JMEPEG (2007) 16:620–625
DOI: 10.1007/s11665-007-9118-z

Corrosion Behavior of Pulsed Gas Tungsten Arc Weldments in Power Plant Carbon Steel

S.P. Kumaresh Babu and S. Natarajan

(Submitted April 7, 2006; in revised form August 28, 2006)

Welding plays an essential role in fabrication of components such as boiler drum, pipe work, heat exchangers, etc., used in power plants. Gas tungsten arc welding (GTAW) is mainly used for welding of boiler components. Pulsed GTAW is another process widely used where high quality and precision welds are required. In all arc-welding processes, the intense heat produced by the arc and the associated local heating and cooling lead to varied corrosion behavior and several metallurgical phase changes. Since the occurrence of corrosion is due to electrochemical potential gradient developed in the adjacent site of a weld metal, it is proposed to study the effects of welding on the corrosion behavior of these steels. This paper describes the experimental work carried out to evaluate and compare corrosion and its inhibition in SA 516 Gr.70 carbon steel by pulsed GTAW process in HCl medium at 0.1, 0.5, and 1.0 M concentrations. The parent metal, weld metal and heat affected zone are chosen as regions of exposure for the study made at room temperature (R.T.) and at 100 °C. Electrochemical polarization techniques such as Tafel line extrapolation (Tafel), linear polarization resistance (LPR), and ac impedance method have been used to measure the corrosion current. The role of hexamine and mixed inhibitor (thiourea + hexamine in 0.5 M HCl), each at 100 ppm concentration is studied in these experiments. Microstructural observation, surface characterization, and morphology using SEM and XRD studies have been made on samples exposed at 100 °C in order to highlight the nature and extent of film formation.

Keywords power plant carbon steel, corrosion testing, pulsed GTA welding

1. Introduction

Gas tungsten arc welding (GTAW) can be used to weld all types of carbon steel, stainless steel, and nonferrous metal pipes used in aircraft, atomic energy and power generation industries. In thick-walled pipes and tubing the control of weld pool is important particularly for depositing the root runs. GTAW normally with filler metal is often used for this purpose in pipework required for high-pressure steam lines. Pulsed GTAW welding is another advanced version of GTAW where the welding current is supplied in pulses rather than at a constant magnitude. This gives better stability of the arc through which controlled heat input is possible. Heating and fusion take place during the pulse current periods while cooling and solidification take place during background current periods. The advantages (Ref 1) claimed through pulsing are: (a) There is very little distortion or warpage on thin materials; (b) easy to weld dissimilar metals or same metal with different thicknesses; (c) laying of root run in pipe welding; and (d) for a given average current level, greater penetration can be achieved with steady current which is useful on metals sensitive to heat input. One set of welding variables can be used on a joint in all positions such as circumferential welds in tube-to-tube sheet welding.

In all arc-welding processes (Ref 2-4), the intense heat source produced by the arc and the associated local heating and cooling result in a number of consequences in material corrosion behavior and several metallurgical phase changes occur in different zones of a weldment. Since the occurrence of corrosion is due to electrochemical potential gradient developed in the adjacent site of a weld metal, it is proposed to study the effects of welding on the corrosion behavior of these steels. The fossil fuel-fired boilers (Ref 5-7) and power generating equipment experience corrosion problems in components such as steam generators, waterwalls surrounding the furnace, and in front and rear portions of the superheater and reheater. These components are often made of carbon and low-alloy steels. The water used for steam raising in any boiler installation often contain gaseous impurities (Ref 5) and dissolved solids. These can cause scaling and corrosion in the boiler plant. Apart from these, some of the inorganic salts may hydrolyze to produce acidity causing corrosion of boiler tubes.

This article describes an experimental work carried out at room temperature (R.T.) and 100 °C to evaluate and compare corrosion and its inhibition of SA 516 Gr.70 carbon steel weldments prepared by pulsed GTAW process in HCl acid medium. Organic compounds such as hexamine and thoiurea were used as inhibitors for the prevention of corrosion. In the present study, hexamine, thiourea, and mixture of these two each at 100 ppm concentration was individually employed as inhibitor. SEM and XRD analyses were also made on samples exposed at 100 °C.

S.P. Kumaresh Babu, Assistant Professor, and **S. Natarajan,** Professor are with Department of Metallurgical and Materials Engineering, National Institute of Technology, Tiruchirappalli, 620015, Tamilnadu, India. Contact e-mail: drs_natarajan@yahoo.com.

