Comparative study of hot corrosion behavior of thermal sprayed alumina and titanium oxide reinforced alumina coatings on boiler steel

Gurdeep Singh, Santosh Kumar and Rakesh Kumar

Abstract
The current work evaluates the effect of hot corrosion on ASTM-SA213-T-22 Steel with a coating of 100Al2O3 and 20TiO2-Al2O3 at 900 °C in the molten salt environment of (Na2SO4-60% V2O5). The coatings were sprayed by plasma spray technique. The bare and coated samples were placed inside the muffle furnace at 900 °C for 50 cycles. Each cycle consisted of heating for 1 h and 20 min of cooling at ambient temperature. The kinetics of hot corrosion was analyzed by measuring mass gain after each cycle. The results were achieved by using visual examination, mass change measurement, XRD and SEM/EDS analysis. The result revealed that bare steel was more affected with corrosion and gained more mass due to the development of iron oxide (Fe2O3) than the coated sample. Fe2O3 and Cr2O3 were found as major phase in oxide scale of T-22 uncoated steel specimen. The 100Al2O3 and 20TiO2-Al2O3 coated specimen indicated the reduction in mass gain by 25.41% and 67.02% respectively as compared to uncoated specimen. Al2O3 coating with the combination of TiO2 showed better adhesion properties. The presence of TiO2 enhanced the durability and strength of Al2O3 coating to withstand high temperatures.

1. Introduction
The degradation of materials usually metals and alloys is serious issue in high temperature aggressive environment applications such as boilers, I.C. engine, gas turbine, fluidized bed combustion and heat exchanger etc [1, 2]. Among these applications, coal fired thermal plant boiler is a major industry in suffering from erosion and corrosion. Since, more than 25% of the boiler failure is owing to the fly ash erosion. Prakash et al [3] reported that more than 50% of boiler tube failure in coal fired thermal power plant boiler were owing to hot corrosion and erosion. The erosion-corrosion of boiler tubes leads to regular thinning of the boiler tubes in the working condition; ultimately result into sudden rupture of the boiler tubes. Erosion corrosion is identified as the major reason of downtime (50%–75% of their total arrest time) at power-generating plants, which leads to huge monetary losses [4–7]. Hence, it has been concluded that surface protection of boilers tubes, is required to avoid their premature failure.

There are distinct methods that have been utilized to reduce the material degradation process, in that thermal spray coating methods have attracted remarkable attention owing to their adaptability to spray almost any type of coating powder (metallic, polymeric, ceramic, composite) onto almost any substrate material [5]. The function of coating is to protect or insulate the component from aggressive conditions and thereby improving the service time of the substrate material. Presently, numerous thermal spraying coating techniques are utilized such as cold spray, flame spraying, high velocity oxy-fuel spraying (HVOF), atmospheric plasma spraying, detonation gun (D-Gun) and arc spraying etc. Among these, plasma spray is one of the most
commonly used thermal spray coating technique [6]. In plasma spraying, the coating material (powder) is supplied into a high temperature plasma jet. Due to very high temperature, the particle gets melted and accelerated towards the base material. Upon impact, the molten powder particle is flattened & quenched on the base material, and produce layered microstructure [7].

Now a days, ceramics coating is widely used to protect parts from high temperature, corrosive conditions and wear [8–10]. Plasma sprayed Al₂O₃ based coatings are mostly utilized for distinct industrial applications owing to their better properties like low production cost, excellent wear, abrasion and erosion resistance. Sundararajan et al [11] observed that thermal sprayed Al₂O₃ and Al₂O₃−TiO₂ coating can be utilized to resist wear. However, the coatings deposited by HVOF processes have indicated good tribological performance [12]. Sapra et al [13] investigated the E-C behaviour of D-Gun sprayed Al₂O₃−TiO₂ coating on boiler steels (T22 and T11) in live boiler condition. The results indicates that Al₂O₃−TiO₂ coating remained stable during the exposure to live boiler condition and offered better resistance against hot corrosion and erosion. The Al₂O₃−TiO₂ coatings possess dense structure and flat lamellas with very low porosity and high bond strength. In the literature study distinct coatings are utilized by the distinct researchers to protect the boiler steels from high temperature corrosion. The researchers also discussed about the techniques of coating for prevention of material to maintain its durability with elevated temperatures. Rani et al [14] studied the accelerated hot corrosion of steel and Fe based alloys. The D-gun sprayed method was used for coating the specimen with Cr₂O₃-50%Al₂O₃ coating. After coating, the specimens were kept in the atmosphere of molten salt environment at 900 °C for 50 cycles. The cycles consisted of 1 h of heating and 20 min of cooling at room temperature. Results were obtained using the thermogravimetric analysis, XRD, SEM/EDS techniques. Uncoated specimen experienced higher mass gain and intensive spallation layer of oxide scale which might be due to the formation of Fe₂O₃. Coated specimen showed lesser mass gain and no spallation of oxide scale was reported. In the coated specimens Cr and Al were the major phases as analyzed by SEM/EDS which might be due to formation of Cr₂O₃ and Al₂O₃ which act as barrier agents against corrosive species. Singh et al [15] investigated the corrosion resistance behaviour of Cr₆C₇−25(Ni-20Cr) and Ni-20Cr coatings on T-22 steel in simulated boiler environment. Specimens were coated with HVOF technique. The specimens were kept in the environment of molten salt (Na₂SO₄-60% V₂O₅) for 50 cycles at 900 °C. The experimentation was conducted in silicon tube furnace. Results were analyzed using the thermo gravimetric analysis, XRD, SEM/EDS techniques. XRD testing for coated specimen with Cr₆C₇−25(Ni-20Cr) showed the formation of NiO and Cr₂O₃ on the surface of sample whereas for the uncoated specimen T-22 showed the formation of major peaks of Fe₂O₃ and minor peaks of Cr₂O₃. Specimen coated with Ni-20Cr showed the formation of NiAl₂O₄, Al₂O₃, Cr₂O₃ and NiC as major phase. The bare specimen suffered higher corrosion rate as compared to the coated specimens. However, the Ni-20Cr coated sample suffered higher corrosion than the specimen coated with Cr₆C₇−25(Ni-20Cr). Bala et al [16] investigated the corrosion resistance behaviour of cold spray Ni-50Cr coating on boiler steels. The experiment was performed under the aggressive condition of Na₂SO₄-60%V₂O₅ at the temperature of 900 °C for 50 cycles which consisted of 1 h of heating and then cooling for 20 min. Specimens were coated with Ni-50Cr using the cold spray technique. Results were obtained using the mass change measurement, XRD, SEM/EDAX. Both the uncoated specimens showed poor resistance to hot corrosion and suffered from intensive spallation. XRD showed that the Fe₂O₃ was present in the major oxide scale in uncoated specimens. Specimens coated with Ni-50Cr showed better resistance to hot corrosion as it showed less.

