Dispersive Spectrometry (SEM/EDS) techniques were used to characterize the oxide scales. The technique was used to establish oxidation kinetics and X-Ray Diffraction (XRD) and scanning electron microscopy/energy-dispersive analysis (SEM/EDAX) techniques have been used to characterize coating and microstructure. Diffraction (XRD) and scanning electron microscopy/energy-dispersive analysis (SEM/EDAX) techniques were used to characterize coating and microstructure.

High temperature oxidation and hot corrosion behaviour of plasma sprayed YSZ coating on SA213 T92 steel in air and salt at 900°C under cyclic condition

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ABSTRACT
Oxidation and hot corrosion has been considered as the principal destructive factors in thermal barrier coating systems during service. Thermal barrier coatings (TBCs) are extensively used to protect turbine blades against high temperature oxidation and corrosion. At the present time, problems of component materials reliability in power plant focus on assessing the potential behavior of coatings, in order to avoid expensive failure in service. Hot corrosion studies were conducted on both coated and uncoated specimen in air and salt (Na2SO4-60% V2O5) at 900°C under cyclic conditions for 50 cycles. An each cycle of one hour heating at 900°C followed by 20 minutes of cooling in air. Yttria-Stabilised Zirconia (YSZ) coatings were deposited on T-92 boiler steel weldments. In this paper present a comparison on the experimental performance of YSZ coating has been made to understand their hot corrosion behavior. This YSZ coatings increase the resistance to corrosion substantially which can be attributed to formation of zirconium oxides (ZrO2) and yttrium oxide (Y2O3). This coating was more significant in salt environment and there is an additional phase of ZrS. Thermo-gravimetric technique was used to establish oxidation kinetics and X-Ray Diffraction (XRD) and scanning electron microscopy/energy-dispersive spectrometry (SEM/EDS) techniques were used to characterize the oxide scales.

Keywords: hot corrosion, yttria-stabilised zirconia, thermal barrier coating.

1. INTRODUCTION
Hot corrosion can be regarded as an accelerated oxidation attack of metals exposed to the flow of combustion gases. Metals and alloy reacts during high temperature service with the surrounding environment, resulting in high temperature corrosion.

Oxidation is the most important high temperature reaction. Oxidation of metals or alloys takes place when they are heated in a highly oxidizing atmosphere such as air or oxygen. An oxidation reaction is represented by the interaction of metals with oxygen to form oxide. There are a variety of factors on which the oxidation behaviors of a metal depends and the reaction mechanism involved may often be quite complex. An oxidation reaction begins with adsorption of oxygen molecules from the atmosphere, nucleation of oxides, formation of a thin oxidation layer, followed by its growth to a thicker scale [1].

In a wide variety of applications, mechanical components have to operate under severe conditions, such as high load, speed or temperature and hostile chemical environment. Thus, their surface modification is necessary in order to protect them against various types of degradation.

Thermal barrier coating (TBC) systems are used in thermal insulating components in the hot sections of gas turbines in order to increase operational temperature with better efficiency [2-8]. Yttria stabilized zirconia (YSZ) has been usually chosen for the top insulating coat material because of its high thermal expansion coefficient, which closely matches that of the substrate. Apart from this application TBC is also useful in aerospace, aircraft and boiler applications.

The different functions of the coating, such as wear and corrosion resistance, thermal or electrical insulation can be achieved using different coating techniques and coating materials. The purpose of a hot corrosion resistant coating is to serve as an effective solid-state diffusion barrier between oxygen (or other gases) and base metal [9]. Mostly metals and alloys experience accelerated oxidation when their surfaces are covered with a thin film of fused salt in an oxidizing gas atmosphere at elevated temperatures. This is known as hot corrosion where a porous non-protective oxide scale is formed at the surfaces and sulphides in the substrate [10].

The research work deals with development of NiCrAlY as bond coat and YSZ as top coat on T-92 boiler steel weldments along with their characterizations. X-ray diffraction (XRD) and scanning electron microscopy/energy-dispersive analysis (SEM/EDAX) techniques have been used to characterize coating and respective corrosion products after hot corrosion at 900°C.

2. RESEARCH SIGNIFICANCE
Material evolution over the last few decades has make progress for large thermal power plants to be built today with steam temperatures of 900°C and supercritical steam pressures. In recent years, the construction of advanced ultra-supercritical fossil-fired power generation plant with higher efficiency has been accelerated by the...
demand of reducing CO₂ emission for the protection of global environment.

There has been greater concern over high temperature oxidation and hot corrosion of ultra super critical boiler tube. No attempts were made so far about hot corrosion behavior of coated T92 boiler steel tube, to fill up the gap an attempt is made to characterize the high temperature oxidation of hot corrosion of T92 boiler steel tube.

