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Performance of Cr_3C_2-25(Ni-20Cr) and Ni-20Cr Coatings on T91 Boiler Tube Steel in Simulated Boiler Environment at 900°C

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Abstract The dangerous process in boiler steel tube is corrosion due to loss of metal by the attack of corrosive agents. In order to prevent this corrosion Cr_3C_2–25 (Ni–20Cr) and Ni-20Cr coatings were deposited on T91 boiler tube steel by high velocity oxy-fuel (HVOF) process. Hot corrosion studies were conducted on uncoated and HVOF-coated T-91 steel specimens after exposure to a molten salt (Na_2SO_4–60%V_2O_5) environment at 900°C under cyclic conditions. Each cycle consisted 1 h of heating in tube furnace followed by 20 min of cooling in air. The weight change measurements were performed after each cycle in order to establish the kinetics of corrosion using thermogravimetric technique. X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDS) were used to analyze the corrosion products. The bare steel experienced higher weight gain due to the formation of unprotective Fe_2O_3 dominated oxide scales. The Cr_3C_2–25(Ni–20Cr) coating was found to be more protective than the Ni-20Cr coating.

Keywords Corrosion, Boiler Steel, Degradation, SEM/EDS, XRD Technique

1. Introduction

Corrosion mainly occurs due to high temperature oxidation, hot corrosion and erosion. The various parts of turbines, boilers, industrial waste and inclinators wastes suffer from degradation at very high temperature [1]. From the view point of chemical thermodynamics the corrosion of metals is a spontaneous process, which can result in loss of functions in construction instrument. Corrosion results in loss of a metal due to the reaction of the corrosive agents in gaseous environment. Low cost alloys can be used for surface modification in order to prevent metal from corrosion. The surface modification can be achieved by coating. The naturally, synthetically or artificially deposited layer of material on the surface of metal is known as coating. It improves the technical and decorative properties of the material. It is one of the mostly used technologies in the world. Almost 80% metals are protected by coating methods. Coating is that technique in which material is added or deposited on the surface of same or different material. It basically has two main purposes [2].Thermal Spray technique was firstly invented by Dr. Schoop by designing a gun, in which O_2 & acetylene were used as a source of heating & for projection of molten metal on the substrate compressed air was used. This technique was further used by George & Herb [3]. Many researchers have developed thermal spray coatings to reduce the corrosion of boiler tube steels. **K.Yamada et.al**. [4] Described that thermal spray prevents oxidation & hot corrosion in gas turbine components & boilers. Ni-Cr alloys were used as coating material. D-gun was used as coating technique which has low porosity. The Inconel-625, SU-310 & SU304 were used as substrate material. Inconel-625 was best coated & carbon steel S5400 was least resistant. Due to high Ni content Inconel-825 & 625 were having best corrosion resistance than steel. **J. Picas et.al.** [5] found that Cr_3-NiCr coating can be used to improve wear resistance. To retain the nanostructure of the coating, the HVOF technique was used. The Cr_2C_3& Cr_2C_3-7NiCr powders were used as coating material. The steel was used as substrate material. The authors concluded that coating done by CrC60-40NiCr powder was more dense & homogeneous than CrC75-NiCr25 powder. The micro hardness of CrC75-NiCr25 was more than that of CrC60-40NiCr. The result revealed that coating done by CrC60-40NiCr was less protective than CrC75-NiCr25. **N.F. AK et al.** [6] described that HVOF technique is capable of producing better carbide-metal coating along with high density, high hardness, good bond strength & low decarburization. The coating produced by this technology was 100-300 μm thick. Value of hardness of HVOF technique depends upon porosity, unmelted & semimelted particles, oxidized & inclusions. The authors concluded that the hardness improved due to reason that coating produced by HVOF was very dense & was having high cohesive strength. **T. Sidhu et.al**. [7] Developed NiCr-BSi coatings on steel substrates and performed high temperature corrosion studies in the salt environment of Na_2SO_4-V_2O_5 at 900°C in cyclic conditions. Porosity was found to be less than 1.4%. XRD analysis showed that very small amount of was formed. EDS showed the formation of small amount of V_2O_5, TiO_2, Al_2O_3 & MnO. The thickness of coating was found to be in the range of 250-300 µm. Coating done by NiCrBs was found to be very effective in decreasing corrosion rate. There was no spallation & peeling of oxide layer. **Sandeep et al. [**8] described that the presence of salt, ash, low grade fuels & hot gases caused the hot corrosion or degradation in metals. Cr_2O_3 was used as coating material & Inconal-625 was used as substrate material in presence of K_2SO_4-NaCl at 800°C for 50 cycles. The thickness was found to be 300 µm. The authors found the formation of scale rich in Ni &Fe but inner layer was mainly of Cr. The uncoated Inconal-625 exhibited highest corrosion followed by air oxidation.Cr_2O_3 Coated Inconal-625 was found to be less corroded due to coating obtained by plasma spray coating. **V. Sharma et al**. [9] described that boiler and turbines must operate at high efficiency for better energy transfer. So their efficiency depends upon operating temperature, which is mainly high due to which oxidation & hot corrosion take place. So coating is needed to be done for their better efficiency. Coating was done by D-gun process. Ni-Cr was used as coating powder & supermi-750 was used as substrate material in salt environment of Na_2SO_4-V_2O_5 at 900°C for 100 cycles. Oxides of Ni, Fe & Ni-Cr were formed in case of bare compared to coated alloys. The corrosion rate was lowered in case of super alloy (SN750).

