Corrosion Effects of Cr and Ni in Thermo-Mechanical Treated Steel Bar in Marine Environments

Sunil Kumar Durgam[1], Ghanshyam Das[2], Anjani Kumar Singh[3]

[1]M.Tech, Department of Materials & Metallurgical Engineering, National Institute of Foundry & Forge Technology, Ranchi, India
[2]Associate Professor, Department of Materials & Metallurgical Engineering, National Institute of Foundry & Forge Technology, Ranchi, India
[3]Research Scholar, Department of Materials & Metallurgical Engineering, National Institute of Foundry & Forge Technology, Ranchi, India

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Abstract - *High strength reinforcing steel bars popularly known as rebar produced by using advance technology such as in-line quenching thermomechanical treatment (TMT) process. These steel rebars are the backbone for general construction and are used in combination with cement concrete for reinforced cement concrete (RCC) structures. The properties of these rebars are usually modified by alloying with suitable elements such as Cr, Cu and Ni for use in specific areas such as seismic prone zones, and corrosive environments: coastal, marine, and industrial. When used in marine, and regions with high humidity content, the rebars should have good corrosion resistance properties. The effect of alloying elements such as chromium, copper, and nickel present in a reinforcing bar steel produced by in-line quenching process has been studied which affects the properties, microstructure, and corrosion resistance of steel in simulated chloride environment. The results have been compared with that of a semikilled C-S-Mn reinforcing bar steel without these alloying elements produced by the same process route. The Cu-P-Cr-Ni exhibited a composite microstructure, and good balance of yield stress, tensile stress, elongation, and ultimate tensile to yield stress ratio. Two conventional test methods, namely, the convectional weight loss method, and potentiodynamic polarization tests, were used for the corrosion test. Also, the free corrosion potential of the Cu-P-Cr-Ni steel was nobler, and the corrosion current was markedly lower than that of a C-S-Mn rebar. The improved corrosion resistance of the Cu-P-Cr-Ni steel has been attributed to the presence of copper, phosphorus, and small amount of chromium in the dense, adherent rust layer on the surface of reinforcing steel bar.*

Key Words: *Thermo-Mechanically-Treated (TMT) steels, Corrosion rate, Potentiodynamic polarization*

1. INTRODUCTION

Thermo-Mechanically-Treated (TMT) bars have recently been used as advancement over the conventional mild steel bars in reinforced concrete structures in order to enhance the durability in corrosive environment. Corrosion of steel reinforcement leads to cracking of reinforced concrete sections and thus may further reduce the load carrying capacity and serviceability of the structural members. Corrosion of rebars may cause reduction in yield strength of steel, affect the bond strength due to delamination of rust formed on the rebar surface [1-4].

Carbon-sulphur-manganese steel rebars are subjected to corrosive attack in the RCC structure, particularly in marine environment when threshold chloride concentrations are exceeded especially at high temperature and humidity. The corrosion is aggravated by diffusion of chloride ions through micropores of concrete element contains calcium hydroxide which produces calcium carbonate in the presence of carbon dioxide, and moisture in the environment. The formation of carbonic acid in the cement micro pores also lowers the pH of water in the pores of concrete close from 13 to 8, making the steel rebar vulnerable to corrosion. The depth of penetration of CO_2 is determined by the rate, which depends primarily upon the temperature, and the concentration of CO_2 at the surface of concrete.

Calcium carbonate also deposits in the pores, and with time the pH of pore water gets reduced to about 8 and may contain products of hydration, namely, silicates, aluminates; and the ferrite in steel becomes unstable, and corrodes. The corrosion products or rust being more voluminous exert pressure on the surrounding concrete and lead to localized spalling. The corrosive attack can be severe due to wind-born chloride ions from sea that can penetrate through the micropores in concrete. The corrosion is aggravated by high humidity and temperature. The addition of corrosion inhibiting alloying elements such as copper, phosphorus, chromium, molybdenum, and nickel in steel[5-10]. In this article, the effect of these alloying elements on the tensile properties, microstructure, and corrosion resistance of a semikilled TMT reinforcing steel bar has been discuss. Premature and rapid failure can be seen much below the design strength values of these steels when put to application in aggressive corrosive environments.

