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Erosion–corrosion behaviour of Ni-based superalloy Superni-75 in the real service environment of the boiler

T S SIDHU[1,*], S PRAKASH[2], R D AGRAWAL[2] and RAMESH BHAGAT[1]

[1]Shaheed Bhagat Singh College of Engineering and Technology, Ferozepur 152 004
[2]Indian Institute of Technology Roorkee, Roorkee 247 667
e-mail: tssidhu@rediffmail.com

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Abstract. The super-heater and re-heater tubes of the boilers used in thermal power plants are subjected to unacceptable levels of surface degradation by the combined effect of erosion–corrosion mechanism, resulting in the tube wall thinning and premature failure. The nickel-based superalloys can be used as boiler tube materials to increase the service life of the boilers, especially for the new generation ultra-supercritical boilers.

The aim of the present investigation is to evaluate the erosion–corrosion behaviour of Ni-based superalloy Superni-75 in the real service environment of the coal-fired boiler of a thermal power plant. The cyclic experimental study was performed for 1000 h in the platen superheater zone of the coal-fired boiler where the temperature was around 900°C. The corrosion products have been characterized with respect to surface morphology, phase composition and element concentration using the combined techniques of X-ray diffractometry (XRD), scanning electron microscopy/energy-dispersive analysis (SEM/EDAX) and electron probe micro analyser (EPMA). The Superni-75 performed well in the coal-fired boiler environment, which has been attributed mainly to the formation of a thick band of chromium in scale due to selective oxidation of the chromium.

Keywords. Erosion–corrosion behaviour; Ni-based superalloy; Superni-75; supercritical boilers.

1. Introduction

High temperature erosion–corrosion of heat exchanger tubes and other structural materials in coal-fired boilers is recognised as the main cause of downtime at power-generating plants, which could account for 50–75% of their total arrest time (Cutler (1971); 1978). Maintenance costs for replacing broken tubes in the same installations are also very high, and can be

*For correspondence

estimated at up to 54% of the total production costs (Chandler & Quigley 1986). Combustion of coal generates erosive–corrosive media particularly near the superheater tubes of the boilers (Weulersse–Mouturat *et al* 2004). A dynamic surface layer consisting of a mechanical mixture of particles from the boiler gases and oxide scale growing from the base metal is formed on boiler tubes. This layer is constantly refurbished and removed at a rate that resulted in an essentially constant thickness of the deposit/scale layer during steady state operation of the boiler (Levy 1993).

The superalloys exhibit outstanding strength and surface stability at temperature up to 85% of their melting points. Usually the superalloys are used at temperatures above 540°C (Metals Handbook 1990). However, compared with steels, erosion–corrosion resistance of the superalloys is relatively less known Sidhu (2006); Smith *et al* (1999); Castello *et al* (2000); Sidhu & Prakash (2006).

In the present investigation, an attempt has been made to evaluate the erosion–corrosion behaviour of Ni-based superalloy Superni-75 in the actual service environment of the coal-fired boiler of a thermal power plant at 900°C under cyclic conditions. This alloy is developed by Mishra Dhatu Nigam Limited, Hyderabad (India) for various applications in boilers and gas turbines and they have designated this alloy as superalloy Superni-75.

2. Experimental

2.1 *Substrate material and sample preparation*

The nickel-based superalloy Superni-75 (19·5Cr-3Fe-0·3Ti-0·1C- Balance Ni) was used as a substrate material in the present study. The specimens with dimensions of approximately $20 \times 15 \times 5\,mm^3$ were ground with SiC papers and subsequently mirror polished down to $1\,\mu m$ alumina on a wheel cloth-polishing machine. Specimens were prepared manually and all care was taken for any structural changes in the specimens.