It is clear from the literature review that investigation of performance of coated boiler steel samples is crucial research area for the researchers, and there is still a scope to increase the corrosion resistance performance of boiler tube steel in boiler environments. Therefore, the present work is focused to study the influence of HVOF sprayed Cr_3C_2-25(Ni-20Cr) and Ni-20Cr coatings on hot corrosion behavior of ASTM–SA213-T-91 steel. XRD, SEM and EDS testing are used to characterize the corrosion products formed after the experimentations.

2. Experimentation

2.1. Substrate Material

ASTM-SAE213-T91 boiler steel has been chosen as the substrate material for the current study. This type of carbon steel was recently introduced as boiler steel in the super heater zone in many regions of India. The material used for this study was procured from Guru Nanak Dev Thermal Plant, Bathinda, Punjab, India. The chemical composition of the material is shown in table 1.

2.2. Preparation of Samples of Substrate Material

Samples of dimensions 20 mm × 15 mm ×5 mm approximately, were cut from the boiler tube steel. The samples were polished with the help of emery papers of 180 grit sizes and subsequently on 1/0, 2/0, 3/0 and 4/0 grades and then mirror polished using cloth. The specimens were prepared manually. Special care was taken to avoid any structural changes in the specimen and finally the deposition of the coating is done by using high velocity oxy fuel process.

2.3. Development of Coating on Material

HVOF process was used to apply coatings on the super alloys at *Metallizing Equipment Co. Pvt. Ltd*. Jodhpur Rajasthan India. Standard spray parameters were used for depositing the Cr_3C_2-25(Ni-20Cr) and Ni-20Crcoatings. All the process parameters including the spray distance, were kept constant throughout the coating Process. The experimentation was performed in silicon tube steel at 900^0C. Table number 2 shows the specifications of the furnace.

Table 1. Nominal Chemical composition (wt %) of ASTM SA213-T91 boiler tube steels.