2. Materials and Experimental Procedure

2.1 Material preparation

In this research work, locally produced high strength 500MPa TMT reinforcing steel bars of Cu-P-Cr-Ni (steel 1) and C-S-Mn (steel 2) 10 mm diameter of two different local industries have been investigated. Here it is to be mentioned that, In this paper, high strength steel bars containing Cu-P-Cr-Ni and C-S-Mn will also be denoted by Steel 1 and 2 respectively(1 and 2 denote two different companies).

2.2. Chemical composition identification

The chemical compositions of the steel bars of two different companies were known by optical emission spectroscopy and are presented in Table 1.

Table-1: Chemical Composition of the steel bars.

Steel ID	Steel 1	Steel 2
C	0.21	0.25
Si	0.17	0.13
Mn	0.9	0.51
S	0.03	0.035
P	0.03	0.035
Cu	0.20	0.09
Cr	0.16	-
Ni	0.03	-

2.3. Metallography

Metallographic samples were also cut and prepared for observation under metallurgical microscope following standard procedure. After complete polishing, the faces of each sample of all high strength steel grades were etched in 2% Nital solution (2ml HNO_3 and 98ml ethanol or methanol).

2.4. Hardness test

Hardness tests were carried measured by out for all steel bars on different zones using a HTM-7510 Vicker tester machine. The effects of corrosion on hardness properties were observed by this experiment.

2.5. Tensile test

Tensile tests were carried out for all steel bars using a Alfred Jamsler Universal Testing Machine. The effects of corrosion on tensile properties were observed by this experiment.

2.6. Corrosion test

For corrosion tests, weight loss method and electrochemical test (Potentiodynamic polarization method) for determining the corrosion rates has been used. The corrosion rates of different types of steel bars of each company in various test media (fresh water and sea water) have been compared. Here it is to be mentioned that for corrosion tests using weight loss method, Steel bars were used in the as received conditions and for all cases, corrosion tests were continued for 70 days. However, after every 7 days (one week) of immersion, test samples were taken out of the solution, washed in water to clean the rusts accumulated on the steel bar surfaces and they were then completely dried. After that the mass losses were measured using a very sensitive digital balance. This experimental cycle has been repeated for 70days, i.e. for each sample, weight losses were measured for eight times. The corrosion rates of these steel bars are also determined by Potentiodynamic polarization method (PDP), the

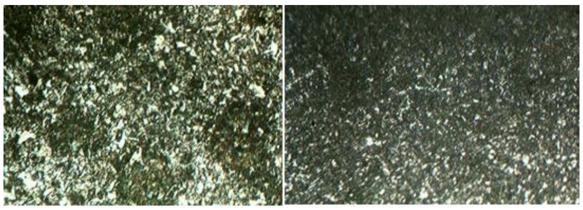
conventional three electrode electrochemical cell system was used. The steel samples were used as the working electrode, platinum rods as the counter electrodes and a silver/silver chloride electrode as the reference electrode.

PDP measurement is performed by slowly scanning the specimen potential through (-1.2V) and then moving to the positive (1.2V) direction in steps height of 0.5 mV, with the scan rate of 5mV/sec in either the anodic or cathodic direction, and the potentials are plotted versus the log of the measured current to generate a polarization curve.

3. Results and Discussions

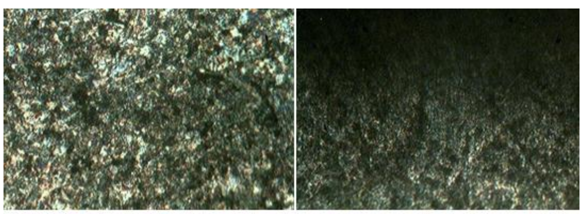
The chemical compositions of the TMT steel bars are presented in Table-1. As per this table the chemical compositions of steel bars supplied by two local companies are not the same. Steel Bars 1 have slightly lower carbon content, and alloying elements chromium, nickel and copper contents are present which are absent in case of steel 2. Both companies produce steel bars maintaining almost similar production process parameters, however, they showed different corrosion rates because of different chemical compositions and resulted final microstructures.