2. Experimental Work

2.1 Preparation of Weldments

Carbon steel in plate form was welded by pulsed GTAW process and it was stress relieved at 630 °C. The studies were made using small coupons measuring 90×8 mm cut from the plate comprising parent metal and weld metal plus narrow HAZ as composite regions.

2.2 Corrosive Medium and Inhibitor

HCl acid solutions of 0.1, 0.5, and 1.0 M concentrations were prepared using analar grade materials. Hexamine at 100 ppm was used as the inhibitor throughout the study. The role of mixed inhibitor (thiourea + hexamine in 0.5 M HCl) each at 100 ppm concentration was also studied separately at high temperature experiments. Each test coupon was surface polished using conventional methods (degreasing, polishing with emery papers of various grades, etc.). Except the desired area of regions of exposure, the other regions were masked using Teflon. Studies were made both at R.T. and at 100 °C .The HAZ was identified by macroetching.

2.3 Electrochemical Polarisation Studies

All studies were made using Model-362 scanning potentiostat (Princeton Applied Research Corp., Princeton, NJ). The studies were made at R.T. and at 100 °C in the absence and presence of inhibitor mentioned above. The following techniques were adopted to find I_{corr} values.

2.4 Tafel Line Exploration

Applications of potential upto ±150 mV from open circuit potential (OCP) were made for Tafel method and a plot of E vs. log i was made in all the experiment and tangents were drawn which on extrapolation to E_{corr} intersected at a point that represented on the X axis, the I_{corr} value.

2.5 Linear Polarization Resistance (LPR)

The open circuit potential in each case was observed after the system became stable at least for 30 min. Accordingly the OCP up to 20 mV potentials were applied in a discrete fashion in increments of 2 mV and corresponding current was read. A plot of E vs. I was made. It was found to be linear almost in all cases. From the above plot, R_p was calculated. I_{corr} values were obtained using the formula

$$I_{corr} = b_a \cdot b_c / 2.303(b_a + b_c) \cdot 1/R_p,$$

where $R_p = \Delta E/\Delta I$, b_a, b_c values were obtained from the Tafel line extrapolation method as described above.

2.6 Impedance Measurements

The well-polished electrode was introduced into 200 mL of deaerated test solution and allowed to attain steady potential values. AC signals were impressed into the system with frequencies ranging from 0.1 to1 kHz. The values of R_s, R_t and C_{dl} were obtained from the plot of the real part (Z') vs. the imaginary part (Z''). The above measurements were made using an electrochemical impedance analyzer.

The values of I_{corr} were obtained by substituting for R_t in Stern-Geary equation.

$$I_{corr} = b_a \cdot b_c / 2.303(b_a + b_c) \cdot 1/R_t$$

2.7 SEM Analysis

Studies on the surface morphologies of carbon steel samples were carried out for the weld root and HAZ region exposed to 0.5 M HCl concentration at 100 °C containing the hexamine inhibitor at 100 ppm level.

2.8 XRD Studies

A computer-controlled wide-angle X-ray diffractometer system JEOL (Japanese make) model; JDX 8030 using Cu-Kα radiation and λ = 1.5418 Å (Ni filter) with a scanning range 3°–65°–2θ was used to investigate the weld region of the specimen.

3. Results and Discussion

The chemical composition and mechanical properties, weld metal chemical analysis, and welding conditions for the SA 516 Gr.70 carbon steel are given in Table 1-3.

3.1 Selection of Electrochemical Technique

The values of I_{corr} for the different electrochemical techniques are given in Table 4 and 5. The Tafel technique shows the maximum corrosion rate in both PM and (WM + HAZ) regions at room temperature and 100 °C.

3.2 Effect of Acid Concentration

The parent metal, (WM + HAZ) all exhibit increase in corrosion rate with respect to the increase in acid concentration. Previous researchers (Ref 8-10) have also found the same trend.

Table 2 Welding parameters for pulsed GTAW process

Parameters	Values
Pulse current (I_p)	180 A
Background current (I_b)	50 A
Voltage (V)	10 V
Pulse frequency	2-7 Hz
Travel speed	100 mm/min
Shielding gas	Argon

Table 1 Chemical composition, mass contents in % and mechanical properties, MPa for SA516 Gr.70 steel

Element	C	Mn	Si	P	S	Mo	Cu	T.S	Y.S
Base metal	0.27	0.85-1.20	0.15-0.40	0.035 max	0.035 max	0.15	0.40	485.0	275.0
Filler wire	0.105	1.41	0.47	0.017	0.01	0.01 max	0.01 max	480.0	400.0