C	Mn	P	Si	S	Cr	Mo	Fe
.05-.15	0.3-0.6	0.025	0.50	0.025	1.9-2.6	0.87-1.13	balance

Table 2. Specification for tube furnace

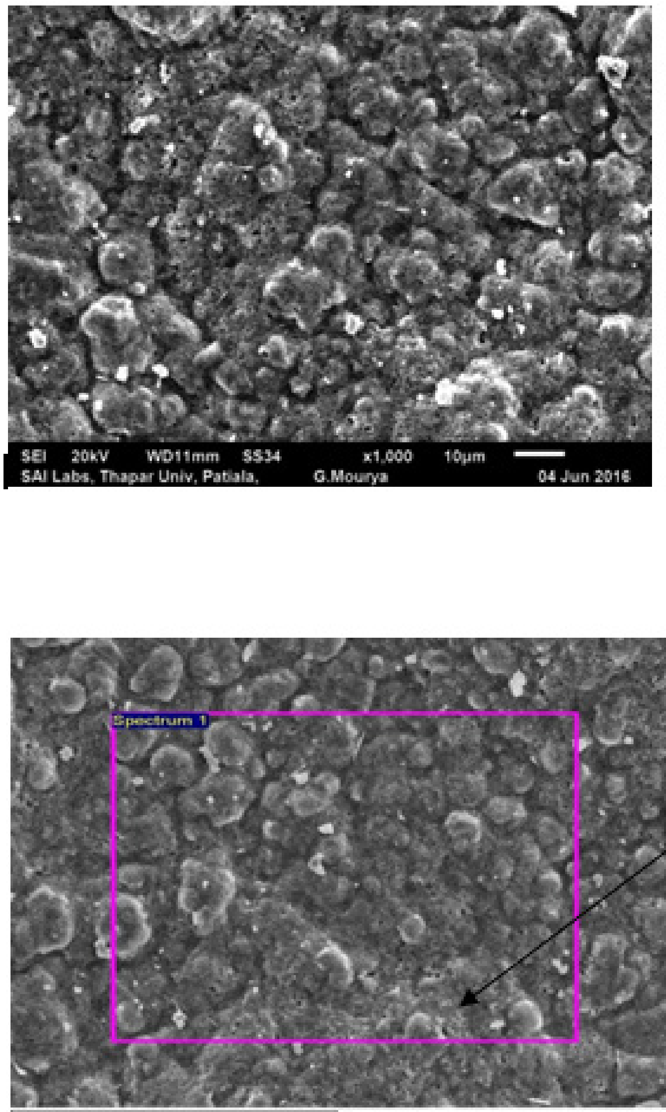
Max Temperature	Power	Heating Elment	Thermocouple	Heating Zone
1200 ±50c	I Kwh	Electric Filament	K_Type	9 Inches

3. Results

The performance of boiler steel T-91 without coating and after coating with Cr_3C_2-25(Ni-20Cr) and Ni-20Cr using High velocity oxy fuel sprayed process is being discussed, under various condition viz. Heating takes place in the tube furnace in aggressive environment of molten salt Na_2So_4- 60% V_2O_5 at temperature of 900°C under cyclic condition. The conditions of surface were observed during the process of heating and weight change was analyzed through thermo gravimetric data [10, 11]. The corrosion products were analyzed by using SEM, EDS and XRD testing.