The microstructure of TMT steel bars was observed under an optical microscope. The microstructure of different zones (core and case areas) of steels are presented Fig-2 and Fig-3, it is revealed that case areas of both TMT steels are composed of tempered martensitic structures. However, in core areas, the microstructures are significantly different.



(a) (b)

Fig-2: Optical image showing microstructure of (a) core and (b) case of steel 1 at 100X



(a) (b)

Fig-3: Optical image showing microstructure of (a) core and (b) case of steel 2 at 100X

For a properly heat treated TMT steel bars, the core microstructures should be fully composed of well developed pearlite (black grains) and ferrite (white grains) and this has been observed for steel 1, Fig-2a. On the other hand, the ferrite-pearlite grains in core of steel 2 are significantly deviated from the standard microstructures Fig-3a. This type of deviation from standard microstructures means that there is residual stress in it. This residual stress is responsible for higher hardness values in the steel bars. From Table 2, it is clear that the case and core hardness of steel 2 is significantly higher than that of steel1.

Table-2: Results of Vicker Hardness testing

Steel ID	Average Case Hardness, HV	Average Core Hardness, HV
Steel 1	338	222
Steel 2	372	246

The case hardness of TMT steels are more than the core hardness. The reason behind this is that case is composed of martensitic structure which is brittle and core is composed of fine pearlite and ferrite which is ductile in nature. From Table 2 it is clear that the core and case hardness values of steel 2 are much higher than that of steel 1. One of the reasons behind this is its higher carbon content.

Table-3: Tensile properties of TMT steel bars used.

Steel ID	Yield Strength(MPa)	Ultimate Tensile Strength(MPa)	Elongation (%)
Steel 1	513.39	580.8	22
Steel 2	585.80	624.5	16

From Table-3, it is very clear that the tensile strength (both yield and ultimate) of steel 2 is much higher than that of steel 1, which is also expected from its hardness values. Whereas the ductility (elongation %) of steel 2 is much lower than that of steel 1. Thus the results show that these types of steels have good combination of ductility and strength. Corrosion of these steels leads to a substantial decrease in the strength parameters. Premature and rapid failure can be seen much below the design strength values of these steels when put to application in aggressive corrosive environments.

(a) (b)

Fig-4: Optical macrograph showing the fracture mode of TMT steels (a) 1 and (b) 2

Fig-4, presents the fracture modes of the steel bars used with as-received ribs on their surface. From this figure it is clear that steel 1 exhibited nearly cup and cone type fracture, which is the typical feature of any ductile fracture mode. However, steel 2 exhibited brittle and shear type fracture mode. In the case of concrete reinforcing applications, ductile failure of the steel bar is very much expected. We know that concrete is a very brittle aggregate. Its compressive strength is very high; however, the bending/tensile strength is very poor. Reinforcing steel bars protects the concrete under tensile loading from easy cracking and also from collapse. Because of non-standard aggregates, casting or improper curing, concrete might be cracked, but reinforcing steel bars resist the sudden collapse of the concrete. As concrete itself is a brittle type material, then reinforcement of the concrete with ductile type steel bars will ultimately increase the safety of the structures. It has been mentioned that steel bar 2 retains more residual stress because of lack of tempering in the heat treatment schedule. It has been found that steel bars with higher residual stress will corrode at a higher rate.

The corrosion behaviour of the TMT steel bars was studied using weight loss measurements in fresh water solution and sea water solution (3.5% NaCl) for a period of 70 days. The variation of corrosion rate (mpy) with exposure time (days) of TMT steels in 3.5%NaCl and fresh water was shown in Fig-5 and Fig-6.

