High Temperature Corrosion Behavior of Boiler Waterwall Tubes in Pyrite and Hematite Mixture Under Solid-Solid and Gas-Solid Reaction State.

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ABSTRACT

The slagging is a common problem of high temperature corrosion in fireside of waterwall tube of steam generator/ boiler of power plant component. The hematite (Fe_2O_3) layer very often exists on the fire side of the waterwall tube. The chemical interaction of hematite on the outer layer of the tube walls with molten pyrite (FeS_2) at high temperature (if the fuel contains sulfur) may cause slagging/fire side tube wastage due to the high temperature corrosion. This is closely similar to slagging/fire side corrosion of the waterwall tubes at high temperature when sulfur bearing fuels are used in boiler. Plain carbon steel ASTM SA210 Grade A1 is widely used for the construction of the waterwall tubes in the boiler. This papers highlights the mechanism and extent of high temperature corrosion of plain carbon steel in 67% of hematite (Fe_2O_3) and 33% pyrite (FeS_2) in solid-solid and gas- solid reaction state. The samples are exposed in high temperature furnace in different reaction states as mentioned at a constant temperature of 923 K=750^{0}C for 5 hours to study the high temperature corrosion behavior. The corrosion rates are calculated by weight gain method. The SEM and EDS study of the external scales of the samples are also carried out to examine the scale morphologies and constituent weight percentage of the elements of the external scales. It can be concluded from the results of the experiments that corrosion rate is much higher in solid-solid reaction state in comparison gas-solid reaction states with same proportion of hematite and pyrite The higher rate of corrosion in solid-solid reaction state is associated with external scale cracking/spalling and presence of appreciable amount of sulfur on the external scale.the lower corrosion rate in gas-solid reaction state is associated with the adherent corrosion resistant scale with finer grains of oxides and sulfides.

Keywords: Corrosion, Boiler, Waterwall, Hematite, Pyrite, Sulfur, Slagging

1. INTRODUCTION

Waterwall tubes in steam generator boiler components are used to produce dry saturated steam from water/1/ and considered to be one of the important

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parts in thermal power plant boiler. Plain carbon steels of ASTM SA-210 Gr A1 are mostly used as water wall tube material in boiler. Molten salt and slag related attack is considered as one of the predominant cause of the fireside corrosion in waterwall tubes/1,2/. The interaction with the protective oxide film in the form of hematite(Fe_2O_3) on the outer surface of the tube with iron sulfide in the form of pyrite (FeS_2) can lead to the accelerated corrosion in waterwall tubes. This type of corrosion becomes operative in the burner area of the furnace zone of the boiler if the fuels contain sulfur. This type of high temperature corrosion problem is due to the formation of low melting eutectic compound /3,4/. Fundamental work has been carried out on slag formation and deposit mechanism.The mechanism of chemical interaction of 67% hematite and 33% of pyrite were studied in detail by differential scanning calorimetry (DSC) combined with simultaneous thermogravimetry/5/. The results indicate that hematite is converted into magnetite in this proportion, which reduces the protective ability and accelerates corrosion of the waterwall tube at 923=700^{0}C. The present work is focused on the studies of the extent of corrosion rate, the morphology of the scale and the mechanism of the corrosion in different powder mixture of pyrite and hematite in solid-solid and gas-solid environment which is very similar to the situation of interaction of pyrite deposits on the protective outer scale of hematite of the waterwall tubes in the thermal power plant boiler.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

The initial material for the investigation is annealed hot finished seamless plain carbon steel tubes (ASME-SA210 GrA-1) which is widely used in construction of waterwall tubes of the thermal power plant boiler. The chemical composition of the tube material is analyzed by atomic Absorption spectrometer (Model Analyst 300, Perkin Elmer) and carbon-sulfur analyzer (Model EMIA-320V, Horiba, Japan) . Small specimens are cut and subjected to grinding, polishing and etching for preparation microstructure and grain size. The polished and etched samples are examined in Inverted Metullurgical Microscope (Olympus GX-51) with image analyzing facility. The chemical analysis and the microstructure are shown in **Table 1** and **Figure 1**. The average grain size measured is found 47 μm. Rectangular pieces are prepared from the tubes for corrosion studies. The prepared samples are subjected to rough grinding followed by subsequent polishing in 120,220,400.500.800 and 1000 grade SiC emery paper followed by cleaning with acetone. The dimensions of the samples are measured and surface areas are calculated .The initial weights of the samples are measured using a electronic digital balance of accuracy (± 0.01 mg) .

