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Mechanics of Corrosion of TRIP-assisted Steels in different NaCl solutions

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ABSTRACT

Mechanics of corrosion of two TRIP-assisted steels designated as A (having no Cr and Cu content) and B (having higher Ni, Cr and Cu content) heat treated at different condition to alter micro-structure phases. After two TRIP –assisted steels 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. Micro-structural characterization of Pre & post corrosive samples and quantitative phase analysis were carried out to arrive at heat treatment-structure-properties co-relation to get knowledge about mechanics of TRIP-assisted steels in different NaCl solutions.

Key words: Corrosion, TRIP-assisted Steel, Electro-chemical test,
Phase analysis, Heat treatment.

INTRODUCTION

From the history of steel development for vehicle, we can see that there were many kinds steels, which had been developed and used. From the 1950's to the 1960's, the rimmed steel was researched and used. From the 1960's to 1970's, many killed steels were developed and employed. From the 1980's to the 1990's, to highly improve the formability of sheet steel , the research of auto steel was mainly centralized in interstitial-free(IF) steel. By the 21st century, most projects of auto steel focused on developing new kinds of HSS and new style steels to meet the needs of the plan of ultra light steel auto body (ULSAB).These steels include double-phase (DP)steel, TRIP-steel and TWIP steel.

The former steels also known as high tensile steels (HT S) 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[5-9]. Due to higher carbon contents these suffer from poor weld ability and for this reason new classes of steels having low carbon content and higher alloy elements were developed. Steels having a fully austenitic microstructure are called TRIP steels (Zackay *et al.,* 1967). These steels tend to be rich in nickel and other expensive austenite stabilising elements. By contrast, austenite is only a minor phase in the overall microstructures of TRIP-assisted steels (Matsumura *et al.,* 1987; Takechi *et al.,* 1987).

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[1-8].

The major factors those effects the corrosion rate of HSLA steel are

i) Chemical composition

ii) Composition of sea atmosphere

iii) Type of exposures

In moderate-velocity and high velocity sea atmosphere, Ni base alloy is frequently used for pumping. It has excellent resistance to cavitations, erosion and exhib its 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 sea 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. It is essential to do more study in corrosion behaviour and performance of the material in order to evaluate and improve the design, cost effectiveness and reliability of each material used. Khoshnaw et al. (2007) have studied fatigue strength of low alloy steels in chloride solution. Turnbull *et al.* (2008) have studied stress corrosion cracking of stainless steel in chloride solutions. Chen *et al.* (2005) have studied mechanical properties of low-alloy steels in atmosphere containing chloride in tension test.

EXPERIMENTAL

Materials

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

Heat treatment

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

Optical Micrography

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 papers. 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.

Phase Analysis

The phase analysis 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 microscope. 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 s 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. The phase analyses ASTM E 566 1245 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 microscope. The acquired images of a multiphase 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.

Electro-chemical study

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.

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 sweep voltammetry was preformed with the help of AUTOLAB 12 PGSTAT , Eco Chemic B.V (the Netherlands) at 0.5 mV/s scan rate within the potential range of -1500 mV to the cathodic potential of 650 mV vs .SCE. Potential scans were conducted in de-aerated conditions by purging the solution with nitrogen for 10min. Tafel analysis was perfomed to determine the corrosion parameters .

Electro-chemical Impedance Spectroscopy

EIS at the respective OCP value were recorded with the help of AUTO-LAB 12 PG STAT, Eco Chemie B.V (the Netherlands) combined with frequency response analyser (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 the solution of different electrolytes at neutral pH. The experiment was performed in three electrode one compartment cell containing the test coupons as working electrode, a large area Pt foil as counter electrode and a s saturated calomel reference.

RESULTS AND DISCUSSION

Micro structural Characteristic

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

A_2 and B_2 reveals granular ferrite plus bainite and granular ferrite plus tempered bainite. A_3 and B_3 revealsaccicular ferrite plus bainite and accicular ferrite. A_4 and B_4 shows ferrite and martensite. Finally A_5 and B_5 reveals ferrite and pearlite. Post corrosion microstructures, taken for a few samples for both steels, reveal adequate corrosion both in the form of grain boundary attack and pitting. However steel having high percentage of Cu and Cr, in case of steel B, this corrosion attack is comparatively less in all heat treatment schedules seemingly due to formation of protective oxide layer. Post corrosion microstructures reveal adequate corrosion both in the form of grain boundary attack and pitting (as shown in Fig.4.and Fig.5).

