CORROSION CONTROL THROUGH SURFACE MODIFICATION

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1.0 INTRODUCTION

Steel is widely used for a broad range of structural and engineering application owing to its excellent mechanical properties and many favourable characteristics. However, it is susceptible to corrosion caused by interaction with the environment. The direct-loss cost of corrosion have resulted in figure corresponding to 3-4% of GNP in developed countries, where the share of industry in GNP is 32 to 41%. In India in a recent year this loss is Rs. 40×10^9. An estimated average of 15 to 20% of these losses could be saved by implementing corrosion control measures.

Methods of corrosion protection employed to protect steel include altering the metal by alloying, changing the environment, controlling electrochemical potential by application of cathodic or anodic currents, applying organic/inorganic coating and by surface modification of material. This paper deals with corrosion control in the area of structural steel and automobile steel sheets.

2.0 STRUCTURAL STEEL

The limitation of plain carbon structural steel in terms of heat-treatment, welding difficulties and rusting problem, have been to a great extent, overcome by the high strength low alloy steels without appreciably adding extra cost compared with special steels. One of the most important developments in combating corrosion in natural environment was the advent of weathering steel. Tata Steel, the largest special steel producer in India, started developmental work over a decade ago to have a suitable grade of weathering steel which has the same mechanical properties and corrosion resistance as the CROTEN-A grade steel but does not contain the costly alloying element Ni. The chemical composition and mechanical properties of Ni-free weathering steel for structural angles are shown in Table-1 & 2 respectively.

The samples of IRSM-41 corten and Ni free weathering steels grades were supplied to a government agency for corrosion testing. The test results supplied by them are shown in Table-3, which clearly reveals that both grades of Ni-free weathering steel are at par with or superior to corten. Although, WS-2 is better than WS-1 in NaCl test, WS-1 is superior in humidity test. This was possibly due to higher P content. Since humidity is more important factor under Indian condition, WS-1 would be a preferred substitute for IRSM-41 grade.

With the commissioning of Hot Strip Mill, in 1995, we took up the development programme to produce corten steel through LD-Slab Caster-HSM route. After optimising the process parameters, we are regularly producing hot rolled coils of corten steel.

2.1 Reinforcing bars

A large amount of steel are used for the reinforcement of concrete in building, bridges and marine structure. These bars when embedded in concrete, the alkaline concrete medium develops a protective passive layer that prevents rusting. This passivation is destroyed when aggressive ingredients like chloride, oxygen, carbon dioxide and moisture reach the metal concrete interface, leading to structural failure.

Realising the severity of the corrosion problems in reinforced concrete structures, Tata Steel look up the development of CRS rebars to impact relatively a layer life to RCC structure through changing the basic composition of metal. Based on trials and initial observation, optimal alloying additions and other compositional adjustments of rebar steels have been made. This has led to the development and commercial production of a new grade of CRS rebars having improved corrosion resistance in both chloride and acidic environments.

2.2 Production alternative

The bar properties depend upon chemical composition as well as on processing parameters. In order to compensate the losses in strength by reducing the carbon content for weldability reasons, there are mainly three different production route namely.

- Cold twisting (CTD).performed of line
- Microalloyed as rolled bar
- Thermal treatment/water quenching and self tempering

The major disadvantage with CTD CRS rebars is the introduction of stress during cold working which accelerate corrosion. Tata Steel is the leading manufacturer of TMT CRS rebars to combat corrosion. TMT rebars are more corrosion resistant owing to its tempered martensitic rim. The addition of corrosion resistant elements further enhances the CRI of rebars.

CRS rebars are produced from continuously cast billets in the range 8mm to 40mm φ by Thermo-mechanical treatment (TMT). This process utilises the heat available in the hot rolled bars to achieve the desired combination of physical properties. The excellent strength and toughness of these bars is principally due to the microstructural combination (Fig.1). The chemistry and mechanical properties are shown in Table-4 & 5 respectively. The bond strength of the rebars embedded in concrete were found to be more than 43.8% over plain bar at 0.025mm slip and more than 96.17% over plain bar at 0.25mm slip. IS-1786 stipulates that bond strength should be more than 40% over plain bars at 0.025mm slip and more than 80% over plain bar at 0.25mm slip.

2.3 Corrosion resistant properties or CRS rebars

Salt spray, alternate immersion SO_2, potentio-dynamic, dipping, concrete compatibility tests in NaCl solution were conducted to assess the corrosion rate of Tiscon TMT-CRS bars with respect to ordinary TMT bars. The same has been reported in the form of Corrosion Resistance Index (CRI) as the ratio of corrosion rate between ordinary TMT bars and corrosion resistant TMT bars.

