Studies on High-Temperature Corrosion resistance of low carbon Steel in Actual boiler environment

Navneetinder Singh1, Supreet Singh2, Manoj Kumar3, Manpreet Kaur4, harprabhjot singh5, sukanta sarkar6
1 Department of Automobile Engineering, Chandigarh University, Mohali, Punjab, India
2, 3 Department of Mechanical Engineering, Chandigarh University, Mohali, Punjab, India
4 Department of Mechanical Engineering, Baba Banda Singh Bahadur Engineering College, Fatehgarh Sahib, Punjab, India
5Department of Mechanical Engineering, Indian Institute of Technology, Ropar
6 Department of Metallurgical Engineering and Material Science, IIT Bombay, Powai, Mumbai, India
Corresponding author: supreet.mech@cumail.in

Abstract: In coal based power generated plants, hot corrosion and erosion are identified as serious problems, resulting in deterioration of boiler tube. In this present study, the High-Temperature Corrosion behavior of bare SA 210 Gr. A1 steel and Friction stir processed Cr3C2-25(NiCr) inserted Gr. A1 steel samples were compared under cyclic condition of 1500 hours in actual both environments. The kinetics of hot corrosion was measured on the base of weight-change after each cycle. The tool rotation speed for three processed samples were recorded as 1600rpm, 2000rpm, 2400 rpm respectively with transverse speed of 30 mm/min processed by three number of passes. Microstructure evolution of base and FSPed was done by electron back scatter diffraction (EBSD). X-ray diffraction (XRD) and scanning electron microscopy (SEM) along with energy dispersive spectroscopy (EDS) were performed on the exposed sample to analyze the corrosion products. The base steel sample suffered extreme erosion-corrosion in actual boiler environment, whereas processed samples exhibits better hot corrosion resistance (64%, 66%, 73%) respectively. The processed samples also showed 4 fold refined grains, as confirmed by (EBSD).

1. Introduction
Hot corrosion is the depletion or deterioration of a material subjected to elevated temperature conditions. High temperature attainment is an inputted factor in several high tech industries for example fossil fuelled power plants, refineries, petrochemical industries and coal fined thermal power plants, with an adverse effect of material degradation and oxidation resulting in reduced life of these industries[1]. In whole world, coal fired thermal plants has predominance in generation of electricity. Coal is burned inside the boiler which further boils the water, and produced steam is used to run the turbines, coupled with a generator [2].
To overcome the corrosion problem number of techniques are used, Friction Stir Processed is one of the advantageous technique which results in microstructure modification and enhanced mechanical properties [3-6].In FSP, depending on processing parameters, i.e. rotational speed,
transverse speed and force applied, the rotating tool induces plastic deformation on base steel. The evolution of microstructure is obtained due to material flow, high temperature in processing zone (PZ), heat affected zone (HAZ) and thermo mechanical affected zone (TMAZ).

In this study, 4 mm thick SA210 grade A1 boiler steel is Friction Stir Processed, after insertion of Cr3C2-25(NiCr) powder at different rotational speeds 1600rpm, 2000rpm, 2400rpm, with three numbers of passes and transverse speed of 30 mm/min. samples are named as S1-1600rpm, S2-2000rpm, and S3-2400 rpm respectively.

2. Experimental Procedure
2.1. Material
In Current study the SA210 grade A1 boiler steel was selected as the base material. The chemical composition of the steel is shown in table 1. The embedded powder was Cr3C2-25(NiCr) with particle size (45±15 μm). The steel plates were cut down into specified dimensions i.e. 76mm ×50mm×4mm, so that the plates can be mounted in specified designed fixture for further processing.

| Elements | C  | Mn  | Si  | S   | P   | Fe   |
|----------|----|-----|-----|-----|-----|------|
| Wt %     | 0.27 | 0.93 | 0.1 | 0.035 | 0.035 | Balance |

2.2. Friction Stir processing
FSP was performed on vertical milling centre VMC (make viper 950, India). The tool used during the process is pinless, made up of tungsten carbide with diameter of 10 mm throughout the experiment. Fixture along with the hold sample was bolted on the VMC bed. FSP was done on the Cr3C2-25(NiCr) powder embedded samples with variable rotational speed of 1600rpm, 2000rpm, 2400rpm for three different plates named as S1, S2 and S3 respectively shown in Figure 1. The feed rate of 30 mm/min and plunger depth 1mm is fixed for all the three samples. Maximum 3 passes were performed on all the samples with exact overlapping on the previous pass. After processing, the specimens were rapidly cool down with the help of dry ice.

