

# Cyclic air oxidation studies on bimetallic combinations of AISI 4140 and AISI 316

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## Abstract

High temperature corrosion is one of the serious, vulnerable problems in the power generation and petrochemical industries. The bimetallic joints of AISI 4140 and AISI 316 is widely used in the aforementioned areas where the greater attention is required to overcome the problems associated with hot corrosion. This paper investigates the hot corrosion behaviour of AISI 4140 and AISI 316 weldments. These dissimilar metals were welded using Gas Tungsten Arc Welding (GTAW) and Pulsed Current Gas Tungsten Arc Welding (PCGTAW) employing ER309L filler wire. Cyclic air oxidation studies were performed on the various coupons of the weldments at 600 °C. The hot corroded products were revealed using the SEM/EDAX analysis.

**Keywords:** Dissimilar metal welding; Hot corrosion; Cyclic air oxidation; SEM/EDAX analysis

## 1. Introduction

Hot corrosion is an accelerated form of oxidation which occurs when metals are heated in the temperature range 700–900 °C in the presence of sulphate deposits formed as a result of the reaction between sodium chloride and sulphur compounds in the gas phase around the metals [Hancock \(1\)](#). [Prakash et al. \(2\)](#) have studied the boiler tube failure in coal fired boilers. A case study covering one-year duration has been conducted by them for a coal fired power plant in northwestern region of India. The number of failures occurred in the study year have been found to be 89 and out of which 50 failures were attributed to the hot corrosion and erosion of ash.

The bimetallic joints of low alloy steel and stainless steel are widely used in high temperature corrosive environments. [Shushan et al. \[3\]](#) and [Tiwari et al. \[4\]](#) reported that the dissimilar joints of low alloy steel and stainless steel are employed in the power generation industries where the weldments are prone to corrosion at the elevated temperatures. Bimetallic joints of low alloy steel and austenitic stainless steel are widely

used in fossil fuel boilers and fossil – fuel fired power generating equipments such as steam generators, water walls surrounding the furnace, economizer assemblies, and in the front and rear portions of the super heater and reheater are usually experience hot corrosion problems in these typical components [5–7]. Muthapandi et al. [8] reported that the micro-segregation which occurs in weld fusion zones of dissimilar metals leads to a situation where inter-dendritic regions are enriched in Fe, Cr and C. Also the segregation within the dendritic structure results in deterioration of the mechanical properties and corrosion resistance of the joints. It was reported by the various researchers [9–11] that a cyclic regime of 50 cycles (cycle of 1 h heating and 20 min cooling) is considered adequate for steady-state oxidation studies involving steel as it provides the severe conditions for oxidation tests. These conditions correspond to the actual industrial environment where breakdown/shutdown occurs frequently. Arivazhagan et al. (12) carried out the hot corrosion studies on the friction welded AISI 4140 and AISI 304 in air oxidation and in the molten salt environment at 650 °C. Further the authors reported that as suggested by Hurdus et al. (13), thermo-gravimetric curve for air oxidation studies showed the tendency of oscillation type reaction and this should be due to changes in reaction rate which are associated with the formation of a laminated inner-oxide layer made up of fine and coarse grain spinel.

As evident from the open literatures, the bimetallic combinations of AISI 304 and AISI 316 have typical applications in the adverse corrosion prone environments. Hitherto no specific work has been carried out on these bimetallic joints. This paper investigates on hot corrosion behavior of GTA and PCGTA welded AISI 4140 and AISI 316 employing ER309L filler wire. The hot corrosion products were systematically characterized using the combined techniques of optical microscopy and SEM/EDAX analysis. The results of this research work will be highly beneficial to the industries employing these bimetallic combinations.

## 2. Experimental Procedure

The chemical composition of the base metals such as AISI 4140, AISI 316 and the filler metal ER 309L is represented in Table 1. The base samples were cut to 100 mm x 50 mm x 5 mm using wire-cut EDM process before welding. Also the parent metal AISI 4140 is pre-heated to 150 °C before welding. Bead on plate welding was carried out by varying the current to optimize the weld parameters adopted in this study. The process parameters employed in this study is listed in Table 2.