2.3.1 Salt spray tests

Marine water containing NaCl is capable of dissolving a large amount of oxygen resulting in a highly corrosive environment. In the laboratory tests, an artificial fog was created using 5% NaCl solution and the samples were tested for 720 hours followed by corrosion rate evaluation, based on weight loss data. The results clearly show that the TMT-CRS bar were 1.6-1.9 times more corrosion resistant than ordinary TMT bars. It may be noted that cold twisted bars show low corrosion resistance than ordinary TMT bars. Low corrosion resistance of the cold twisted bars is due to a ferritic – pearlitic structure and the higher stress on the surface introduced during cold working TMT rebars have a rim with lath martensitic structure. It is well established that the tempered lath martensitic structure is more corrosion resistant than the pearlite-ferrite microstructure.

An additional feature observed after the test was that the rust in ordinary TMT bars was loose and flaky in nature whereas in CRS-TMT bars, it was adherent and required more time to pickle. It was further observed that CRS-TMT bars show superior resistance to pitting corrosion that ordinary rebars in NaCl atmosphere.

2.3.2 Test in sulphur dioxide atmosphere

In an industrial environment, sulphur dioxide gas is most corrosive in the presence of humidity. SO_2 gas was generated by adding sodium thiosulphate in dilute acid and the samples were suspended in a sealed chamber for 720 hours. The corrosion rate was evaluated using the weight loss method. CRI was found to be in the range of 1.55-1.8.

2.3.3 Alternate immersion test

Steel structure in the splash zone of the sea get wet and dry alternately and the corrosion rate in such condition is accelerated by the abundance of oxygen as the wet surface is exposed to air. Samples suspended to a wheel rotating at 3 rpm, was used for 720 hours in 3.5% NaCl solution, simulating the alternate wetting and drying condition. The CRI was found to be 1.6 (minimum).

CRS and ordinary rebars were embedded in concrete cubes of 150mm square of M15/20 quality concrete having cement / sand / aggregate in the ratio of 1:2:4:4. In each cube, $CaCl_2$ (2% of cement) was added to accelerate the corrosion attack on the rebars. Cubes were cured in water for 21 days. After curing, the concrete blocks were immersed in 5% NaCl solution for 3 days and subsequently dried in the atmosphere for 4 days. This cycle continued for two years. A fresh solution of sodium chloride was added every month to maintain a constant P_H of the NaCl solution. At the end of the test it was observed that crack appeared in the concrete blocks that used mild steel, whereas no crack was observed in the blocks that used CRS rebars.

2.3.4 Electro-Chemical Behaviour Study

The accelerated Electro-chemical corrosion behaviour of metals was studied by the polarisation technique where the surface current density of the sample is scanned over a potential range. TMT-CRS rebars were tested in 3.5% NaCl solution and in natural seawater. The tests were carried out at room temperature on cathodically cleaned samples at a scan rate of 10 mv/min for 500 seconds. It was found that CRS rebars were 2.3 times more corrosion resistant in 3.5% NaCl and 1.7 times more corrosion resistant in natural seawater than ordinary rebars.

2.3.5 Atmospheric exposure test

The marine environment of Digha was selected for the field exposure test. Industrial tests were carried out at Jamshedpur. Extensive field exposure tests were carried out for two years on CRS-TMT bars are atleast 1.6 times more corrosion resistant than ordinary TMT bars.

2.3.6 Fatigue tests of CRS bar and concrete beam

Bars used in reinforced concrete structure particularly in seismic zones must meet the requirements of fatigue. Fatigue tests were conducted on the bare rebars and in reinforced concrete beams. The cyclic load tests on the virgin bars showed that the TISCON-CRS rebars withstood the deformation under cyclic strains of $\pm 4\%$ without fracture. This satisfied one of principal requirements of rebars for their use in seismic regions. The cyclic load test on concrete beams have also shown that the load levels were maintained with a maximum loss of 18.5% which is within reasonable levels of variation. Based on the above findings, it may be concluded that TISCON-CRS bars of Grade 500 and 415 can be used as a reinforcement material in seismic zones.

3.0 Steel in Automobiles

The use of coated steels in automobiles has undergone a dramatic change in last 30 years involving billions of dollars in the steel industry. The combination of various metallic coating and finishing capabilities on the part of the steel industry with a broad range of application requirements and of stamping, assembly, and painting capabilities among the car companies has led to a very large number of coated products being available in the market today.