2.3 High temperature Erosion-Corrosion tests
The specimens for the high temperature corrosion were prepared in the dimensions 10x10x4 mm from the FSPed plates. All the six sides of the samples were polished with the help of disc polishing machine from grit size 120 to 1500 grades. To get the weight gain per unit area graph all the dimension is noted and initial weight of bare and processed steel is measured.
2.4 Erosion-Corrosion Studies in actual Coal-Fired Boiler

The processed and base samples were hung through soot blower dummy points in the low
temperature zone of stage-II boiler in Guru Gobind Singh Super Thermal Power Plant
(GGSSTPP), Ropar, Punjab (India) for erosion-corrosion studies under cyclic conditions. In this
zone, 700 tones/hr volumetric flows of flue gas and temperature about 700±10°C were recorded.
The chemical composition of the ash inside the boiler is mainly silica 55%, aluminum oxide 30%
and oxides of magnesium, sulphur, calcium, sodium and potassium with % in between 0.2 to 1.5
approx. The oxidation-erosion study was conducted for 15 cycles, with 100 hour exposure for
each cycle, followed by 1 hour ambient air cooling. At the end of each cycle, the hanged samples
were carefully examined regarding spalling tendency, color change and then subjected to weight
change measurements.

3. Results and Discussions

3.1. Microstructure

The optical microstructure of substrate SA 210 Gr. A1 steel with grain size of 25μm is consisted
of light colored ferrite and dark colored pearlite grains as shown in Figure 2(c3). FSP resulted in a
considerable refinement inside the Nugget Zone as confirmed by Electron Back Scattered
Diffraction (EBSD) as shown in Figure 2(a-d). The FSPed steel grain size caused decrement from
25μm down to about 11.705μm, 9.447μm and 6.36μm for samples S1, S2 and S3 respectively.
This means that the maximum grain size reduction is upto 4 times with the plastic deformation of
FSP inside the NZ. The refinement of grains i.e. fragmentation was seen due to dynamic
recrystallization as temperature was increased by friction stir processing followed by rapid
cooling and severs plastic deformation and temperature during FSP and refined by the effect of
severe plastic deformation. The Cr presence was confirmed, which leads to increase in hardness
and -strength of FSPed steel samples. Such a grain refinement was also was also seen by authors
[7-10].
Figure 2. EBSD images showing nugget zone of (a1) base steel (a2) S1 (a3) S2 (a4) S3; (b1) base steel (b2) S1 (b3) S2 (b4) S3 graph for grain size diameter; (c2), (c3), (c4) showing % of Ni and Cr in FSPed SA 210 Gr. A1 steel; (d2), (d3), (d4) shows the chromium and nickel composition in FSPed region; (c1) shows Optical microstructure of SA 210 GrA1 boiler steel
3.2 Hot Corrosion Studies in Actual Boiler Environment

3.2.1 Visual Examination
After exposure of processed sample to actual boiler environment, due to the formation of porous oxides scale, the bare SA 210 Gr. A1 steel suffered corrosion attack. The scale appeared on the surface of the bare steel is grey in color, with settled blotches of ash (grayish brown) after 2nd cycle. At the end of 4th cycle, it is observed that on side is turned reddish brown, the predictable indication of corrosion. The corrosion was subsequently increased during cycles. By the end of 6th cycle, scale puffiness was started and uneven surface was observed, continued for 1500 hours of experimentation. An asymmetrical oxide scale was left on the bare steel sample. Cr$_3$C$_2$-25(NiCr) imbedded SA210 GrA1 steel, after exposure to boiler environment, no sign of degradation was noticed during the experimental study. A smooth and homogeneous surface was found except the patches of deposited ash. No sign of deterioration was detected on the samples even after exposure of 1500 hours.