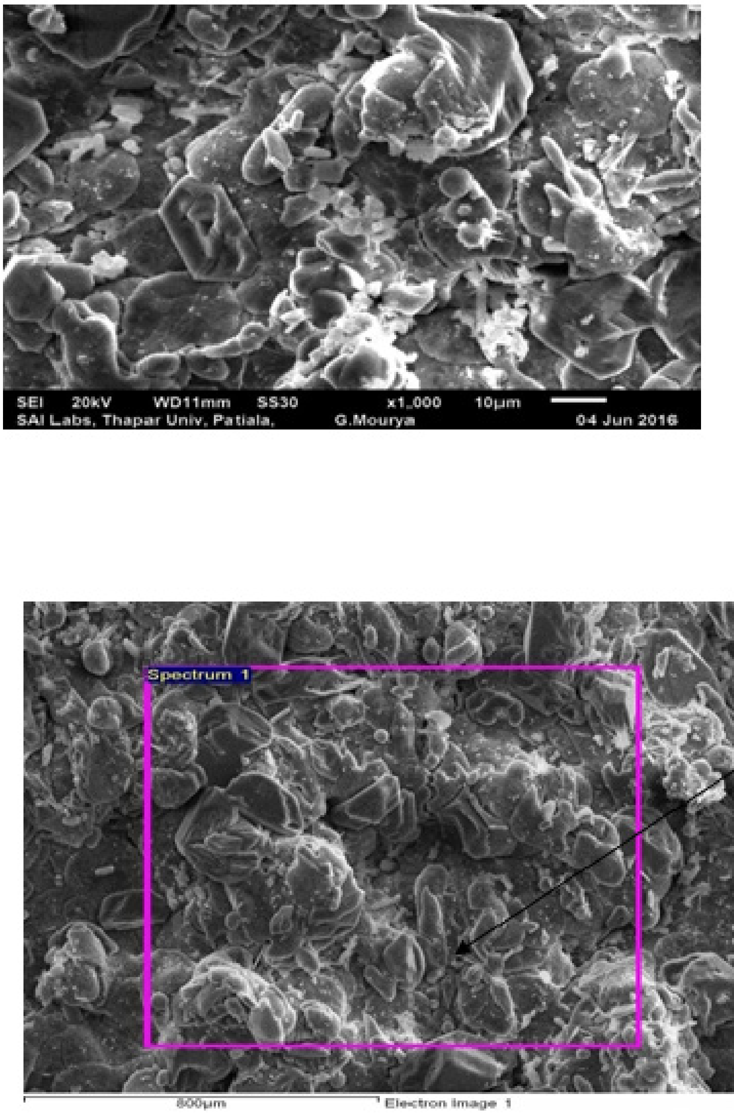
3.1 SEM/EDS Analysis of Un-Coated T-91 Boiler Steel in Molten Salt Environment

The SEM micrograph showing the surface morphology of Un-Coated T-91 boiler Steel in molten salt environment is shown in Figure 1. Furthermore EDS analysis corresponding to spectrum shows the formation of Fe_2O_3 and Cr_2O_3 on sample. The excessive particles are Fe and O.



C	1.75
O	36.72
Al	0.07
Si	0.02
Ti	0.09
Mn	0.97
Fe	60.31
Ni	0.05

Figure 1. SEM images and EDS analysis for Un-Coated T-91 boiler Steel in salt environment