3.1 Zinc coating

Hot dip-zinc coated steel sheet, also called galvanised, is by far the most widely used coated sheet product. For general-purpose galvanised sheet, 19 μm per side is the usual thickness. In the automotive industry, where formability and weldability are key considerations, lighter coatings such as 90 g/m^2 are more typical. Galling and Coating pick off can also occur in severe forming application. The build up of particulate material on die surfaces may cause impressions and poor appearance on the surface of the formed parts.

The life of spot welding electrodes is reduced by zinc coating. Galvanised sheet is used in both bare and painted condition. For galvanised components that are painted after fabrication, such as automobile body components, zinc phosphate is commonly used. Zinc coatings product steel in three ways:

- Initially, a continuous film of zinc at the surface of steel serves as a barrier to separate the steel from environment

- At voids in the coating, such as scratches and cut edges, the zinc behaves as a sacrificial anode to provide galvanic protection.

- After anodic dissolution of the zinc metal, zinc hydroxide can precipitate at the cathodic areas of exposed steel, thus forming a secondary barrier.

3.2 Zinc-Iron alloy coating

Also known as galvanneal, is produced by the thermal diffusion and alloying of a galvanised coating with a steel substrate. Today, galvanneal is used increasingly often by the automobile industry because of its improved paintability and spot weldability relative to a pure hot dip zinc coating of equal thickness. The iron content of the alloyed coating is usually in the range of 9 to 12%. For automobile body panels, the typical coating thickness for galvanneal is 7 μm (coating mass 50 g/m^2). The corrosion resistance of galvanneal is similar to that of a pure zinc coating. However, because of the iron in the coatings, the galvanic potential is not as great as that of pure zinc. Also, the corrosion products are reddish brown. The addition of an organic barrier coating, both significantly improves perforation corrosion resistance and provides an opportunity for lower cost coatings.

The question remains, however, "why do we have so many different coated product?" Table-6 summarises most of the issues involved. This throws a challenge for optimisation of the combination of materials to meet customer's requirements at the lowest possible cost. The opportunity to tailor make coated products to meet specific customer requirements is a strength that the steel industry must more aggressively utilise as we continue to strive to keep steel the material of choice in automobile bodies.

Table 1. Chemical Compositions of the Experimental Heats of Corrosion Resistant Structurals

Elements	IRS-M41 (CORTEN-A)		Ni-free weathering steel 1	Ni-free weathering steel 2
	Specified	Achieved	Specified	Specified
C	0.10 max.	0.07	0.10 max.	0.15 max.
Mn	0.25/0.45	0.33	0.90 max.	0.60 max.
S	0.04 max.	0.028	0.04 max.	0.04 max.
P	0.08/0.12	0.12	0.12 max.	0.04 max.
Si	0.30/0.70	0.39	0.40 max.	0.70 max.
Cu	0.35/0.50	0.38	0.50 max.	0.40 max.
Cr	0.35/1.20	0.95	0.90 max.	1.00 max.
Ni	0.28/0.62	0.37	-	-
V	-	-	0.10 max.	0.10 max.

Table 2 Mechanical Properties and Microstructural Analysis of Corrosion Resistant Structurals

	Specified in	Achieved		
	IRS M-41	IRS M-41	Ni-free W.S.1	Ni-free W.S.2
Y.S kg/mm2	35 min.	39.0 39.4	42.3 42.2	37.6 37.2
UTS kg/mm2	49 min.	52.3 52.1	54.7 54.4	50.0 49.0
Elongation. %	22 min.	28.7 28.0	32.5 30.0	32.5 28.7
Bend	2 T	1 T OK	1 T OK	1 T OK
Grainsize ASM	5 - 8	7.5	7 - 7.5	7.5
Micro-structure	-	Pearlite Ferrite	Pearlite Ferrite	Pearlite Ferrite

Table 3 : Corrosion Evaluation test of Ni-free Weathering Steel and CORTEN-A grade steel for 168 hrs.

Humidity test (wt.loss mg/100 mm2)			Salt spray test (3% Nacl) (wt.loss mg/100 mm2)		
Corten	WS-1	WS2	Corten	WS-1	WS-2
3.23	2.06	3.01	5.91	5.06	2.90

Table – 4

Chemical Composition of CRS rebar, %						
C	Mn	Si	S	P	Cr	Cu
0.15 max.	1.00 max.	0.45 max.	0.04 max.	0.10 max.	0.80 max.	0.3 – 0.5