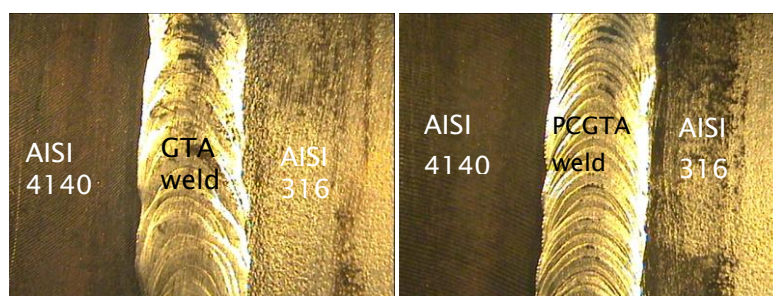
Metallographic examination on the composite region [parent metals + weld + HAZs] was carried out after polishing with emery sheets of SiC with grit size varying from 220 to 1000 and followed by disc polishing using alumina and water to obtain a mirror finish of  $1\mu$  on the surface weldments. Nital (5 % Con. HNO<sub>3</sub> and 95% distilled water) was used to examine the microstructure of AISI 4140 whereas a mixture containing hydrochloric acid nitric acid and acetic acid (at 3:1:1 ratio) was employed on AISI 316 side to reveal the microstructure of the weldments. The welded samples were further sliced according to ASTM E8 standards to assess various mechanical properties obtained from both destructive and non-destructive tests. Coupons used for corrosion studies were mirror polished down to  $1\mu$  before the corrosion run. Cyclic hot corrosion studies were performed on the different regions of the welded samples exposed under air oxidation at 600°C. These corrosion studies were performed on the different regions of dissimilar welded samples of AISI 4140 and AISI 316 each measuring 10 mm x 10 mm x 5 mm; also on the composite region [Base Metal + HAZ + Weld] measuring 30 mm x 10 mm x 5 mm to estimate the corrosion behaviour for 50 cycles (each cycle consists of 1 hour heating followed by 20 minutes of cooling to room temperature). The weight changes have been measured for all regions for each cycle using electronic weighing balance with a sensitivity of 1 mg. The weight gain or loss of the spalled scale was also included at the time of measurement to determine the rate of corrosion. The corroded samples of various regions were characterized for XRD and SEM/EDAX analysis.

### 3. Results

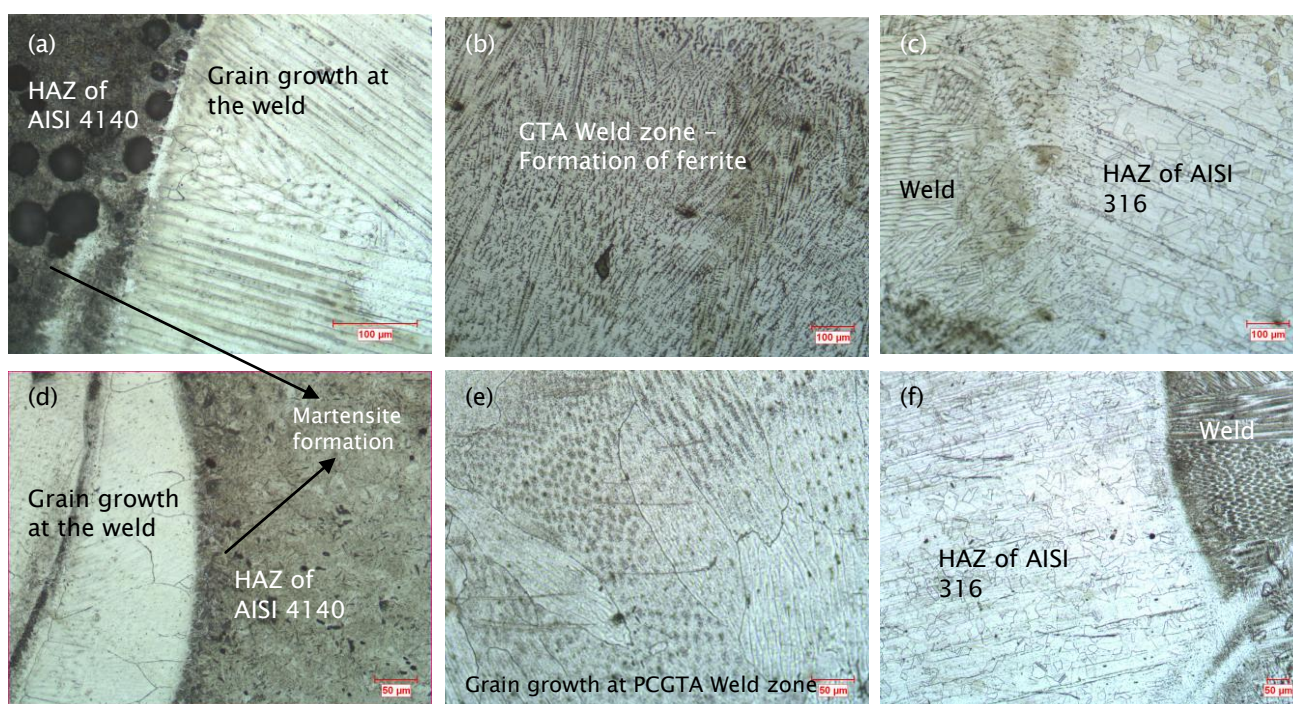
#### 3.1 Macro and Micro-structure Examination

