

A Study of Hot & Aqueous Corrosion of an Iron Phosphorous Alloy

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Abstract—Advances in the development of high-temperature materials are expected to increase the life time of gas turbines, boilers, and industrial waste incinerators with their improved strength, creep and fatigue properties. Hot corrosion is an accelerated form of high temperature oxidation of materials, induced by a thin film of fused salt deposit. Alloys used for high temperature applications should possess good mechanical properties along with corrosion - erosion resistance. In the present work, a comparative study of Grade A-1 and P-1 steels has been conducted with respect to their high temperature oxidation and hot corrosion behaviour. The specimens were subjected to cyclic oxidation in air and in molten salt environment of Na₂SO₄ - 60% V₂O₅, at 900°C, for 30 cycles and 10 cycles respectively. Visual, optical and thermo-gravimetric techniques were used to study the oxidation and hot corrosion effects and analyse the corrosion products. It was observed that both the samples exhibited similar hot oxidation resistance in case of oxidising environment. But, in case of molten salt environment, the deterioration occurred to a larger extent in the A-1 sample as compared to P-1. In aqueous environment, the P-1 sample showed slightly better corrosion resistance in comparison to A-1 grade.

Keywords: Hot Corrosion, Aqueous corrosion, metallography, Iron-phosphorous alloy.

1. INTRODUCTION

Corrosion is costly and can also lead to hazardous failures. Crores of rupees are spent annually for the replacement of corroded structures, machinery, pipelines, etc. Other costs associated with corrosion are maintenance to prevent corrosion, inspections, and the upkeep of cathodically protected structures and pipelines. Plant shutdowns, loss of efficiency, product contamination, etc., are the indirect cost of corrosion.

Advances in high-temperature materials are expected to increase the life time of gas turbines, boilers, and industrial waste incinerators with their improved strength, creep and fatigue properties. The combination of high temperature with contaminants of environment and low-grade fuels, such as sodium, sulphur, vanadium, and chlorine, leads to the phenomenon of hot corrosion. The corrosive nature of the gaseous environment may cause rapid material degradation and result in the premature failure of components [1]. The

corrosive nature of gaseous environments in coal gasification pilot plants which contain oxygen, sulphur and carbon may cause rapid material degradation and result in the premature failure of metallic components [2]. Technical literature available is evidence that corrosion and deposits on the fireside of boiler surfaces or in gas turbines represent important problems [3]. Oxidation is a type of corrosion involving the reaction between a metal and air or oxygen at high temperature in the absence of water or an aqueous phase. It is also called dry corrosion. The rate of oxidation of a metal at high temperature depends on the nature of the oxide layer that forms on the surface of metal [4]. Metals and alloys may experience accelerated oxidation when their surfaces are coated by a thin film of fused salt in an oxidizing gas. This mode of attack is called hot corrosion, and the most dominant salt involved is Na₂SO₄ [5]. Corrosion of metals costs the United States over \$300 billion per year according to recent estimates—more than the cost of annual floods and 2 fires [6]. An estimated 40% of total US steel production goes to replacement of corroded parts and products. High temperature degradation is one of the main failure modes of hot-section components in the gas turbines, so an understanding of this high temperature oxidation is very necessary [7]. In the past, a number of materials such as T - 11, T - 12, T - 22, Grade A-1, SS - 347 etc. have been employed for the application in boilers. The research work is continuously being done, in order to improve the performance of these materials, by coating techniques or by introducing new materials for such applications.

The present study is an attempt to evaluate the high temperature corrosion behaviour of uncoated A-1 boiler steel and P-1 samples in a comparative manner. The tests were planned to be carried out in air and in salt mixture of Na₂SO₄-60% V₂O₅ reported to be most aggressive environment at an elevated temperature of 900°C for 30 cycles (each cycle of 1 hour heating followed by 20 min. cooling in air) in silicon-carbide tube furnace. The temperature of study was kept high than the actual operating temperature as this would also take into consideration the overheating effect in case of boilers.

The cyclic conditions were employed as these conditions constitute more realistic approach. This will also take into account the stress that is developed due to difference in the coefficient of expansion of the base alloy and coating. Thermo-gravimetric studies were to be done to understand the corrosion kinetics of hot and aqueous corrosion as well as corrosion in a molten steel bath..

2. EXPERIMENTAL PROCEDURE

In this section, the experimental techniques and procedure employed for the study, has been summarized. It includes the selection of substrate material and high temperature oxidation and hot corrosion studies and the analysis of corrosion products.