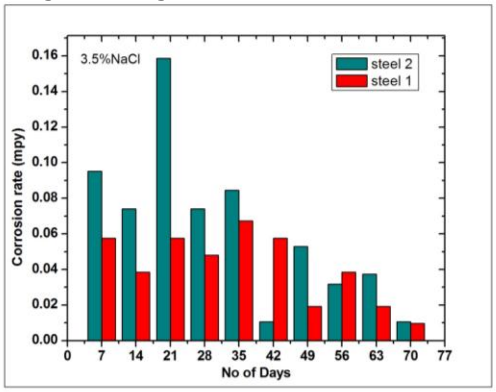


Fig-5: Variation of corrosion rate (mpy) with exposure time (days) of TMT steels in 3.5%NaCl

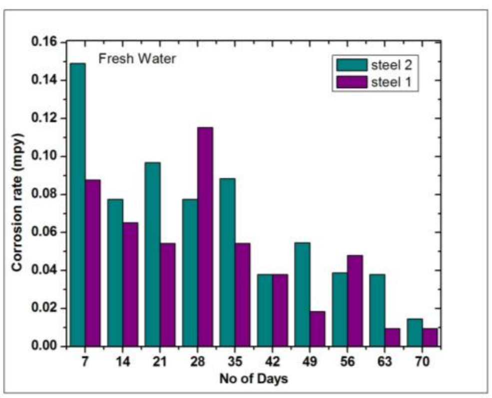


Fig-6: Variation of corrosion rate (mpy) with exposure time (days) of TMT steels in fresh water

The variation of corrosion rate (mpy) with exposure time (days) of TMT steels in 3.5%NaCl and fresh water was shown in Fig-5 and Fig-6 respectively. It was observed that the corrosion rates of steel bar in the solutions first linearly increased with an increase in immersion time and then gradually decreases. The steel 2 bar exhibited weight loss in 3.5%NaCl solution and fresh water is more than the steel 1 as shown in Fig-5 and Fig-6. This is in agreement with the corrosion behavior exhibited by steel 2 not compose of chromium and copper content and retains higher residual stress which will corrode at a faster rate while nickel is not as effective in sea water as in aggressive atmosphere.

The Tafel Potentiodynamic polarization curve of TMT steels in 3.5% NaCl and fresh water are presented in Fig-7 and Fig 8.

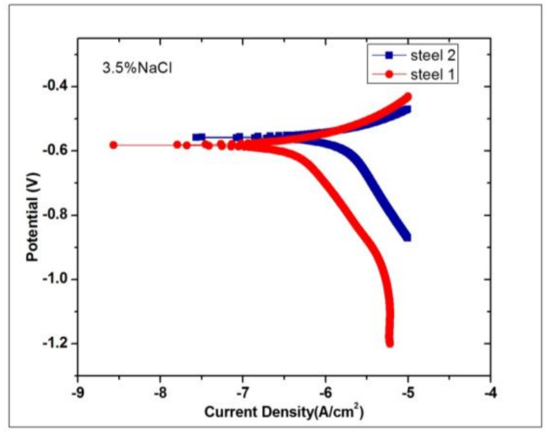


Fig- 7: Tafel polarization curve of TMT steels in 3.5% NaCl

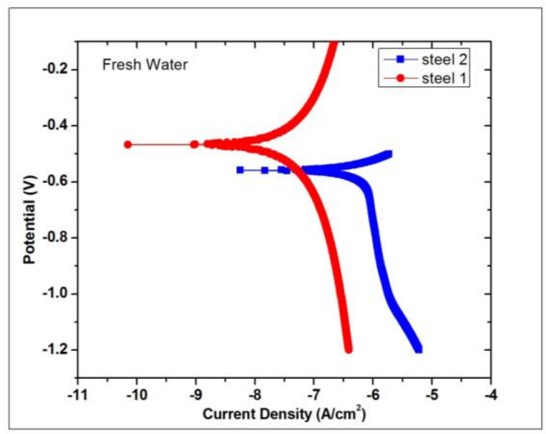


Fig- 8: Tafel polarization curve of TMT steels in Fresh water

The passivity of steels seems to remain unstable with passivity breakdown and pitting in concentrations of all the solutions. E_{corr} of the steels in all the solutions reached a stable value after a certain period of exposure. This indicates that the corrosion processes of the steels remain constant with time and they formed relatively stable corrosion products in the media studied.