2.2 *Studies in coal-fired boilers*

Three samples were hung through the soot blower dummy point in the middle zone of platen superheater of the Stage-II boiler at Guru Nanak Dev Thermal Plant, Bathinda, Punjab (India). The samples were kept in the zone where temperature was 900 ± 10°C. The study was conducted for 10 cycles; each cycle consisted of 100 h exposure followed by 1 h cooling at ambient conditions. Cyclic study provides the severest conditions for testing and may represent the real plant operation where breakdown or shutdown occurs frequently depending on the power requirement. The average volumetric flow of flue gases was around $122\,m^3/sec$. At the end of each cycle, the specimens were visually observed for any change on surface. The weight of specimens was measured subsequently. After 1000 h exposure under cyclic conditions, the samples were subjected to XRD, SEM, EDAX, scale thickness and depth of internal corrosion attack measurement, and EPMA analysis. Due to similar erosion–corrosion behaviour of all the specimens, analysis of only representative micrographs is presented here.

2.3 *Erosion–corrosion evaluation*

Measuring the weight change per unit area and the extent of erosion–corrosion of the specimens assessed the erosion–corrosion behaviour of the superalloy Superni-75 in the given environment. The weight change consists of weight gain owing to the formation of oxide scale and weight loss due to the erosion, spalling and fluxing of the oxide scale. The net weight change represents the combined effects of these two processes. The extent of erosion–corrosion was assessed by measuring: (i) the scale thickness lost due to erosion, spallation or possible evaporation during experimentation; (ii) the average thickness of the scale left after 1000 h of exposure to the boiler environment. The depth from the surface to scale-substrate interface is taken as the scale thickness; and (iii) the depth of internal corrosion attack which is taken as the distance from the scale-substrate interface to the site up to which the corrosive species penetrated into the substrate.

The sum of the scale thickness loss, the average scale thickness left, and the depth of internal corrosion attack gives estimation of the material depth affected by the erosion–corrosion and thereby of the remaining sound metal.

2.4 *Measurement of scale thickness and depth of internal corrosion attack*

The scale thickness lost due to the erosion, spallation or evaporation was assessed by finding the difference in thickness of the specimens before and after 1000 h exposure to the aggressive environment of coal-fired boiler. The thickness was measured with a micrometer and every represented value was taken as the average of 10 measured values.

Average thickness of the scale and depth of internal corrosion attack were measured from the back-scattered electronic (BSE) image. The eroded–corroded specimens were cut across the cross-section and polished down to 1 μm alumina on a wheel cloth-polishing machine. A Scanning Electron Microscope (LEO 435VP) with attached Robinson Back Scattered Detector (RBSD) was used to obtain the BSE Images.

3. Experimental results

3.1 *Erosion–corrosion rate*

The weight change per unit area (mg/cm^2) verses time plot for 1000 h cyclic exposure of the Superni-75 to the boiler environment is shown in figure 1. During the first cycle, the weight of the specimen increases due to the formation of oxides from the base metal as well as interaction of these oxides with the ash deposits from the boiler gases. Subsequently, the

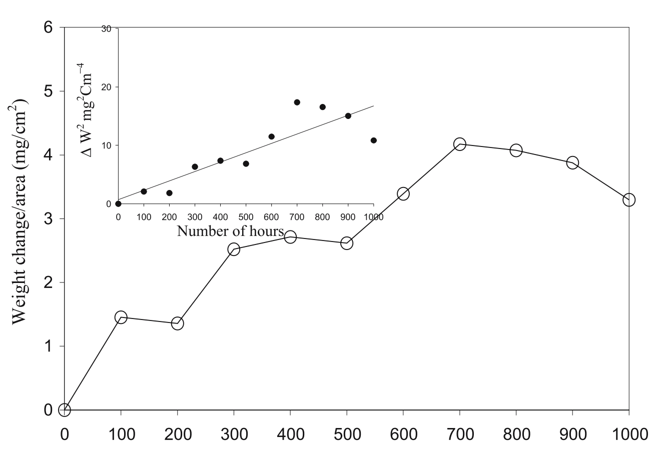

Figure 1. Weight change vs. time plots for Superni-75 during cyclic study in the real service environment of the coal-fired boiler. Insert is fitted for (weight change/area)^2 vs time plots.

