Paper No. RCC12



Corrosion Behavior of Dual Phase Steel in Different Pore Solution in RCC Structure

SubhadraSahoo^{1*} and Amit Sarkar²

Metallurgical and Material Engineering Department, Veer Surendra Sai University of Technology, Burla, Sambalpur, India.

> Metallurgical and Material Engineering Department, Jadavpur University, Kolkata-700032

e-mail: subhadrasahoo007@gmail.com

ABSTRACT

Dual Phase steels (DP) consist in a ferritic matrix with a fraction of dispersed in different percentage, which gives the material a good combination of strength and ductility, with a significant capacity to absorb energy and corrosion property. The purpose of this paper is to present results of an evaluation of dual-phase and different rebar steel reinforcements in corrosive environments. Low carbon steels were intercritically annealed at 740°C followed by iced water quenching to obtain dual-phase structures with different per cent volume fraction of martensite dispersed in ferrite matrix. Corrosion property of dual phase steel and rebar tested in different pore solution. Corrosion rate, tensile and macro as well as micro hardness tests were performed. From all of the tests carried out it was found that dual-phase steels exhibited better corrosion resistant properties and superior strength compared to rebar. The results reported show that dual-phase steel can be a good candidate for reinforcement in concrete especially in aggressive and corrosive environments.

Key words: dual Phase steels; corrosion rate; macro as well as micro hardness; rebar

1. Introduction

Technology breakthroughs in various fields, such as energy, automobile, safety and construction had been enabled through application of steel, which are most important structural materials for humankind. Overpowering progress in the above-mentioned domains has been achieved through the development of advanced dual phase steel, which have both high strength and good formability. Where most steels have primarily one microstructural phase, like ferrite, DP typically has a combination of martensite, bainite and ferrite phases. These unique microstructures of DP impart high-strength and high-ductility characteristics to the alloy. The engineering and scientific interest in dual-phase (DP) steel, one of the earliest and most prominent examples of AHSS, has been especially strong in the last decade [1]. DP steels are a group of high strength steels characterized by having a microstructure consisting of a matrix of fine ferrite containing small islands of a second harder phase. This second phase is mainly martensite, even though a small percentage of retained austenite or bainite might also be present. Usually, the volume fraction of the martensite in the microstructure is between 10 to 20% (even though ranges from 5 to 30% are also found in literature). The hard martensite islands provide substantial strengthening while the ductile ferrite matrix gives good formability [2-8]. Dual phase in reinforced concrete structures, the

ferrite matrix gives good formability [2-8]. Dual phase in reinforced concrete structures, the local ductility of elements subjected to bending moment is strongly influenced by the geometrical and mechanical parameters of the cross sections and the materials used, in particular, the concrete's mechanical properties, the strength, ductility and bonding of the reinforcement, the section's geometry, the percentages of longitudinal and transverse reinforcement, the structural details, the elements' slenderness, the boundary and loading conditions and the magnitude of the axial forces. Steel has very good corrosion resistance.

The intercritical quenching process introduces a harder phase into the ferrite matrix, which causes (in part due to the considerable volume differences) high residual stresses and an increase in the density of the mobile dislocations in correspondence to the ferrite–martensitic interface. The particular mechanical behaviour of the DP steel stems precisely from the formation of a two-phase ferrite–martensitic structure [9-11].

2. Experimental procedure 2.1 Metallography

Small specimens were cut from the as received sample and heat-treated samples for optical metallography. For this purpose, the thorough thickness cutting specimens was done along the perpendicular direction of longitudinal axis of each specimen using a StruersSecoTom10 machine. These specimens were polished in successively finer grade silicon carbide base abrasive papers from 320, 400, 600, 800, 1000, 1200, 1500, 2000, and 2500. After through paper polishing is done then the samples are manually cloth polished. Cloth polishing is done in automatic cloth polisher SPECTRUM SYSTEM[™] 1000 (Figure 3.5) successively to make sample completely scratch free. Ferrous alumina is used as a lubricant during cloth polishing. The specimens were then thoroughly cleaned with water and then in ethanol, and dried. The scratch free polished specimens were etched with 2% pctnital solution and observed in an optical microscope, Leica DM 2500M. Figure 3.6 shows the optical used for observing the microstructure. The finely polished and smoothly etched samples were ready for investigation. Analyser, Leica Application Suite, Version V4.4, has been used. Ten different fields were observed in optical microscope and the digital images of the

microstructures were used for quantitative characterization of microstructure of the steels. For this purpose, an automatic Image Viewer Version 4.4 is used for analysis.