Gain and protective oxides of Ni and Cr were found. Singh et al [17] evaluated the hot corrosion on T-91 boiler steel tubes coated with Al₂O₃. D-gun spray method was used for coating the substrate. The coated and uncoated specimens were exposed to molten salt environment at 900 °C for 10 cycles. The thermo gravimetric study method was used to study the change in mass of each specimen, after exposing them in the molten salt condition. It was analyzed that coated specimen gained 2.69% less mass as compared to bare specimen. The SEM/EDS results showed that the corrosion rate was more in bare specimen. The coating of Al₂O₃ was found protective for T-91 boiler steel tube. Jagadeeswaran et al [18] examined hot corrosion study on T-31 boiler steel coated with Al₂O₃ + CoCrAlTaY. The coating was fabricated by high velocity oxy fuel (HVOF) technique. The experiment was conducted under molten salt condition of (Na₂SO₄−V₂O₅) at 800 °C. Results were analyzed using the thermo gravimetric analysis, XRD, SEM/EDS techniques. XRD and SEM analysis showed that the surface of uncoated T-31 was rich with iron oxides and the surface coated with HVOF coating was max. in oxides of Cr, Co & Al. These protective oxides provided the resistance to hot corrosion and reduced the rate of corrosion by 5 times as compared to uncoated specimens. Wang et al [19] examined the thermal barrier coating of aluminum rare earth coating in mixed sulfate on nickel based super alloy GH4033 at 1050 °C. Aluminum rare earth coating method was used for coating the substrate. Substrates were exposed to corrosive environment of (75%wtNa₂SO₄−25%wtV₂O₅) and were kept in muffle furnace for required 10 cycles of 10 h, followed by air cooling. The x-ray, SEM/EDS techniques were used to determine the corrosive components and microstructure of specimen after experiment. The distinct steps were observed by coating were: 1st the dissolution of surface oxide, 2nd was oxidation state and 3rd was spallation. Therefore this coating was used under 1000 °C of
temperature. Singh et al [20] examined the performance of ASTM SA213 T-22 boiler steel tube with coating of TiO2-Ni3Al. The coating was sprayed by high velocity oxy fuel (HVOF) technique. High temp. corrosion studies were done on the coated and bare samples for 50 cycles in the Na2SO4-60%V2O5 environment at 900 °C for.