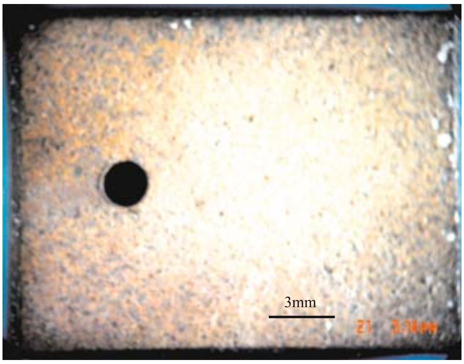

Figure 2. Macrographs of the Superni-75 after 1000 h exposure to platen superheater zone of the coal-fired boiler at 900°C.

weight of the specimen increases and decreases erratically. The increase and decrease in weight is due to the formation and erosion of the oxide scale, respectively. The oxide scale grew from the base metal and eroded due the striking of ash particles from the boiler gases. It can be observed from the (weight change/area)^2 vs. time plot (insert in figure 1) that the weight change indicates significant deviation from the parabolic rate law, thereby indicating the refurbishing and removal of a dynamic surface layer which is formed on the specimen during steady state operation of the boiler. The parabolic rate constants for the bare superalloys could not be calculated, as it did not follow the parabolic rate law.

Visually, it was observed that after exposure of 100 h, light grey scale was appeared on the surfaces of Superni-75. Subsequently, colour of the scale turned to brownish-grey. Symptoms of erosion were visible from the surface of Superni-75, as can be seen from figure 2.

From the back scattered electron image shown in figure 3, the depth of internal corrosion attack and the average scale thickness left after 1000 h of cyclic exposure of the specimen to platen superheater region of the coal-fired boiler has been measured. The sum of the scale thickness lost during experimentation, the depth of internal corrosion attack and the average scale thickness left are found to be as 80 μm, 10 μm and 65 μm respectively. Therefore, the thickness of material lost due to erosion–corrosion of the specimen after 1000 h of exposure to platen superheater regions of the coal-fired boiler is about 155 μm.

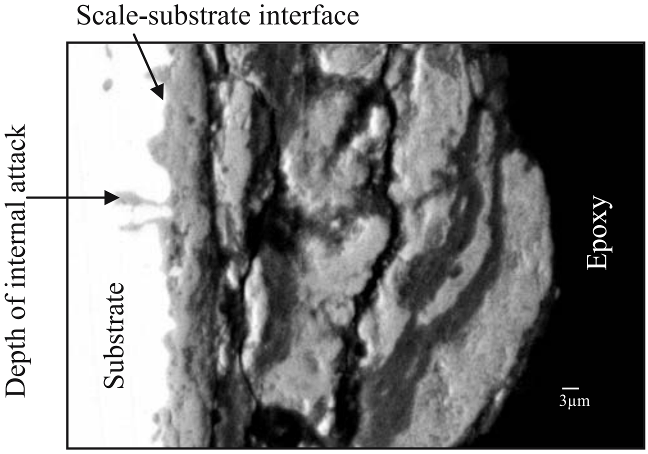

Figure 3. BSE image for the Superni-75 after 1000 h exposure to platen superheater zone of the coal-fired boiler at 900°C.

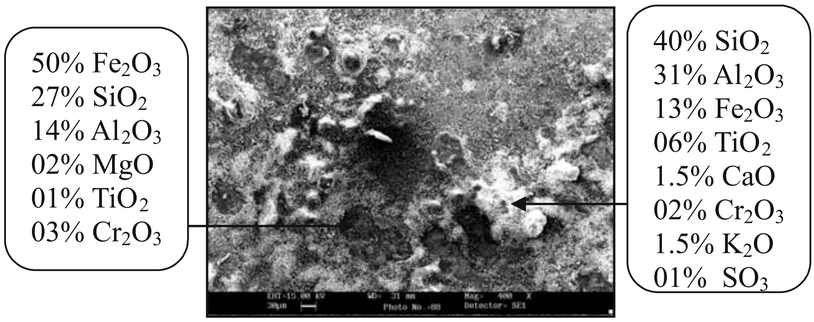

Figure 4. SEM/EDAX analysis showing elemental composition (wt.%) for the Superni-75 after 1000 h exposure to platen superheater zone of the coal-fired boiler at 900°C.