2.2 Hardness measurement

The hardness of the as received and intercritically quenched samples was measured using a Vickers's hardness tester (Figure 3.8) at an applied load of 30 kg for 15 seconds. An average of five different fields was considered in this study.

2.3 Volume fraction calculation

Volume fraction of intercritically quenched specimen was determined using an automatic image analyser, Leica material works station. At least 10 fields on surfaces of the polished and etched specimens were studied at a suitable magnification to acquire a statistically reliable result. The data obtained were averaged to find the volume percentage of martensite.

2.4 Corrosion test

Small specimens were taken out from the mid region of these heat-treated samples. Corrosion behaviour has been studied by potensiodynamic polarization (Figure 3.10), electrochemical impedance spectra, and cyclic polarization and potentiostatic tests in 3.5% NaCl solution using potentiostat. Before starting the electrochemical experiments one side of each specimen was metallographically polished. Experiments were carried out by using a conventional three electrodes cell with a graphite rode and a saturated calomel electrode (SCE). In those experiments, polished sample was worked as a working electrode, graphite as a counter electrode and SCE as a reference electrode. Potensiodynamic Polarization curves were recorded at a constant scan rate of 1 mV/s at the interval from - 1500 to +2500 mV_{SCE}. Cyclic polarization involves sweeping the potential in a positive direction until a predetermined value of current or potential is reached, then the scan is immediately reversed toward more values that are negative until the original value of potential is reached.

3. Results

3.1 Microstructural analysis

As received sample, microsture contains ferrite and pearlite but after heat-treatment microstructural changes occurs to ferrite and martensite.



Fig 3.1 Tata Tiscon (as received) NIGIS * CORCON 2017 * 17 – 20 September 2017 * Mumbai,India



30;µm

Fig 3.3 Optical micrographs of as received sample Concast Maxx.



Fig 3.4 optical micrograph of as received DP steel.

Hardness:

Rebar	Hardness(VHN)
Tata Tiscon (as received)	170

4. Potensiodynamic polarization curve

a. 0.9 M NaOH (pH=13.9) + 0.2% Cl⁻solutions:

Fig.4.1a shows examples of the anodic polarisation curves obtained for Tata Tiscon in 0.9 M NaOH solution and in the same solution with the addition of different concentrations of chloride ion. Rebar segments immersed in 0.9 M NaOH solutions were in the passive state at the free corrosion potential. The presence of higher chloride concentrations has a substantial effect on the anodic behavior of the steel. The anodic polarization curves showed a passive zone, where the passive current density increased with increasing chloride concentration and a passivity breakdown potential or pitting potential above which high current increases were observed and pitting nucleated on the metallic surface. The pitting potential was a function of the chloride concentration. The higher the chloride concentration, the lower is the pitting potential. In addition, the corrosion potential shifted toward lower values with increasing chloride concentration. The behavior DP to the above solution is shown in fig4.1b Corrosion rate of DP lower than DP steel in same Solution.



Fig4.1a Corrosion behavior of Tata Tiscon



Fig 4.1b Corrosion behavior of DP steel

b. Saturated Ca(OH)₂ (pH=12.5) + .2% Cl⁻ solutions:

The anodic polarisation curve obtained for carbon steel in saturated $Ca(OH)_2$ solution was similar to those found in 0.9 M Na (OH) solution. The major difference was a displacement of the curve towards higher potentials that was most probably associated to the lower pH of the $Ca(OH)_2$ solution. The behavior Tata Tiscon to the above solution is shown in fig.4.2a.and DP steel fig no 4.2b



Fig4.2a Corrosion behavior of Tata Tiscon





c. 0.3 M NaHCO₃ + 0.1 M Na₂CO₃ (pH=9.0) solution:

The rebar polarization behavior in the solution containing high levels of carbonates and bicarbonates was also found to be analogous to that observed in the more alkaline solutions. The formation of green corrosion products on the metallic surface was seen above the pitting potential. Similarly, to the behavior in more alkaline solutions, the pitting potential will be a function of the chloride ion concentration, and the higher the concentration the lower will be the pitting potential. In addition, the corrosion potential will shift to the less noble direction with increasing chloride. Corrosion rate of DP is lower than Tata Tiscon in this solution. The behavior Tata Tiscon to the above solution is shown in fig.4.3a and DP steel fig no 4.3b