Each cycle composed of 1 h of heating in silicon tube furnace and then cooling in air (20 min) at room temperature. The XRD, SEM/EDS testing were utilized to analyse the corrosion characteristics of specimens. In bare T-22 boiler steel, Fe2O3, Cr2O3 and Fe3O4 were observed as main phase and in TiO2 coated T-22 sample TiO, Ti4O7 and Ti3O14 were observed as primary phases. The uncoated specimen experienced high corrosion rate than coated T-22 specimens. The TiO2-Ni3Al coating was found suitable and preventive against corrosion on boiler steels. Garg et al [21] experimented on prevention of hot corrosion on SAE 213 T-22 boiler steel tube coated with differentiated weight percentages of tungsten carbide and chromium (10WC-Cr) and (12WC-Cr). The coatings were deposited by high velocity oxy fuel (HVOF) technique. Each specimen was kept in the condition of Na2SO4-60%V2O5 for 50 cycles at 900 °C. The thermo gravimetric technique was used to examine the coating behaviour. The result revealed that, the uncoated T-22 specimen gained much more mass because of formation of Fe2O3 on its surface. The 12%WC-Cr coated T-22 have gained less mass than 10% WC-Cr coated specimen. It was found that the addition of tungsten carbide helped in preventing the hot corrosion. Muthu et al [22] analyzed the hot corrosion and oxidation performance of pulsed current gas tungsten arc weldment of Fe based superalloy A-286 in air and Na2SO4-7.5%NaVO3-5%NaCl condition at 700 °C. The corrosion kinetics of the weldments were determined using thermogravimetric analysis. From the mass change data, it was concluded that oxidized weldment exhibits less mass gain than hot corroded weldment after 50 cycles. However, from the cross-sectional analysis it was observed that in both the cases higher rate of oxidation rate is observed in the base metal zone. Mahu et al [23] analyzed the influence of plasma sprayed Al2O3-13TiO2 coating on a C45 steel (crankshaft material). The different testing techniques such as XRD, optical and electronic microscopy were used to analyze the as sprayed coating. The coated samples showed higher hardness than the C45 steel. The result showed that spraying of appropriate powders into the plasma jet can be an alternative to classical thermal treatments on the crankshaft journals. Chen et al [24] used sol-gel with plasma surfacing to prepare TiO2/Al2O3/Incone1625 composite coatings on Q235 alloys. To examine the corrosion resistance of this coatings, samples with TiO2/Al2O3/Incone1625 composite coating and Inconel 625 single coating were corroded with Na2SO4 and NaCl salts in air at 900 °C with the weight ratio of 1:1 for one day. Results showed that the composite coatings offered lower oxidation mass gain than the sample with single coating. Wang et al [25] studied the effect of laser remelting on thermal shock and microstructure of plasma sprayed Al2O3-13wt%TiO2 Coatings. The SEM and XRD show that after laser melting, lamellar structure disappears and particles on the ceramic coating are refined, thus enhancing density and getting a remelting coating basically without defects like cracks. In addition, the laser-remelted coating exhibited better thermal shock resistance than plasma sprayed coating. Duran et al [26] evaluated the wear and corrosion of flame sprayed Al2O3-TiO2 coating on AISI 1020 carbon steel. The electrochemical techniques (Tafel) were used to estimate the resistance against corrosion. The coated samples showed better corrosion resistance than bare steel. Thus ceramic coating is a better choice to resist corrosion, wear, high temperature oxidation [27–29]. The surface coating of Al2O3 and TiO2 are widely used to enhance the resistance of material against erosion, wear, cavitation and corrosion. Addition of different quantity of TiO2 in Al2O3 are utilized in combustion chamber of CI engines, cutting tool, and other industrial applications. Since, Al2O3 powder particles are stable in alpha form that reduce the mechanical characteristics but enhance the toughness and hardness of the coating. However, the hardness and toughness of Al2O3 coating can be changed with the addition of TiO2 [30]. The reason for low mechanical characteristics without bond coat may be owing to thermal expansion mismatch between the substrate and coating material. Although, the composites of Al2O3 with TiO2 have exhibited better performance under different environment than those of the individual oxides [31]. But, ceramic coating exhibit poor adhesion strength with the metallic substrate owing to the difference in coefficient of thermal expansion between metallic substrate and ceramic coating [32]. Hence, it is essential to spray a bond coat between the ceramic coating and substrate. Since, a very high anisotropy occur between the metallic substrate and ceramic coating due to the variation in the coefficient of thermal expansion. Thus bond coat reduce the stress at the substrate-coating interface and improve the adhesion strength of the coating [33]. The another reason to use bond coat is to provide a good thermal expansion match between these two different layers [34]. The coefficient of thermal expansion for bare T-22, coating powder Al2O3 and 20TiO2-Al2O3 is 13 × 10−6 K−1, 5.4 × 10−6 K−1 and 4.1 × 10−6 K−1 respectively.

From the overview of hot corrosion studies especially in the field of thermal power plant, it has been concluded that the development and identification of high corrosion resistant materials are the areas of prime interest in this field. Since, hot corrosion in industries, power plants, IC engines, gas turbines and boiler steels is major problem due to corrosive environments at elevated temperatures. Various materials such as; T-11, T-22, T-91, T-92 and Gr-Al steels are majorly used in the power plants and industries, so it is very important to protect these steels from hot corrosion. The various studies and experimentation are done by distinct researchers to minimize...
the effect of hot corrosion. It is observed from the literature study that various types of coatings are used on the specimens with different deposition methods [35–44]. The thermal spray coatings have porosities through which aggressive chemicals may attack the substrate to induce corrosion. The reinforcements in conventional coatings may help to block porosities to block the penetration of aggressive oxides to attack substrate steel. The TiO2 is a hard material, which may be used as reinforcement in conventional Al2O3 coatings. Therefore it was decided to reinforce the conventional Al2O3 coating with different weight percentages of TiO2 and further to study the hot corrosion behaviour of these TiO2-Al2O3 coatings in molten salt environment (Na2SO4-60% V2O5) at 900 °C. In addition, there is no reported literature on hot corrosion performance of Al2O3-TiO2 coating deposited on commonly used boiler steel using plasma spray technique. However Rani et al [14] deposited Cr2O3-50%Al2O3 coating on T-22 and SF800H boiler steel to evaluate the hot corrosion behaviour in molten salt condition at 900 °C using D-Gun spray technique. The result showed that Cr2O3-50%Al2O3 coating on T22 steel was better than SF800H steel to resist hot corrosion. Thus, T22 and Na2SO4-60% V2O5 is used as a substrate and salt material in the current investigation. The selection of Na2SO4-60% V2O5 salt is due to the fact that it simulates similar conditions of the deposits of molten sulfate-vanadate, which are ensuing from the condensation of the combustion products of low-grade fuels in boilers. Further, thermogravimetric technique was used to study the kinetics of the hot corrosion of the aforementioned coating and base boiler steel. The following objectives were finalized:

1. To deposit Al2O3 and 20TiO2-Al2O3 coating on T-22 steel with plasma spray coating method.
2. To investigate the change in mass of T-22 steel specimens after exposing it to molten salt environment at 900 °C for 50 cycles.
3. To investigate the microstructure of corroded specimens with XRD, SEM/EDS techniques.