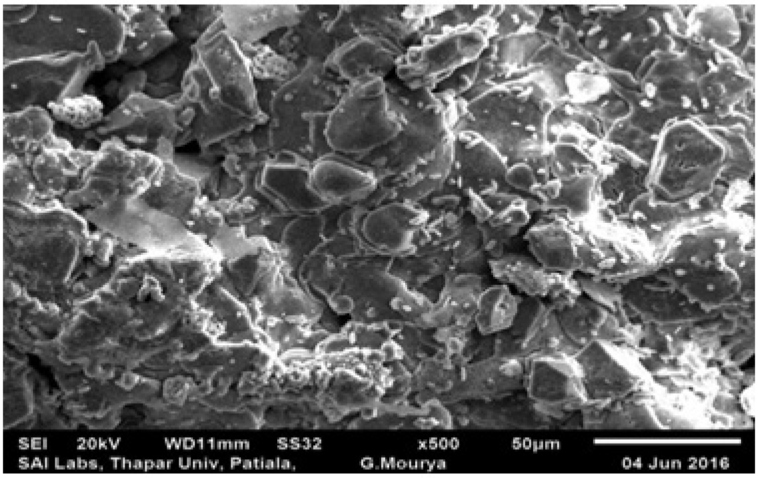


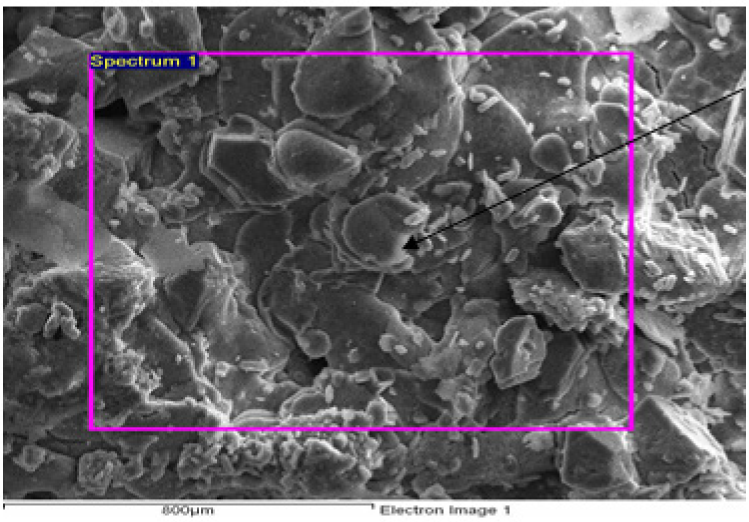
C	4.88
O	43.57
Na	2.47
Cr	31.50
Si	0.19
V	0.84
Al	1.86
Ni	14.69

Figure 2. SEM images and EDS analysis for Cr_3C_2-25(Ni-20Cr) Coated T-91 boiler Steel in Salt environment

3.2. SEM/EDS Analysis of Cr_3C_2-25(Ni-20Cr) Coated T-91 Boiler Steel in Salt Environment

The SEM micrograph showing the surface morphology of HVOF-spray Cr_3C_2-25(Ni-20Cr) Coated T-91 boiler Steel in salt environment is shown in Figure 2. Furthermore EDS analysis corresponding to spectrum indicates the formation of Cr_2O_3 and NiO on sample. There is presence of some globular particles in the scale, as could be perceived from the excessive presence of O, Ni and Cr.





C	9.62
O	44.26
Na	1.95
Ni	30.62
Si	0.92
V	0.40
Al	0.80
Cr	9.38

Figure 3. SEM images and EDS analysis for Ni-20Cr Coated T-91 boiler Steel in salt environment

3.3. SEM/EDS Analysis of Ni-20Cr Coated T-91 Boiler Steel in Salt Environment

The SEM micrograph showing the surface morphology of HVOF-spray Ni-20Cr Coated T-91 boiler Steel in salt environment is shown in Figure 3. Furthermore EDS analysis corresponding to spectrum indicates the formation of NiC and NiO on sample. There is presence of some globular particles in the scale, as could be perceived from the excessive presence of O, Ni and Cr.

3.4. XRD Analysis of Un-coated T-91 Boiler Steel in Salt Environment

The X-ray diffraction of un-coated sample of T-91 as shown in fig 4 is subjected to testing in molten salt enviroment. The oxide scale of coated T-91 steel is found to have the presence of Cr_2O_3 at higher peaks while Fe_2O_3 and FeV_2O_4 at lower peaks.