Table 3 **Chemical analyses of weld metal and base metal in SA 516 Gr.70 carbon steel-pulsed GTA weldments**

Sample ID	C	Mn	Si	S	P	Cr	Ni	Mo	Cu
BM	0.09	0.88	0.10	0.033	0.025	<0.10	<0.10	<0.05	<0.10
WM	0.03	0.96	0.25	0.020	0.032	<0.10	<0.10	<0.10	<0.10

Table 4 **I_{corr} in mA/cm^2 at R.T. for CS/pulsed GTAW/HCl/hexamine**

		Parent metal (PM)		(WM+HAZ)	
Concentration of HCl		Tafel	LPR	Tafel	LPR
0.1 M	WOI	1.50	0.97	1.15	0.40
	WI	1.05	0.65	1.32	0.41
	PIE	(30.0)	(33.0)	(IAC)	(IAC)
0.5 M	WOI	5.06	2.5	2.81	0.66
	WI	3.09	0.96	3.65	0.79
	PIE	(34.0)	(61.6)	(IAC)	(IAC)
1.0 M	WOI	7.05	1.87	4.85	1.16
	WI	3.24	0.36	5.99	0.75
	PIE	(54.0)	(81.0)	(IAC)	(35.3)

Note: PIE—Percentage Inhibitor efficiency; ( )—PIE for pulsed GTAW process; WoI—without inhibitor; IAC—Inhibitor accelerates corrosion; WI—with Inhibitor

Table 5 **I_{corr} in mA/cm^2 at 100 °C for CS/pulsed GTAW/HCl/hexamine**

		Parent metal		(WM+HAZ)	
Concentration of HCl		Tafel	LPR	Tafel	LPR
0.1 M	WoI	1.7	1.66	1.6	1.21
	WI	3.0	1.25	1.1	1.06
	PIE	(IAC)	(24.6)	(31.2)	(12.4)
0.5 M	WoI	5.0	2.1	4.4	3.6
	WI	3.6	4.32	1.7	1.42
	PIE	(28.0)	(IAC)	(61.3)	(60.5)
1.0 M	WoI	10.0	4.1	4.6	1.95
	WI	3.6	1.03	2.0	2.2
	PIE	(64.0)	(74.8)	(65.0)	(IAC)

3.3 Influence of Welding Process, Microstructure, and Hardness

The (WM + HAZ) composite region shows minimum corrosion current compared to parent metal, which indicates that pulsed GTAW process is beneficial to carbon steel. The microstructures of PM, WM, HAZ, and hardness plot are shown in Fig. 1-4. The weld metal microstructure predominantly consists of acicular ferrite, bainite, and peartlite. The microstructure of HAZ shows the presence of widmanstatten ferrite and peartlite. The controlled heat input of pulsed GTAW process leads to the formation of acicular ferrite in the weld metal region. It is in this morphology of ferrite the surface area exposed to the corrosive atmosphere is less and also the presence of bainite in the weld metal region leads to less corrosion damage (Ref 11, 12). At this juncture it will be worthwhile to compare the earlier work of Natarajan et al. (Ref 13), wherein it is found that weld root region corrodes less than other regions.

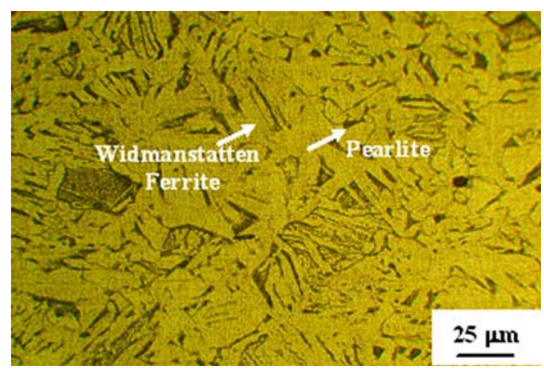

Fig. 1 Microstructure of HAZ consisting of widmanstatten ferrite and pearlite

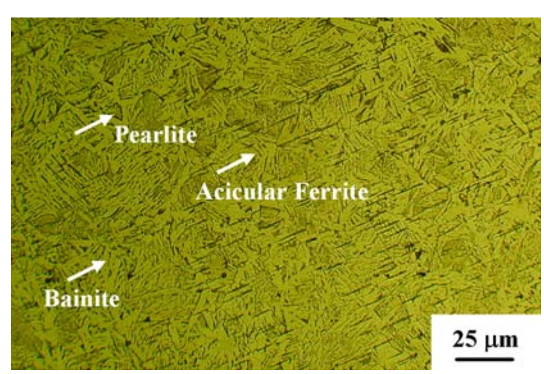

Fig. 2 Microstructure of WM consisting of acicular ferrite, bainite, and pearlite