3.2.2 Weight Change Data
The net weight loss after the exposure of samples in actual boiler environment represents the combination of weight loss and weight gain due to the spallation of the oxide scales and the formation of oxidation scale respectively. The overall weight loss by the bare steel has been found to be (-7.8824 mg/cm$^2$). Due to formation of thick oxide scale, and continue oxidation-erosion of bare SA210 Gr. A1 steel showed higher weight loss than the Cr$_3$C$_2$-25(NiCr) imbedded steel in actual boiler environment. However, among the all Cr$_3$C$_2$-25(NiCr) imbedded, S3 sample showed the minimum weight loss (-2.12033 mg/cm$^2$), followed by S2 (-2.62452 mg/cm$^2$) and S1 (-2.7975 mg/cm$^2$) shown in Figure 3.

![Figure 3. Weight change vs. number of cycle plots for the base sample and powered inserted FSPed samples exposed to actual boiler environment at 700 °C for 1500 hours.](image-url)
3.2.3 Thickness Monitoring

After 1500 hours the 0.06433 of the thickness loss is observed in bare steel when exposed to the boiler environment. Based on this thickness data the oxidation rate will be calculated in terms of miles per year (mpy). The thickness loss data as shown in figure 4 represents the oxidation rate of SA 210 Gr A1 steel is 14.731. In the case of processed samples, thickness loss was 0.0229 mm for sample S1, sample S2- 0.0199 mm, sample S3- 0.0153 mm and the erosion-corrosion rate indicated by these samples were 5.224 mpy, 4.557 mpy, 3.503 mpy respectively.

![Figure 4. Bar Graph shows the thickness change in mils per year (mpy) for the Base sample and powered inserted FSPed samples exposed to actual boiler environment at 700 °C for 1500 hours.](image)

3.2.4 X-ray Diffraction Analysis

Fig 5. shows the X-ray diffraction analysis of FSPed bare and Cr3C2-25(NiCr) imbedded SA210 Gr. A1 steel samples which were exposed on the coal-fired boiler at 700°C for about 1500hr. Fe2O3, SiO2 and Al2O3 have been identified as the strong intensity phase in bare SA210 Gr. A1 steel samples are shown in Fig. 5 (a). In the case of processed samples, for sample S1, XRD revealed the presence of Cr2O3 and Cr3C2 as the main phases with Fe2O3 and Al2O3 as weak phases (Fig. 5 (b)). For S2 sample, XRD revealed the formation of Cr2O3, Cr3C2 and Cr2C as main phases and addition of SiO2, Fe2O3 and Al2O3 phase as weak intensity phases (Fig. 5(c)). XRD analysis for the S3 revealed a prominent phase of Cr2O3, NiO, and Cr3C2 whereas SiO2 and Al2O3 phase as weak intensity phases (Fig. 5(d)). The FSPed samples oxidize along the margin of the splat during corrosion and for the processed splat FSPed samples traits to form oxidation at a rapid rate resulting in better resistance in the hot corrosion of the samples.
3.2.5 Surface analysis of the scale

The scanning electron microscopy (SEM) analysis of corroded boiler steel and FSPed sample S1, S2 and S3 is as shown in Figure 6. The SEM of the base sample showed (Fig 6 (a)) corroded scale with the presence of Fe$_2$O$_3$ on the surface as revealed by XRD. The presence of this harmful phases leads to formation of cracks which is formed due to penetration of more oxygen on the surface of base steel and causing high temperature corrosion. Friction Stir processed samples S1, S2 and S3 shows densely packed fiber structure on the surface. The chromium splats were seen on S3 (Fig. 6 (d)) samples as confirmed by EDS, these presences of Cr and Ni may have lead to the existence of sacrificial phases as confirmed by XRD (Fig 5 (d)). Sample S2 and S1 also showed good protection against oxidation due to strong bounded composition of Ni-Cr and capability to act as effective barriers. The SEM micrograph of the S3 sample represents in Fig. 6 (d) shows us dense crack free surface. The white colored particles are observed in scale.
Figure 6. Surface morphology and EDS analysis for bare sample and powered inserted FSPed samples exposed to actual boiler environment at 700 °C for 1500 hours. (a) base steel (b) S1 (C) S2 (C) S3. 

