OXIDATION BEHAVIOR OF CNT REINFORCED AL₂O₃ COATED GRADE A-1 BOILER STEEL IN AIR AT 900°C

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Abstract- The oxidation surface behaviour of bare and CNT reinforced Al₂O₃ coated Grade A-1 boiler steels has been studied in air at a temperature of 900°C in a cyclic manner. Oxidation kinetics was established for the bare and coated Grade A-1 steel in air at 900°C under cyclic conditions for 50 cycles by thermogravimetric technique. Each cycle consists of 1 hour heating at 900°C followed by 20 min of cooling in air at room temperature. X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive X-ray (SEM/EDAX) techniques were used to characterise the oxide scales of surface. The CNT reinforced Al₂O₃ coated Grade A-1 steels were found to be more corrosion resistance than bare T-11 steel in air oxidation for 50 cycles.

Keywords: Oxidation; Bare and CNT reinforced Al₂O₃ coated Grade A-1 boiler steel

I. INTRODUCTION

Degradation of metals and alloys due to hot corrosion or erosion has been identified as a serious problem for many high temperature aggressive environment applications, such as boilers, internal combustion engines, gas turbines, fluidized bed combustion, and industrial waste incinerators [1 and 2]. Due to depletion of high-grade fuels and for economic reasons, residual fuel oil along with coal is used extensively in the energy generation systems such as turbines, boilers, and industrial waste incinerators.

Oxidation occurs when metals or alloys are heated in oxidizing environments, such as combustion atmospheres with excess of air or oxygen [3]. The stainless steels used for the tubes face the acute problem of degradation by high-temperature oxidation [4]. Susceptibility of particular metal surface to oxidation is dependent upon the free energy of formation of its metallic oxide [5]. Surface oxidation of metals is difficult to suppress at high temperature since oxide formation is thermodynamically favourable for most metals even in the presence of extremely small amount of oxygen [5]-[7]. Oxidation rates can be reduced through the formation of protective oxide layers from the selective oxidation of alloying elements thereby suppressing the oxide formation of the other elements which have less affinity for the oxygen. In the initial stages of high temperature oxidation exposed metal atoms on the surface compete in oxide formation until the most thermodynamically stable oxide dominates [8].

High temperature oxidation is the main failure modes of above mentioned components in the hot sections [9]. Therefore, the development of wear and high-temperature oxidation protection systems in industrial boilers is a very important topic from both engineering and an economic perspective [10 and 11].

Coatings play significant role to protect the materials used in aggressive environment against the oxidation and corrosion attack [12]. Recent studies reveal that coating application used 80% of the total cost for the protection of metals [13]. Coatings extend the life of materials by protecting them against wear, oxidation and corrosion. Various coating process are used to improve the surface property of various metals for different application. Thermal spray coating process is well known process to improve the wear resistance of surface. Thermal spray process carried out in a different way like plasma spray, arc spray, detonation gun spray, flame spray etc. [14]-[16].

Detonation gun (D-gun spray) process is a thermal spray coating process, which gives an extremely good adhesive strength, low porosity and
coating surface with compressive residual stresses [17]. Detonation gun sprayed of Al2O3 powder provides a typical layer structure similar to that of coatings deposited using other thermal spraying processes. However, the high particle velocity results in the formation of a rough surface on the spray splat, which may be effective in enhancing interlocking between flattened particles [18].

Oliker et al. (2006) studied the formation of detonation coatings based on titanium aluminide alloys and aluminium titanate ceramic sprayed from mechanically alloyed powders Ti- Al [19]. Wang et al. (2009) designed the separation device for detonation gun spraying system and studied its effects on the performance of WC-Co coatings. The results showed that the use of the separation device resulted in better properties of the D-gun sprayed WC Co coatings, because of lower the surface roughness, lower the porosity, higher the micro hardness, higher the elastic modulus, and higher the interfacial adhesive strength. Also, the tribological performance of the WC-Co coatings was improved [20].