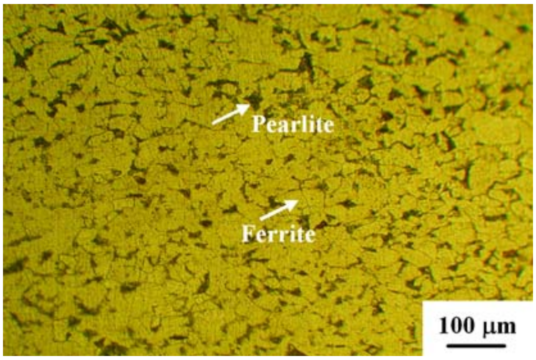

Fig. 3 Microstructure of PM consisting of ferrite and pearlite

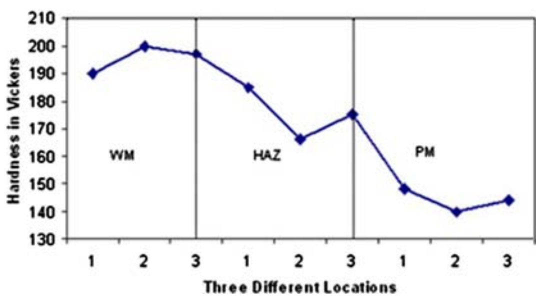

Fig. 4 Hardness survey for carbon steel-pulsed GTA weldments

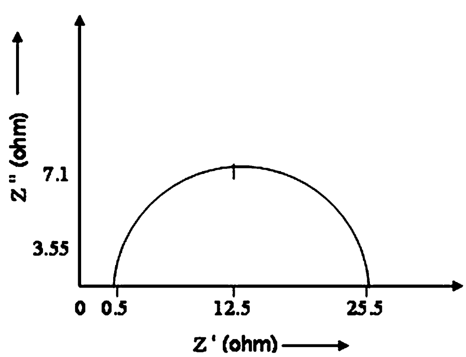

Fig. 5 Impedance plot for pulsed GTAW/(WM+HAZ)/CS/0.5 M HCl+hexamine

The weld metal chemistry and the hardness values are not significantly influencing the corrosion parameters under test conditions.

3.4 Role of Inhibitor

Hexamine: It is the weld root region which always carries the corrosive fluid during the operation of any plant. Hexamine shows 35.3% efficiency at R.T. and 65.0% efficiency at high temperature (100 °C) for (WM + HAZ) whereas for parent metal region it shows 81.0% efficiency at R.T. and 74.8% at high temperature (100 °C).

Thiourea: The I_{corr} values are given in Table 6. An efficiency of 44.8% efficiency is shown by thiourea for the WM + HAZ region at 100 °C and 80.6% efficiency at R.T.

Table 6 I_{corr} **in mA/cm^2 for CS/pulsed GTAW/0.5 M HCl/thiourea/mixed inhibitor**

Concentration of HCl		R.T. (WM+HAZ) Tafel	R.T. (WM+HAZ) LPR	100 °C (WM+HAZ) Tafel	100 °C (WM+HAZ) LPR
0.5 M	WOI	2.81	0.66	4.4	3.6
	WI (thio)	1.55	0.70	0.9	0.86
	PIE	(44.8)	IAC	(79.5)	(76.1)
	WI (mixed)	1.60	0.33	0.85	0.42
	PIE	43.0	58.4	80.6	88.3

Table 7 Comparison of PIE for 0.5 M HCl at R.T. and 100 °C for hexamine, thiourea and mixed inhibitor for (WM+HAZ) composite region

Concentration of HCl (0.5 M)	R.T. Tafel	R.T. LPR	100 °C Tafel	100 °C LPR
Hexamine	IAC	IAC	61.3	60.5
Thiourea	44.8	IAC	79.5	76.1
Mixed	43.0	58.4	80.6	88.3

Note: PIE—Percentage Inhibitor efficiency; ( )—PIE for pulsed GTAW process; WoI—without inhibitor; IAC—Inhibitor accelerates corrosion; WI—with Inhibitor.

Table 8 Impedance parameters for pulsed GTAW/(WM+HAZ)/CS/0.5 M HCl+hexamine/R.T.