TMT steel 1 was more resistant in fresh water and 3.5 % NaCl solution as compared to steel 2. In the polarization lead to the conclusion that TMT steel 2 corroded more than steel 1 in fresh water and 3.5% NaCl solution.

Table- 4: Experimental data of electrochemical test result

Corrosion media	Sample	E_{corr} (V)	$i_{corr}(A/cm^2)$	Corrosion Rate (mpy)
3.5% NaCl	Steel 1	-0.582	0.0026665	0.49226
	Steel 2	-0.558	0.0026750	1.818060
Fresh water	Steel 1	-0.467	0.00019033	0.129346
	Steel 2	-0.559	0.0020784	0.38369

From Table-4, it is clear that corrosion resistance of steel 1 was better than that of steel 2 in fresh water and 3.5wt% NaCl solution. The corrosion rates of the steels were observed to be more in 3.5wt% NaCl solution as compared to fresh water.

The surface texture of the TMT steels studied by the Scanning electron microscopy after corrosion is shown in Fig-9and Fig-10. By the surface analysis, it was observed that there is formation of pits on the surface of steels that is steels are mainly subjected to pitting corrosion.

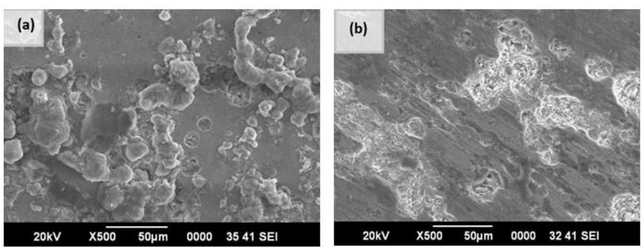


Fig-9: SEM micrographs of surfaces of steel 1(a) and steel 2(b) at 500X after corrosion test.

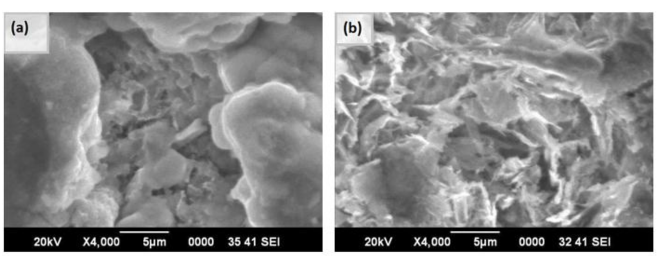


Fig-10: SEM micrographs of surfaces of steel 1(a) and steel 2(b) at 4000X after corrosion test.

4. CONCLUSIONS

The Corrosion effects of Cr and Ni in Thermo-Mechanical Treated steel bar in marine environments was studied and the following conclusions have been finally drawn.

1. Steel 1 containing Cu-P-Cr-Ni is more corrosion resistant than steel 2 containing C-S-Mn for use in marine environment.
2. Based on the results obtained from the weight loss tests carried out to assess the corrosion behavior of TMT steel in 3.5 % NaCl solution and fresh water, it can be concluded that the steel 2 bar exhibited weight loss in 3.5%NaCl solution and fresh water is more than the steel 1. This is in agreement with the corrosion behavior exhibited by steel not compose of chromium , and copper content and retains higher residual stress which will corrode at a faster rate while nickel is not as effective in sea water as in aggressive atmosphere.
3. Also from potentiodynamic polarization method it is clear that corrosion resistance of steel 1 was better than that of steel 2 in fresh water and 3.5wt% NaCl solution. The corrosion rates of the steels were observed to be more in 3.5wt% NaCl solution as compared to fresh water.
4. The steel shows different corrosion behavior with considerable difference in their corrosion resistance in two different environments. This was confirmed by the different patterns in cumulative weight loss of the steel as well as the Tafel polarization curves from the electrochemical techniques potentiodynamic polarization method. The steels shows different active to passive transition behavior in polarization.
5. The steel samples that were analyzed after corrosion using the scanning electron microscopy and it was observed that there is formation of pits on the surface of steels, hence the steels were subjected to pitting corrosion.

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