$Cu + Cr + P \geq 0.5\%$

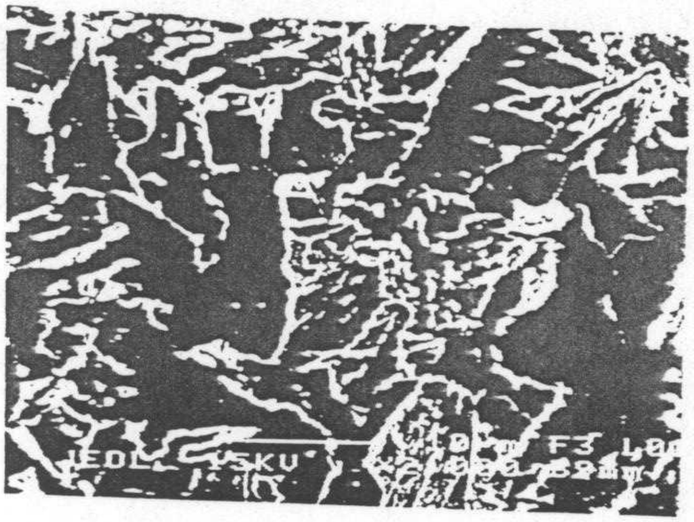
Carbon equivalent < 0.42

Table – 5 : Typical tensile properties of TMT-CRS rebar

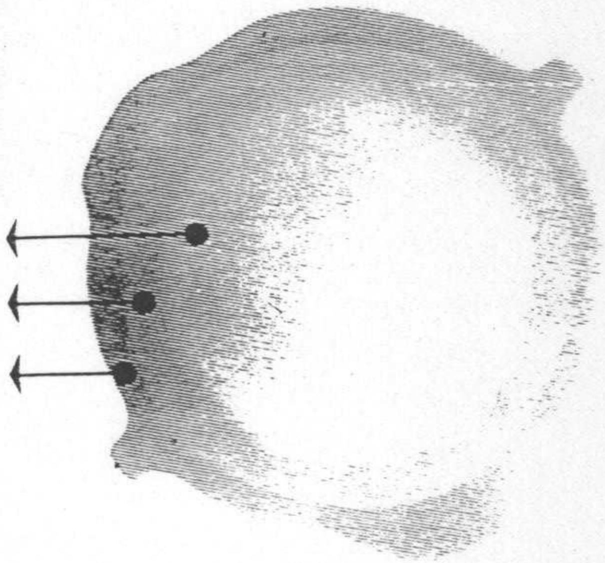
	Fe 415 specified. min.	TMT-CRS	Fe 500 specified. min.	TMT-CRS
YS N/mm^2	415	460	500	540
UTS N/mm^2	485	520	545	620
% Eln.	14.5	24	12	22

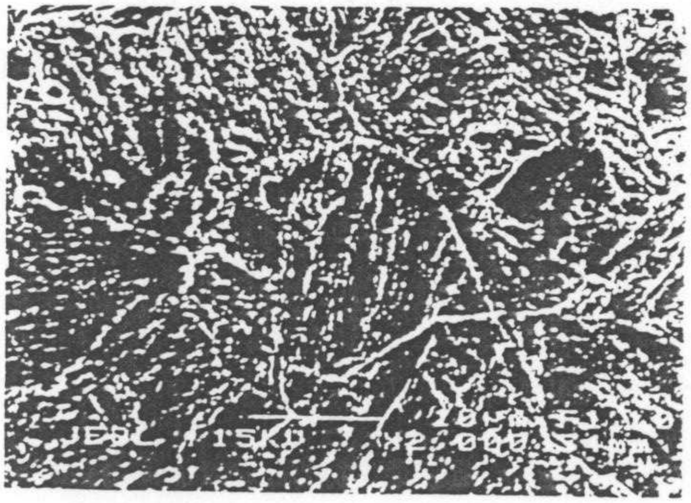
Auto industry issues	Steel product issues
Forming	EDDQ, DDQ, DQSK, CQ
- mechanical properties	Bake hardening, dent resistant, high strength, dual-phase
- surface	Roll preparation
- lubrication	- shot blast
	- electrical discharge
Die build-up	- laser
	- electron beam
Surface quality	Zinc alloy phase control
Welding	Zinc/zinc alloy coatings hardness control
Bonding	Wide range of coating types
- adhesive	Wide range of coating masses
- sealants	Improved coating mass uniformity
- sound damping	
Phosphating	Improved substrate thickness uniformity
Electrocoating	Coating surface compositional control
Paint appearance	Variety of coating textures and appearances
Corrosion	Variety of non-metallic coatings in combination with metallic coatings
- perforation	
- cosmetic	

Table 6: *Auto industry and steel product issues that affect the choice of coated products*



x 2000
Ferrite-pearlite





x2000
Tempered martensite

Fig. 1 : Micro-structure of TMT-CRS rebar