Macro-structure studies on the GTA and PCGTA weldments shown in Fig.1 clearly inferred that the proper fusion had occurred on the base metals while employing ER 309L filler and NDT analysis also confirmed that no macroscopic and microscopic defects were obtained on the GTA and PCGTA weldments of AISI 4140 and AISI 316. Micro-structure examination on the GTA and PCGTA welded coupons revealed the formation of needle shaped acicular martensite at the HAZ of AISI 4140 on both the weldments. This could be probably due to the higher heat inputs developed during the welding and also due to the low cooling rates. However the martensite observed on the GTA weldments were appeared to be lath type; whereas in PCGTA weldments, uniform sized, fine clusters of martensite were observed. The weld interface of the PCGTA weldments at AISI 4140 side has the formation of columnar austenite grains. This is in agreement with the work of other researchers [10].





**Fig. 1 Photo–Macrograph of the GTA and PCGTA weldments of AISI 4140 and AISI 316 employing ER 309L filler**



**Fig. 2 Microstructure of the various zones of the GTA weldments (a, b, c) and PCGTA weldments (d, e, f) employing ER 309L filler metal**

### 3.2 SEM/EDAX analysis on the as-welded samples

SEM/EDAX analyses were performed on the various zones of both GTA and PCGTA weldments to understand the elements present in the various zones of the weldments. It is well understood that the HAZ of AISI 4140 of GTA and PCGTA weldments has significant amounts of Fe, Cr and C. Nickel is found almost absent in HAZ of AISI 4140 GTA and PCGTA weldments. The weld region and the HAZ of AISI 316 are enriched with the presence of Fe, Cr and Ni in both the cases. It was evident that the carbon migration from carbon steel to

stainless steel weld metal will be higher on using a filler metal contains more chromium [12, 13]. The presence of higher amounts of Cr and C at the weld interface of AISI 4140 contribute for the precipitation of chromium carbides and due to the higher inputs in GTAW and rapid cooling rates result in the formation of lath and coarse martensite at the HAZ of AISI 4140. The next chapter describes in detail on the hot corrosion behavior of the dissimilar weldments of AISI 4140 and AISI 316

### 3.3 Hot Corrosion

#### 3.3.1 Visual Examination

Visual examination on the hot corroded samples clearly showed that a slight blackish oxide layer formed on the parent metal of AISI 4140 at the end of 5<sup>th</sup> cycle. This black oxide layer turned to brown tarnish color during the course of the corrosion run and at the end of 50<sup>th</sup> cycle, orange reddish layer was formed on the parent metal of AISI 4140. The greyish spots formed on the HAZ of AISI 4140 on the GTA weldments continued to grow and turned to dark reddish spots at the end of the corrosion whereas the HAZ of AISI 4140 on the PCGTA weldments showed a scale of greyish black color was formed. The weld region of GTA weldments typically shown a bluish red color spots which originated from 1<sup>st</sup> cycle and at the end of 5<sup>th</sup> cycle, multi-color spots were pronounced on the entire sample and continued till 50<sup>th</sup> cycle. Whereas the weld region of PCGTA weldments had shown slight blue tarnish color spots at the end of 5<sup>th</sup> cycle and tarnished to black from 10<sup>th</sup> cycle and retained till the end of corrosion. Black spots in the golden yellowish background is formed on the HAZ of AISI 316 of GTA weldments at 5<sup>th</sup> cycle and turned to greyish from 6<sup>th</sup> cycle and became blackish from 10<sup>th</sup> cycle till the end of the corrosion run.

#### 3.3.2 Thermogravimetric Analysis

The corrosion kinetics of specimens in the air oxidation is depicted in [Fig. 2](#) as a plot of weight gain per unit area vs. function of time (number of cycles). These figures indicate that the weight gain kinetics under air oxidation shows a steady-state parabolic rate law. In case of GTA weldment employing filler ER309L, all the zones showed minor weight changes with small fluctuations. And it is observed that, from 12<sup>th</sup> cycle onwards there is a weight gain in all the zones continued till the end of the cycle. The thermogravimetric graph showed that the weld zone is more oxidation resistance as compared to the other zones. In case of PCGTA weldment employing filler ER309L, the HAZ of AISI 4140 shows a lot of fluctuations with a trend of increase in weight gain from the beginning till the end of the cycles and the thermogravimetric graph showed that HAZ of AISI 4140 has been more prone to corrosion