Many materials such as T-11, T-22, GrA1, SS-347 and T-91 have been employed for the application in boilers. In order to improve the performance of these materials in boilers, the study of behaviour and performance of these materials at high temperature became an important issue. Also it was important to study, if the performance of Gr A-1 could be improved by coating. So it has been planned in the present work, to study the behaviour and performance of Gr A-1 material in uncoated as well as coated condition by examining its surface by heating it at 900°C under cyclic conditions. In this study detonation gun thermal spraying process is used for coating of CNT reinforced Al2O3 powder on Grade A-1 boiler steel. The coated and uncoated samples are subjected to cyclic oxidation for 50 cycles in laboratory. The SEM/EDAX, XRD and thermo gravimetric techniques are used to analyse the corrosion products.

II. EXPERIMENTAL MATERIAL AND PROCEDURE
A. SUBSTRATE STEEL

The boiler tube steel Grade A-1 (ASTM-A210A450-Grade A-1) has been selected as the substrate materials for the experimental work. The Grade A-1 steel alloys were acquired from Guru Nanak Dev Thermal Power Plant, Bathinda (Punjab, India) for protecting them against high temperature corrosive environment applications. The chemical composition of Grade A-1 boiler steel is as reported in Table 1.

B. PREPARATION OF SUBSTRATE MATERIALS

Specimens with dimensions of approximately 20mm X 15mm X 5mm were cut from the boiler tubes. The specimens were polished using emery papers of 220, 400, 600 grit sizes and later on 1/0, 2/0, 3/0 and 4/0 grades. These substrates are then grit blasted with alumina powders (Grit 45) prior to the deposition of the coatings by detonation gun thermal spray process.

C. FEEDSTOCK MATERIALS FOR THE COATINGS

Four types of coatings were selected in this study. The Al2O3 powder was chosen for D-Gun spray coating with reinforcement of CNT (1.5%wt, 2%wt and 4%wt) on Grade A-1 boiler steel. An additive CNT of different composition with 99.99% purity and Al2O3 powder were dry-ball milled in a conventional rotating ball mill with stainless steel balls as a grinding medium for 10 hrs to form a uniform and homogeneous mixture.

D. FORMULATION OF COATINGS

The D-gun spray process was used to apply coatings on the superalloys at SVX Powder M Surface Engineering Pvt. Ltd, Greater Noida (UP, India) as shown in Fig.1. Standard spray parameters were designed by the above mentioned firm for depositing the coatings in the present work. All the process parameters, including the spray distance (200mm), were kept constant throughout the coating process. The standard spray parameters as mentioned in the manual of Detonation gun spray system were used for the deposition of the coating as shown in Table 2.

E. HIGH TEMPERATURE OXIDATION STUDY IN AIR
Oxidation studies were conducted at 900°C in a laboratory using silicon carbide tube furnace (Digitech, India make). The furnace was calibrated to an accuracy of ±5°C using Platinum/Platinum-13% Rhodium thermocouple fitted with a temperature indicator of Electromeck (Model-1551 P), India. The bare as well as the coated specimens were polished down to 1μm alumina wheel cloth polishing to obtain similar condition of reaction before being subjected to corrosion run. The physical dimensions of the specimens were then recorded carefully with digital vernier caliper to evaluate their surface areas. Subsequently, the specimens were washed properly with acetone and dried in hot air to remove the moisture. During experimentation, the prepared specimen was kept in an alumina boat and the weight of boat and specimen was measured. The alumina boats used for the studies were pre-heated at a constant temperature of 1200°C for 12 hours and it was assumed that their weight would remain constant during the course of high temperature cyclic oxidation study.