3. PRELIMINARY INVESTIGATIONS

3.1. Substrate steels

The experimental work was performed by using samples of T-92 steel. The spectroscopy was done on samples which were taken for experiment, this showed chemical composition in wt. % which is given below:

Table 1. Chemical composition of T92 material (wt %).

<table>
<thead>
<tr>
<th>Element</th>
<th>C (W)</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Al</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.11</td>
<td>1.53</td>
<td>0.45</td>
<td>0.37</td>
<td>0.002</td>
<td>0.009</td>
<td>8.91</td>
<td>0.38</td>
<td>0.20</td>
</tr>
</tbody>
</table>

3.2. Execution of weldments

3.2.1. Edge preparation

The boiler tube was cut into approximation length of 100 mm each. Each tube was machined to obtain a single conventional V- groove, with 37.5° bevel angle for SA213 T92 steel with root and face 1mm as shown in Fig. 1.

![Figure 1](image1)

Figure 1. Schematic view of weldment design for SA213 T92 boiler tube steel. Here t = 5 mm, h = 3 mm, b = 37.5°, w= 15 mm, g = 1 mm.

3.2.2. Welding processes

The tubes were preheated to 200°C for ½ hr. All weld joints were made by Gas Tungsten Arc Welding (GTAW) process. Prior to welding the boiler tube were thoroughly cleaned with brush and acetone so as to remove any oxide layer and dirt or grease adhering to the boiler plate. All process parameters including the root were constant throughout the welding process. The conditions were as reported in Table-2.

Table 2. Welding parameters for GTAW weldments.

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre heating</td>
<td>200°C</td>
</tr>
<tr>
<td>Joint design</td>
<td>single “V”</td>
</tr>
<tr>
<td>Shielding gas</td>
<td>Argon</td>
</tr>
<tr>
<td>Current</td>
<td>85 Amp</td>
</tr>
<tr>
<td>Voltage</td>
<td>16 Volts</td>
</tr>
<tr>
<td>Filler wire</td>
<td>F92 Flux core wire</td>
</tr>
<tr>
<td>Plate thickness</td>
<td>5 mm</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>5 min⁻¹</td>
</tr>
</tbody>
</table>

3.2.3. Preparation of sample materials

The samples are cut in the Weld Zone (WZ) and Base Metal (BM). The samples were polished by 220 grit silicon carbide papers and followed by 1/0, 2/0, 3/0, and 4/0 grade emery papers and finally wheel polished.

3.2.4. Coating powders

Yttria stabilised zirconia (YSZ; ZrO₂ - 8wt. % Y₂O₃) and NiCrAlY (Ni-22Cr-10Al-1Y) is been used for TBC coating which were applied on samples by plasma spray process. The chemical composition and particle size for these powders are given in Table-3.

Table 3. Composition, mean particle size.

<table>
<thead>
<tr>
<th>Coating Powder</th>
<th>Composition (wt %)</th>
<th>Mean particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCrAlY</td>
<td>Cr (21), Al (7),</td>
<td>35-100</td>
</tr>
<tr>
<td></td>
<td>Y (0.8), Ni</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Balance)</td>
<td></td>
</tr>
<tr>
<td>YSZ</td>
<td>Y₂O₃(8), ZrO₂</td>
<td>0.027</td>
</tr>
<tr>
<td></td>
<td>(Balance)</td>
<td></td>
</tr>
</tbody>
</table>

3.2.5. Coating formulation

Samples were grit blasted before plasma spraying. Argon was used as powder carrying and shielding gas. All the process parameters were kept constant throughout coating process. Ni-22Cr-10Al-1Y
powder was sprayed as a bond coat of around 150 μm thickness before applying the final coatings of YSZ around 200μm and the process parameters were as reported in Table 4.

Table 4. Parameters of argon shrouded plasma spray process.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc current (A)</td>
<td>750</td>
</tr>
<tr>
<td>Arc voltage (V)</td>
<td>50</td>
</tr>
<tr>
<td>Powder flow rate (rev/min)</td>
<td>3.2</td>
</tr>
<tr>
<td>Spraying distance (mm)</td>
<td>85–105</td>
</tr>
<tr>
<td>Plasma arc gas (argon) (psi)</td>
<td>57</td>
</tr>
<tr>
<td>Carrier gas (psi)</td>
<td>42</td>
</tr>
</tbody>
</table>

4. CHARACTERISATION OF WELDMENTS

4.1. Micro hardness measurements

The hardness data across the welds in the central region for both similar and dissimilar combinations are represented. The micro hardness of the weldment was measured using a ZWICK hardness testing. A load of 1000 gms (1 kg) was applied for duration of 15 sec. Hardness was measured at a distance of 1mm across the interface and 1mm along the base metal. Hardness survey was performed across the weld in the axial direction. The maximum hardness was distinguished at interface of dissimilar weld metal, minimum hardness was observed on the base metal side.