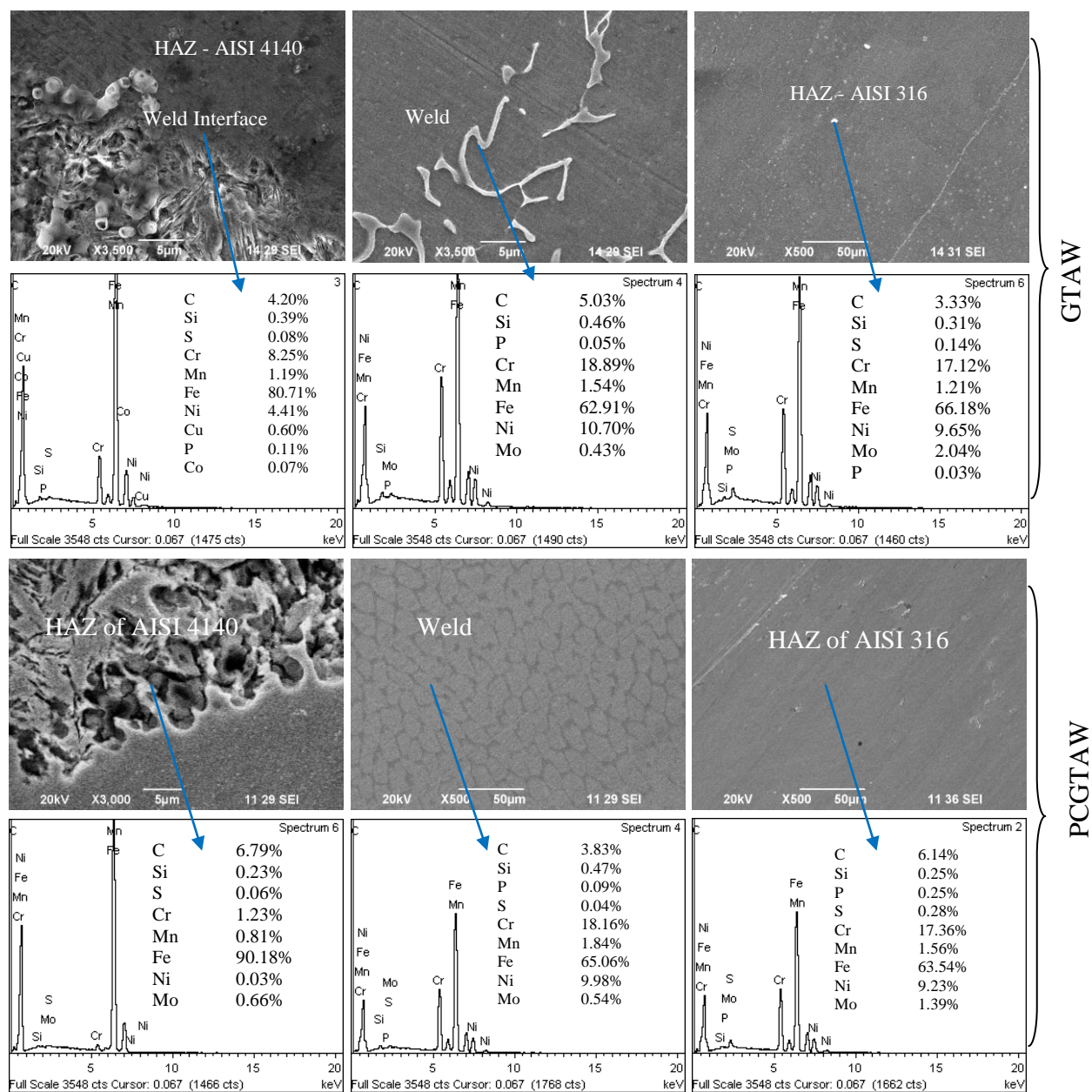
than the PM of AISI 4140. The HAZ of AISI 316 had shown better corrosion resistance and on the safe side which has maintained the uniformity and below the horizontal axis stating that which has better resistance to oxidation at 600 °C

