Universal Journal of Mechanical Engineering 7(4): 224-230, 2019 http://www.hrpub.org
DOI: 10.13189/ujme.2019.070411

Evaluations of Hot Corrosion Behavior of Al_2O_3 Thermal Spray Coatings with ZrO_2 Reinforcements on T-91 Steel

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Abstract Different coating with varying quantities of Al_2O_3 and ZrO_2 were fabricated on the SA213 T-91 steel using plasma spray method to study hot corrosion resistance behavior. Experiment was conducted under the molten salt environment of 60% Na_2SO_4-40%V_2O_5 at a temperature of 900°C inside a furnace for 50 cycles. Each cycle consisted of 1hr heating and 20 min cooling at room temperature. Results were examined using the visual inspection, weight change measurement, X-ray diffraction technique and Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy (SEM/EDS) analysis. Results showed that uncoated T-91 steel was more prone to hot corrosion as compared to coated steel specimens. It was noticed that ZrO_2 reinforcements in Al_2O_3 coating matrix helped to enhance corrosion resistance of these coatings. The corrosion resistance increased with increase in ZrO_2 content in coating matrix.

Keywords Plasma Spray, ZrO_2 Coating, Al_2O_3 Coating, Porosity, Boiler Steel

1. Introduction

At elevated temperature, accelerated oxidation is experienced by metal and alloys when they are exposed to corrosive environment which leads to deposition of thin film of fused salt on the surface of metal. This leads to the formation of porous non protective oxide layer on the surface and sulphides inside the substrate as described by the Gond D *et al* [1]. In boiler of a thermal power plan, corrosion occurs due to presence of sulphur in coal and oil fuels, which produce SO_2, which further oxidizes partially to SO_3 [2, 3]. Sulphur present in fuel reacts with NaCl to form Na_2SO_4 within the boiler tube as reported by DeCrescente and Bornstein [4]:

$$2NaCl + SO_3 + 1/2O_2 \rightarrow Na_2SO_4 + Cl_2$$

As the higher grade fuels are being depleted at a faster pace, therefore for production of energy, residual fuels are being used. Impurities such as Na, K, S and V are present in the residual fuel which forms low melting point compounds [5, 6]. Corrosion is initiated by these low melting compounds as they get deposited on the surface of the material. These melting compounds react with oxygen to form Na_2SO_4 and V_2O_5. These compounds are known as ash. Protective oxide layer is deteriorated by these molten compounds during the boiler/gas turbine operations at high temperatures [7-9]. Different ceramics coating materials help in preventing the corrosion at elevated temperatures. Al_2O_3 and ZrO_2 are preferred among the all ceramics materials because they have better chemical stability, wear resistance, superior hardness and corrosion resistance properties. Different methods of thermal coating processes are available, but plasma spray method coating is chosen because of low cost, simplicity and high deposition rate. However, fabrication of ceramic coating using plasma spray method leads to higher inherent porosity which helps the electrolyte to attack on substrate which in turn leads to corrosion. To overcome this issue bilayered coatings of Al_2O_3 and ZrO_2 has been used in recent past [10, 11]. For fabrication of Al_2O_3 coating, ZrO_2 is referred as underlying material for adhesion as it increases the adhesion strength as studied by Chang and Yen [12]. Even the alumina whisker is added to increase the adhesion and cohesion strength of composite coatings in the conventional coating methods. It is observed that adding ZrO_2 coating to aluminum alloy has sharply increased the corrosion resistance property in the salt environment. Number of cracks and black spots were also reduced and surface quality is increased by increase in weight percentage of ZrO_2 [13]. In the automobile industry, exhaust manifold handles high temperature and different contents of harmful gases causes the material to develop thermal stress and

corrosion [13].

It is clear from the literature study that Al_2O_3 and ZrO_2 bilayered coating effectively reduced the boiler steel corrosion at higher temperature but there is a chance of inherent porosity in the substrate. There is a scope to further improve the corrosion resistance by reinforcing alumina coating matrix with ZrO_2 powder, instead of bilayered coatings. Therefore, it was decided to fabricate different composite coatings by reinforcing ZrO_2 in Al_2O_3 coating matrix. And subsequently, their hot corrosion behavior has been studied at high temperature (900°C) in molten salt environment. So very few research have done on reinforced coating ZrO_2 with Al_2O_3.