3.2 *X-ray diffraction analysis*

XRD analysis was performed on the corroded specimens to identify the various phases present on its surface. Diffraction patterns were obtained on a Bruker AXS D-8 Advance Diffractometer (Germany) with CuK_α radiation and nickel filter at 20 mA under a voltage of 35 kV. The specimens were scanned with a scanning speed of 1 Kcps in 2θ range of 10° to 110° and the intensities were recorded at a chart speed of 1 cm/min with 2°/min as Goniometer speed. XRD analysis showed the presence of Cr_2O_3, Fe_2O_3, Al_2O_3, FeS. and SiO_2 as the major phases. The presence of Al_2O_3 and SiO_2 phases are due to the deposition of ash particles in the outer layer of the scale.

3.3 *SEM/EDAX analysis of the scale*

3.3a *Surface analysis:* The SEM micrograph showing surface morphology of the scale formed on the Superni-75 is shown in figure 4. The black areas present on the surface of Superni-75 indicate that erosion of the scale has occurred during experimentations. The EDAX analysis shows that the white phase of the scale consists mainly of SiO_2, Al_2O_3, Fe_2O_3 and some amounts of TiO_2, Cr_2O_3, SO_3, CaO, MgO and K_2O. It is inferred that the composition of the white phase is almost similar to ash composition along with some other oxides of the scale. The spalled regions are found to be rich in Fe_2O_3, with SiO_2 and Al_2O_3 markedly decreased relative to white phase.

3.3b *Cross-sectional analysis:* The BSE image and EDAX analysis at some selected point of interest across the cross-section of corroded Superni-75 are shown in figure 5. About 45 μm thick corrosion scale formed on the bare Superni-75 has a duplex structure. The inner layer is continuous and adherent with the substrate, whereas adherence loss can be seen in the intermediate zone of the outer layer. EDAX analysis indicated that the inner layer (Point 3) contains mainly chromium, nickel and oxygen with small amounts of iron, titanium, and sulphur; and the outer layer (Points 4 and 5) exhibit presence of silicon, aluminium and oxygen-rich zones which indicate the interaction and deposition of ash particles with the outer scale. The Point 2 indicates the little penetration of oxide scale into the substrate. The EDAX analysis shows that this contrast grey phase (Point 2) consists mainly of Cr, which has increased, whereas Ni has decreased substantially in this phase. The existence of significant quantity of oxygen (42 wt%) points out that this gray phase is rich in Cr_2O_3.