### 3.3.3 SEM/EDAX analysis on the hot corroded samples

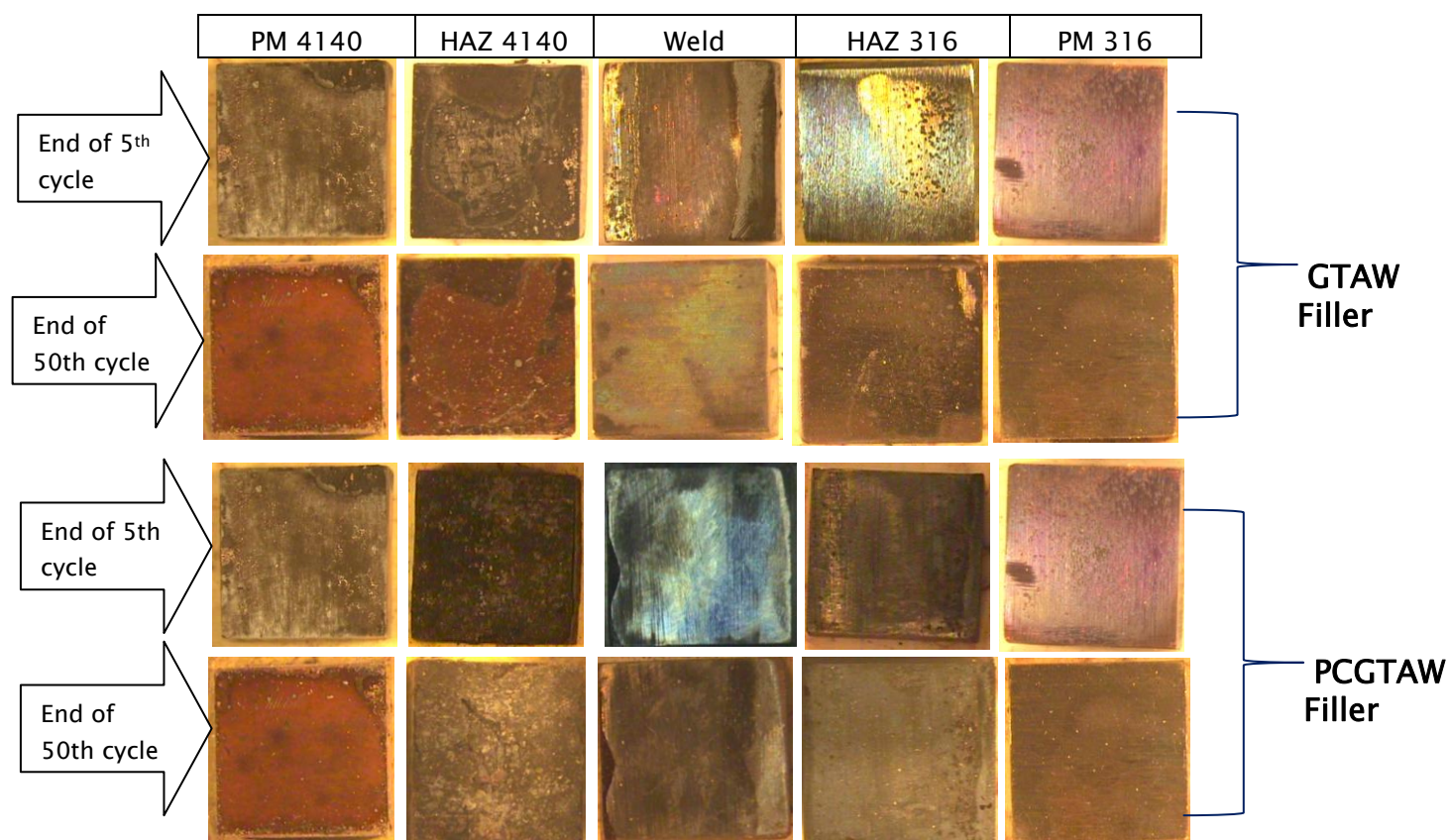
SEM/EDAX analysis of the hot corroded GTA and PCGTA weldments employing ER309L filler wire clearly depicted the formation of predominant oxide scales such as  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{NiO}$  on the HAZ of AISI 316 and weld zones. Nominal weight gain has occurred till 10th cycle across all the zones of the GTA weldments. At the end of 11th cycle, vigorous weight gain has been observed in all the zones of the GTA weldments.

Similarly in the PCGTA weldments, the formation of the major oxides including  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{MnO}$  at the HAZ of AISI 316, parent metal of AISI 316 and the weld region had been witnessed. The HAZ of AISI 4140 and parent metal side of AISI 4140 has shown least corrosion resistance towards air oxidation. Spallation is also observed at these zones as indicated in the visual examination. In specific, the weld zone of the PCGTA weldments were found to be better in terms of corrosion resistance compared to the weld zone of the GTA weldments (Fig. 5).





**Fig. 3 SEM/EDAX analysis on the GTA and PCGTAW weldments in the as-welded conditions**



**Fig.4 Macrographs of the corroded samples of GTA and PCGTA weldments employing ER309L filler subjected to air oxidation at 600° C**