2. Materials and Methods

2.1. Composition of Substrate Material

In this research work, SA213T-91 steel has been used as the substrate material, because this steel alloys has been commercially used to manufacture boiler components in Indian Thermal Power Plants. The material was obtained from Guru Gobind Singh Super thermal power plant, Ropar. The chemical composition of T-91 steel alloy is given in Table 1. The sample size of substrate is 20mm×15mm×5mm were prepared by cutting the boiler steel tube.

2.2. Formulation of Coating

Table 2 depicts compositions and particle sizes of ZrO_2 and Al_2O_3 feedstock powders used to fabricate different composite coatings.

The different coatings were fabricated at Metallizing Equipment Corporation Private Ltd. Jodhpur, Rajasthan. Plasma spray arc method was used for depositing the coatings on the substrates of T-91 boiler steel tube. All the process parameters for plasma spray method were kept at constant rate and are mentioned in Table 3.

Table 1. Composition of T-91 steel boiler tubes

Type of steel	ASME code	Composition	C	Mn	Si	S	Nb	P	Cr	Mo	V	Ni	Fe
T-91	SA213T-91	Actual	0.12	0.41	0.28	0.01	0.08	0.02	8.2	0.87	0.20	0.13	Bal

Table 2. Different coating composition on T-91 steel

Substrate Material T-91	Composition of Al_2O_3 (in percentage)	Composition of ZrO_2(in percentage)	Particle size
Coating 1	100	0	40±10µm
Coating 2	97	3	40±10µm
Coating 3	87	13	40±10µm
Coating 4	80	20	40±10µm

Table 3. Parameter used for Plasma spraying

Parameters	Values
Plasma current/A	600 A
Plasma voltage/V	50 V
Powder flow rate	50 gm/min
Arc gas (primary gas) flow rate	62 psi
Carrier gas flow	50 psi
Spray distance/mm	50

2.3. Experimental Set up for Hot Corrosion

The hot corrosion experiments were performed in silicon tube furnace at metallurgy lab of Chandigarh University, Mohali. The experiments were conducted at 900°C. Using the platinum- rhodium thermocouple, standardization of furnace was done and deviation of ±10°C of temperature was shown by the indicator. Uncoated samples were mirror polished before exposing to corrosion environment and their dimension were taken using the vernier caliper so as to calculate the surface area. Samples were placed within the ceramic boats which then placed inside the furnace to carry out the hot corrosion study.

The study on coated and uncoated samples was conducted in presence of corrosive molten salt environment of Na_2SO_4 and V_2O_5 periodically with 50 cycles. One cycle of experiment was consisted of 1 hour of heating at 900°C followed by cooling for 20 minutes at room temperature. With number of repetitions, hot corrosion become more aggressive. Na_2SO_4 and V_2O_5 salts were opted, because in the lower grade fuels impurities such as sodium and vanadium are present. Mixture of Na_2SO_4-60%V_2O_5 melts at lower temperature i.e. at 500°C, hence becomes highly corrosive in nature.

The study was conducted on uncoated and coated substrate and the results were compared after completion of the experiment. On all six sides of specimen mixture of Na_2SO_4 and V_2O_5 was applied using the camel hair brush to create a similar environment as the actual environment. The weight of each specimen after each experimental cycle was measured using the electronic weigh measuring gauge. Results were examined using the visual inspection, weight change measurement, X-ray diffraction technique and Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy (SEM/EDS) analysis.

3. Results

3.1. Visual Observation

The macrographs of uncoated and coated substrate of different coating compositions (100Al_2O_3, 97Al_2O_3 -3ZrO_2, 87 Al_2O_3 -13 ZrO_2, 80 Al_2O_3-20ZrO_2) are shown in figure 1 after 50 cycles of exposure to hot corrosion environment. In case of T-91 uncoated substrate, blackish gray color scale started to appear after the 2nd cycle and spalling of scale was also noticed which continued up to the 50th cycle. On the other hand yellowish color started to appear on the surface of coated substrates after 5th cycle and no spallation was recorded. The variation in color indicated oxidation probability.

