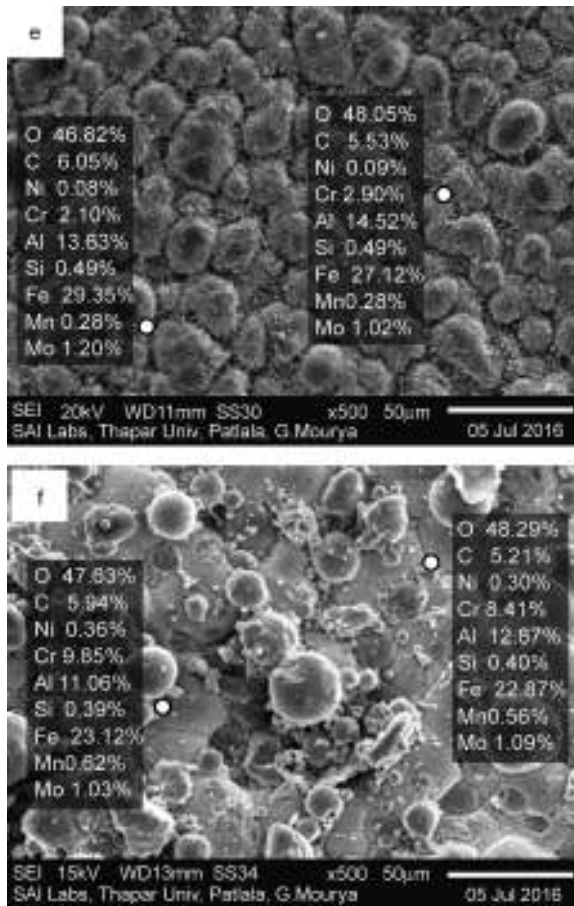


Fig. 5(a-f). Surface morphology and EDS analysis after 10 cycles in superheater of boiler at 900 °C for T22 (a) 93(WC-Cr₃C₂)-7Ni coated T22 (b) 93(WC-Cr₃C₂)-7Ni coated T91, (c) 86WC-10Co-4Cr coated T22, (d) 86WC-10Co-4Cr coated T91 (e) T22 uncoated (f) T91 uncoated.

- The improved corrosion resistance of 86WC-10Co-4Cr coated on ASME SA213 T22 steel alloys may be due to the formation of thin band of oxides of nickel, chromium and carbides of tungsten.

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