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CORROSION BEHAVIOUR OF TRIP-ASSISTED STEELS FOR INDUSTRIAL APPLICATION IN SEA ATMOSPHERE

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Abstract : Corrosion behaviour of two moderately low carbon high strength low alloy steels designated as A (having no Cr and Cu content) and B (having higher Ni, Cr and Cu content) heat treated at different conditions to alter micro-structure phases, have been studied under the simulated condition of sea atmosphere in the laboratory scale in different level of salinity under the influence of neutral pH as well as exposing them in real sea water condition by using electrochemical test. Pre and post corrosion micro-structural studies and quantitative phase analysis were carried out to arrive at structure-stoichometry-corrosion co-relation for designing of steels for industrial application in sea atmosphere.

Keywords: Corrosion, TRIP-assisted steel, electro-chemical test, phase analysis, heat treatment.

1. INTRODUCTION

Development of newer types of low alloy high strength corrosion resistance steel has been attempted by many researchers all over the world for industrial application in sea atmosphere [1-6]. Major factors that effect corrosion rate of HSLA steel are:

i) chemical composition,

ii) composition of sea atmosphere and

iii) type of exposures and supply of oxygen in corroding surface.

In moderate-velocity and high velocity sea atmosphere, Ni base alloy is frequently used for pumping. It has excellent resistance to cavitations, erosion and exhibits corrosion rates of less than 0.025 mm/year. Other Ni-base alloys containing Cr and Mo offer increased resistance to localized corrosion in stagnant sea atmosphere. Sea water is a highly conductive environment with 3.4% salt (NaCl) concentration [3-6]. Approximately 91.1% of the dissolved salts are chlorides. There are other commonly occurring constituent, dissolved gases, living organisms and various other materials found in s ea water. Keeping in view of the above study on corrosion behaviours to moderately low carbon steel having Si, Mn, Ni, V, Nb, Mo, Cu and Cr designed and develop for industrial application in sea atmosphere has been attempted in this study. No data base being available in literature on the systematic study on the effect of corrosion on multi-phase microstructure. Here attempts are being made to find out a correlation with post and pre-corrosion microstructure with corrosion behaviour of the steels. Prior to the development of high strength low alloy steels ferrite-pearlite and quenched and tempered steels were used in structure where high strength is required. The former steels also known as high tensile steels (HTS) have moderate strength (350MPa) and increased strength through pearlite strengthening by the addition of carbon upto 0.2%. In 1960's quenched and tempered (Q and T) steels were developed to improve the performance of industrial applications [5-7]. Due to higher carbon contents these suffer from poor weldability and for these reason new classes of steels having low carbon content and higher alloy elements were developed.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Two moderately low carbon high strength low alloy steels for sea atmosphere application is designated as A and B having composition given in Table 1 were supplied by DMRL, Hyderabad.

2.2 Heat Treatment

Steels were heat treated as per schedules as shown in below in Table-2 to develop different microstructure.

Table 1: Composition of alloy elements

Steel	**Composition of Alloy Elements**									
	C	**Mn**	**Si**	**P**	**Ni**	**Cr**	**Cu**	**V**	**Nb**	**Mo**
A	0.11	1.35	0.32	0.02	0.75	0	0	0.03	0.03	0
B	0.10	0.47	0.28	0.02	2.02	0.4	0.6	0.03	0	0.44

Table 2: Heat treatment of steels

Steel	Schedule No.	Heat treatment	Designation
A	1	As received (oil quenched and tempered)	A1
	2	Held at 950°C for 1/2hr, air cooled, Held at 700°C for 2 hrs, quenched to 400°C (salt bath), held for 900s and oil quenched.	A2
	3	Held at 950°C for half an hour, oil quenched in an oil of 0.123 centistokes viscosity.	A3
	4	Held at 950°C for half an hour then cooled in water	A4
	5	Held at 950°C for half hour then cooled in air	A5
	6	Held at 950°C for 1/2hr., and then cooled in furnace by switching off.	A6
B	1	As received (water quenched and tempered)	B1
	2	Held at 970°C for 1/2hr,air coo led, Held at 800°C for 2 hrs, quenched to 400°C (salt bath), held for 900s and oil quenched.	B2
	3	Held at 970°C for half an hour , oil quenched in 0.123 centistokes viscosity	B3
	4	Held at 970°C for half an hour, cooled in water	B4
	5	Held at 970°C for half an hour , then cooled in air	B5
	6	Held at 970°C for 1/2hr., and then cooled in furnace by switching off.	B6

2.2 Optical Micrograph

The micro-structural characterizations of the steels were carried out using an OLYMPUS CK4OM-CP optical microscope. The optical metallographies of all these samples were carried out in the usual way. Samples were cut from plates of theses steels. These samples were polished on polishing wheel after 1 to 6 (rough to fine) emery paper. The polished surface appeared like mirror having no scratches and the etchant was used 2% nital. The washed and dried samples were observed carefully in Microscope at different magnification and some selected photomicrographs were taken.