2 Experimental detail/ Methods

2.1. Selection of specimen material
ASTM-SA213-T-22 steel has been used as the base material having sample sizes of 20 mm × 15 mm × 5 mm. The material in the form of boiler tube was obtained from Guru Gobind Singh Thermal Power station, Rupnagar, Punjab. Detailed specifications of T-22 boiler steel are given in table 1.

2.2. Fabrication of coatings
The coatings were fabricated at Metalizing Equipment Company Private Ltd Jodhpur, Rajasthan. Before coating the samples, the emery paper of 200, 400, 600, 800 and 1000 grit sizes were used to remove the surface irregularities on the surface of samples. The Al2O3 and Al2O3-20TiO2 coatings were sprayed on T22 boiler steel by plasma spray. A bond coat of Ni-20wt% Cr was deposited between the base steel and coating, since it decrease the stress at the coating substrate interface and enhance the adhesion strength of the coating. The composition of coatings is given in table 2. The parameters used to spray plasma spray coating as shown in table 3.

2.3. Hot corrosion studies in molten salt environment (Na2SO4-60% V2O5)
The hot corrosion behavior of Al2O3 and Al2O3 coatings on T-22 boiler steel at 900 °C in the molten salt condition was examined. The experiment was consisted of 50 cycles. Each cycle consisted of 1 h heating and 20 min of cooling in air at room temperature. Before conducting the experiment, the physical dimensions of
each specimen was measured with the help of vernier caliper. The de-burring operation was performed on each surface to remove any foreign particles at the microscopic level. The plasma spray coating was performed before the application of molten salt on the surface of specimens. The $\text{(Na}_2\text{SO}_4-60\% \text{ V}_2\text{O}_5)$ salt was mixed with distilled water and was applied on each face of the specimen after washing all specimens with acetone. The layer of molten salt was applied gently on each face of specimen with the help of camel hair brush. To make the proper adhesion of molten salt on each surface of the specimen, all specimens were heated up to 250 °C in the oven. The molten salt environment becomes more aggressive to react with metals with the increase in temperature and the rate of reaction also increases. The increase in temperature causes the faster rate of corrosion on the surface of the metal. The aggressiveness of corrosion was examined with a number of repetitions in cycles. After hot corrosion study, all the samples were analyzed by the XRD, SEM and EDS. The test was conducted in metallurgy laboratory of Chandigarh Engineering College, Landran (Mohali), Punjab.

2.4. Analysis of corroded samples
The following techniques were used for analyzing the specimen after hot corrosion process:

2.4.1. Visual observation
After every cycle, each specimen was examined visually for any change in colour, cracks formation and surface properties. After completion of 50 cycles, each specimen was examined and their macrographs were prepared. The physical visual examination (spallation and formation of cracks) on the surface of sample were studied by macrographs.

2.4.2. Mass change analysis
The kinetics of hot corrosion was determined by the measurement of mass change values of each sample after each cycle. Then the graph was plotted between mass change data and number of cycles.

2.4.3. XRD analysis
The x-ray diffraction analysis of the uncoated and coated specimen were carried out with x-ray diffracto-meter at Thapar University, Patiala, Punjab (India) to examine the various phase formed on surface of each specimen. With the scanning speed of 2° mm$^{-1}$ in 2θ range of 20° to 120°, the intensities were recorded.

2.4.4. SEM/EDS analysis
The uncoated and coated specimen were analyzed and scanned by using SEM/EDS technique after cyclic study was done by exposing it to molten salt environment. The surface morphology of the samples was examined by inserting each specimen in Scanning Electron Microscope. The different percentages of composition were examined at different phases. To find the element composition wt% at specific area or point, the EDAX genesis software was used, SEM with EDAX Genesis software is used to scan each specimen at Thapar University, Patiala, Punjab (India).