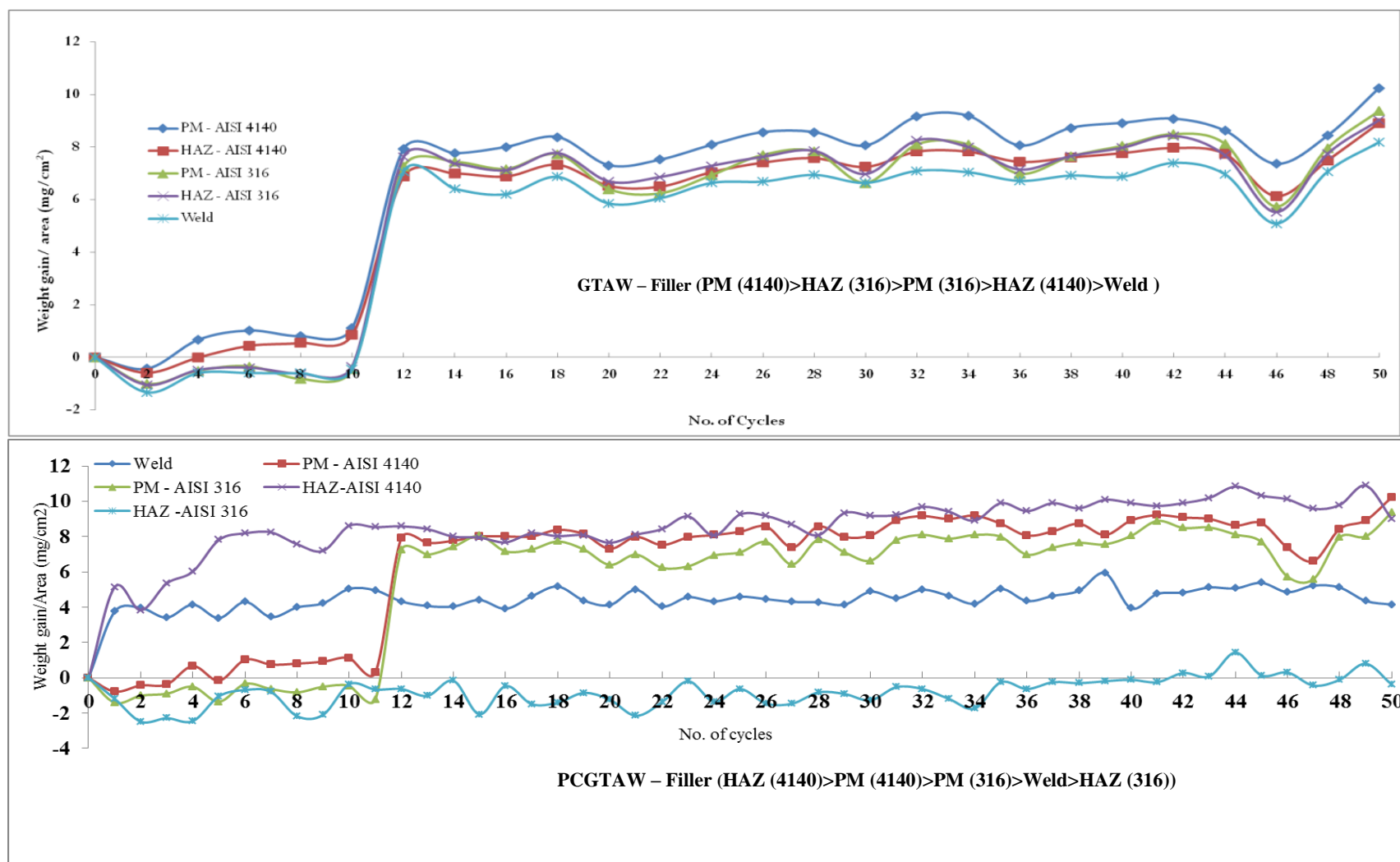
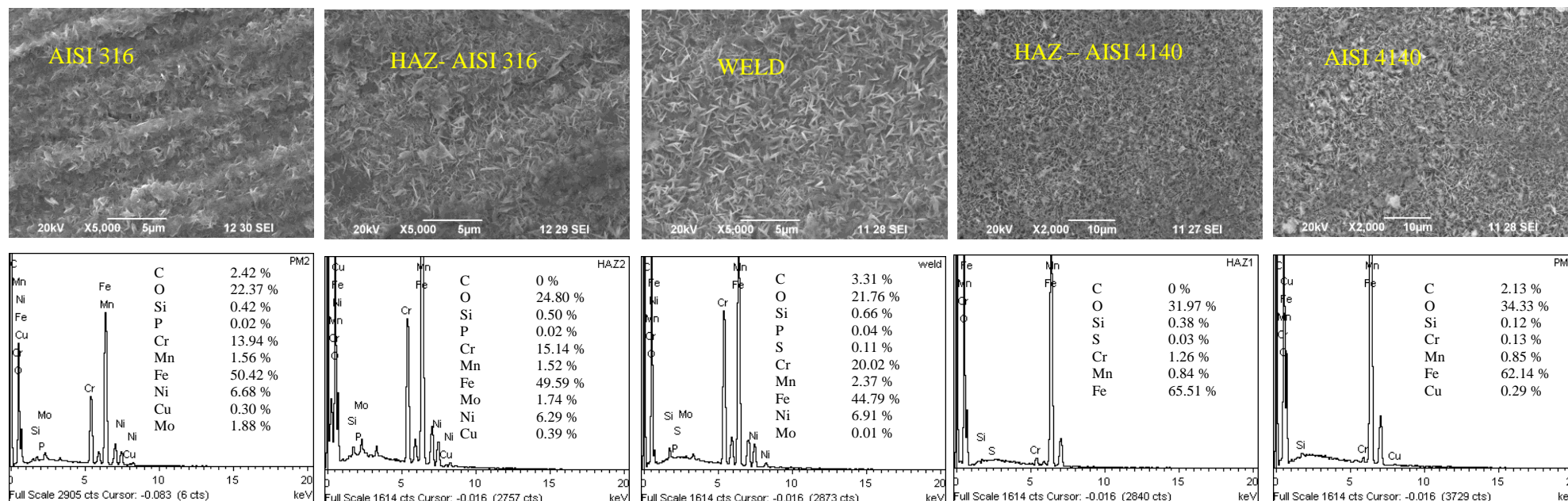
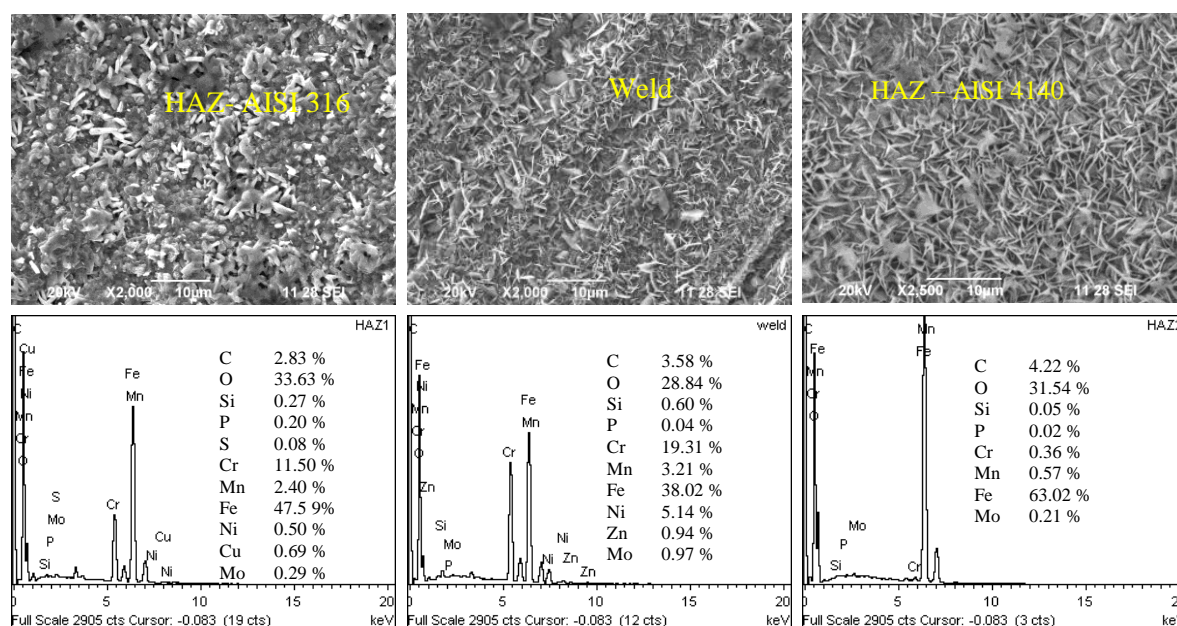