2.1 Selection of substrate material

Boiler steel has been selected as the substrate material for the present study. This carbon steel is used as a boiler tube material in the super heater zone in thermal power plants. The behaviour of this material in corrosive media has been studied in comparison with P-1 samples.

2.1.1 Preparation of substrate material

The specimens of the steel samples were cut with dimensions of approximately 20 mm x 15 mm x 5 mm. The specimens were polished by using 100, 400, 800 and 1000 grade SiC emery papers and subsequently cloth polishing with iron oxide powder.

2.2 Hot corrosion and aqueous corrosion oxidation studies

2.2.1 Experimental setup and procedure:

The high temperature oxidation and hot corrosion study was conducted at a temperature of 900°C using silicon carbide tube furnace in laboratory. Firstly, the furnace was calibrated and a temperature indicator with a variation of $\pm 5^\circ\text{C}$. Heating zone in the tube was found out for 900°C with the help of a thermocouple. The steel specimens were mirror polished using iron oxide paste on a wheel cloth before study. After polishing, the samples were washed properly and dried in hot air to remove the moisture. The dimensions of the specimens were measured with the help of a Vernier calliper, to calculate the surface area and other dimensions. Alumina (Al_2O_3) boats were used to place the samples in furnace for corrosion studies. The boats were pre-heated at a constant temperature of 1200°C for 10-12 hrs. It was done to ensure that their weight will remain constant during the high temperature corrosion study. For conducting the experiment, each sample was kept in the boat and the weight of boat and sample was measured. Then, the boat with sample was inserted into the heating zone in the furnace at 900°C. The holding time in the furnace was 1 hr and after that the boat with sample was taken out and cooled in ambient air for 20 min. Then the weight of the boat with sample was measured with the help of electronic

weight balance meter. This constituted one cycle of the study. The study was carried out for 30 such cycles. The scale formed and fell in the boat was also taken into consideration for weight change measurement.

2.2.2 Oxidation and hot corrosion studies:

(1) The two specimens (conventional: A-1 and new composition: P-1) were taken and their dimensions were measured with the help of Vernier Callipers and scale. Alumina boat was placed in furnace at 900°C for 12 hours and its constant weight was obtained. The boat along with the sample was placed into the hot zone of the furnace. The boat along with specimen was weighed after each cycle. Holding time in furnace is 1 hr followed by cooling in still air at ambient temperature for 20 minutes. The specimen was subjected to visual observations carefully after the end of each cycle with respect to colour or any other physical aspect. The procedure was repeated for 30 cycles.

(2) The two specimens (conventional: A-1 and new composition: P-1) were taken and their dimensions measured.

The specimens were coated with a mixture of Na_2SO_4 and V_2O_5 . Alumina boat and samples was weighed after alumina boat had been placed in the furnace at 900°C for 12 hours so that its constant weight was obtained and maintained throughout the 10 cycles. Subsequently, the boat along with sample was placed into the hot zone of the furnace. The boat was weighed along with specimens after each cycle. Holding time in furnace was 1 hr followed by cooling in still air at ambient temperature for 20 minutes. The specimen was subjected to visual observations carefully after the end of each cycle with respect to colour or any other physical aspect. The procedure was repeated for 10 cycles.

2.2.3 Aqueous corrosion studies:

Preparation of solution: the solution was prepared for aqueous corrosion by dissolving 3.5 grams of NaCl in 100 ml of water. Therefore for 300ml we need 10.5 grams of NaCl. The conventional and the new composition specimens were suspended in the corrosive aqueous media (NaCl soln.) with a thread after their dimensions have been checked by using Vernier Callipers and scale. The specimens were kept at rest in the media for a time period of 30 days after which they were taken out. It was observed that a fine powdery yellowish brown layer of oxide was formed on both samples. This layer was removed using a stripping solution. A solution of Antimony trioxide (20gms) and stannous chloride (50gms) in 1000ml hydrochloric acid (according to ASTM-G1-03) was used as a stripping solution. The specimens were then weighed to calculate the weight loss due to aqueous corrosion.

2.3 Analysis of corrosion products

The specimens subjected to high temperature air oxidation and hot corrosion at 900°C for 30 cycles were analyzed for the identification of corrosion products. The resulting corroded

specimens were subjected to visual examination & thermo-gravimetric analysis.

2.3.1 Visual examination:

A visual examination of the specimens was made after each cycle and changes in appearance, colour, cracks and tendency of spalling were noted. Specimens were photographed and examined carefully after the completion of each cycle.

2.3.2 Thermogravimetric studies:

The weight change measurements were taken at the end of each cycle using an electronic weight balance meter to understand the kinetics of corrosion. The weight change with respect to number of cycles was plotted for each specimen in hot corrosion, aqueous corrosion as well as hot corrosion in salt bath. The graphs of the samples for comparative study were also plotted.