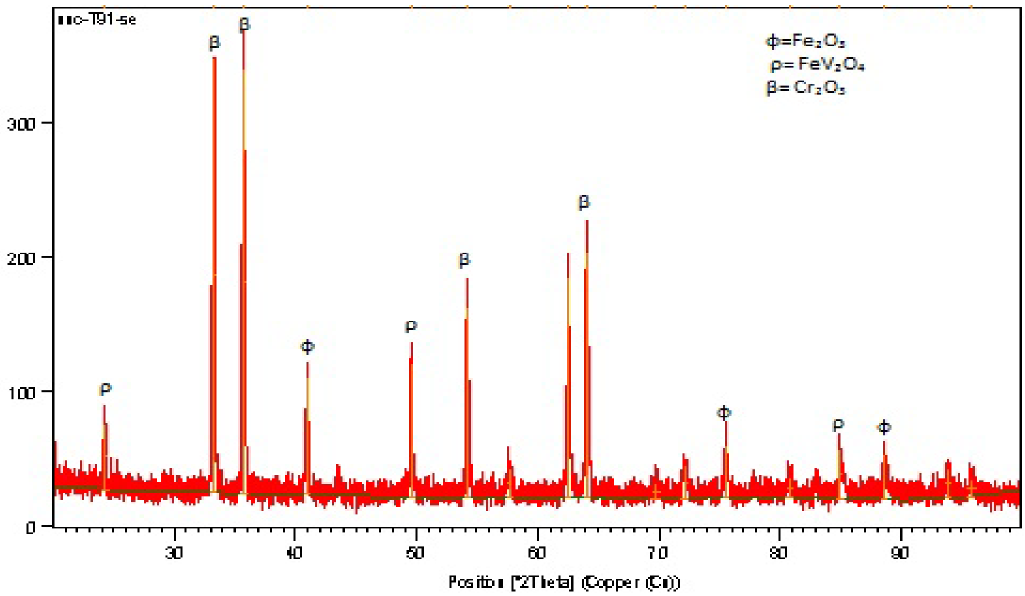


Figure 4. XRD analysis of Un-coated T-91 boiler steel in salt environment

3.5. XRD analysis of Cr_3C_2-25(Ni-20Cr) coated T-91 boiler steel in salt environment

The X-ray diffraction of Cr_3C_2-25(Ni-20Cr**)** coated sample of T-91 as shown in fig 5. subjected to molten salt testing in salt enviroment. The oxide scale of coated T-91 steel is found to have of presence of Cr_3C_2, Cr_7C_3 at different peaks.

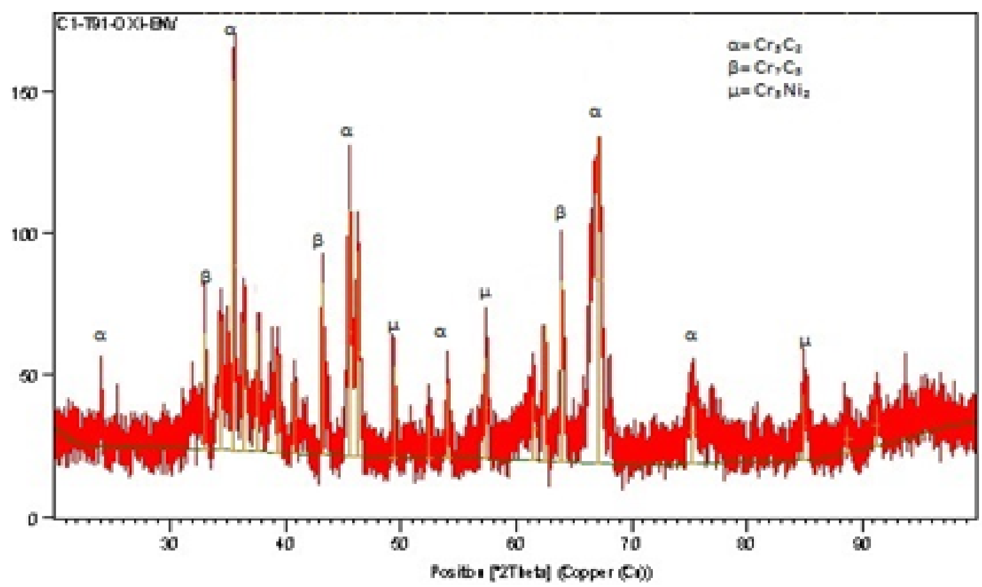


Figure 5. XRD analysis of Cr_3C_2-25(Ni-20Cr) coated T-91 boiler steel in salt environment

3.6. XRD Analysis of Ni-20Cr coated T-91 Boiler Steel in Salt Environment

The X-ray diffraction of Ni-20Cr coated samples of T-91 as shown in fig 6 is subjected to oxidation testing in salt enviroment. The oxide scale of coated T-91 steel is found to have a presence of NiO, Cr_2O_3 and $NiCr_2O_4$ at major peaks while Fe_2O_3 at minor peaks.