3. Results
The performance of uncoated and coated ASTM-SA213-T-22 boiler steel has been discussed in this section. The T 22 steel samples were coated with $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$-$\text{Al}_2\text{O}_3$ by adopting plasma spray technique. The experiment was done in molten salt environment under the cyclic conditions at 900 °C. During the experiment, the each specimen was inspected after each cycle. The condition of surface of each specimen was observed and the change of mass is analyzed with the use of thermogravimetric data. The corrosive products were checked by using XRD and SEM/EDS techniques.
3.1. Visual examination
Before conducting the experiment, all samples were in perfect condition. The experiment was conducted in a molten salt environment (Na$_2$SO$_4$-60% V$_2$O$_5$) kept in silicon tube muffle furnace at 900 °C. During the experiment, after the 4th cycle, the uncoated T-22 specimen started to change in brownish colour and after 13th cycles dark black colour is formed on the surface of the sample. However, after 25 cycle, formation of cracks near corners of the specimen propagate. Then, after 32th cycles the huge spallation takes place along with material start removing in powder form. Further, after 35th cycles material starts removing in chip form. Subsequently, after 38th cycles, formation of cracks on the top surface of the specimen take place. At the end of 40th cycles, crack propagates and this phenomena continue till the end of 50th cycles. The image of bare T22 after 50 cycles is shown in figure 1 (a). On the other side, for 20TiO$_2$-Al$_2$O$_3$ coated T-22 steel, only change in colour was observed till 50th cycle, there was no development of cracks found even after 50 cycles as shown in images figure 1 (b). But in the case of Al$_2$O$_3$ coated T-22 coated sample, minor spallation of scale was seen after 40th cycles on the surface and side of the sample. However, after 46th cycles, sputtering from the top surface along with material starts removing in chip form till 50th cycles as indicated in figure 1 (c). The image of test samples after 50 cycles of study is shown in figure 1.

From the micrograph of test samples it was observed that 20TiO$_2$-Al$_2$O$_3$ coatings was found durable; almost no deration of material occurred due to the corrosive environment under elevated temperature.

3.2. Thermo gravimetric study
The thermo gravimetric study was done to find the mass change characteristics showed by coated and uncoated T-22 boiler steel. The change in mass of uncoated and coated T-22 steels were analyzed after exposing each specimen in the molten salt environment (Na$_2$SO$_4$-60% V$_2$O$_5$) for 50 cycles at 900 °C. The change in mass showed the kinetics of corrosion. The high mass gain is identified as a high rate of corrosion. The graph indicates that bare sample experienced the higher mass gain, than coated samples.

The mass change is observed after each complete cycle shown in figure 2.

From the mass change graph, it was observed that 20TiO$_2$-Al$_2$O$_3$ coated sample get less mass gain than Al$_2$O$_3$ coated samples. However, both the coating reduced more mass gain than uncoated steel. The cumulative mass gained by coated and uncoated specimens are shown in figure 3.

From figure 3, the uncoated specimen showed maximum cumulative mass gain of 54.61 mg cm$^{-2}$. The least cumulative mass gain for coated specimen of 80Al$_2$O$_3$-20TiO$_2$ was 18.01 mg cm$^{-2}$ after exposure in molten salt.

![Figure 1](image1.png)

**Figure 1.** Image of samples after 50 cycle of study (a) uncoated T22 (b) 20 TiO$_2$-Al$_2$O$_3$ coated T22 steel (c) Al$_2$O$_3$ coated T22 steel.

![Figure 2](image2.png)

**Figure 2.** Mass gain in (mg cm$^{-2}$) for uncoated and coated specimens during the experiment. (UC = Uncoated, C1: Al$_2$O$_3$ coated T22 steel and C2: 20TiO$_2$-Al$_2$O$_3$ coated T22 steel).

![Figure 3](image3.png)
environment. The specimen C1 coated with 100 Al₂O₃ gained the cumulative mass of 40.73 mg/cm² and gained 25.41% less mass gain as compared to uncoated specimen when exposed in corrosive environment for same period of time. The C2 specimen coated with 80Al₂O₃-20TiO₂ measured the least cumulative mass gain of 18.01 mg cm⁻² and it resulted in 67.02% less mass as compared to uncoated specimen.

The result showed that the coating of 20TiO₂-Al₂O₃ was found more protective than Al₂O₃ according to the thermo gravimetric study of cumulative mass gain.

3.3. Investigation of parabolic rate constant (Kp) at 900 °C

The parabolic rate constant (Kp) was calculated by a linear least-square algorithm to a function in the form of \( (W/A)t = Kpt \), where \( W/A \) is the mass gain per unit surface area (mg/cm²) and \( t \) indicates the number of cycles representing the time of exposure. Figure 4 indicates the mass gain for bare and coated sample as a function of time (no. of cycles) at 900 °C for bare and coated sample. (UC: Bare T22 steel; C1: Al₂O₃ coated T22 steel; C2:Al₂O₃-20TiO₂ coated T22 steel).

The value of Kp for bare sample (T22 steel) was higher than the Al₂O₃ and 20TiO₂-Al₂O₃ coated T22 steel. The lower value of kp was due to the spinel layer that is protective against oxidation. However, the uncoated T22 steel oxidizes without any protection, thus result in higher value of kp.
3.4. XRD analysis

X-Ray diffraction analysis was conducted to figure out the metallurgy of material affected due to corrosive environment at high temperature as indicated in figure 5.

The XRD graph, figure 5(a) shows that in uncoated T-22 specimen, the XRD spectrum shows the formation of Fe$_2$O$_3$ at oxide scales. The higher mass gain of uncoated T22 steel was due to the existence of iron oxide in their oxide scales. The higher growth rate of iron oxide result in less cohesion strength among their layers and provide less corrosion resistance [46]. The XRD spectrum of the specimen with the coating of pure Al$_2$O$_3$ shows the Al$_2$O$_3$ peaks along with Na$_2$SO$_4$ and Fe$_2$O$_3$ as shown in figure 5(b). The XRD spectrum of Al$_2$O$_3$-20TiO$_2$ coated specimen shows presence of TiO$_2$, Na$_2$SO$_4$ and Al$_2$O$_3$ along with of V$_2$O$_5$ and no peak of Fe$_2$O$_3$ is found on the surface of coated specimen as shown in figure 5(c). The XRD graph clearly shows that the uncoated specimen mostly affected by the formation of Fe$_2$O$_3$ and nearly no formation of Fe$_2$O$_3$ found on the surface of the specimens coated with 20TiO$_2$-Al$_2$O$_3$ coatings.