R_s, Ω	R_s+R_t, Ω	I_{corr}, mA/cm^2	C_{dl}, F/cm^2
0.5	25.5	0.83	4.09×10^{-5}

Mixed Inhibitor (thiourea + hexamine): The I_{corr} values are given in Table 6. The WM + HAZ region shows 88.3% efficiency at 100 °C and 58.4% efficiency at R.T. From the above it is inferred that both thiourea and the mixed inhibitor are preferable for CS/Pulsed GTAW weldments. From earlier work and a comparison from reports of case studies (Ref 14-16) it is confirmed that use of hexamine and mixed inhibitor is beneficial to carbon steel weldments. A comparison of P.I.E. for 0.5 M concentration HCl at R.T. and 100 °C of different inhibitors is shown in Table 7.

3.5 Impedance Measurements

Impedance measurements were taken for WM + HAZ of pulsed GTAW carbon steel weldment in HCl at 0.5 M concentration using an electrochemical impedance analyzer. Nyquist plot was obtained and the impedance diagrams are shown in the Fig. 5. The I_{corr} values of WM + HAZ is found to be 0.83 mA/cm^2. The typical Nyquist plot indicates that the corrosion reactions are activation controlled. The C_{dl} value is found to be 4.09×10^{-5} F/cm^2. The impedance parameters are furnished in the Table 8.

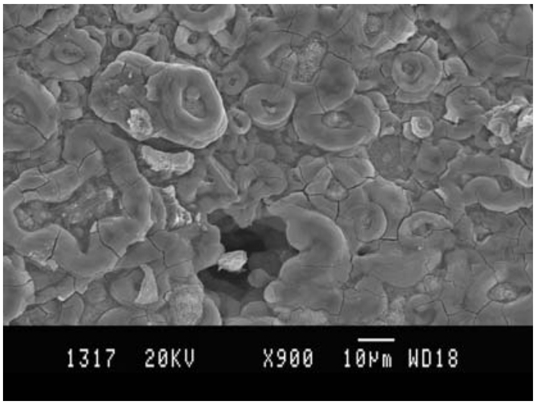

Fig. 6 SEM photograph of WM showing spongy nature of film with transgranular cracks in between

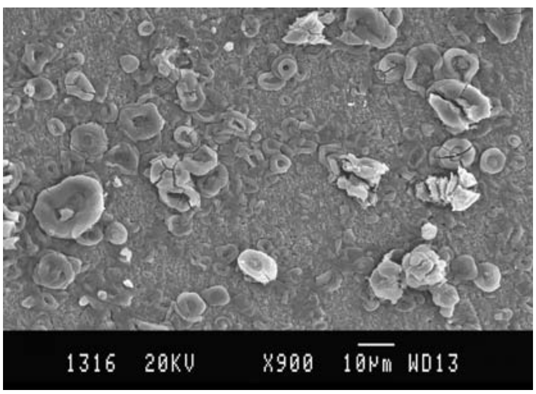

Fig. 7 SEM photograph of HAZ showing steam chimneys with micro fissures on the film

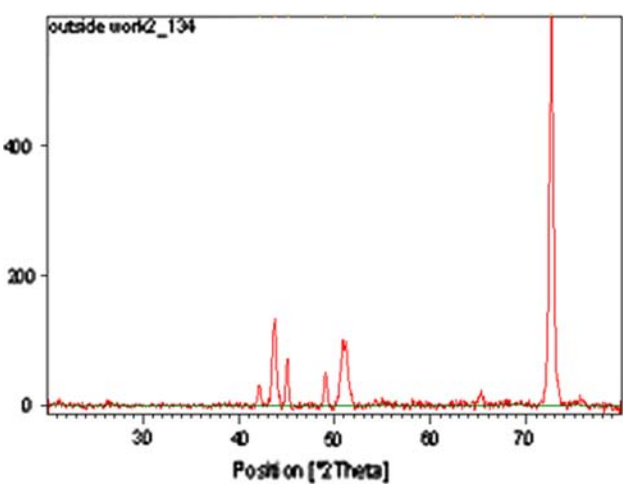

Fig. 8 XRD pattern of CS/pulsed GTAW/WM/0.5 M HCl+100 ppm hexamine/100 °C (The peaks were identified as (1) $\Upsilon FeMn_3$, (2) FeO, (3) Fe_3N, and (4) Fe_3Si)

3.6 SEM Analysis

The WM and HAZ regions exposed at 100 °C in 0.5 M HCl containing 100 ppm was subjected to SEM examination and the features are provided in Fig. 6 and 7. In terms of surface morphology by SEM, much work has been reported (Ref 17-20) pertaining to case studies. In the present investigation SEM photo resembles the corrosion products obtained on carbon steel during case studies.