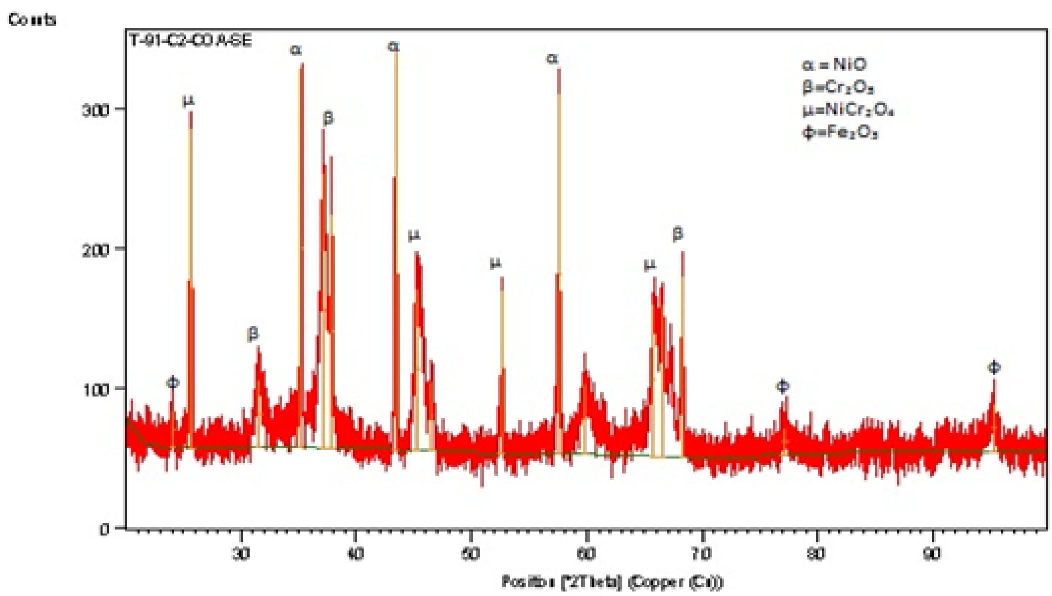


Figure 6. XRD analysis of Ni-20Cr coated T-91 boiler steel in salt environment

3.7 Weight Change for T-91 in Salt Environment

The graph of the weight change and number of cycles is plotted for uncoated T-91, Cr_3C_2-25(Ni-20Cr) coated T-91 and Ni-20Cr coated T-91 in salt environment