3. RESULTS AND DISCUSSIONS

In this section, the performance of boiler steel of ASTM-SA 210 Grade A-1 and P-1 steels are compared under various conditions viz. heating in the presence of oxygen and in aggressive environment of molten salt Na_2SO_4 - 60% V_2O_5 , at 900°C , under cyclic conditions has been evaluated. The surface conditions were observed during heating and the weight change was analyzed using thermo gravimetric data. The results obtained have been reported and discussed in the following sections.

3.1 Results:

3.1.1 Characterization of substrate steel

Chemical Composition of Substrate Steels: The chemical composition of substrate steels Grade A-1 and P-1 is as given in Table 3.1.

Table 3.1. The chemical composition of substrate steels Grade A-1 and P-1

Alloy	%C	%Mn	%Si	%P	%Cr	%Fe
A-1	0.307	0.598	0.287	0.009	0.00	Rest
P-1	0.145	0.206	0.182	0.281	0.15	Rest

Optical microscopic analysis: The microstructures of both the steels contain ferrite (Figures 3.1 and 3.2).

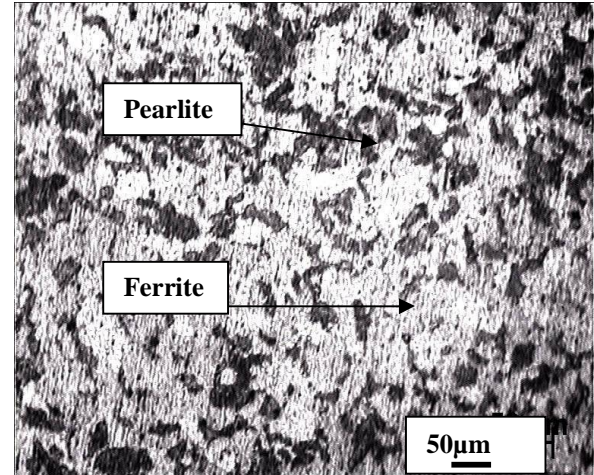


Figure 3.1. ASTM-SA210 Grade A-1 boiler steel, 200X

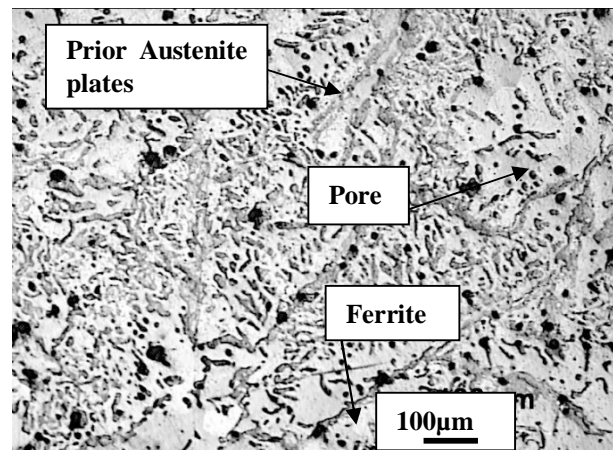


Figure 3.2. Rolled and forged alloy P-1, 100X

3.1.2. High temperature oxidation study

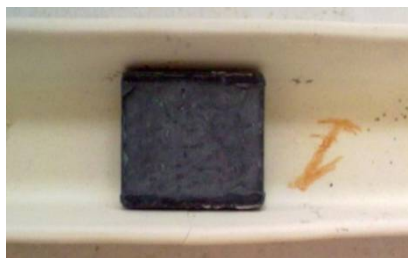
Visual Examination: The high temperature oxidation behaviour of uncoated A - 1 steel was visually examined for 30 cycles at 900°C . Uncoated A - 1 steel showed rapid deterioration till the completion of 5 cycles. Scale started to form on the surface due to rapid oxidation on the surface. After the 5th cycle of heating, scaling rate of the surface deteriorated till the 10th cycle was completed. Scale from the surface started peeling off in the form of thin layers. The layers showed a dull steel grey colour throughout the 30 cycles. The sample started to disintegrate by gradual peeling off of thin layers from the surface which started first at the larger surface of the sample while it gradually proceeded to the smaller areas. Deterioration of material continued at a decreasing rate till 30th cycle of heating. The cycle wise macrographs of oxidation of A-1 are shown in figure 3.3.