All the above microstructure when subjected to image analysing 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.

Corrosion Characteristic

Corrosion results have been shown in Table 3, Table 4 & 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 A_2 and B_2 in 0.1% Na Cl shows (as shown in Fig.8) that B2 is characterized with a narrow but distinct passive region while in A_2 there is no such region (as shown in Fig.9.A samples are more resistant than B samples Rp (A) > Rp (B) as shown in Table no-5. It may be predicted that matrix / grain boundary of A is more reactive than that of B in neutral conditions and that may be due to formation of thicker and stern passive layer (oxide film) in alloy B. This gets disrupted immediately in contact with Cl-. In most of A and B samples 10-fold decrease is observed when exposed to 0.1% NaCl. However this decrease is much restricted in case of B_2 and B_3 samples. With further increase in Cl- ion Rp decrease as usual.A more or less similar behavior is reflected with polarization studies.

Table 1: Composition of materials

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	0.1	0.47	0.28	0.02	2.02	0.4	0.6	0.03	0	0.44

Table 2: Heat treatment of steels

Steel	ScheduleNo	Heat treatment	Designation
A	1	As received (oil quenchedand temp ered)	A_1
	2	Held at 950°C for1/2hr,air coo led, Held at700°C for 2 hrs, quenched to 400°C(salt bath), held for 900s and oil quenched.	A_2
	3	Held at 950°C for half anhour, oil quenched in an oil of 0.123 centistokes viscosity.	A_3
	4	Held at 950°C for half anhour then cooled in water	A_4
	5	Held at 950°C for halfhour then cooled in air	A_5
	6	Held at 950°C for 1/2hr.,then cooled in furnace by switching off.	A_6
B	1	As received (waterquenched and tempered)	B_1
	2	Held at 970°C for1/2hr,air coo led, Held at800°C for 2 hrs, quenched to 400°C (salt bath), heldfor 900s and oil quenched.	B_2
	3	Held at 970°C for half anhour , oil quenched in0.123 centistokes viscosity	B_3
	4	Held at 970°C for half anhour, cooled in water	B_4
		Held at 970°C forhalf an hour , then cooledin air	B_5
	6	Held at 970°C for 1/2hr.,then cooled in furnace by switching off.	B_6

Table 3: Corrosion rate (CR)

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 4: Polarisation resistance (R_p)

Sample		CR(mm/yr) in Various %of NaCl			
		0 % NaCl	0.1% NaCl	1% NaCl	3% NaCl
A	A_1	47.5	4.36	2.2	0.35
	A_2	66.7	5.2	1.1	0.35
	A_3	74	7.3	0.9	0.43
	A_4	-	1.041	0.359	0.159
	A_5	-	1.309	0.447	0.248
	A_6	-	1.39	0.82	0.356
B	B_1	31.5	3.5	1.3	0.6
	B_2	55.3	20.1	5.5	1.2
	B_3	23	16.5	1.2	0.4
	B_4	-	0.72	0.47	0.158
	B_5	-	1.913	0.535	0.286
	B_6	-	2.23	1.08	0.52

Table 5: Corrosion current

Sample		CR(mm/yr) in Various %of NaCl			
		0 % NaCl	0.1% NaCl	1% NaCl	3% NaCl
A	A_1	4.7	7	71	-
	A_2	1.4	3.6	27.2	-
	A_3	1.5	5.8	44.7	-
	A_4	-	3.127	9.378	9.589
	A_5	-	2.207	7.081	9.493
	A_6	-	1.143	5.518	7.788
B	B_1	2.4	2.3	93.6	-
	B_2	2.9	1.9	10	-
	B_3	4.7	3.9	9.2	-
	B_4	-	2.812	8.288	9.261
	B_5	-	2.511	7.4	7.848
	B_6	-	1.418	3.269	0.163

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 then B ones. Interestingly enough, in case of B2 and B3 samples corrosion rates are not that significantly accelerated with Cl ion as in case of A samples. EIS measurement reveals the Nyquistplot (as shown in Fig.10 and Fig.11) where half circles diameter represent the circuit resistance of the material.