Table 1

Chemical composition of boiler waterwall tube

Grade	C	Mn	P	S	Si	Fe
Mass percent	0.28	0.77	0.023	0.035	0.12	Balance

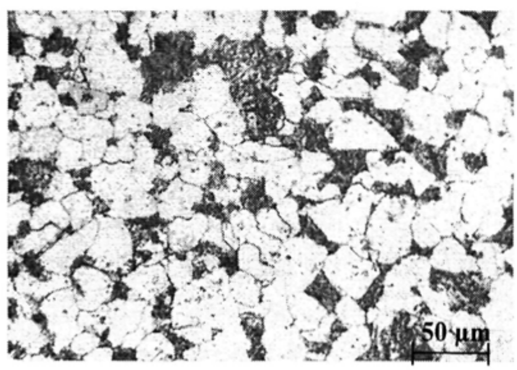


Fig. 1: Optical Microstructure of as received material

Tablets of pyrite and lumps of hematite are manually powdered in dry ball mill. Both are powdered to a size of 106μm. The solid mixture of 33% pyrite and 67% hematite is taken in weight basis for experimental study. Sample 1 is placed in a crucible submerged in a solid mixture of 33% pyrite (FeS_2) and 67% hematite (Fe_2O_3). The sample 2 is suspended with help of thin nicrome wire over a crucible filled up to 1/3 its volume containing a solid mixture of 33% Pyrite (FeS_2) and 67% hematite (Fe_2O_3). The former case allows the corrosion under solid-solid reaction of metal with mixture of hematite and pyrite. This situation is closely similar to the practical situation where waterwall tube is exposed in a mixture of hematite with pyrite (if the fuels contains sulfur)at high temperature. Generally layer of solid pyrite sticks to the outer scale of hematite of the waterwall tube in burner area of the thermal power generation boiler. The later case is the gas –solid interaction of metal with the same mixture of hematite and pearlite. This situation exists when the tube metal is allowed to react with oxygen and sulfur9gasious phase) generated from the mixture of pyrite and hematite.The two samples are placed in the furnace at 973K=700^0 C for 5 hours.

The scope of the experimental work covers

- Calculation of corrosion rate in terms of weight gain.
- Scanning Electron Microscope study of the external scale to examine the scale morphology.
- EDS X-ray microanalysis to estimate the chemical composition of the constituent element in weight percent.of the external scale.

3. RESULTS AND DISCUSSION

The results of chemical analysis (Table 1) shows that the chemical composition of the tube material conforms to the specification SA-210 GrA1 (plain carbon steel)which is normally used in waterwall tube of the boiler. The microstructure shows polygonal grains of ferrite and pearlite. The average grain size measured is of 47 μm. The corrosion rate of the two samples in terms weight gain is shown in **Figure 2.**

