Study of Corrosion Behavior of SA213T91 Boiler Steel in the Environment of Air and Molten Salt of $Na_2SO_4 - 60\%$ $V_2O_5$ at 900°C

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Abstract
The hot corrosion behavior of boiler steel SA213T91 (T91) after exposure to environment of air and molten salt of $Na_2SO_4 - 60\%$ $V_2O_5$ is investigated at a temperature of 900°C in a cyclic manner. Thermo-gravimetric technique was used to establish oxidation kinetics for T91 at 900°C under cyclic conditions for 50 cycles. X-Ray Diffraction (XRD) and scanning electron microscopy/ Energy Dispersive Spectrometry (SEM/EDS) techniques were used to characterize the oxide scales. The hot corrosion behavior of T91 steel was found to be better in air condition than oxidation under salt condition.

Keywords
Boiler Steel T91, hot corrosion, $Na_2SO_4 - 60\%$ $V_2O_5$, SEM/EDS, XRD

I. Introduction
Many components used in thermal power plants, various power generating industries and mills have to operate under severe conditions such as high load, speed, temperature and hostile chemical environment. According to the findings of Uustilo and co-workers [1], the power plants are one of the major industries suffering from severe corrosion problems resulting in the substantial losses. The performance of materials used in high-temperature environments is related to their ability to form protective oxide scales on their surfaces. Metals and alloys experience accelerated oxidation when their surfaces are covered with a thin film of a fused salt in an oxidizing environment at elevated temperatures. This mode of attack is commonly known as hot-corrosion, which takes place at an accelerated rate [2]. A common manifestation of hot-corrosion at elevated temperatures is the development of a porous non-protective oxide scale and sulphide precipitates in the substrate [3]. In coal fired boilers and power generating plants, corrosion at elevated temperature is recognized as the main cause of down time. So, the behavior of materials at elevated temperature is gaining technological importance. Ferritic steels, containing chromium and molybdenum are well known for their excellent mechanical properties combining high temperature strength and creep resistance with high thermal fatigue life, as well as with good thermal conductivity, weldability, and resistance to corrosion. Because of these characteristics, this type of steels have attracted special interest for application in industrial processes related to carbon-chemistry, oil refining, carbon gasification and energy generation in thermal power plants, where components like, heat exchangers, boilers and pipes operate at high temperatures and pressures for long periods of time [4-5]. Among these the T91 ferritic steel has widespread use in the boilers of power plants of northern India. As per the actual study of boiler of unit-4 of G.N.D.T.P. Bathinda, Punjab, India T91 is used in the secondary section of the boiler. At high temperature exposure, the interaction between a metal or an alloy and the surrounding gases and combustion products leads to corrosion, thus leading to failure for materials and structures [6-7]. It is commonly reported that as a result of oxidation process under isothermal conditions a protective Cr-containing oxide and Fe-containing oxide is developed over the surface of the steel causing a decrease of the oxidation rate with time. Oxide scale is constituted by a layered structure with compositional and microstructural variations from the substrate to the outer interface with the outer surface [8]. On the other hand, depending on the oxidation temperature and the chemical composition of the steel, both, the mechanisms of formation and the microstructural characteristics of the oxide scale, along with the degree of protection it provides, are different [9].

This paper is an attempt to access the corrosion behavior of the T91 ferritic steel in the atmosphere of Air and $Na_2SO_4 - 60\%$ $V_2O_5$ at temperature of 900°C in cyclic manner. This experimental study is the part of the work carried by the authors in the study of dissimilar metal weldments exposed to high temperature in the boilers of power plants.

II. Experimental Procedure

A. Substrate Material
SA213T91 (T91) was used as a substrate material in the experimental work. This material is used as boiler tube material in some of power plants in northern India. When the service conditions are stringent from the point of temperature and pressure, this steel finds wide applications in power plants and other higher temperature operative industries. The chemical composition of the steel is reported in Table 1.