3.2. Weight Change Measurement

The hot corrosion kinetics was determined from weight change (mg/cm^2) versus time plot for uncoated and coated specimens of T-91 steel. The specimens were subjected to 50 cycles of heating exposing them in molten salt environment in furnace at 900°C. The weight change data has been shown in figure 2. From the data and graph it was observed that uncoated T-91 steel experienced highest weight gain as compared to coating specimens. However it was also been noticed that with increase in percentage of ZrO_2, resistance to hot corrosion increased. From figure it was clearly visible that weight gain by specimen was reduced with increase in the ZrO_2 in alumina matrix. The data shows that ZrO_2 reinforced coated specimens showed better corrosion resistance than uncoated specimen.

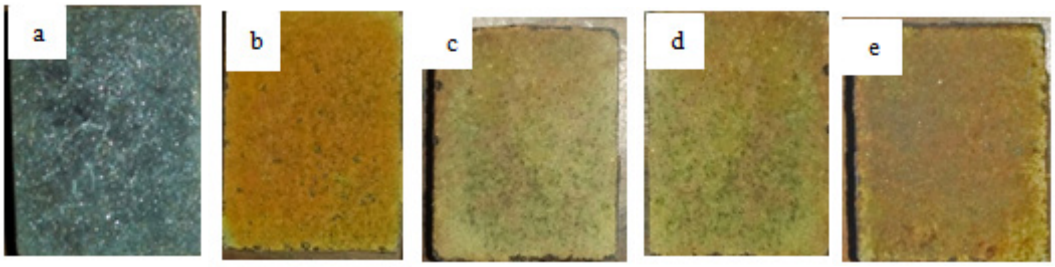


Figure 1. (a) T-91 uncoated (b) T-91 Al_2O_3 (c) T-91 Al_2O_3-3Wt% ZrO_2 (d) T-91 Al_2O_3-13Wt% ZrO_2 (e) T-91 Al_2O_3-20Wt% ZrO_2