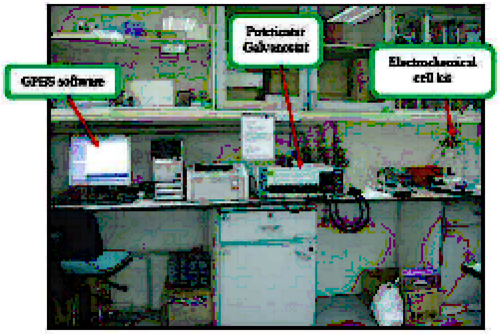

Fig.1: Electro-chemical test set up

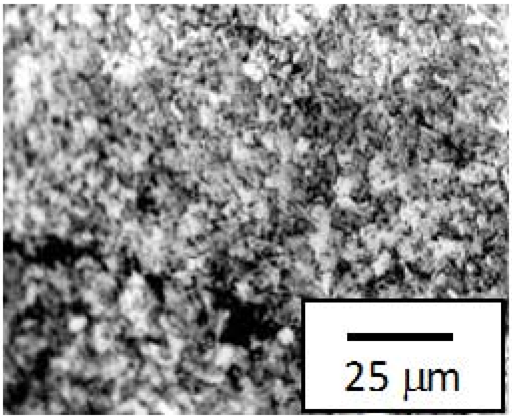

Fig. 2: Optical microstructure A1 as per schedule 1

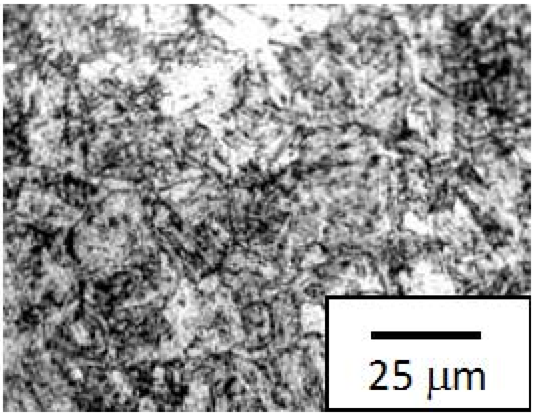

Fig. 3: Optical microstructure B1 as per schedule 1

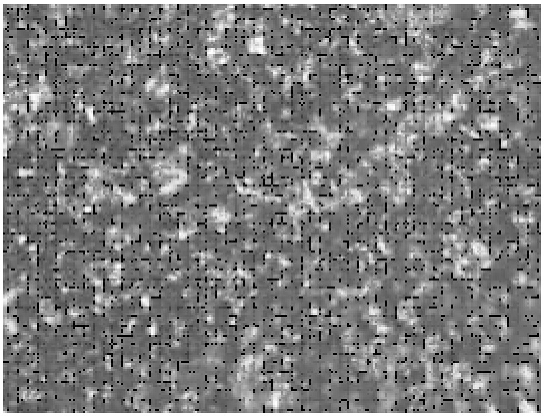

Fig. 4: Optical microstructure A1 in 0.1% NaCl (500X)

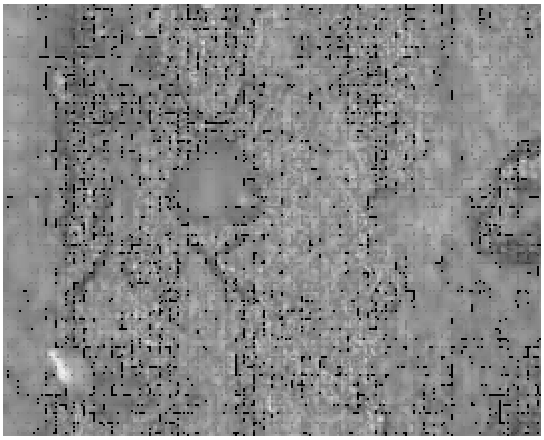

Fig. 5: Optical microstructure B1 in 0.1% NaCl (500X)