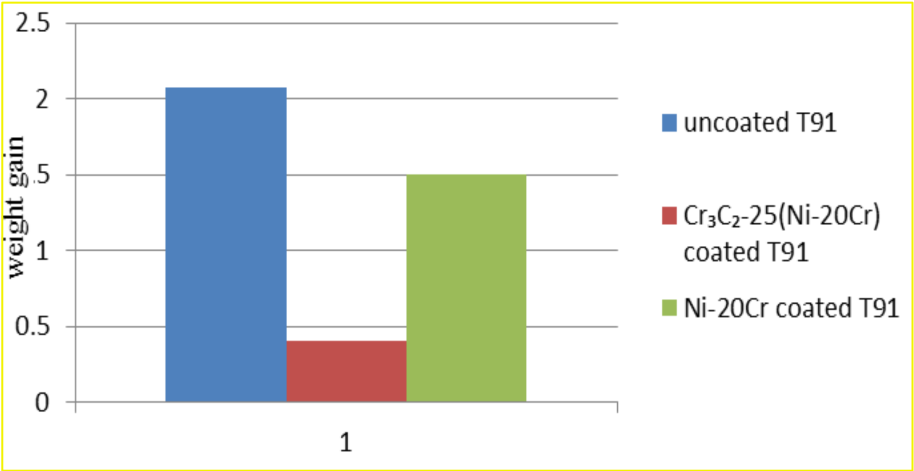


Figure 7. Bar graph shows the total weight gain of uncoated T-91 , Cr_3C_2-25(Ni-20Cr) coated T-91 and Ni-20Cr coated T-91 in salt environment

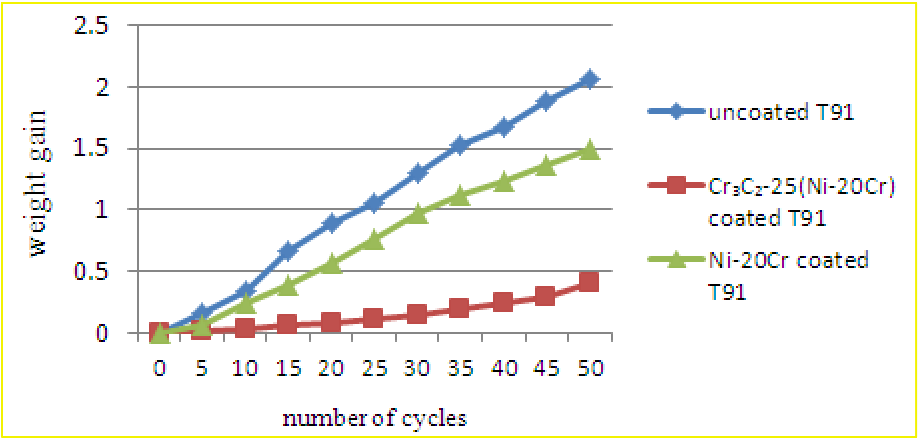


Figure 8. Line graph shows the comparison of uncoated T-91, Cr_3C_2-25(Ni-20Cr) coated T-91 and Ni-20Cr coated T-91 in salt environment

It can be seen from the graphs that total weight gained in uncoated T-91 is 2.07gm, 0.4gm in Cr_3C_2-25(Ni-20Cr) coated T-91 and 1.5 gm in Ni-20Cr coated T-91 in salt environment.

4. Conclusions

1) Cr_3C_2-25(Ni-20Cr) and Ni-20Cr coatings have been successfully deposited by HVOF technique on ASTM-SAE213-T91 boiler steel. The coating thickness was in the range of 250-300 µm.

2) In case of uncoated T-91 boiler steel Fe_2O_3, Cr_2O_3 and Fe_3O_4 were indicated as main phase by XRD and SEM/EDS in salt environment.

3) In Cr_3C_2-25(Ni-20Cr) coated T-91 substrate NiO, Cr_2O_3 and $NiCr_2O_4$ were identified as major phases in oxidation and salt environment at 900 ℃.

4) In Ni-20Cr coated T-91 substrate, NiO, $NiCr_2O_4$ and, NiC were identified as major phases in oxidation and salt environment at 900 ℃.

5) The bare T-91 boiler steel suffered high corrosion rate as compared to coated T-91 boiler steel in molten salt environment. The corrosion loss is more in Ni-20Cr coating as compared to Cr_3C_2-25(Ni-20Cr) coating.

6) Ni-20Cr coating may be recommended as a suitable coating process combination for salt environment whereas HVOF sprayed Cr_3C_2-25(Ni-20Cr) was found to be best among studied coating. The formation of oxide scale might have imparted better corrosion resistance to coating

7) The corrosion rate for uncoated and coated T-91 boiler steel specimens in molten salt environment is as follow-

Cr_3C_2-25(Ni-20Cr) > Ni-20Cr> uncoated T-91

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