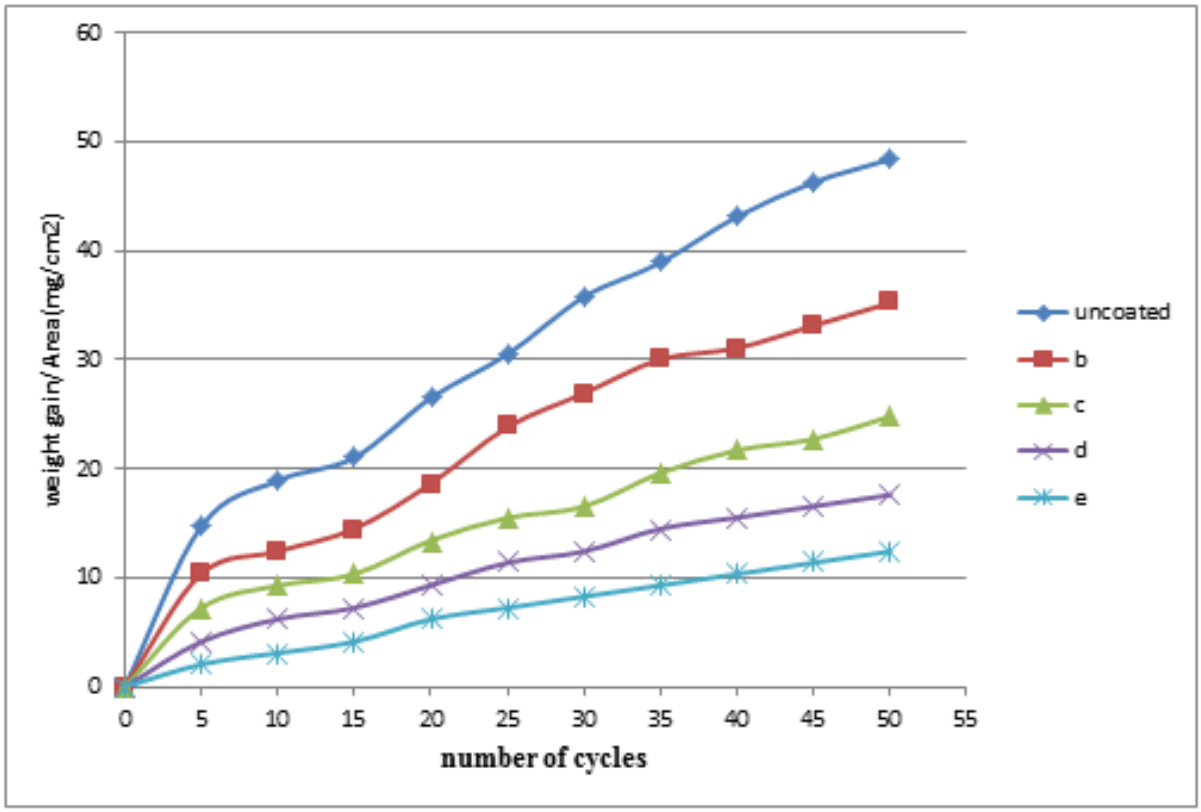


Figure 2. Weight gain plot for (a) T-91 uncoated (b) T-91 Al_2O_3 (c) T-91 Al_2O_3-3Wt% ZrO_2 (d) T-91 Al_2O_3-13Wt% ZrO_2 (e) T-91 Al_2O_3-20Wt% ZrO_2

3.3. X-ray Diffraction Analysis

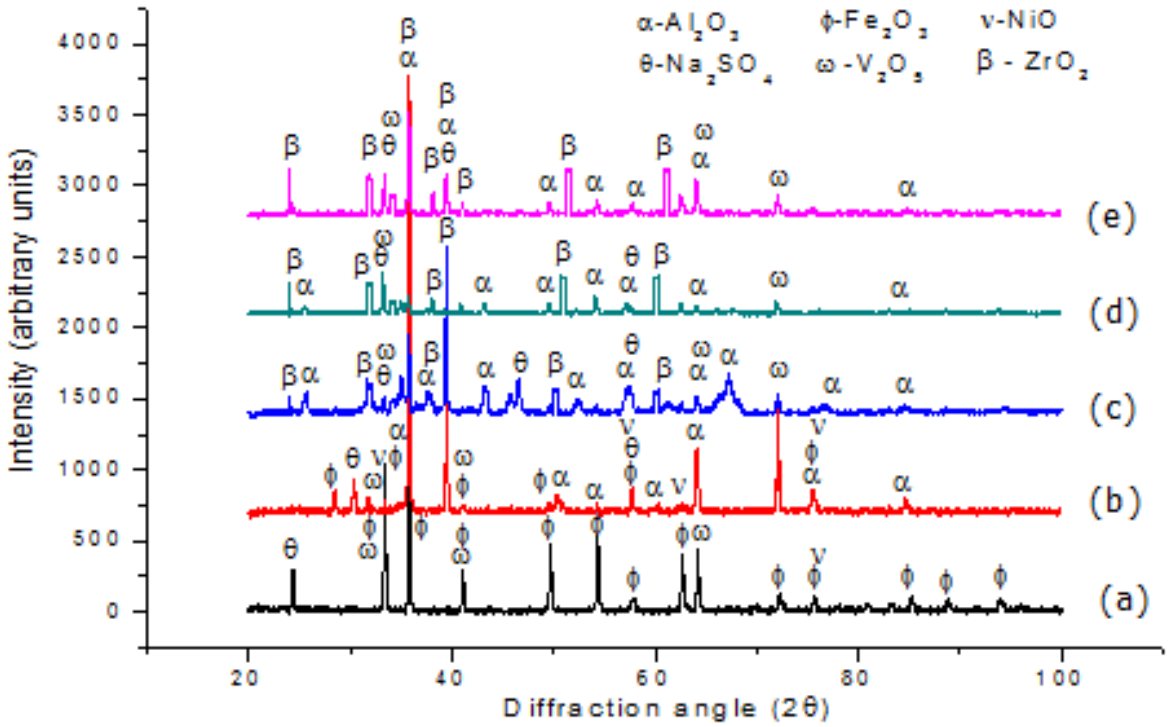
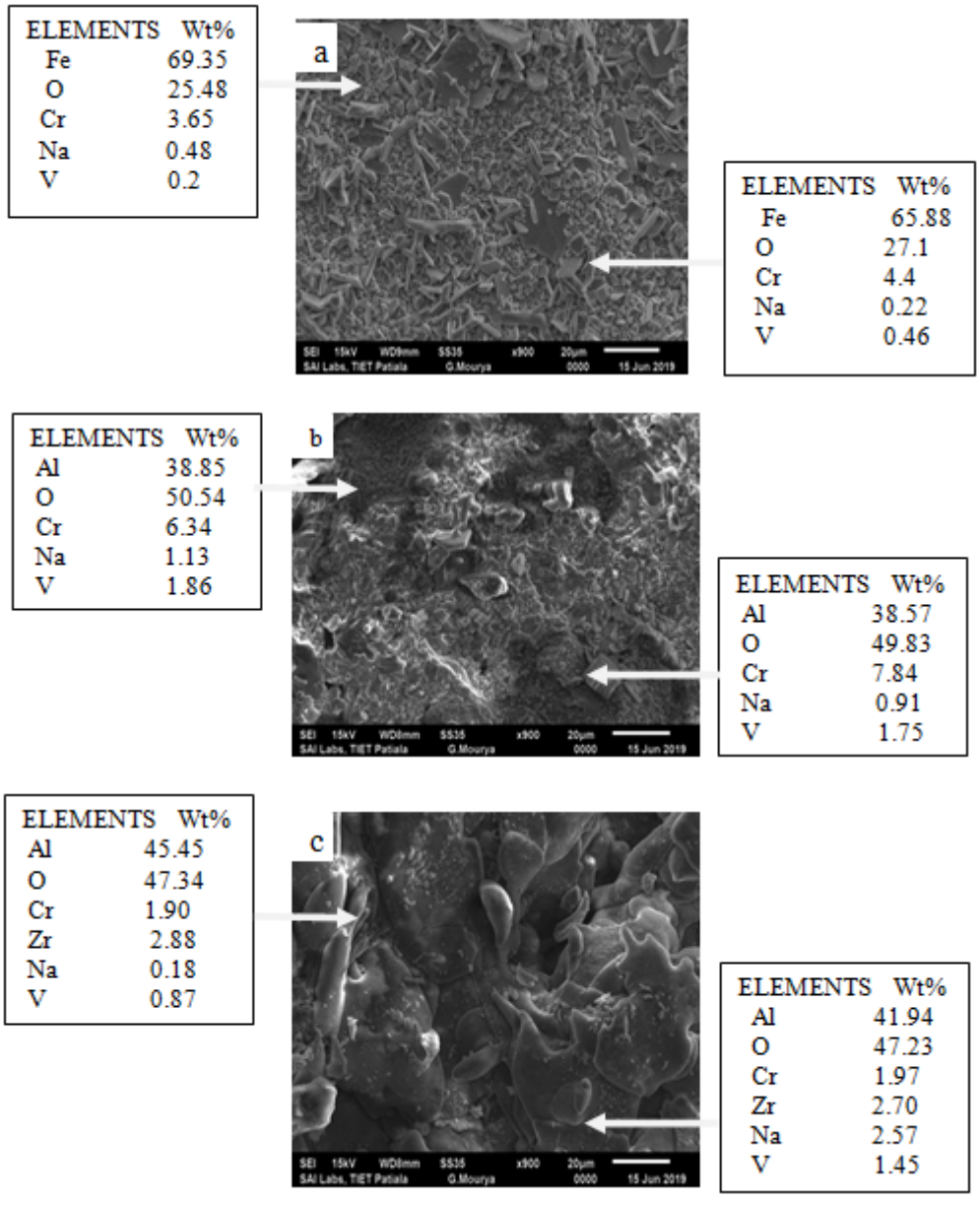