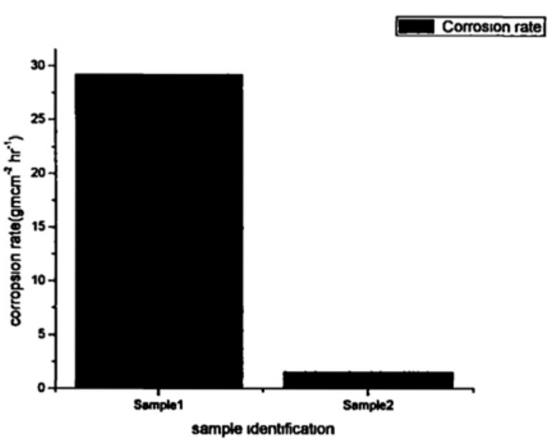


Fig. 2: Corrosion rate of different samples

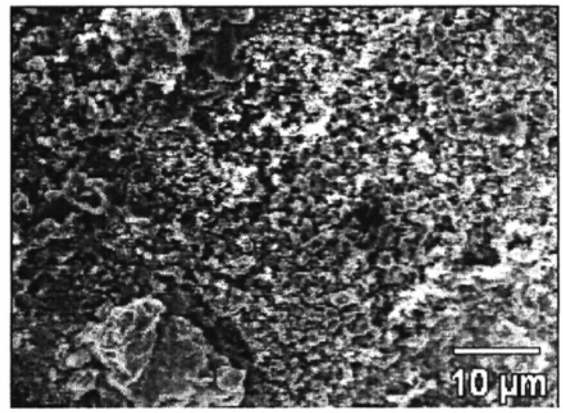


Fig. 3: SEM Micrograph of external scale of sample-1

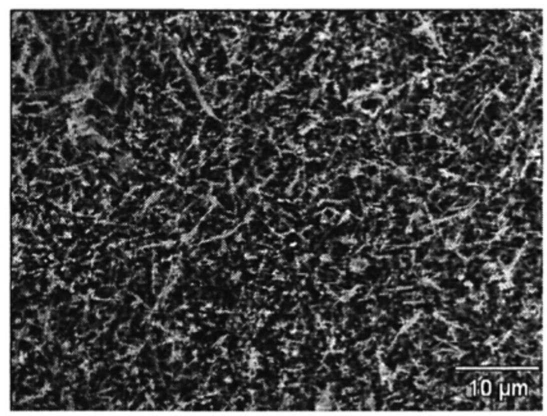
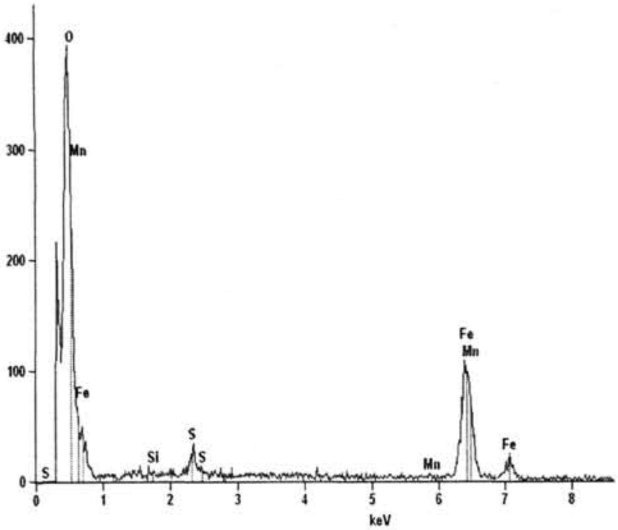


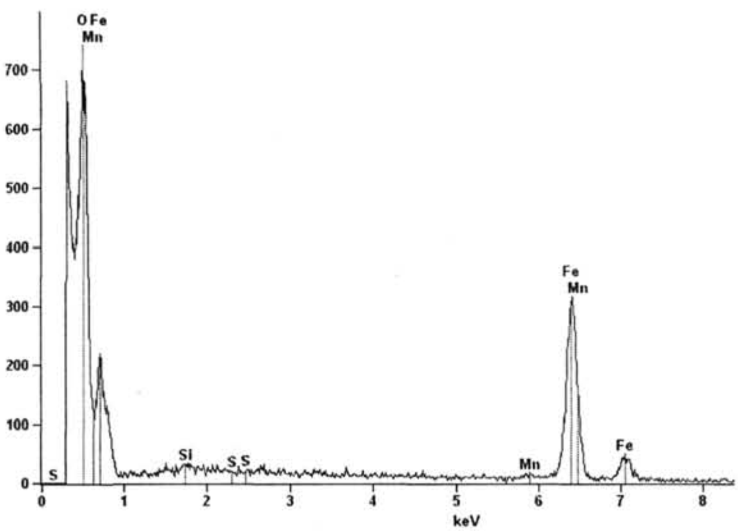
Fig. 4: SEM Micrograph of external scale of sample-2