2.4 Phase Analysis

The phase analyses have been done by using Olysia m3 software. Samples were prepared as like as preparation of sample for optical microscope observation. Then images were taken in optical micros cope. The acquired images of a multi- phase object were taken for analysis. Phase analysis will be conducted on a gray-value image. The image is selected and threshold is set to define the gray value ranges for the separate phases. The OLYSIA software created a measurement sheet showing the absolute area and proportional area (in %) of all the phases. The measured values are taken.

2.5 Electro-Chemical Study

2.5.1 Samples and Solution Preparation

Samples were cut from plates of these steels. These samples were polished on belt followed by polishing on polishing wheel with 1 to 6 (rough to fine) emery papers . The polished surface appeared like mirror having no scratches. They were then degreased with acetone before exposing to the electro - chemical test. Solution of 0%, 0.1%, 1% and 3% NaCl at pH 6.5 were prepared with triple distilled water. Electrochemical test set up has shown in Fig.1.

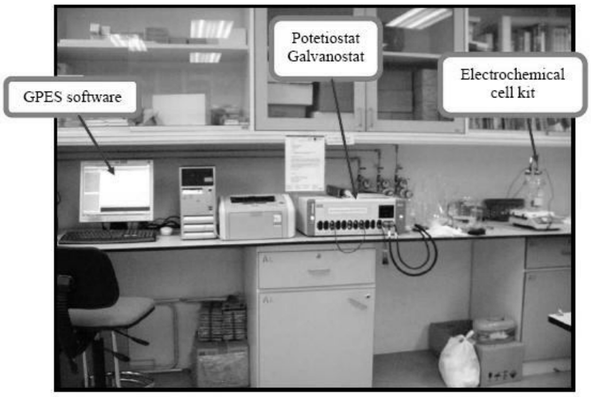

Fig.1 Electro-chemical test set up

2.5.2 Polarization Study

Samples were taken in an area of 0.204 square cm size coupons for performing potentiodynamic polarization studies in de-aerated condition in cells with three electrode configuration and using aqueous saturated calomel SCE (W) as the reference electrode and Pt foil as counter electrode. Linear s weep voltammetry was preformed with the help of AUTO LA B 12 PGSTAT, Eco Chemic B.V (the Netherlands) at 0.5 mV/s s can rate within the potential range of -1500 mV to the cathodic potential of 650mV vs. SCE. Potential s cans were conducted in de -aerated conditions by purging the solution with nitrogen for 10min.Tafe l analysis was performed to determine the corrosion parameters.

2.5.3 Electro-Chemical Impedance Spectroscopy

EIS at the respective OCP value were recorded with the help of AUTO-LA B 12 PG STAT, Eco Chemie B.V (the Netherlands) combined with frequency response analyzer (FRA) module. The sinusoidal perturbation of 5mV amplitude was applied at the cell over the frequency range of 100 KHz to 10 MHz EIS measurements were conducted at open circuit conditions after a steady state potential was attained in aerated solution of different electrolytes at neutral pH. The experiment was formed in three electrode one compartment cell containing the test coupons as working electrode, a large area Pt foil as counter electrode and a saturated calomel reference.

3. RESULTS AND DISCUSSION

3.1 Micro structural Characteristic

Pre-corrosion microstructures for steel A1 and B1 reveal polygonal ferrite plus tempered bainite and blocky polygonal ferrite plus tempered bainite (as shown in Fig.2 and Fig.3).