3.5. SEM/EDS analysis

Figure 6(a) shows the SEM micrograph of T-22 uncoated steel substrate after exposing it in molten salt environment for 50 cycles of heating inside a silicon tube muffle furnace. The EDS analysis on spectrum indicates the presence of Fe and Cr which might of the formation of Fe$_2$O$_3$ and Cr$_2$O$_3$. SEM Micrograph shows the spallation in the coating layer. The Fe, O along with small percentage of Cr. For Al$_2$O$_3$ coated T-22 specimen the EDS analysis spectrum shows the presence of Al, O, Cr and Fe as depicted in figure 6(b). The presence of Al and Fe might cause the formation of Al$_2$O$_3$, Cr$_2$O$_3$, and Fe$_2$O$_3$. In case of 20Wt% TiO$_2$-Al$_2$O$_3$ coated specimen, it shows the morphology of surface coating of specimens and the EDS analysis shows the major formation of Al$_2$O$_3$ and TiO$_2$. The TiO$_2$ was well spotted with bright particle in darker region of Al$_2$O$_3$. The presence of Na and V might be due to the presence of molten salt elements in the oxide scale as shown in figure 6(c).

The SEM/EDS result showed that the coated specimens formed preventive elements such as Al, Cr and Ti on their surface, but in uncoated specimen the formation of Fe and Mo was found. The presence of Fe and Mo on the surface of uncoated specimen, might have caused the formation of iron oxide layer on the surface, and led to maximum mass gain. The corrosion occurred at very early stages of the cycles in molten salt the environment at 900 °C. On the other hand, the coated specimen showed absence of Fe and molybdenum.

3.6. Cross-sectional analysis of as sprayed Al$_2$O$_3$ and 20TiO$_2$-Al$_2$O$_3$ coating

The cross-sectional SEM image and of as sprayed Al$_2$O$_3$ and 20TiO$_2$-Al$_2$O$_3$ coating on T-22 boiler steel is shown in figures 7(a) and (b).

Both the coating along with bond coat exhibit dense appearance. The average coating thickness of the top coat (Al$_2$O$_3$ and 20TiO$_2$-Al$_2$O$_3$) and bond coat (Ni-20Cr) on T22 steel was 250 to 300 μm, which is suitable for boiler application. In addition, the average microhardness of bare T22 steel, Al$_2$O$_3$ and 20TiO$_2$-Al$_2$O$_3$ coating was measured to be 190 Hv, 840 Hv and 750 Hv respectively. However, for bond coat (Ni-20Cr), for both coating has an average microhardness value of 240 Hv.
The digital micro hardness tester at 100g load and dwell time of 10 s. was used to measure the mean micro hardness. During hardness testing, five points were taken at a distance of 50 μm, 100 μm, 150 μm, 200 μm and 250 μm from the interface between coat (top coat + bond coat) and the base steel. The calculated value of average micro hardness graph is shown in figure 8.

4. Discussion

In this experiment, the hot corrosion behaviour of Al₂O₃ and 20TiO₂-Al₂O₃ coating on T-22 boiler steel was examined. Each specimen was kept in molten salt environment (Na₂SO₄-60% V₂O₅). After the successful completion of experiment the result were obtained. The macrograph showed that the rate of corrosion was high.
in uncoated T-22 specimen as compared to coated specimens. The change in colour to brownish was found in early stage in uncoated T-22 specimen. After 25th cycle the development of cracks and sputtering initiated and continue till 50th cycles. The sample image of bare T22 steel after 50th cycles is shown in figure 1(a). The thermo gravimetric study revealed that the uncoated specimen gained maximum mass in the experiment as compared to other specimens. The change in mass showed the kinetics of corrosion in the molten salt environment at elevated temperature. The thermo gravimetric graph (figure 2) and histogram (figure 3) showed that mass gained by the uncoated specimen was 54.61 mg cm$^{-2}$. The XRD (figure 5) graph indicated the formation of Fe$_2$O$_3$ in oxide scale on the surface of uncoated specimen. The SEM/EDS analysis indicated the presence of Fe, Mo and V on the surface of uncoated T-22 specimen (figure 6). These elements are highly responsible for the hot corrosion [2]. The molybdenum oxide is found in molten state at 550 °C. At 900 °C the liquid molybdenum oxide dissolves the protective layer of chromium, which causes corrosion on the surface of substrate. The protective oxide layer of chromium helps to resist the corrosive species to react with the surface of metal [16]. The iron oxide reacts with the base metal with time, due to this the mass of substrate increases with respect to time. The thick iron oxide layer forms on the surface of specimens which is responsible for corrosion [19]. Al$_2$O$_3$ coated specimen showed 25.41% less mass gain as compared to uncoated specimen. Small pores were noticed on the surface of the specimen after exposing it to the molten salt environment for 50 cycles. XRD graph indicated the presence of Al$_2$O$_3$, Cr$_2$O$_3$, and Fe$_2$O$_3$ oxide layers. The less mass gain by the specimen is might be due to the formation of Al$_2$O$_3$ and Cr$_2$O$_3$ which resist the corrosive element to attack the base metal. However, porosities in Al$_2$O$_3$ coatings might have abled the corrosive elements to attack the base metal. SEM/EDS analysis also showed presence of Al, Cr and Fe which validated the XRD results. The spallation produced on the specimen was might be due to the formation of Fe$_2$O$_3$ oxide layer. However, the specimen coated with Al$_2$O$_3$-20TiO$_2$ showed least...
mass gain of 18.01 mg cm\(^{-2}\) and gained 67.02% less mass as compared to uncoated specimen showed by thermo gravimetric method shown in (figure 3). The XRD graph (figure 5) showed the presence of Al\(_2\)O\(_3\), Cr\(_2\)O\(_3\) and TiO\(_2\) oxides on the surface of coated specimens. These elements are corrosion resistant in nature. In SEM/EDS analysis, the coated specimen showed the presence of Ti, Al in major phase. There were no traces of Fe and Mo found on the surface of coated specimens even after 50 numbers of cycles in molten salt environment at elevated temperatures as shown in figures 6(b) and (c).