4.2. Metallographic studies

For metallographic studies the weldments and unwelded samples were cut along the cross-section with diamond cutter (low speed saw, Buehler, USA make). The samples were polished by using SiC metallographic emery papers up to 1000 grit. After manual polishing the samples were polished on high speed polishing wheel using diamond polishing series of 6 μm and 3 μm sizes. The final polishing is carried out on a sylvet-cloth using 1 μm size alumina powder suspension on polishing wheel machine. Sample was etched with picric reagent for 30 second, washed, dried and finally examined optical microscope. The typical microstructures of the different regions of welded samples were photographed.

4.3. High temperature oxidation and hot corrosion study

The studies were conducted at 900°C using silicon carbide tube furnace having PID temperature controller. The samples were subjected to polishing which will provide uniformity of reaction while oxidation process. Then dimensions measured by digital vernier to calculate area which required for plotting of graph of weight gain per unit area verses number of cycle. Finally specimens were cleaned i.e. degreased by ethanol and kept in alumina boat. This alumina boat prior to performing of experiment was kept in oven for 5hr at 250°C in oven and then kept in furnace at 900°C for 2hr so that moisture is totally removed from boat. After this the sample was kept in boat and weight was taken initially and then placed in tubular furnace.

Sample of T-92 bare steel were kept in alumina boat and then inserted in tubular furnace. These samples were kept in furnace for 1 hr at a temperature of 900°C.
and then they were removed and cooled further for 20 minutes at room temperature and their weight were taken by electronic balance (make Contech, India) having sensitivity of 0.001 gms. Spalled scale was also taken into consideration which used to fall into the boat i.e. the weight was taken along with the boat. This cycle was repeated for 50 times.

Samples of T-92 steel were kept in alumina boat and heated in an oven along with alumina boat up to 150°C and the salt mixture of 40wt%Na₂SO₄ + 60wt.% V₂O₅ dissolved in distilled water was coated on the warm polished samples with the help of a camel hair brush. The amount of the salt coating in the range 3.0–5.0mg/cm². The salt coated samples were then dried at 250°C for 2½ hrs in an oven to remove the moisture and then weighed, after this sample of T-92 were inserted in tubular furnace. These samples were kept in furnace for 1 hr at a temperature of 900°C and then they were removed and cooled further for 20 minutes at room temperature and their weight were taken by electronic balance having sensitivity of 0.001 gms. This cycle was repeated for 50 times i.e. 50 cycles. The weight of samples was measured at the end of each cycle and spalled scale was also taken into consideration which used to fall into the boat i.e. the weight was taken along with the boat.

5. ANALYSIS OF CORROSION PRODUCTS

All the samples subjected to hot corrosion were analyzed for the identification of corrosion products for the surface. The analysis was performed for surface of corroded samples. Corroded samples were subjected to SEM/EDAX analysis.

5.1. Visual inspection.

Visual examination was made and recorded after each cycle for any change in color, luster, adherence-spalling tendency and development of crack in the scale etc. After the completion of 50 cycle (each cycle of 1 hr heating and 20 minutes cooling) in laboratory furnace and then their macroscopic views were taken.

5.2. Thermo gravimetric studies

The weight change values were measured at the end of each cycle with the aim to understand the kinetics of hot corrosion and oxidation. The data was plotted with respect to number of cycles for each sample and the plots are given in the subsequent sections. In many cases spalling and scaling occurred in the alumina boat and the same is also added in the weight change values.

5.3. SEM/EDAX analysis

Corroded samples from salt oxidation were analysed by XRD and SEM/EDAX and the oxide scale which fell into the boat were also analysed by XRD. Cu radiation was used in XRD at a step of 2°/min and the range of angle was 5-100°.

5.4. Behaviour in air and salt at elevated temperature

The weight gain plots for the substrate without coating and with coatings have been shown in Fig. 6 in the presence of air and salt layer of Na₂SO₄–60% V₂O₅ at 900°C. On x-axis “number of cycles” and on y-axis “weight gain/area (mg/cm²)” was taken. In case of air oxidation, hot corrosion behaviour of T-92 bare steel in air was somewhat linear because the oxide layer formed on substrate used to peel of very easily and as compared to this oxidation rate of T-92 YSZ coated sample was very less nearly 40% less as compared to bare steel. In case of salt oxidation, T-92 bare steel behaviour was parabolic but T-92 YSZ coated sample showed more resistance to oxidation than the bare sample nearly 60% less as compared to bare steel. The graph reveals that T-92 YSZ coated steel is better than T-92 bare steel in an environment of air and salt for 50 cycles. Fig. 7 shows plot of (weight gain/area)² vs. Number of cycles. In this plot every curve is associated with straight line of same colour. This straight line is trend line and it is used to calculate rate constant (Kp) which is given in Table 5.