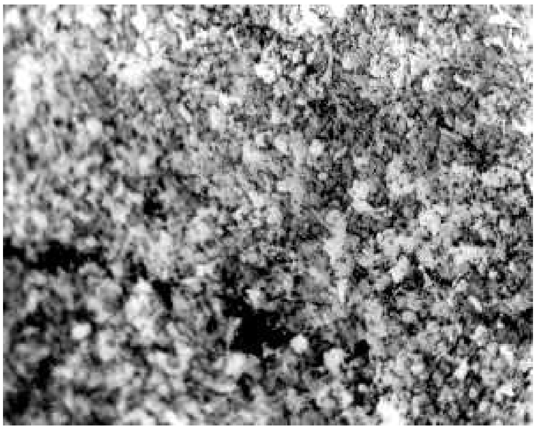

Fig.2 Optical microstructure A1
as per schedule 1

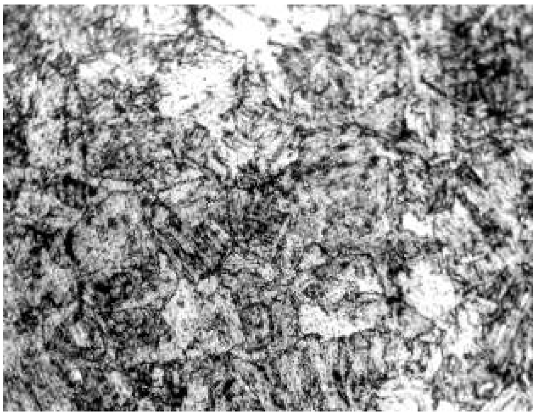

Fig.3 Optical microstructure B1
as per schedule 4

A2 and B2 reveal granular ferrite plus bainite and granular ferrite plus tempered bainite. A3 and B3 reveals accicular ferrite plus bainite and accicular ferrite. A4 and B4 show ferrite and martensite. Finally A5 and B5 reveal ferrite and pearlite. Post corrosion microstructures reveal adequate corrosion both in the form of grain boundary attack and pitting (as shown in Fig.4 and Fig. 5).

However, steels having high percentage of Cu and Cr (Steel B) face corrosion attack comparatively less in all heat treatment due to formation of protective oxide layer.

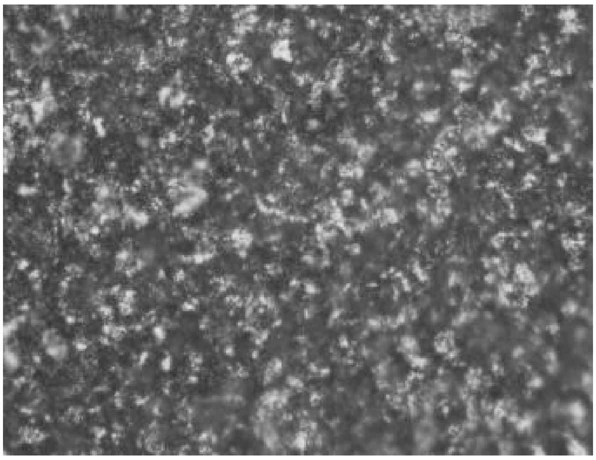

Fig. 4 Optical microstructure A1
in 0.1% NaCl (500X)

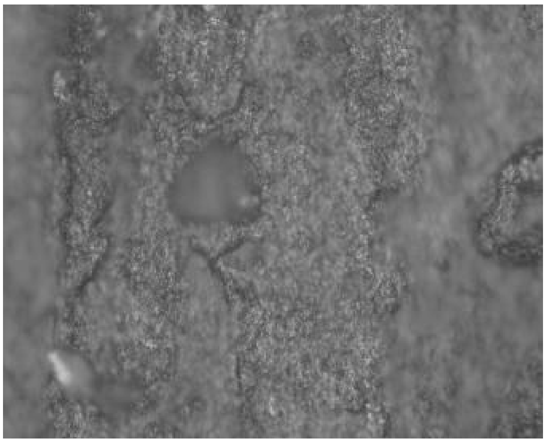

Fig. 5 Optical microstructure B1 in
0.1% NaCl (500X)

All the above microstructure when subjected to image analyzing system (as shown in Fig.6.and Fig.7).

It is seen that high % of martensite and/ or pearlite in ferrite matrix during water and air cooling.

3.2 Corrosion Characteristic

Corrosion results have been shown in Table 3, Table 4 and Table 5.