Fig. 5 Thermogravimetric analysis of the weldments subjected to Air Oxidation at 600° C (a) GTA (b) PCGTAW weldments employing ER309L filler wire.



**Fig. 6 SEM/EDAX for PCGTA weldment employing filler under Air Oxidation at 600° C for 50 cycles**



**Fig. 7 SEM/EDAX for GTA weldment employing filler under air Oxidation at 600° C for 50 cycles**

## 5. Discussions

It is a well known fact the constituent Nickel is a good austenite stabilizing element and also evident from the SEM/EDAX analysis that the Ni constituent is found to be less at the HAZ of AISI 4140 and hence the martensite formation is favored in both the weldments; whereas the presence of Ni at the HAZ of AISI 316 is greater and favored for the formation of austenite columnar grains. Also due to the pulsing of current, heat input is controlled which resulted in the formation of fine, uniformly dispersed high carbon content martensite at the HAZ of AISI 4140 (Fig. 2). On the other hand, the columnar austenite growth is witnessed at the weld interface with equiaxed austenite grains at the center of the weld at AISI 316 side. This result is also in agreement with the work carried out by other researchers [10].

Thermogravimetric analysis revealed the formation of  $\text{Cr}_2\text{O}_3$  at the HAZ of AISI 4140, which are found to be very lower in both the weldments. It is also evident that the protective layer  $\text{NiO}$  is almost absent in the parent metal and HAZ of AISI 4140. Similarly the protective oxide scale  $\text{Cr}_2\text{O}_3$  is found almost in lower traces in the parent metal and HAZ of AISI 4140. It is also witnessed that the weight gain is almost higher in case of the HAZ of AISI 316 and it is evident that the HAZ of AISI 316 has lesser amounts of Cr and Ni as indicated in the SEM/EDAX analysis. Weld zone of the GTA weldments showed better oxidation resistance



and this could be probably due to the enrichment of the oxide layers of NiO and Cr<sub>2</sub>O<sub>3</sub> as reported from the SEM/EDAX analysis.