### TABLE 1 CHEMICAL COMPOSITION (WT %) OF GRADE A-1 BOILER STEEL (ASTM-A210/450-GR ADE A-1)

<table>
<thead>
<tr>
<th>Standard</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Actual</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The boats containing the bare or coated specimen were inserted into hot zone of the furnace maintained at a temperature of 900°C. The weight of the boat loaded with the specimen was measured after each cycle during the corrosion run, the spalled scale if any was also considered during the weight change measurements. Holding time in the furnace was one hour in still air followed by cooling at the ambient temperature for 20 minutes. Following this, weight of the boat along with specimen was measured and this constituted one cycle of the oxidation study. The specimens were subjected to visual observations carefully after the end of each cycle with respect to colour or any other physical aspect of the oxide scales being formed. This cycle was repeated for 50 times i.e. 50 cycles were made for each sample. Corroded samples from air oxidation were analysed by XRD (BRUKER-binary V3) and SEM/EDAX and the oxide scale which fell into the boat were also analysed by XRD.

### III. EXPERIMENTAL RESULTS

#### A. BEHAVIOUR IN AIR AT ELEVATED TEMPERATURE

1) **Visual Examination**

The macrographs of bare and coated Grade A-1 boiler tube steel after cyclic oxidation in air at high temperature of 900°C for 50 cycles are shown in Fig. 2.

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**Fig. 1 D-Gun Thermal Spray Process Used In The Current Research Work**

**Table 2 Spray Parameters of D-Gun Spraying**

<table>
<thead>
<tr>
<th>Variant</th>
<th>D-Gun Spraying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen flow rate</td>
<td>4800 l/h</td>
</tr>
<tr>
<td>Fuel (acetylene) flow rate</td>
<td>1920 l/h</td>
</tr>
<tr>
<td>Carrier gas (nitrogen) flow</td>
<td>300 l/h</td>
</tr>
<tr>
<td>Spray distance</td>
<td>300 mm</td>
</tr>
<tr>
<td>Flame temperature</td>
<td>3900°C</td>
</tr>
<tr>
<td>Deposition frequency</td>
<td>3 shots/sec</td>
</tr>
</tbody>
</table>
Colour of oxide scale formed on the bare alloy Grade A-1 [Fig.2(a)], after oxidation for 50 cycles at 900°C was mixture of dark and light grey scale along with large cracks. Some cracks was also examined on the corners and edges of specimen. Initially, colour of scale appeared as brownish. Subsequently, it converted into light black and grey mixture along some cracks on the surface on bare Grade A-1. The scale formation was noticed at the end of 3rd cycle and swelling of which was examined at the end of 16th cycle. Spalling of scale started at the end of 22th cycle; however, the scale formation continued till 50th cycle.

Whereas Al₂O₃ coating alloy [Fig.2(b)] show initially white colour. As the oxidation went on, the colour of oxide scale turned into mixture of redish and brownish colour on luster dark grey background after 50 cycles. Some coating remained on the corners and edges of the specimen after completion of 50 cycles.

Alloy with coating Al₂O₃+1.5% CNT [Fig.2(c)] also show initially white colour. After the completion of 50 cycles of oxidation, coating remained on two sides of surface with white colour. Some white bubbles also appeared on the surface. The spallation of coating suffered along the corners and edges of the specimen.

Al₂O₃ +2% CNT [Fig.2(d)] coating posses white colour initially. As the oxidation went on, after 23 cycles spallation of coating start and the colour of oxide scale turned into small brownish colour. Some white colour is apperead on the surface with luster grey backgrounds and colour of oxide scale turned into brownish colour after 50 cycles of oxidation. Here, coating suffered spallation along the corners and edges of specimen with brownish colour.

But in case of Al₂O₃+4% CNT [Fig.2(e)] spallation of coating start after 25th cycles and colour of oxide turned into small brownish. After completion of 50 cycles, colour of oxide scale turned into small white colour mixture with brownish colour on one side of the surface with light black background. On the other side brownish colour appeared as major part on the surface with luster grey background after 50 cycle of oxidation along with only half side coating of surface. All the edges and corners shows luster grey colour.