In case of P-1 steel, deterioration of the surface started rapidly due to the formation of oxide scale at the surface. The deterioration was not uniform unlike in A-1 sample. Cracks

appeared all over the surface during cooling after 5th cycle. Layers peeled off from the surface from 10th cycle onwards, in the form of small pieces and this peeling off continued for the rest of the cycles. Inner layers were grey in colour and dull in appearance. This deterioration slowed down in subsequent cycles. The cycle wise macrographs of oxidation of P-1 are shown in figure3.4.



Cycle 2



Cycle 20

Figure3.3. The cycle wise macrographs of oxidation of A-1 in air



Cycle 2



Cycle 20

Figure3.4. The cycle wise macrographs of oxidation of P-1 in air

Thermo gravimetric study: The thermo gravimetric analysis was done for grade A-1 and P-1 steels for high temperature oxidation. The change in weight after each cycle was calculated and was plotted against number of cycles as shown in figure3.5. The rate constants for the high temperature oxidation of Grade A-1 and P-1 steels were calculated from figure 3.5 as $6.23 \times 10^{-13} \text{ gm}^2/\text{cm}^4\text{s}^{-1}$ for Grade A-1 and $4.53 \times 10^{-13} \text{ gm}^2/\text{cm}^4\text{s}^{-1}$ for P-1 steel. This is indicative of better resistance to high temperature corrosion, of P-1 steel, as compared to Grade A-1.

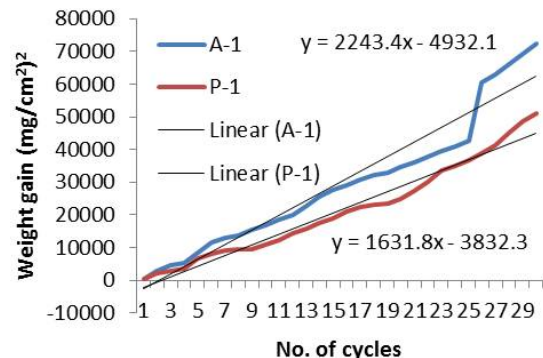


Figure3.5. (Weight gain/area)² plot for Grade A-1 and P-1 steel after high temperature oxidation at 900 °C for 30 cycles

3.1.3. Hot corrosion studies in molten salt environment

Visual Examination: A-1 was visually examined for 10 cycles at 900 °C in aggressive environment of molten salt Na_2SO_4 - 60% V_2O_5 . The A-1 steel sample showed small cracks in 1st cycle. The cracks increased in size onwards along with the spalling of scale. It was observed that A-1 steel severely deteriorated with considerable sized scale pieces, which peeled off. Dull grey coloured layers were formed on the steel surface. The 5th cycle macrograph of corrosion of A-1 in molten salt environment is shown in figure3.6.

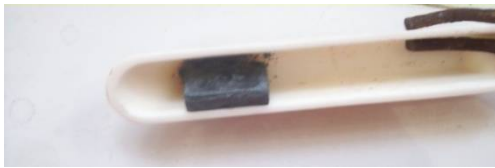


Cycle 5

Figure3.6. The 5th cycle macrograph of oxidation of A-1 in molten salt environment

In the case of P-1 steel, blister-like spots started forming on the surface right after the 1st cycle. Gradually some pieces of outer layer chipped off from the surface and scattered in the boat. Material started peeling off from inner layers in small pieces with grey colour from 6th cycle onwards. Specimen further deteriorated after the completion of the 10 cycles. The

cycle wise macrographs of corrosion of P-1 in molten salt environment are shown in figure 3.7.



Cycle 5

Figure 3.7. The cycle wise macrographs of oxidation of P-1 in molten salt environment

It may be observed that the base material was not able to withstand the salt at 900°C after the 1st cycle itself as it underwent rapid spalling. However, the P-1 steel scale did crack after the 1st cycle, but the deterioration was to a lesser extent than A-1. After which the scale started chipping off. This may be due to the difference in coefficient of thermal expansion of the substrate and the coating applied, which resulted initially the separation of the coating from the substrate exposing the substrate to the molten salt.

Thermo gravimetric Study: The corrosion kinetics for A-1 and P-1 steels in molten salt environment at 900°C have been studied. The weight gain data have been plotted for number of cycles.