Figure 3. XRD pattern for (a) T-91 uncoated (b) T-91 Al_2O_3 (c) T-91 Al_2O_3-3Wt% ZrO_2 (d) T-91 Al_2O_3-13Wt% ZrO_2 (e) T-91 Al_2O_3-20Wt% ZrO_2 exposed to molten salt environment for 50 cycles at a temp of 900°C

The formation of elements on the surface of corroded samples was examined using XRD analysis. Analysis indicates that the uncoated T-91 steel specimen had the presence of Fe_2O_3 in the oxide scale (Fig. 3a). In case of Al_2O_3 coated specimen, the peaks of Al_2O_3 were identified along with peaks of Fe_2O_3 (Fig. 3b). The Fe2O3 might have been formed due to porosity in the alumina coating. The XRD analysis of Al_2O_3-3Wt% ZrO_2, Al_2O_3-13Wt% ZrO_2, Al_2O_3-20Wt% ZrO_2 coated specimens indicated presence of Al_2O_3 and ZrO_2 elements in the oxide scale, with no traces of ferrous oxide (Fig. 3c-e).

3.4. SEM/EDS Analysis

Figure 4(a) shows the SEM micrograph of T-91 uncoated steel specimen after exposing it in molten salt environment for 50 cycles of heating inside a furnace. Also EDS analysis indicated the formation of Fe_2O_3 and Cr_2O_3. Micrograph shows spalling of topmost layer with badly damaged oxide scale. The scale was rich in Fe and O and small amount of Cr can be seen in the elemental analysis (Fig 4a). In case of Al_2O_3 coated specimen (Fig. 4b), micrograph shows that it consisted of the surface morphology similar to that of plasma spray coatings. EDS analysis shows the formation of Al_2O_3 and Cr_2O_3, along with presence of Fe and O. For coatings of Al_2O_3-3Wt% ZrO_2, Al_2O_3-13Wt% ZrO_2, Al_2O_3-20Wt% ZrO_2, the micrographs respectively indicate no traces of corrosion and EDS analysis shows the presence of Al, Zr and O elements. ZrO_2 is well spotted with bright particle in darker region of Al_2O_3 (Fig. 4c-e). Globular particles in the scale can also been observed, which might be because of the presence of excessive O, Cr.



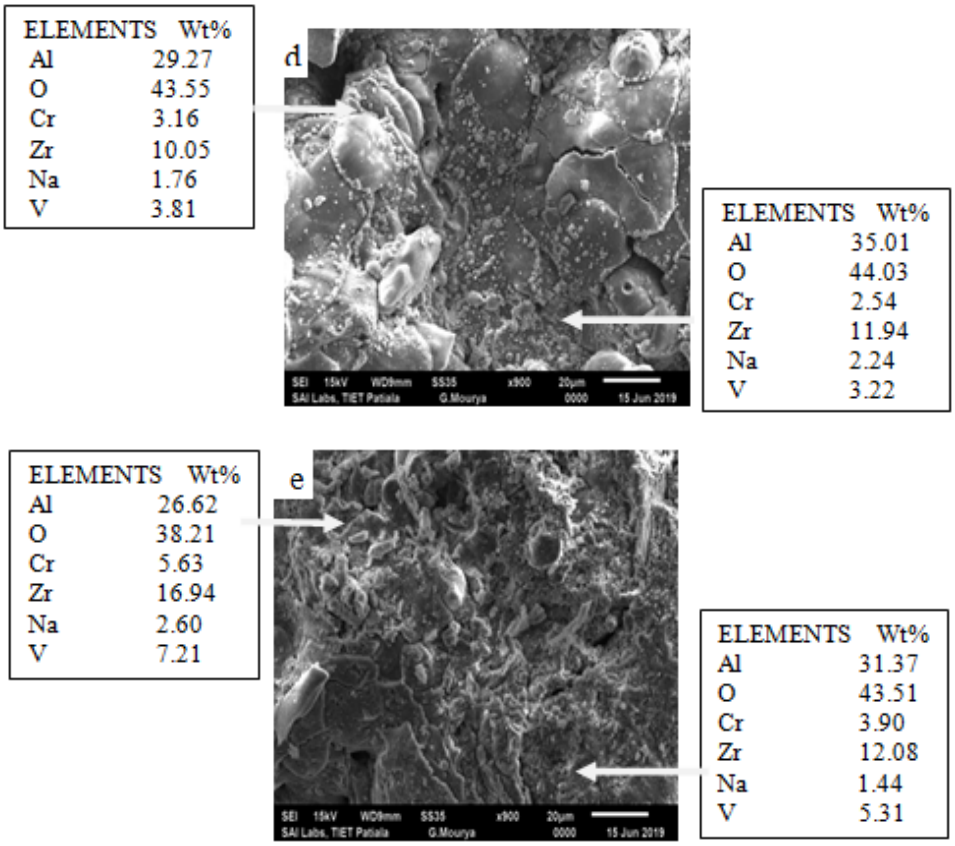


Figure 4. Surface scale morphology SEM images and EDS analysis for (a) T-91 uncoated (b) T-91 Al_2O_3 (c) T-91 Al_2O_3-3Wt% ZrO_2 (d) T-91 Al_2O_3-13Wt% ZrO_2 (e) T-91 Al_2O_3-20Wt% ZrO_2

4. Discussion

In this research work, different coating with varying quantities of Al_2O_3 and ZrO_2 were fabricated on the SA213 T-91 steel using plasma spray method to study hot corrosion resistance behavior. Experiment was conducted under the molten salt environment of 60% Na_2SO_4-40%V_2O_5 at a temperature of 900°C inside a furnace for 50 cycles. Each cycle consisted of 1hr heating and 20 min cooling at room temperature.