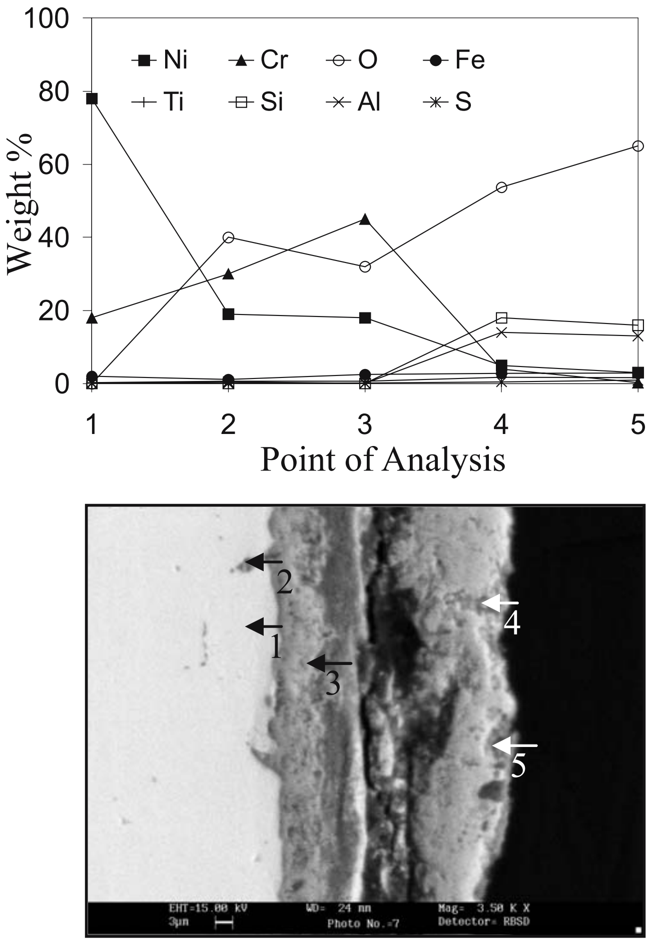

Figure 5. Oxide scale morphology and variations of elemental composition (wt%) across the cross section of Superni-75 after 1000 h exposure to platen superheater zone of the coal-fired boiler at 900°C.

3.4 *EMPA analysis*

BSE image and elemental X-ray maps for the Superni-75 after cyclic exposure to the given environment are shown in figure 6. The BSE image of the Superni-75 shows the penetration of oxide scale into the substrate to about 30 μm. Elemental maps show that the ash particles of Al, Si, K and Ca are present in the topmost part of the scale. Underneath of these deposits, Fe forms a nearly continuous thin layer, whereas Cr along with Ti forms a thick band. Titanium also shows a tendency to form clusters in the areas of internal attack, where Ni gets depleted.

4. Discussion

The (weight change/area)^2 graph indicates significant deviation from the parabolic rate law (insert in figure 1), as the surface scale is constantly removed due to erosion caused by fly ash and refurbished due to growth of the oxide scale from the base metal and fly ash. The weight change per unit area and (weight change/area)^2 verses time plots shown in figure 1 suggest that the mechanism of erosion–corrosion degradation is the main cause of failure of the boiler tubes used in the platen superheater zone of the boiler.