Table-5. Value of the rate constant Kp

<table>
<thead>
<tr>
<th>Description</th>
<th>Kp (10⁶ g² cm⁻⁴ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-92 bare air oxidised</td>
<td>64</td>
</tr>
<tr>
<td>T-92 bare salt oxidised</td>
<td>19</td>
</tr>
<tr>
<td>T-92 YSZ coated air oxidised</td>
<td>10</td>
</tr>
<tr>
<td>T-92 YSZ coated salt oxidised</td>
<td>17</td>
</tr>
</tbody>
</table>

Every line or curve in graph is having its approximate equation which is given below.

For T-92 air oxidised bare sample the approximated curve equation is

\[ Y = -6.85324 + 2.59654X -0.00792X^2 \]

For T-92 air oxidised YSZ coated sample the approximated curve equation is

\[ Y = 1.53659 - 0.12986X -0.0198X^2 \]

For T-92 salt oxidised bare sample the approximated curve equation is

\[ Y = 29.59635 - 2.19512X -0.02X^2 \]

For T-92 salt oxidised YSZ coated sample the approximated curve equation is

\[ Y = 0.55236 - 0.14963X -0.00398X^2 \]

(Where X is number of cycle and Y is weight gain/area and these equation are calculated by using analysis mode of Origin software)
Figure-6. Weight gain vs. number of cycles plot for coated and uncoated T-92 steel subjected to cyclic oxidation for 50 cycles in air and salt at 900°C.

Figure-7. (Weight gain/area)^2 vs. number of cycles plot for coated and uncoated T-92 steel subjected to cyclic oxidation for 50 cycles in air and salt at 900°C.

5.5. X-Ray Diffraction analysis

The samples and their scales after oxidation were removed from boat and 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.

Figure-8. XRD patterns for T-92 steel subjected to cyclic oxidation in air at 900°C after 50 cycles. (p) T-92 bare sample (q) T-92 bare sputtered scales (r) T-92 YSZ coated sample (s) T-92 YSZ coated sputtered scales.

Figure-9. XRD patterns for T-92 steel subjected to cyclic oxidation in Na₂SO₄–60% V₂O₅ salt at 900°C after 50 cycles. (x) T-92 bare sample (y) T-92 bare sputtered scales (z) T-92 YSZ coated sample.

In case of coated samples the case of accelerated corrosion was absent due to the overlay coating of Yttria stabilised zirconia (YSZ). In T-92 YSZ coated air oxidised sample Figure-8(r and s) and T-92 YSZ coated salt oxidised sample Figure-9(z) there is formation of mainly ZrO₂, Y₂ZrO₃ and in case of YSZ coated salt oxidised sample apart from this ZrS was also formed.

5.6. XRD result for T-92 bare and YSZ coated air and salt oxidised sample

From the X-Ray Diffraction analysis it is found that ferrous oxide (Fe₂O₃), chromium ferrous oxide (Cr, Fe)₂O₃ are mainly formed along with Cr₂O₃ in T-92 bare air oxidised sample Figure-6 (p and q) and T-92 bare salt oxidised sample Figure-7 (x and y). Fe₂O₃, Cr₂O₃ form a protective oxide layer at surface due to which further oxidation is prevented as it acts as barrier for further corroding media to interact with substrate but at initial stage as the substrate material was in direct contact of corroding media so there was accelerated corrosion at initial stage.

5.7. Energy dispersive X-Ray (EDAX) studies

The SEM/EDAX analysis for T-92 bare sample after oxidation in air for 50 cycles at 900°C is shown in Figure-10 (a). The oxide scale reveals the dominance of Fe₂O₃ and along with this compounds of Mo₂O₃ and Cr₂O₃ are also formed. The obtained morphology indicates that
the oxide formed is layer-wise i.e. one below the other and the weight wise composition is approximately same but it greatly differs in case of Cr content. The upper layer contains nearly no Cr but the lower layer is rich in Cr content. T-92 bare salt oxidised sample Fig 8(b) reveals that the oxide formed is layer wise and it contains granules. Analysis of these granules revealed that they were formed when the amount of chromium oxide was less in it i.e. at about 1-2%, and it showed some cracking in oxide layer.

b) The measured porosity value of plasma sprayed coating was 0.63% and this YSZ coated layer has yield very high resistance to corrosion as compared to bare sample subjected to corrosion in both condition i.e. air and Na2SO4-60% V2O5 salt environment.

c) The oxidation rate of T-92 YSZ coated air oxidised sample was very less nearly 40% less as compared to bare steel and in case of T-92 YSZ coated salt oxidised sample more resistance to oxidation than the bare sample was achieved i.e. nearly 60% less at 900°C for 50 cycles.

REFERENCES