2) Weight Change Measurements:

Weight gain /unit area(mg/cm²) versus number of cycles plot for the bare as well as D-gun sprayed coated boiler tube steel Grade A-1 alloys oxidised at 900°C in air upto 50 cycles are shown in Fig 5.3. Uncoated Grade A-1 shows the maximum weight gain among all the alloys. The coated Al₂O₃+4% CNT Grade A-1 steel alloy show much lower weight gain among all the coated specimens and Al₂O₃ coated Grade A-1 alloy indicate higher weight gain among all the Grade A-1 coated alloys in given environment.
savings in weight gain for $\text{Al}_2\text{O}_3 + 2\%$ CNT coated and 94.5% weight saving for $\text{Al}_2\text{O}_3 + 4\%$ CNT coated Grade A-1 respectively in comparison with uncoated Grade A-1. Further, the weight gain square (mg$^2$/cm$^4$) data is plotted as a function of time (number of cycles) as shown in Fig. 5.17 to establish the rate law for the oxidation. All the CNT reinforced $\text{Al}_2\text{O}_3$ coated Grade A-1 followed a parabolic rate law of oxidation at 900°C (Fig 5.12). The values of the parabolic rate constant ($k_p$) are shown in Table 5.2. It is inferred that the $k_p$ values for the coated Grade A-1 steel are less than the bare Grade A-1.

Fig. 3 Weight Gain Plot For Bare And Coated Grade A-1 Boiler Steel Exposed to Cyclic Oxidation Study In Air At 900°C For 50 Cycles

Fig. 4 Weight Gain Square Plot For Bare And Coated Grade A-1 Boiler Steel Exposed To Cyclic Oxidation Study In Air At 900°C For 50 Cycles

Table 3 Parabolic Rate Constant ($K_p$) Values For Bare And D-Gun Sprayed Coated Grade A-1 Boiler Steel Subjected To Cyclic Oxidation In Air For 50 Cycles At 900°C

<table>
<thead>
<tr>
<th>Grade A-1(Oxidation)</th>
<th>$K_p$ (g$^2$cm$^{-4}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>$3759.17 \times 10^{19}$</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$216.05 \times 10^{19}$</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$ + 1.5% CNT</td>
<td>$25.74 \times 10^{19}$</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$ + 2% CNT</td>
<td>$25.59 \times 10^{19}$</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$ + 4% CNT</td>
<td>$11.23 \times 10^{19}$</td>
</tr>
</tbody>
</table>

B. X-RAY DIFFRACTION ANALYSIS

The samples after oxidation were removed from boat and their oxide scales which were separated from surface were also removed. Then they were analysed separately by XRD and after that only oxidised sample were analysed by SEM/EDAX. The results of XRD analysis contained graph indicating peak values (i.e. d values) which were used to identify various phases with the help
of inorganic X-ray Diffraction data card from Powder diffraction file of JCPDS. Help of software named Philips X’pert High score and Eva was also taken for finding out compounds at respective peaks.

1. XRD Result for Bare and Coated Grade A-1 Samples

The various phases identified from X-ray diffraction patterns of surface oxide formed on uncoated and D-gun sprayed coated steel alloys of Grade A-1 after cyclic oxidation in air at 900°C for 50 cycles are shown in Fig 5. The main phases identified for the oxidised uncoated Grade A-1 alloy is Fe$_2$O$_3$ [Fig. 5(a)]. The surface oxides on all CNT reinforced Al$_2$O$_3$ coated Grade A-1 steel alloys indicated the formation of mainly Al$_2$O$_3$ (aluminum oxide). The existence of large amount of Fe$_2$O$_3$ on uncoated Grade A-1 steel alloys indicates the diffusion of Fe from the substrate during oxidation at temperature of 900°C [Fig. 5(a)].