The results indicates that the corrosion rate of sample 1 (solid-solid reaction) is much higher in comparison of the sample 2 (gas-solid reaction) with same proportion of mixture of hematite and pearlite. The results also clearly indicates that corrosion rate in solid-solid reaction is much faster than in gas-solid reaction state with same proportion of pyrite and hematite. The external scales of two samples are examined in Scanning electron microscopy (Model-S-3000N, Hitachi Ltd, Japan) and Energy Dispersive Spectroscopy (EDS) (ThermoNoran USA). The SEM studies of the external scales of the two samples are shown in **Figure 3** and **Figure 4.** The corresponding EDS results are shown in **Figure 5** and **Figure 6.**



Element	Mass percent
O	58.47
Si	0.19
S	1.76
Mn	0.38
Fe	39.21

Fig. 5: EDS analysis of sample-1



Element	Mass percent
O	51.84
Si	0.13
S	0.29
Mn	0.38
Fe	47.35

Fig. 6: EDS analysis of sample 2

The scale morphology of sample-1 reveals highly porous scale. Significant spalling/ scale cracking is also observed **(Figure 3)** .The EDS analysis of the external scale confirms appreciable sulfur (1.76% mass)along with oxygen and iron. **(Figure 5)** The external scale of sample 2 shows adherent external scale with no significant scale cracking and spalling **(Figure 4)**. Finer grains of oxide and traces of sulfide grains are detected on the external scale in both the cases. The EDS analysis of the external scale of sample 2 confirms traces amount of sulfur(0.29%mass) along with oxygen and iron **(Figure 6)**.

The interaction of 33% pyrite(FeS_2) with 67% hematite at 973K=700^{0}C was studied in the past /5/. The following reaction occurs during the interaction of pyrite and hematite at high temperature, when pyrite is directly in contact with the outer scale of hematite of the water wall tube.

$FeS_2 + 6\ Fe_2O_3 = Fe + 2SO + 4\ Fe_3O_4$ (1)

Thus the conversion of hematite(Fe_2O_3) into magnetite(Fe_3O_4) at 973K=700^{0}C reduced the protective ability of corrosion at the great extent in sulfidation and oxidation mixed environment. . The above mechanism justifies the maximum corrosion rate of sample 1 in solid-solid reaction state. The highly porous scale and significant spalling/scale cracking supports the maximum corrosion. The presence of sulfur in the external scale indicates the more of sulfidation rather than oxidation. Sulfide scale grows rapidly and spalls more easily compared to oxide scale and responsible for higher corrosion rate. On the other hand, the slower corrosion rate in gas-solid reaction state sample 2 is due to the lower concentration of sulfur in the vapor phase in gas –solid reaction state as compared to direct reaction with the solid powder mixture(solid-solid reaction state).The lower corrosion rate of sample 2 can be attributed to adherent corrosion resistive scale with finer grains of sulfide and oxide grains. The presence of more oxide grains rather than the sulfide grains indicates more oxidation rather than sulfidation. Oxide scales are more protective and corrosion resistant. The presence of traces amount of sulfur on the external scale supports also the fact of lower rate of corrosion by sulfidation.

4. CONCLUSION

On the basis of the results and discussion the following conclusions can be made.

1. The corrosion rate is maximum when the sample is placed inside the powder mixture of 33% pyrite and 67% hematite (sample-1 in this case). Here the corrosion takes place in solid-solid reaction state. The external scale formed is highly porous in association with cracking/spalling. The higher corrosion can be attributed due to higher sulfur potential and lower oxygen potential in solid-solid reaction state. temperature The corrosion rate is faster in sulfidizing atmosphere than in oxidizing atmosphere because of cation diffusion in corresponding oxides. Sulfide scale grows rapidly and spalls more easily than oxide scale. This situation is similar to fireside corrosion of waterwall tube where the metal with outward hematite scale interacts with molten pyrite (if fuel contains sulfur) at high temperature.
2. The corrosion rate is lower when the sample is placed above the powder mixture of 33% pyrite and 67% hematite(sample-2).Here the corrosion takes place in gas-solid interaction state. The lower corrosion rate can be attributed due to slower reaction rate in vapor phase due to much less concentration of S and O_2 in the crucible atmosphere, compared to direct reaction with the same mixture powder(solid-solid reaction state). No significant spalling/scale cracking is observed on the outer scale. Finer grains of oxides mostly on the outerscale makes the scale more protective and resistance to corrosion.

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