This reinforcement of TiO\(_2\) in Al\(_2\)O\(_3\) might have helped to reduce the porosity in the coating layer. It is observed that the composition of Al\(_2\)O\(_3\)-20TiO\(_2\) showed better results. It has been analyzed that with the addition of TiO\(_2\) in Al\(_2\)O\(_3\) coating, the hot corrosion resistance increases. The TiO\(_2\) along with Al\(_2\)O\(_3\) showed better adhesion properties with base metal and found preventive from hot corrosion. The rate of hot corrosion resistance showed the following trend: Uncoated T-22 steel < Al\(_2\)O\(_3\) < 20Wt%Ti-Al\(_2\)O\(_3\).

5. Conclusion

In this research, the hot corrosion behaviour of Al\(_2\)O\(_3\) and 20TiO\(_2\)-Al\(_2\)O\(_3\) coatings on T-22 specimens is investigated at the temperature of 900 °C for 50 cycles inside a silicon tube muffle furnace under the molten salt environment. The following conclusions are drawn from above study.

1. Both the coating (100Al\(_2\)O\(_3\) and 20TiO\(_2\)-Al\(_2\)O\(_3\)) were successfully deposited on T-22 with plasma spray coating technique.

2. The uncoated T-22 coated specimen showed maximum mass change whereas the specimen coated with 20TiO\(_2\)-Al\(_2\)O\(_3\) showed least mass change.

3. The XRD and SEM/EDS analysis indicates that uncoated T-22 steel specimen contained Fe\(_2\)O\(_3\) and Cr\(_2\)O\(_3\) as major phase in oxide scale.

4. In the case of coatings of 20TiO\(_2\)-Al\(_2\)O\(_3\), the major phases of TiO\(_2\) and Al\(_2\)O\(_3\) were found in XRD, SEM/EDS analysis.

5. The 20TiO\(_2\)-Al\(_2\)O\(_3\) coating provide more hot corrosion resistance than Al\(_2\)O\(_3\) coating in molten salt environment (Na\(_2\)SO\(_4\)-60% V\(_2\)O\(_5\)) for 50 cycles at 900 °C.

6. The 100Al\(_2\)O\(_3\) and 20TiO\(_2\)-Al\(_2\)O\(_3\) coated specimen indicated the mass gain reduction by 25.41% and 67.02% respectively, as compared to uncoated specimen.

7. During the exposure, the formation of cracks, peeling and spallation occurred in the uncoated T-22 boiler steel near 15th cycle and coated T-22 showed no formation of cracks after experimentation done in molten salt environment (Na\(_2\)SO\(_4\)-60% V\(_2\)O\(_5\)) at 900 °C.

5.1. Future scope

- Hot corrosion behaviour of TiO\(_2\)-Al\(_2\)O\(_3\) coatings can be investigated in actual boiler environment.
- TiO\(_2\)-Al\(_2\)O\(_3\) coatings can be fabricated with different thermal spray techniques, other than plasma spray method.
- TiO\(_2\)-Al\(_2\)O\(_3\) coatings may be deposited on different alloy steels to investigate their hot corrosion behaviour.
- The composition of TiO\(_2\) can be varied in Al\(_2\)O\(_3\) matrix to fabricate different coatings.