The uncoated T-91 boiler tube steel specimen underwent intense spalling of scale and deterioration of surface, along with color of the specimen turned to blackish grey due to severe corrosion and formation of ferrous oxide in the scale. The formation of ferrous oxide has been indicated in XRD analysis and SEM/EDS analysis. Uncoated steel experiences the internal oxidation which leads to spalling of scale, because in scale different oxides has different thermal expansion coefficient as described by Niranatlumpong et al [14]. Higher weight gain and intense spalling was due to the formation of Fe_2O_3 which penetrated through the cracks and attacked the base metal [15]. X ray diffraction analysis indicated the formation of Fe_2O_3 as the main constituent in uncoated steel specimen which has also been reported by Sidhu *et al* [7, 16].

The Al_2O_3 coating on the steel alloy helped to reduce corrosion rate. The formation of Fe_2O_3 might be due to diffusion of Fe from the base alloy through the porosities in the alumina coating. The ZrO_2 reinforced Al_2O_3 coated specimens showed no deterioration of surface and no spalling of scale was noticed. Presence of ZrO_2 coating increases the hardness and along with Al_2O_3, it increases the adhesion to the substrate steel. This helps to reduce porosities in the composite coatings. Corrosion behavior of coating and oxidation of specimens in hot corrosion is governed by mass gain. Figure 2 indicated sudden increase in mass of all specimens at initial stage. This might be due to the sudden oxygen pick-up during diffusion of oxygen at high temperature [15]. Uncoated T-91 steel specimen showed maximum increase in weight gain and Al_2O_3-20Wt% ZrO_2 showed least weight gain among all specimens. This may be due to rapid formation of oxides at grain boundaries and through small pores these oxides enters during early cycles in uncoated T-91 steel specimen as described by Niranatlumpong et al [14]. The presence of all these elements can also seen in the SEM/EDS analysis. SEM/EDS showed the higher amount of Fe_2O_3 in uncoated steel specimen while Al_2O_3 and ZrO_2 as the major element in coated specimens. ZrO_2 was well spotted with bright particle in darker region of Al_2O_3. Rate of corrosion showed the following trend: T-91 steel uncoated > Al_2O_3 > Al_2O_3-3Wt% ZrO_2 > Al_2O_3-13Wt% ZrO_2 > Al_2O_3-20Wt% ZrO_2.

5. Conclusions

The following conclusions have been drawn from this research work:

1. Using plasma spray process, different coatings of Al_2O_3 and ZrO_2 have been successfully deposited on ASTM-SAE213-T-91 steel boiler.
2. XRD, SEM/EDS analysis indicated that oxide layer of uncoated T-91 steel specimen contained Fe_2O_3 as main phase along with traces of Cr_2O_3.
3. Higher weight gain and intense spalling of uncoated boiler steel alloy was due to the formation of Fe_2O_3 which penetrated through the cracks and attacked the base metal.
4. In Al_2O_3 coating, Al_2O_3 was noticed as major phase while Fe2O3 was found as minor phase by XRD, SEM/EDS analysis. The formation of Fe_2O_3 might be due to diffusion of Fe from the base alloy through the porosities in the alumina coating.
5. In case of Al_2O_3-3Wt% ZrO_2, Al_2O_3-13Wt% ZrO_2, Al_2O_3-20Wt% ZrO_2 coatings, Al_2O_3 and ZrO_2 were found as major phase by XRD, SEM/EDS analysis. Small amount of globular particle was also been observed this might be because of excessive O, Cr.
6. The corrosion rate was higher for the uncoated T-91 steel as compared to the coated steel specimens.
7. The rate of corrosion was found decreasing with increase in ZrO_2 in alumina coating matrix and has followed following trend:
   T-91 steel uncoated > Al_2O_3 > Al_2O_3-3Wt% ZrO_2 > Al_2O_3-13Wt% ZrO_2 > Al_2O_3-20Wt% ZrO_2.

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