This SEM/EDAX results confirmed that due to the absence of these high protective oxide layers, the weight gain is vigorous in the aforementioned zones of the weldments. The increase in the weight gain is due to the spallation of the oxide layers which in turn provide the porous zones in the weldments and the oxygen has been trapped inside during the corrosion run. In case of PCGTA weldments, the HAZ of AISI 316 weldments offered better oxidation resistance owing to the formation of Cr<sub>2</sub>O<sub>3</sub>, NiO, Fe<sub>2</sub>O<sub>3</sub> and MoO

## Conclusions

The major conclusions obtained from the research work are reported as follows:

- [1] Successful, defect free dissimilar welding of AISI 4140 and AISI 316 could be obtained by both GTA and PCGTA welding process employing ER309L filler metal using the process parameters as shown in Table 2.
- [2] Martensite formation is prominent at the HAZ of AISI 4140 in all the cases
- [3] From the SEM/EDAX analysis, it is understood that the formation of protective predominant oxide scales such as Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, NiO on the HAZ of AISI 316 and weld zones of the hot corroded GTA and PCGTA weldments
- [4] The corrosion resistance of the various zones of the PCGTA Weldments employing ER 309L filler could be sequentially arranged as follows:

**HAZ of AISI 316 > Weld > Parent metal AISI 316 > Parent metal AISI 4140 > HAZ of AISI 4140**

- [5] Similarly the corrosion resistance of the various zones of the GTA Weldments employing ER 309L filler could be sequentially arranged as follows:

**Weld > HAZ of AISI 4140  $\cong$  Parent metal AISI 316 > HAZ of AISI 316 > Parent metal AISI 4140**

## References

1. 'Vanadic and Chloride Attack of Superalloys', *Hancock, P.*, (1987), Mater.Sci. Technol., Vol. 3, pp. 536–44.

2. 'Tube Failures in Coal Fired Boilers', *Prakash, S., Singh, S., Sidhu, B. S. and Madeshia, A.*, (2001), Proc. National Seminar on Advances in Material and Processing, 9–10<sup>th</sup> Nov., IIT, Roorkee, India, pp. 245–53.
3. 'The Environment Assisted Cracking Of Diffusion Bonded Stainless Steel To Carbon Steel Joints In An Aqueous Chloride Solution', *Shushan S.M, Charles E. A and Congleton J.*, (1996), corrosion science, vol. 38, No 5, pp 673.
4. 'Hot Corrosion Behaviour of an Iron–Base Superalloy in Salt Environment at Elevated Temperatures,' *Tiwari, S. N. and Prakash, S.*, (1996), Proc. of Symp. on Metals and Materials Research, IIT, Madras, 4–5<sup>th</sup> July, pp. 107–17.
5. 'Corrosion in Power Generating Equipment', *G.J. Theus and P.L. Daniel*, (1983), Proc. 8 The International Brown Boveri Symposium, Baden, Switzerland, p.185.
6. 'Corrosion Estimating of Chemical Cleaning Solvents", NACE publication, Material Performance' *NACE*, (1982), "3M: 182
7. 'Materials of construction for steam power plants' *Wyatt L.M*, (1982), , ISBN 085334 661 5, London,.
8. 'Effect of weld metal chemistry and heat input on the structure and properties of duplex stainless steel welds', *Muthupandi, V., Bala Srinivasan, P., Seshadri, S.K., Sundaresan, S.* (2003), , Materials Science and Engineering, A358, p9
9. 'Mechanism of oxidation of dilute nickel–chromium alloys', *G.C. Wood, T. Hodgkiss*, Nature, 211 (1996), pp. 1358–1361
10. 'Evaluation of the corrosion behavior of plasma–sprayed Ni<sub>3</sub>Al coatings on steel in oxidation and molten salt environments at 900 °C', *B.S. Sidhu, S. Prakash* Surf Coat Technol, 166 (2003), pp. 89–100
11. 'Some studies on hot corrosion performance of plasma sprayed coatings on a Fe–based superalloy', *H. Singh, D. Puri, S. Prakash*, Surf Coat Technol, 192 (1) (2005), pp. 27–38

12. High temperature corrosion studies on friction welded low alloy steel and stainless steel in air and molten salt environment at 650 °C', *N. Arivazhagan S. Narayanan, Surendra Singh, Satya Prakash, G.M. Reddy*, Materials & Design Vol. 34, February 2012, Pages 459–468
13. 'Observation of oscillating reaction rates during the isothermal oxidation of ferritic steels', *M.H. Hurdus, L. Tomlinson, J.M. Tichmarsh* Oxid Metals, 34 (1990), p. 5