<table>
<thead>
<tr>
<th>Metal</th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Mo</th>
<th>Si</th>
<th>V</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91</td>
<td>0.096</td>
<td>8.76</td>
<td>0.47</td>
<td>1.03</td>
<td>0.37</td>
<td>0.26</td>
<td>88.7</td>
</tr>
</tbody>
</table>

B. Sample Preparation
The experiment was performed on samples which were made to specified dimensions of approximately 40 x 12 x 3.5 mm³ from tubular sections. The specimens were polished on SiC emery paper down to 2000 from 80 grades and finally cloth polishing with alumina paste on rotating disc. Polishing was carried out on all six faces. The specimens were degreased (by ultrasonic cleaning in ethanol) and dried, then they were accurately weighed and measured to determine the total surface area exposed to the oxidative environment.
C. Optical Microscopy

The microstructure of the T91 steel sample is revealed after following a standard metallographic procedure of polishing and etching. The microstructure of T91 was revealed with marble’s reagent (CuSO₄ (4g) + HCl (20ml) + distilled water (20ml)). As depicted in fig. 1, the microstructure of T91 consists of tempered lath martensite. The prior austenite grain boundaries as well as lath boundaries are decorated with precipitates, the white spots represent the ferrite phase and rest is other phase [10].

Fig. 1: Optical Microstructure of Substrate T91

D. Molten Salt Corrosion Test

Hot corrosion studies were performed in a molten salt (Na₂SO₄-60%V₂O₅) for 50 cycles under cyclic conditions. Each cycle consisted of 1h heating at 900°C in a silicon carbide tube furnace followed by 20 min cooling at room temperature. The furnace was calibrated to an accuracy of ±5°C using a platinum/platinum–13% rhodium thermocouple. The purpose of imposed cyclic loading was to create severe conditions for testing as these conditions constitute more realistic approach towards solving the problem of metal corrosion in actual applications [11-12]. The cyclic study was performed for 50 cycles as this duration is considered to be adequate to achieve the steady state of oxidation for most of the materials [13-14]. The studies were performed for both the specimens for comparison. Before testing the physical dimensions of the specimen were recorded carefully with a digital vernier caliper (Mitutoyo, Japan make, resolution 0.01 mm) to evaluate the specimens for comparison. Before testing the physical dimensions of the specimen were recorded carefully with a digital vernier caliper (Mitutoyo, Japan make, resolution 0.01 mm) to evaluate the specimens for comparison. Before testing the physical dimensions of the specimen were recorded carefully with a digital vernier caliper (Mitutoyo, Japan make, resolution 0.01 mm) to evaluate the specimens for comparison.

During hot corrosion runs, the weight of boat and specimen was constant during the course of high temperature cyclic study. It can be inferred from the plot that the substrate steel T91 steel showed parabolic nature of weight gain in air as well as in salt oxidation. It is obvious from the weight gain graph that T91 steel oxidized in molten salt environment has shown much higher corrosion rates as compared to T91 steel oxidized in air. Comparative analysis indicate that the T91 steel oxidized in molten salt has the tendency to have higher mass gain continuously without showing any indication of steady state corrosion rate. The cumulative weight gain of both the substrates oxidized in air as well as in molten salt is presented in fig. 2(b), which depicts the higher weight gain of 62.18 mg/cm² for oxidation in salt than weight gain of 39.82mg/cm² for oxidation in air.

B. Thermo-Gravimetric Data Analysis

Thermo-gravimetric data for boiler steel T91 subjected to cyclic oxidation in Air and molten salt is presented in fig. 2 (a) in the form of a graph between weight gain per unit area (mg/cm²) versus time expressed in number of cycles. The mass change data serve as a good index to compare the corrosion rates under similar conditions of exposure. It can be inferred from the plot that the substrate steel T91 steel showed parabolic nature of weight gain in air as well as in salt oxidation. It is obvious from the weight gain graph that T91 steel oxidized in molten salt environment has shown much higher corrosion rates as compared to T91 steel oxidized in air. Comparative analysis indicate that the T91 steel oxidized in molten salt has the tendency to have higher mass gain continuously without showing any indication of steady state corrosion rate. The cumulative weight gain of both the substrates oxidized in air as well as in molten salt is presented in fig. 2(b), which depicts the higher weight gain of 62.18 mg/cm² for oxidation in salt than weight gain of 39.82mg/cm² for oxidation in air.
D. SEM/EDS Analysis of the Specimens

1. Surface Analysis of the Scale

The oxide scale on the surface of T91 steel oxidized in air (fig. 5(a)) has a granular scale which is composed mainly of Fe, O and Cr, thereby indicating the formation of Fe\textsubscript{2}O\textsubscript{3} rich oxide scale along with pocketed presence of Cr\textsubscript{2}O\textsubscript{3} in the scale. The oxide scale observed on the surface of T91 steel seems to be uniform and well adhered. The surface SEM/EDS of the T91 subjected to molten salt of Na\textsubscript{2}SO\textsubscript{4}-60\%V\textsubscript{2}O\textsubscript{5} at 900°C for 50 cycles is presented in fig. 5(b). The morphology of scale seems to be uniform and of globular texture having a large thickness of scale. The EDS analysis shows the presence of Fe, Cr, O and other reacting species justified by the XRD of the sample.