(a) Base steel: 54% Fe, 20% O, 09% C, 08% Al, 07% Zn, 02% Si

(b) S1 (C) S2 (C) S3: 30% O, 28% Cr, 17% Ni, 12% Fe, 06% Al, 05% Fe, 02% Mn

(c) S1 (C) S2 (C) S3: 36% Ni, 23% Cr, 14% O, 11% Al, 09% C, 05% Fe, 02% S

(d) S1 (C) S2 (C) S3: 34% Ni, 31% Cr, 14% C, 10% O

57% Fe, 22% O, 08% Al, 07% C, 05% Zn, 01% S

48% Fe, 28% O, 08% Si, 08% Zn, 07% Al

32% Cr, 19% Ni, 14% Al, 13% Si, 08% Fe, 06% O, 06% C, 02% S

44% Cr, 22% Ni, 18% O, 09% Al, 04% Fe, 03% Si

34% Ni, 31% Cr, 14% C, 10% O
4. Conclusions

- The significant refinement in the grain size is observed after FSP in the microstructure as confirmed by EBSD. The grain size in that zone decreases from 25μm down to 6.36μm this may be attributed due to plastic deformation.
- The maximum corrosion resistance was for sample S3 i.e. 73%, S3 sample showed the minimum weight gain (-2.12033 mg/cm²), followed by S2 (-2.62452 mg/cm²) and S1 (-2.7975 mg/cm²). Dense surface scale, rich in Chromium, along with significant amount of Nickel and Oxygen as revealed by the SEM microstructure, this may attribute to the probable formation of oxides and spinels of Ni and Cr.
- S3 sample revealed the presence of Cr₂O₃, NiO, and Cr₃C₂Cr and Ni may have lead to the formation of sacrificial phases and reduced corrosion rates.

References

[1] A.S. Khanna, “Introduction to high temperature oxidation and corrosion”, ASM International, ISBN 0-87170-762-4, SAN: 204-7586, 2002, pp 1-322.
[2] John Stringer, “High temperature corrosion problems in coal based power plant and possible solutions”, Proceedings International conference on corrosion ‘CONCORN’ 97, Dcember 3-6, Mumbai, India, pp 13-23.
[3] R.S. Mishra, M.W. Mahoney, S.X. McFadden, N.A. Mara, A.K. Mukherjee, ScriptaMater. 42 (2000) 163.
[4] R.S. Mishra, M.W. Mahoney, Mater. Sci. Forum 357-3 (2001) 507.
[5] W.M. Thomas, E.D. Nicholas, J.C. Needham, M.G. Murch, P. Templesmith, C.J. Dawes, GB Patent Application No. 9125978.8, December 1991.
[6] M. Hajian, A. Abdollah-zadeh, S.S. Rezaei-Nejad, H. Assadi, S.M.M. Hadavi, K. Chung, M. Shokouhimehr, Microstructure and mechanical properties of friction stir processed AISI316L stainless steel, Mater. Des. 67 (2015) 82-94.
[7] H.S. Grewal, H.S. Arora, H. Singh and A. Agarwal, Applied Surface Science., 268 (2013) 547-555.
[8] H.S. Arora, H. Singh, B.K. Dhindaw, Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science 43 (2012) 92–108.
[9] P.Xue, B.L.Xiao, W.G.Wang, Q.Zhang, D.Wang, Q.Z.Wang and Z.Y.Ma, Mater.Sci. Eng.A 575 (2013) 30–34.
[10] P. Xue, W.D. Li, D. Wang, W.G. Wang , B.L. Xiao and Z.Y. Ma, Materials Science & Engineering., 670 (2016) 153–158.