C. FE-SEM/EDS ANALYSIS OF SURFACE MORPHOLOGY

Fe-SEM micrographs with EDS spectrum reveals the surface morphology of uncoated Grade A-1 boiler tube steel sample as well as four types of coated Grade A-1 boiler tube steel samples i.e. Al$_2$O$_3$, Al$_2$O$_3$ +1.5% CNT, Al$_2$O$_3$ +2% CNT and Al$_2$O$_3$+4% CNT after cyclic oxidation in air for 50 cycles at 900°C as show in Fig. 6, 7, 8, 9, 10 respectively.

Micrograph of corroded uncoated Grade A-1 reveals the oxide scale developed on the surface is massive and with large cracks. The oxide scale produced is of white contrast and dark black region which is irregular in size and non-uniformly distributed. The EDS analysis of bare corroded Grade A-1 steel alloy at 900°C reveals the scale rich in Fe and O, which indicates the possibility of formation of Fe$_2$O$_3$.

On the other side, Micrograph of corroded Al$_2$O$_3$ coated Grade A-1 steel alloy is with small cracks and appears to be dense and continuous.
EDS analysis revealed the scale rich in O and Al at the point of analysis. Similarly, the scale formed on coated Al₂O₃+1.5%CNT and Al₂O₃+2%CNT, is also dense and continuous like Al₂O₃. Surfaces also show some cracks with globules. The EDS analysis of Al₂O₃+1.5%CNT and Al₂O₃+2%CNT clearly show the scale rich in Al and O, which shows the possibility of formation of Al₂O₃ as predominant oxides. Micrograph of corroded Al₂O₃+4%CNT coating show dense and continuous with small cracks like other coatings with globules at some parts of surface. The EDS analysis of scale also revealed O and Al oxide at the point of analysis like other above coating studied.
During oxidation surface study of CNT reinforced Al₂O₃ coating of Grade A-1 boiler steel in air at 900°C for 50 cycles resemble that corrosion resistance property of CNT reinforced coated Grade A-1 specimen is better than uncoated Grade A-1 boiler steel as weight gained by bare Grade A-1 is much more throughout the 50 cycles than the all four types of coated T-11 samples (Al₂O₃, Al₂O₃+1.5%CNT, Al₂O₃+2%CNT, Al₂O₃+4%CNT). The coated Al₂O₃+4% CNT steel alloy show much lower weight gain among all the coated specimens and Al₂O₃ coated Grade A-1 alloy indicate higher weight gain among all the Grade A-1 coated alloys in given environment. The weight gain by coated Grade A-1 (Al₂O₃), after 50 cycles is nearly 77.1% less than that of uncoated Grade A-1. It is found that 91.4% saving in weight gain for Al₂O₃+1.5% CNT coated, 91.6% saving in weight gain for Al₂O₃+2% CNT coated and 94.5% weight saving for Al₂O₃+4% CNT coated Grade A-1 respectively in comparison with uncoated Grade A-1. The oxidation rate (total weight gain values after 50 cycles) of bare and coated Grade A-1 boiler steel follows the sequence as given below:

**Uncoated > Al₂O₃ coating > Al₂O₃+1.5% CNT coating > Al₂O₃+2% CNT coating > Al₂O₃+4% CNT coating**

Due to different value of thermal coefficient, cracks in the oxide scale (Fig.5) and spalling of coating might be occurred during cyclic testing of coating and substrate as reported by [3]. Various elements have different value of thermal coefficient of expansion. Due to this, much stress produced which will be responsible for more cracks and spalling and corrosive gas can easily penetrate through these cracks which will lead to significant grain boundary corrosion attack [21]-[24]. The Al₂O₃ coating layer on surface of substrate suppresses the diffusion of oxygen from the outer environment and hence plays a significant role in the oxidation resistance [25]-[27]. Presence of wide range of tensile and compressive stresses in the alumina layer has also been reported by Evan and Taylor [28]. The development of similar type of cracks in the coating and subsequent oxidation of base metal had also been reported by D. Wang [29].
for the aluminized coating on 2 1/4Cr-1Mo (SA-213T-22) type of steel. Uncoated and coated boiler steel shows the formation of Fe$_2$O$_3$ and Al$_2$O$_3$ respectively at the surface of specimens exposed to cyclic oxidation as indicated by SEM/EDAX analysis and equally supported by XRD analysis as shown in Fig.5. Most metals are unstable and react spontaneously with oxygen at high temperature, to form the thermodynamically favoured metal oxide. However, once a layer of oxide has developed on the metal surface, it acts as a barrier between the metal and the environment; further reaction takes place only if one or both of the reactants are able to penetrate the layer, leading to formation of new oxide at either the scale-gas or scale-metal interface, [30]. In case of uncoated “ASTM-SA210 Grade A1”, there is no thermal barrier coating available. The higher weight gain during the first few cycles might be attributed to the rapid formation of oxides at the splat boundaries and within the open pores due to the penetration of the oxidizing species [31]-[34]. There is continuous formation of thin oxide scale with subsequent depletion by spallation and corrosion under cyclic test conditions. The top surface may contains inclusions, which leads to vertical cracks through which the corrosive species might have penetrated alongthe crack and between the metallic layers as reported by [35 and 36]. Formation of Fe$_2$O$_3$ as shown by XRD might be due to the reaction of iron with oxygen since iron is the main constituent of boiler steel. Formation of such type of oxides has also been analyzed by [36 and 37] during the failure analysis of super heater tubes caused by fireside corrosion. The Al$_2$O$_3$ layer also suppresses the formation of other oxides and hence protects the surface from degradation. The EDS analysis of bare and CNT reinforced Al$_2$O$_3$ coated Grade A-1 boiler steel after oxidation consist Al$_2$O$_3$ oxide layer (Fig. 6, 7, 8, 9, 10). The XRD spectra of D-Gun coated CNT reinforced Al$_2$O$_3$ after 50 cycles of oxidation as shown in Fig 5, which shows Al$_2$O$_3$ as a predominant oxide. Hence, the existence of large amount of Al$_2$O$_3$ will suppress the further oxidation of coating surface supportively and this is main lead to protection of surface from degradation.

V. CONCLUSIONS

The high temperature oxidation behaviors of uncoated and CNT reinforced Al$_2$O$_3$ coated grade A-1 boiler steel have been investigated in air at 900 °C for 50 cycles. The behavior of uncoated and CNT reinforced Al$_2$O$_3$ coated was studied and the following conclusions are made:

1. The oxidation rate (total weight gain values after 50 cycles) of the coated and uncoated grade A-1 boiler steel follows the sequence as given below:

   Uncoated > Al$_2$O$_3$ coating > Al$_2$O$_3$+1.5% CNT coating > Al$_2$O$_3$+2% CNT coating > Al$_2$O$_3$+4% CNT coating

2. The CNT reinforced Al$_2$O$_3$ coated grade A-1 steel has shown resistance to oxidation as the overall weight gain is less than as compared to the uncoated Grade A-1 boiler steel.

3. In case of uncoated grade A-1 boiler steel, the weight gain is highest with thickest scale. Severe spalling and cracking is also observed in case of bare Grade A-1 steel.

4. The coated Al$_2$O$_3$+4% CNT steel alloy show much lower weight gain among all the coated specimen. Small spalling and cracking is also observed on edges and corners. The weight gain by coated Grade A-1 (Al$_2$O$_3$+4%CNT), after 50 cycles is nearly 94.5% less than that of uncoated Grade A-1.

5. Al$_2$O$_3$ coated Grade A-1 boiler steel indicate higher weight gain among all the Grade A-1 coated alloys in given enviornment. Small spalling is also observed on the corner of coated specimen. The weight gain by coated Grade A-1 (Al$_2$O$_3$), after 50 cycles is nearly 77.1% less than that of uncoated Grade A-1.

6. The appearance of cracks/peeling off in the coatings during oxidation studies may be attributed to the different values of thermal expansion coefficients for the coating, substrate steel and oxides.

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