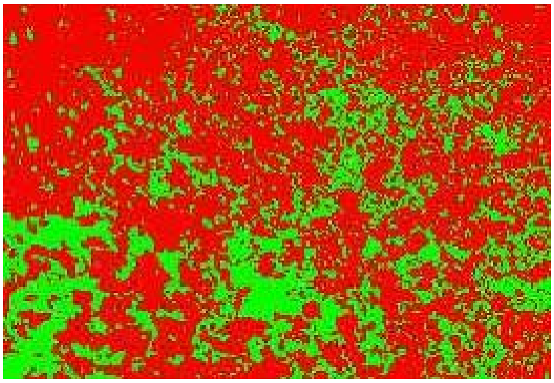

Fig. 6: Corresponding threshold image A1 as per schedule1

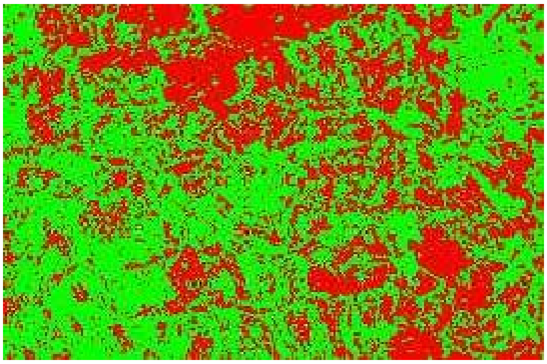

Fig. 7: Corresponding threshold image B1 as per schedule 1

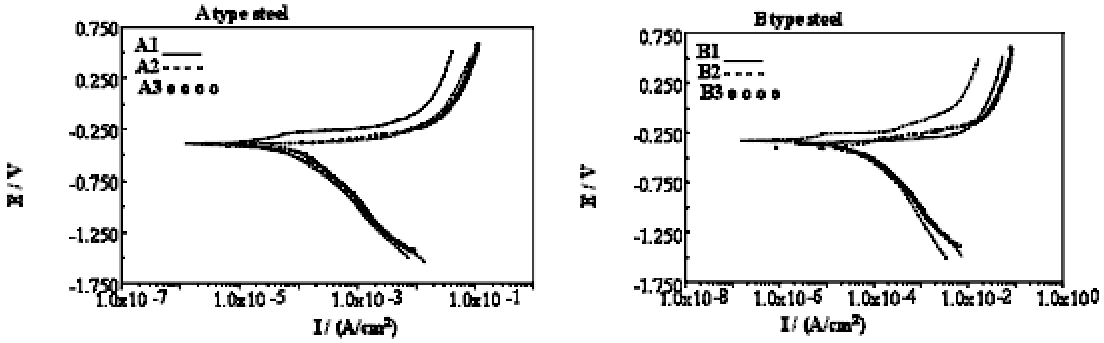

Fig. 8: Polarisation plot for corrosion studies in 0.1%

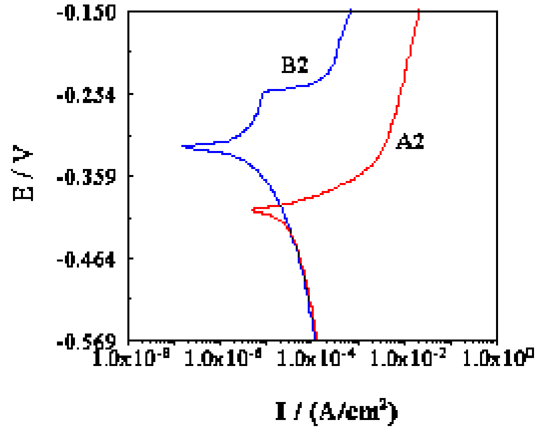

Fig. 9: Polarisation plot for Steel A2 and B2 in 0.1% NaCl

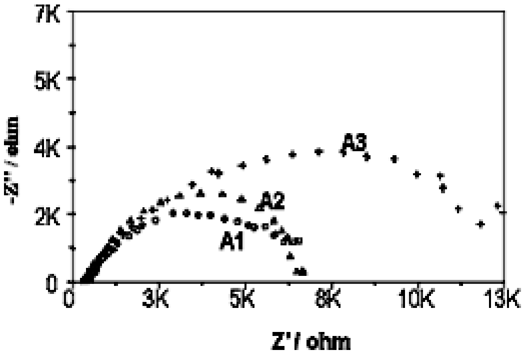

Fig. 10: Nyquist plot for A steel in 0.1% NaCl

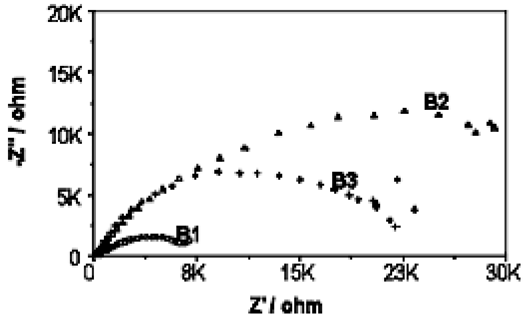

Fig. 11: Nyquist plot for B steel in 0.1% NaCl

CONCLUSIONS

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 and other non equilibrium are more corrosion. 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. The retained austenite in non-Niobium steel is more stable, the non-Niobium steel has shown the optimum combination of mechanical properties.

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