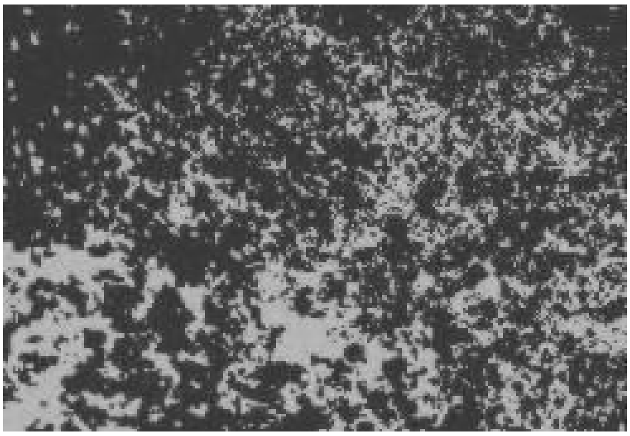

Fig. 6 Corresponding threshold image A1 as per schedule 1

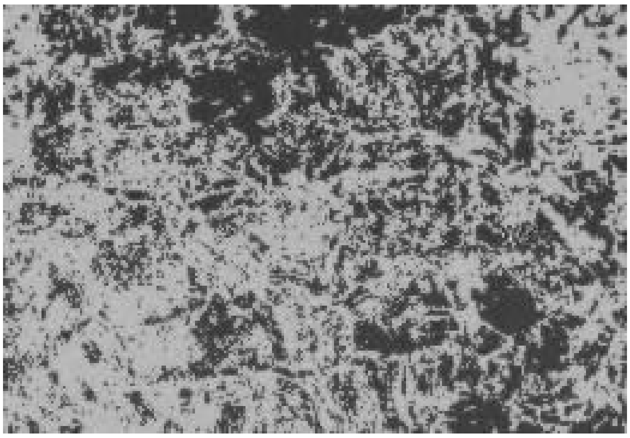

Fig. 7 Corresponding threshold image B1 as per schedule 4

Table 3: Corrosion Current (C.C.)

Sample		**Corrosion current, Icorr (A/cm^2 X 105) in various % of NaCl.**			
		0 % NaCl	**0.1% NaCl**	**1% NaCl**	**3% NaCl**
A	A1	4.7	7	71	-
	A2	1.4	3.6	27.2	-
	A3	1.5	5.8	44.7	-
	A4	-	3.127	9.378	9.589
	A5	-	2.207	7.081	9.493
	A6	-	1.143	5.518	7.788
B	B1	2.4	2.3	93.6	-
	B2	2.9	1.9	10	-
	B3	4.7	3.9	9.2	-
	B4	-	2.812	8.288	9.261
	B5	-	2.511	7.4	7.848
	B6	-	1.418	3.269	0.163

Table 4: Corrosion rate (C.R.)

Sample		**CR (mm/yr) in various % of NaCl**			
		0 % NaCl	**0.1% NaCl**	**1% NaCl**	**3% NaCl**
A	A1	0.361	0.539	5.467	-
	A2	0.107	0.277	2.094	-
	A3	0.115	0.446	3.441	-
	A4	-	0.351	2.704	1.076
	A5	-	0.247	1.313	1.066
	A6	-	0.128	0.619	0.874
B	B1	0.185	0.178	7.207	-
	B2	0.223	0.146	0.77	-
	B3	0.362	0.301	0.708	-
	B4	-	0.316	0.9303	1.826
	B5	-	0.282	0.831	1.042
	B6	-	0.159	0.367	0.881

Table 5: Polarisation resistance (RP)

Sample		**Polarization resistance (RP in Kohm) at various % of NaCl**			
		0 % NaCl	**0.1% NaCl**	**1%NaCl**	**3% NaCl**
A	A1	47.5	4.36	2.2	0.35
	A2	66.7	5.2	1.1	0.35
	A3	74	7.3	0.9	0.43
	A4	-	1.041	0.359	0.159
	A5	-	1.309	0.447	0.248
	A6	-	1.39	0.824	0.356
B	B1	31.5	3.5	1.3	0.6
	B2	55.3	20.1	5.5	1.2
	B3	23	16.5	1.2	0.4
	B4	-	0.716	0.475	0.158
	B5	-	1.913	0.535	0.2858
	B6	-	2.226	1.084	0.516

A_2 and B_2 in 0.1% NaCl shows (as shown in Fig.8 and Fig. 9) that B_2 is characterized with a narrow but distinct passive region while in A_2 there is no such region (as shown in Fig.10).

In neutral pH when EIS represents dual character A samples are more resistant than B samples. With further increase in Cl ion resistance decrease usual. Corrosion current /corrosion rate are much higher for A samples than B ones. Interestingly enough, in case of B_2 and B_3 samples corrosion rates are not that significantly accelerated with Cl ion as in case of A samples. EIS measurement reveals the Nyquist plot (as shown in Fig.11 and Fig.12) where half circles diameter represent the circuit resistance of the material.