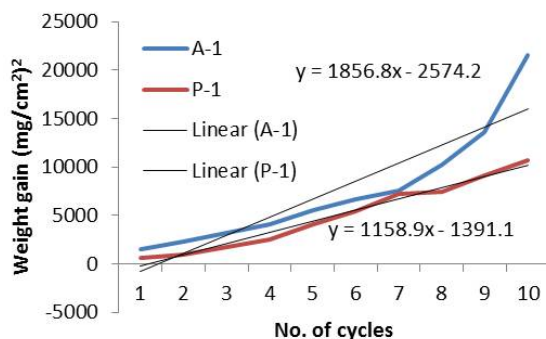


Figure 3.8. (Weight gain/area)² plot for Grade A-1 and P-1 steel in molten salt environment for 10 cycles

The rate constants for Grade A-1 and P-1 steels were calculated from figure 3.8. It was found to be $5.155 \times 10^{-13} \text{ gm}^2/\text{cm}^4 \text{ s}^{-1}$ for Grade A-1 steel and $3.216 \times 10^{-13} \text{ gm}^2/\text{cm}^4 \text{ s}^{-1}$, which indicates better corrosion resistance of P-1 steel.

3.1.4. Aqueous corrosion studies

Visual examination: The sample of grade A-1 was visually examined after keeping in a salt solution for 30 days (Figure 3.9). It was found that the corrosion took place with the formation of a thin, porous, rusty brown film consisting of oxides. This unstable oxide film formation leads to a decrease in weight of the sample.

The sample of P-1 steel was visually examined after immersion in aqueous salt solution for 30 days (Figure 3.9). A rust coloured, thin porous and unstable layer of oxide formed on the surface on dissolution.



Figure 3.9. A-1 and P-1 suspended in salt solution

Thermo gravimetric analysis: The corrosion kinetics for A-1 and P-1 steels in aqueous environment at room temperature have been studied. The weight loss data have been plotted as shown in figure 3.10 below.

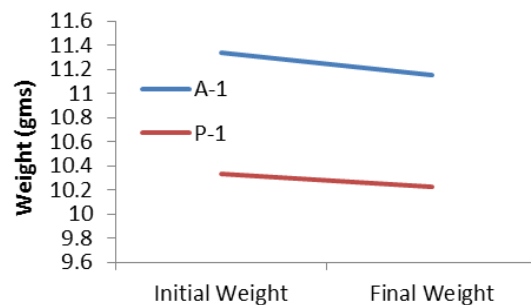


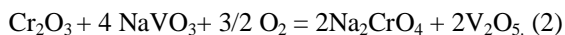
Figure 3.10 Plot of weight loss observed after aqueous corrosion

3.2 Discussion

The weight gain of A-1 and P-1 steels increases continuously with the progress of cycles. The weight gain of the coated specimens is relatively high during the first 10-15 cycles of oxidation and hot corrosion, but subsequently the increase in weight gain is gradual. The rapid increase in weight gain during the initial cycles of study may be attributed to the formation of NaVO_3 as a result of following reaction at 900°C [8].



This NaVO_3 (melting point 610°C) acts as a catalyst and serves as an oxygen carrier to the base steel, therefore leads to rapid oxidation of the base elements of the base steel to form protective oxide scale during initial cycles. Simultaneously the protective scale is destroyed by molten salts as per the reaction:



The Na_2CrO_4 gets evaporated and the metal surface is exposed to direct action of aggressive environment [9]. Therefore, higher weight gain during the subsequent cycles is probably due to the growth of oxides, and simultaneously dissolution of Cr_2O_3 .

A-1 steel shows the formation of scale with significant spalling. Higher spalling of the scale can be attributed to severe strain developed due to the precipitation of Fe_2O_3 from the liquid phase during cooling period of thermal cycles, and interdiffusion of intermediate layers of iron oxide [10]. The P-1 specimen has showed similar spallation of the scale. The P-1 sample has performed much better against corrosion in molten salt environment than in air.

4. CONCLUSIONS

The conclusions from the present study have been enumerated below:

- (1) Higher corrosion rate was observed in both the samples during the initial hours of hot corrosion, which might be attributed to the rapid reaction of metal directly with the salt.
- (2) The A-1 grade boiler steel has undergone intense spalling, peeling and enormous weight gain during oxidation in air after 30 cycles and hot corrosion by Na_2SO_4 -60% V_2O_5 at 900°C after 10 cycles.
- (3) The P-1 grade steel underwent less weight gain as compared to grade A-1 steel when subjected to oxidation in air.
- (4) The corrosion resistance of P-1 sample is more in the molten salt environment (Na_2SO_4 - 60% V_2O_5) than the conventional A-1 grade steel currently being used in boilers.
- (5) The behaviour of A-1 and P-1 samples in aqueous media (3.5 wt% NaCl) is almost same as both show almost equal amount of weight loss after a time period of 30 days.
- (6) Thus, in case of high temperature oxidation as well as corrosion in molten salt environment, the P-1 steel shows improved resistance to corrosion in comparison to the grade A-1 steel.

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