2. Cross-Sectional Analysis of the Scale

The SEI image showing the cross sectional oxide scale morphology and corresponding EDS analysis at some selected points of the T91 substrate subjected to molten salt of Na\textsubscript{2}SO\textsubscript{4}-60\%V\textsubscript{2}O\textsubscript{5} at 900°C for 50 cycles have been compiled in fig. 6(a, b). The scale in this paper has been referred as the material present above the substrate steel, which may include oxidized/ partially oxidized layers plus any other layer found on the surface, as could be seen from the cross-sectional micrographs. As per cross-sectional SEM micrograph of hot corroded T91 steel and its compositional elemental point analysis shown in fig. 6(a), the penetration of O and other elements can be analyzed. While moving from the substrate to oxide layer elemental percentage of O is seen along with the presence of Fe and Cr which justifies the formation of ferrous oxide Fe\textsubscript{2}O\textsubscript{3} and Cr\textsubscript{2}O\textsubscript{3}. This postulates the outward diffusion of Fe and Cr from substrate to oxide layer. While moving from point 5 to point 6 minor increase in composition of Fe and Cr is observed. Minor presence of Na, V and S is also seen in oxide scale and substrate.
3. X-ray Mapping of Exposed Specimens

Compositional Image (SEI) and X-ray mapping of the cross-section of hot corroded T91 substrate subjected to Na$_2$SO$_4$-60%V$_2$O$_5$ at 900°C for 50 cycles has been presented in fig. 7. The analysis of T91 steel in fig. 7, indicates that the base metal is mainly composed of Fe and some percentage of Cr. The oxide scale of the T91 steel has the presence of O, Fe and Cr confirming the presence of Fe$_2$O$_3$ and Cr$_2$O$_3$ as major phase, where as the minor presence of Ni, S, V and Na is also observed. Minor presence of these elements is said to responsible for the minor phases of (Cr,Fe)$_2$O$_3$, FeV$_2$O$_4$, FeS,CrS.
IV. Discussion
The corrosion of the T91 substrate is observed under the influence of environment of air and salt of Na$_2$SO$_4$-60%V$_2$O$_5$ at 900°C for 50 cycles. The T91 substrate exposed to salt showed higher rate of corrosion in comparison to its counterpart T91 exposed to air (Fig. 2(a), 2(b). As the environment of Na$_2$SO$_4$-60%V$_2$O$_5$ salt is more severe in its effect than of air. So same is observed in the conditions of T91 exposed to cyclic studies in air. Kotla et. al. [16] described that Na$_2$SO$_4$ and V$_2$O$_5$ will react at 900°C to form NaVO$_5$ which acts as a catalyst and works as an oxygen carrier to the substrate through pores present on the surface, which causes oxidation of elements of the substrate. Through pores on the surface and cracks in oxide layer, corrosive gases can penetrate to the substrate and allow significant grain boundary corrosion of FeS and CrS phases predicts the sulphidation of Fe and Cr elements of the substrate. Hence it makes the attack more severe and add to more increase of weight gain of T91 oxidized in salt.

Moreover, the surface SEM/EDS analysis (Fig. 5(b) of oxide of T91 substrate along with cross-sectional point analysis (Fig. 6(a) and elemental x-ray mapping (Fig. 7) supported the formation of these oxides reported in XRD analysis of T91 substrate, which showed that scale is primarily composed of Fe, Cr and O elements along with presence of Na, V and S elements.

V. Conclusion
The cyclic oxidation behavior of substrate T91 boiler steel in air and molten salt of Na$_2$SO$_4$-60%V$_2$O$_5$ is exhaustively elaborated. The molten salt of Na$_2$SO$_4$-60%V$_2$O$_5$ has more severe effect on the physical condition of the T91 substrate. The corrosion resistance of T91 boiler steel is better in air than in salt.

References

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