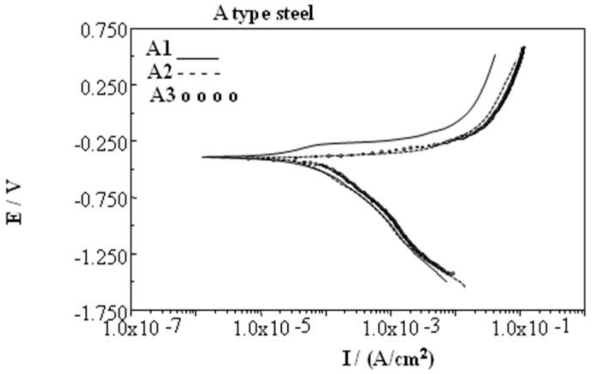

Fig. 8 Polarization plot for Steel A in 0.1% NaCl

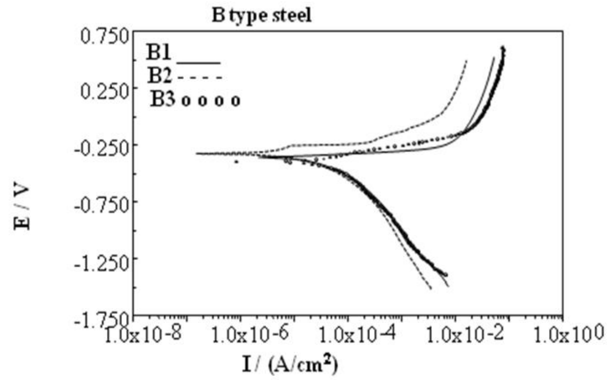

Fig. 9 Polarization plot for Steel B in 0.1% NaCl

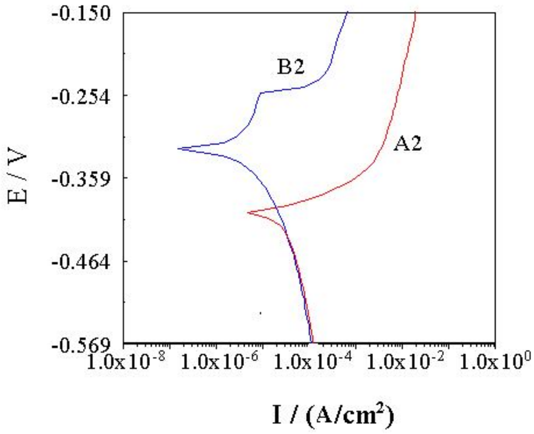

Fig. 10 Polarization plot for Steel A2 and B2 in 0.1% NaCl

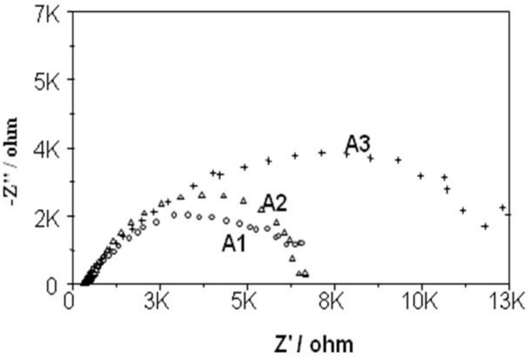

Fig. 11 Nyquist Plot of Steel A in 0.1% NaCl solution.

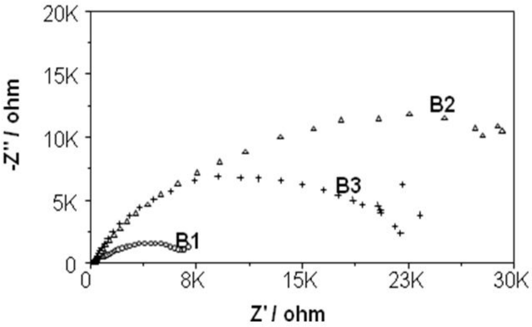

Fig. 12 Nyquist Plot of Steel B in 0.1% NaCl solution

4. CONCLUSION

The EIS is a powerful technique to investigate the corrosion protection of TRIP steel. Localized corrosion is a serious problem of TRIP steels when they are exposed to chloride solutions. As high-energy regions are prone to corrosion, microstructure having finer grains, which is more grain boundary, has less corrosion resistance. Microstructure contains more low temperature transformation products like bainite and/or martensite phases are more corrosive due more grain boundary. Steel containing more Cu, Ni and Cr is less corrosive compared to other steels having same processing or microstructure. Steels in rolled condition are more corrosive in both the case, probably due to high dislocation density.

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