Acknowledgments

Authors are highly thankful to Dr Khushdeep Goyal, Assistant Professor, Department of Mechanical Engineering, Punjab University, Patiala for his unfailing inspiration, whole-hearted cooperation and guidance, Dr Rakesh Goyal, Assistant Professor, CUIET, Chitkara University, Rajpura & Dr IPS Ahuja, Professor, Department of Mechanical Engineering, Punjab University Patiala for completing this research work. In addition, I am deeply thankful to Er Santosh Kumar, Assistant Professor, Deptt. of Mechanical Engineering, Chandigarh Group of Colleges, Landran for guiding and providing the opportunity to conduct the experimental work at CGC Landran Mohali.
ORCID iDs
Santosh Kumar @ https://orcid.org/0000-0003-4414-3305
Rakesh Kumar @ https://orcid.org/0000-0002-7806-6208

References
[1] Sidhu T S, Malik A, Prakash S and Agrawal R D 2007 J. Therm. Spray Technol. 16 844–9
[2] Kumar S, Kumar M and Handa A 2018 Journal of Engineering Failure Analysis 54 1–13
[3] Prakash S, Singh S, Sidhu B S and Madeshia A 2001 Proc. of the National Seminar on Advances in Material and Processing, Nov. 9–10, IIT Roorkee, India, pp. 245–253. p 245
[4] Hidalgo V H, Vareda F J and Rico E F 1997 Trib. Int. 30 641–9
[5] Pawlowski I 2008 The Science Engineering of Thermal Spray Coatings 2nd edn (London: Wiley)
[6] Fauchais P L, Heberlein J R and Bouldo M I 2014 Thermal Spray Fundamentals—From Powder to Part (Berlin: Springer) (https://doi.org/10.1007/978-0-387-68991-3)
[7] Girolamo G D, Brentari A, Blasic C and Serra E 2014 Ceram. Int. 40 12861–7
[8] Wang Y, Jin Y and Wen S 1989 Wear 129 223–34
[9] Leivo E M, Vippola M S, Sorsa P P A, Vuoristo P M J and Mantyla T A 1997 Journal of Thermal Spray Technology 6 205–10
[10] Pantelis D I, Psyllaki P and Alexopoulos N 2000 Wear 237 197–204
[11] Sundararaj G, Sen D and Sivakumar G 2005 Wear 258 377–91
[12] Liu Y, Fischer T E and Dent A 2003 Surface and Coatings Technology 107 68–76
[13] Sapra P K, Singh S, Prakash S and Arivazhagan N 2009 Int. J. Surface Science and Engineering 13 145–56
[14] Rani A, Bala N and Gupta C 2017 Oxidation of Metals 88 515–28
[15] Singh S, Goyal K and Goyal R 2016 Journals of Thin Films, Coatings Science Technology and Applications 3 19–26 ISSN: 2455-3344
[16] Bala N, Parkash S and Singh H 2006 Materials and Design 31 244–53
[17] Singh G and Singh T 2014 Journal of Science and Research 2 2319–7064
[18] Jegadeeswaran N, Ramesh M and Udaya B 2013 Procsia Engineering 64 1013–9
[19] Wang H, Zaho O and Kan P 2018 Corrosion Science 135 99–106
[20] Singh S, Goyal K and Goyal R 2016 Journal of Mechanical Engineering 46 54–61
[21] Garg B and Kumar N 2013 Environment Nanotechnology 2 30–6
[22] Muthu S M and Arivarasu M 2019 Mater. Res. Express 6 116577
[23] Mahu G et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 444 032010
[24] Tuchun C et al 2019 IOP Conf. Ser.: Mater. Sci. Eng. 631 022059
[25] Dongsheng W 2019 IOP Conf. Ser.: Mater. Sci. Eng. 385 012021
[26] Forero-Duran M et al 2017 J. Phys.: Conf. Ser. 935 012021
[27] Evan H F 2011 Surf. Coat. Technol. 206 1512
[28] Guo Q Q, Jiang B L and Li J P 2010 Trans. Nonferrous Met. Soc. China 20 2204
[29] Wang D S, Tian Z J, Shen L D, Liu Z D and Hua Y H 2009 Appl. Surf. Sci. 255 4606
[30] Hazar H and Ozturk U 2010 Renew. Energy 35 2211
[31] Gao X S, Tian Z J, Liu Z D and Shen L D 2012 Trans. Nonferrous Met. Soc. China 22 2498
[32] Han J C 2007 Acta Mater. 55 3573
[33] Tiemann R B 1996 Plasma Sprayed Coatings—principles and Applications (New York: VCH Publishers Inc.) 2nd edn
[34] Yilmaz S, Ipek M, Celebi G F and Bindal C 2005 Vacuum 77 315–21
[35] Kumar R and Kumar S 2018 I-manager’s Journal on Material Science 6 43–56
[36] Kumar M, Kanti S and Kumar S 2019 Materials Research Express 6 1–29
[37] Kumar S, Handa A and Kumar R 2019 A Journal of Composition Theory 12 900–7
[38] Kumar R, Kumar R and Kumar S 2018 IJSMS 1 1–6
[39] Ghaour A F A, Raza M A, Baig M S and Ibrahim S 2017 Mater. Res. Express 4 1–22
[40] Gurrapa I 2007 Material and Manufacturing Processes 15 761–773
[41] Panwar V, Grover N K and Chawla V 2019 Materials Research Express 6 10–9
[42] Cesárez Z, Houšková S a and Lukáš F 2018 Materials Research Express 6 10–4
[43] Bedi TS, Kumar S and Kumar R 2020 Materials Research Express 7 015402
[44] Singh S, Kaur M, Kumar M, Singh H and Singh S 2019 Materials Research Express 6 1–11
[45] Kumar M, Singh H and Singh N 2013 Therm. Spray Technol. 23 692–707
[46] Sidhu B S and Prakash S 2003 Surf. Coat. Technol. 166 89–100