3.7 XRD Studies

The XRD pattern on WM shows peaks which correspond to formation of $\Upsilon FeMn_3$, FeO, FeN, and Fe_3Si as shown in the Fig. 8.

4. Conclusions

- The WM + HAZ composite region registers lower corrosion rate compared to parent metal.
- The impedance test shows that corrosion reactions are activation controlled.
- Pulsed GTAW process is beneficial to carbon steel weldments.
- The SEM examination reveals spongy nature of film formation with transgranular cracks and steam chimneys.
- The XRD peaks indicate the presence of $\Upsilon FeMn_3$, FeO, FeN, and Fe_3Si.

References

1. R.L.O. Brien, Welding Processes, *Welding Handbook*, Vol. 2, 8th ed., AWS, Miami, Florida, USA,1995
2. T.G. Gooch, The Effect of Welding on Corrosion, *Process Industry Corrosion – Theory and Practice*, NACE Publication, 1982, p 739–755
3. M. Henthorne, Corrosion Testing of Weldments, *Corrosion – NACE*, 1974, **30**, p 39
4. G.E. Linnert, Welding Metallurgy, *Carbon and Alloy Steels*, Vol. 1, 4th ed., AWS, Miami, Florida, USA, 1994
5. G.S. Theus and P.L. Daniel, Corrosion in Power Generating Equipment, *Proc. 8th International Brown Boveri Symposium* (Baden, Switzerland), 1983, p 185–188
6. NACE, Corrosion Testing of Chemical Cleaning Solvents, NACE Publication 3M, *Mater. Perform.* **21**, 1982, p 48
7. A.N. Rothwell, Weld Corrosion: Causes and Solutions, *J. Corros. Prevent. Control*, 1992, **39**(5), p 113–118
8. S. Natarajan, "Studies on Corrosion Behaviour of Boiler Steel Weldments in Acid Medium," Ph.D. Thesis, Bharathidasan University, Tiruchirapalli, India, 1990
9. P.J. Antony, S. Natarajan, and R. Vaideeswaran, Corrosion and its Inhibition in the Carbon Steel Induction-Pressure Weldments used in Power Plants, *J. Corros. Prevent. Control*, 2003, **50**(4), p 181–188
10. S. Natarajan and V. Sivan, High Temperature Corrosion and its Inhibition in Carbon Steel Fusion Weldments used in Power and Process Plants, *Int. J. Join. Mater.*, 2003, **15**(3), p 17–23
11. S. Kou, *Welding Metallurgy*, 2nd ed., John Wiley & Sons, 2003
12. S.P. Kumaresh Babu and S. Natarajan, Influence of Heat Input on Corrosion Behaviour of FCA Weldments in Power Plant Carbon Steel, *Proc. of International Conference*, Chennai, NACE, CORCON-2005, 2005
13. S. Natarajan and V. Sivan, Weldment Corrosion and its Control in Power Generating Components, *J. Corros. Prevent. Control*, 2003, **50**(1), p 7–19

14. S.P. Kumaresh Babu and S. Natarajan, Corrrosion Behaviour of Flux Cored Arc Weldments in Carbon Steel Used in Power Plants, *J. STEEL-GRIPS*, 2006, **4**(3), p 207–211
15. G.M.W. Mann, History and Causes of On-Load Water Side Corrosion in Power Boilers, *Br. Corros. J.*, 1977, **12**(1), p 6–13
16. D. Jones, *Principles and Prevention of Corrosion*, 2nd ed., Prentice Hall of India, 1996
17. L. Kayafas, Corrosion Product Removal from Steel Fracture Surfaces for Metallographic Examination, *J. Corros.*, 1990, **25**, p 443
18. P. Mayer and A.V. Manolesu, Growth and Structure of Indigenous Magnetite on Boiler Tubes, *Proc.7th ICMC* (Ontaria, Canada), Trans Tech Publications Inc., 1980, p 1480–1487
19. W.M.M. Huijbregts, Protection Effectiveness of Magnetite Layers in Relation to Boiler Corrosion, *5th ICMC* (Tokyo), Trans Tech Publications Inc., 1972, p 857
20. P.H. Effertz, Morphology and Composition of Magnetite Layers in Boiler Tubes Following Long Exposure, *Proc. 5th ICMC* (Tokyo, Japan), Trans Tech Publications Inc., 1972, p 920