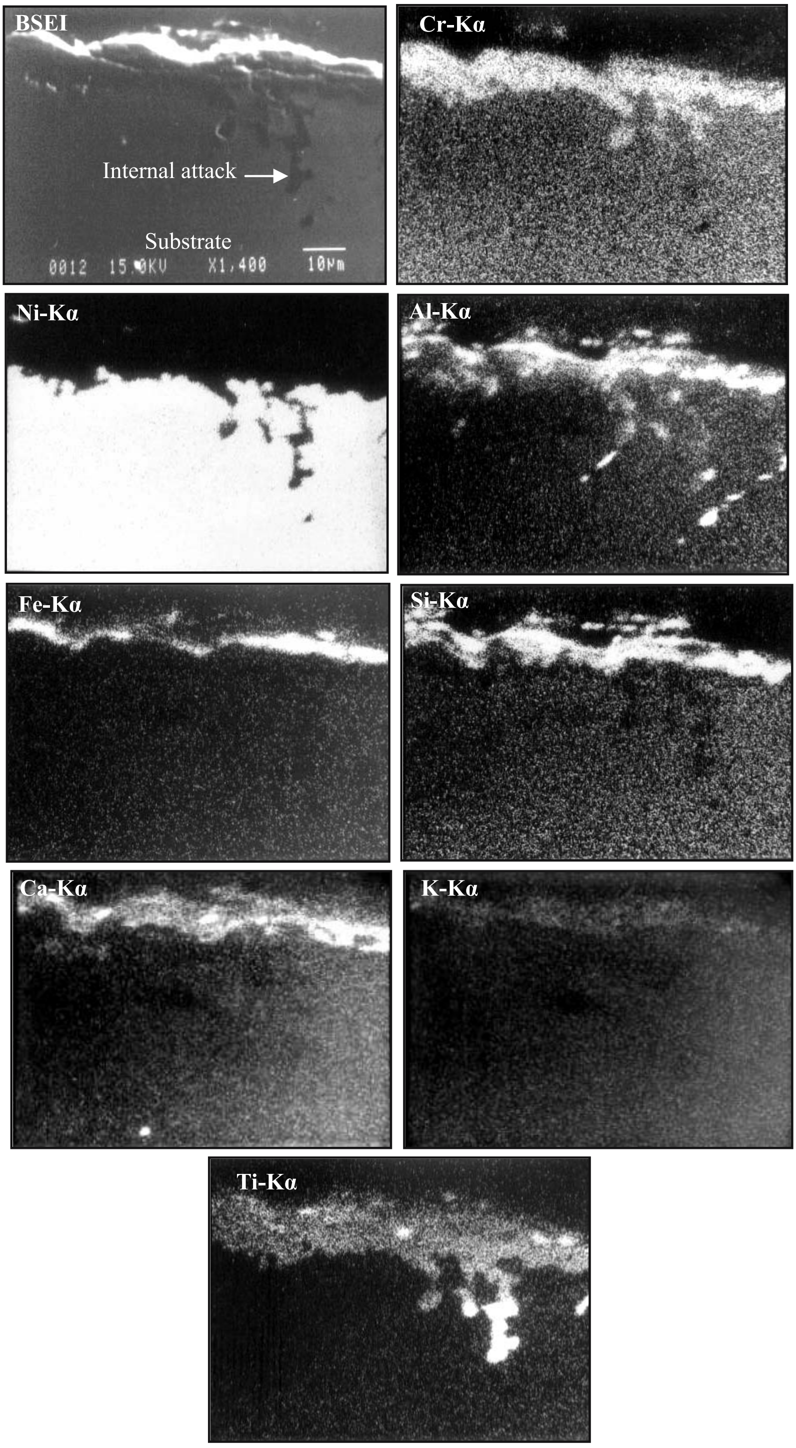

Figure 6. Composition image (BSEI) and X-ray mappings across the cross-section of Superni-75 after 1000 h exposure to platen superheater zone of the coal-fired boiler at 900°C.

The superalloy Superni-75 performed effectively in the boiler environment and has shown much less degradation, as there was only about 155 μm material thickness loss due to erosion–corrosion even after 1000 h of exposure in the coal-fired boiler environment under cyclic conditions. The erosion–corrosion rate for this superalloy is found to be about 53·46 mils per year, which is quite less than erosion–corrosion rate of about 378, 370, 338 mils per year for boiler steel grade GrA1, T11 and T22 respectively (Sundararajan *et al* 2003).

The XRD and EDAX analysis show the presence of ash deposits on the surface of the specimen, which are interacting with the oxide scale growing from the base metal. Cross-section EDAX analysis also indicates the presence of ash deposits, which is further confirmed by EPMA analysis. From these analyses, it can be inferred that the effect of corrosion is more prominent as compared to erosion in the platen superheater zone of the coal-fired boiler. The EPMA analysis indicates that the formation of a thick layer of chromium oxide has mainly contributed for the better erosion–corrosion resistance of Superni-75 during exposure to the real service environment of the coal-fired boiler. The mechanism of Cr_2O_3 formation in the nickel-based alloys is due to the fact that though both NiO and Cr_2O_3 are stable oxides at 1 atm pressure of oxygen, various factors, particularly thermodynamics and kinetics influence the overall scale development. Chromium has higher affinity for oxygen than nickel and forms more stable oxide. NiO is less stoichiometric oxide than Cr_2O_3. This thick layer of chromium oxide is responsible for blocking the penetration of degrading species from the boiler environment to the base alloy. This infers that the oxidation of nickel-based superalloy is solely based on the formation of Cr_2O_3. The threshold concentration required to form Cr_2O_3 is around 15%. In the present superalloy, the concentration of chromium is 19·5%.

5. Conclusions

(i) The nickel-based superalloy, Superni-75, is resistant to erosion–corrosion mode of degradation in the real service environment of the coal-fired boiler.
(ii) The formation of a continuous, regular and thick Cr_2O_3-rich band just above the scale-substrate interface has mainly contributed for better performance of the Superni-75 in the given environmental conditions. This thick oxide layer of chromium acts as diffusion barrier to the inward diffusion of corrosive species.
(iii) The effect of corrosion is more prominent as compared to erosion in the platen superheater zone of the coal-fired boiler.

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