Fig4.3a Corrosion behavior of Tata Tiscon



Fig 4.3b Corrosion behavior of DP steel

a. 0.015 M NaHCO₃ + 0.005 M Na₂CO₃ (pH=9.0) solution:

The anodic polarisation curve of the rebar steel in the solution containing low levels of carbonates and bicarbonates was different from that obtained in the more concentrated solution. In this medium, the corrosion potential was lower than the one measured in solution (c) and no passivity was found. As the potential was raised from the corrosion potential, instead of a low passive current density, a current density that increased rapidly with the potential was observed. Further increase in potential led to a limiting current density. This limiting current was attributed to the limiting value of the transport of ions across a thick film of green corrosion products, clearly seen on the metallic surface. The behavior Tata Tiscon and DP steel to the above solution is shown in fig.4.4a and fig 4.4b. Corrosion rate of DP steel lower than Tata Tiscon in this solution.



Fig4.4a Corrosion behavior of Tata Tiscon



Fig 4.4b Corrosion behavior of DP steel

5. Discussion

The low instantaneous corrosion rate values calculated from polarisation resistance measurements and the corrosion potential values measured in saturated $Ca(OH)_2$ and 0.9 M NaOH solutions, indicated that in these highly alkaline solutions the rebar steel was in the passive state at the free corrosion potential. This result is in agreement with the predictions of the equilibrium potential–pH diagram for the Fe–H₂O system. According to this diagram, a passive oxide film should be stable in both solutions. In highly alkaline solutions, such as saturated $Ca(OH)_2$ solutions, NaOH, KOH or mixtures of these solutions,

the passive state of steel is provided by the presence of a thin oxide film that protects the metal from active corrosion. Kruger and Calvert suggested that the main component of the passive film formed in alkaline solutions were Fe_3O_4 or Fe_2O_3 oxides while Smialowska and

co-workers, by using ellipsometry, concluded that the composition of the passive film formed in both calcium and sodium hydroxide solutions was similar to an oxihydroxide (FeOOH) rather than to Fe₃O₄ or c-Fe₂O₃. Finally, Yonezawa et al. found that in saturated Ca(OH)₂ solution a discontinuous layer of Ca(OH)₂ was present on the metal surface. The addition of chloride ions has a noticeable effect on the corrosion behavior of Tata steel in high alkaline solutions, since in the presence of this ion a passivity breakdown process took place above a certain potential that decreases with the chloride concentration. A critical chloride concentration above which pitting occurred on the metallic surface was evaluated from the results of the potensiodynamic tests. The critical chloride content was defined as the highest chloride concentration that can be tolerated without causing pitting corrosion of the steel up to the oxygen evolution potential. The chloride threshold was 1% (0.28 M) in the solution with pH 13.9 but decreased to 0.1% (0.028 M) in the saturated Ca(OH)₂ solution at pH 12.5. Thus, the critical chloride concentration for pitting initiation increases when the solution pH increases. The beneficial effect of alkalinity on chloride induced localized corrosion of carbon steel is accounted for by the pitting mechanism developed by Galvele, in which the maintenance of a local acidification on the metal solution interface is required as the necessary condition for pitting initiation and propagation. The local acidification is caused by the hydrolysis of metal ions inside of micro-cracks already existing in the passivation film. For each metal and alloy, a critical acidification is necessary to render re-passivation unlikely and sustain pit activity. The presence of high concentrations of OH- ions in the solution hinders the formation of the localized acidification, producing inhibition of the pitting process. The results obtained in solutions simulating carbonated concrete pore solution showed that, at constant carbonate/bicarbonate ratio and constant pH, the corrosion behavior of the steel varied with the concentration of these ions. The instantaneous corrosion rate and the E_{corr} values measured in the solution containing high levels of carbonates and bicarbonates suggested that a protective passive film was formed on the metal surface at the free corrosion potential. Likewise, the potensiodynamic polarisation curve exhibited a large potential range in which the current density was relatively low and no attack was detected on the surface of the samples after polarisation. On the other hand, the behavior of the steel during anodic polarisation in 0.015 M NaHCO₃ + 0.005 M Na₂CO₃ solution indicated that the rebar steel undergone generalized corrosion when exposed to а diluted carbonate/bicarbonate solution. The high corrosion rate values attained as well as the relatively low value of the corrosion potential during the long-term exposition to this solution confirmed this conclusion. In addition, the corrosion potential of the steel in the 0.015 M NaHCO₃ +0.005 M Na₂CO₃ solution was found to fall into the generalized corrosion zone of the Pourbaix diagram for the Fe-H₂O system. Thomas and Davies suggested that the increase in the stability of the Fe (III) passive film on iron with increased bicarbonate concentration was due to the shift of the Flade potential towards lower values. Thus, a high bicarbonate concentration will prevent the dissolution of the passive film. Several authors have reported the existence of two current density peaks in the anodic polarisation curve of carbon steel in bicarbonate solutions. The first peak, at E < -0.2 V was associated with the dissolution of metallic iron (Fe) to ferrous ion (Fe²⁺) and the formation on the metallic surface of a pseudo-passive layer of Fe(OH)² and/or FeCO₃:

 $Fe + 2H_2O = Fe (OH)_2 + 2H_2 + 2e^{-1}$

 $Fe + HCO^{3-} = FeCO^3 + H^+ + 2e_-$

By further increasing the potential, a second current density peak was observed, at

0.1 V, and a passive film was formed $3Fe (OH)_2 \rightarrow Fe_3O_4 + 2H_2O + 2H^+ + 2e_-$

Mao et. al. suggested that the changes in the shape of the polarisation curves with the bicarbonate concentration were mainly related to differences in the stability of the FeCO₃ pseudo-passive film. When the HCO_3^{-} concentration is low, the pseudo-passive film of FeCO3 could be formed on the metal surface as a result of local saturation. However, the local equilibrium of Fe²⁺ and CO₃²⁻ with FeCO3 could be broken by the diffusion of the Fe²⁺ ion away from the surface, resulting in the dissolution of the film. If this was the case, the FeCO3 film would have gone through a competition between formation and dissolution processes, and thus, the polarisation curve in low-concentration HCO³⁻ solutions showed a broad anodic current peak of relatively high current density value. If at higher potentials, passivation did not occur, the metal would continue to dissolve as Fe (II) under diffusion control and the current density would remain high. Transport process analysis inside a pit showed that anions of weak acids salts, because of their buffer properties, act as an impediment for the development of the locally acidified zone in the same way as OH- ions. Therefore, in the presence of anions of weak acid salts, it is more difficult to reach the low pH conditions necessary to promote pitting. In all solution DP steel show low corrosion rate. As received sample have pearlite and ferrite structure. Dual phase have ferrite martensite structure.

6. Conclusions

- In high alkaline solutions and in the more concentrated carbonate plus bicarbonate solution carbon steel remains passive even if the potential is raised up to the potential range of the oxygen evolution reaction.
- In the presence of low levels of carbonate and bicarbonate carbon steel does not passivate and generalized corrosion occurred at all potential higher than the free corrosion potential.
- From a mechanistic point of view, the pitting process in high alkaline solutions and in the more concentrated carbonate plus bicarbonate solution is different from that in the less concentrated solution.
- In the first solutions, pitting was originated by the localized rupture of a passive film whereas in the less concentrated solution, pitting occurred not on a passive metal surface, but on a metal, that is undergoing generalized corrosion.
- An increase in pH as well as the presence of high levels of carbonate and bicarbonate has a beneficial effect on the chloride threshold and improves the resistance of carbon steel to localized corrosion.
- Some problem with the result occurred due to some technical problem. Therefore, we did get exact graph.
- Cl- increases the corrosion rate by breaking the passive layer.
- For protecting a structure from corrosion we have to increase the alkalinity of the solution (pH to be very high)
- DP steel have low corrosion rate than Tata steel rebar.

References

- Tasan, C. C., Diehl, M., Yan, D., Bechtold, M., Roters, F., Schemmann, L., Zheng, C., Peranio, N., Ponge, D., Koyama, M., Tsuzaki, K. & Raabe1, D. (2015). An overview of dual-phase steels: advances in microstructure-oriented processing and micromechanically guided design. Annual Review of Materials Research, 45, 391-431.
- Evaluation of reinforcing bars in old reinforced concrete structures, Engineering Data Report, 2001, 48, 1-4.
- 3. Dieter, G.E., (1988) Mechanical Metallurgy. Material Science and Engineering, 2ndedition.
- 4. Kuziak, R., Kawalla, R., &Waengler, S. (2008). Advanced high strength steels for Auto motive industry. Archives of civil and mechanical engineering, 8(2), 103-117.
- 5. Zackay, V. F., Parker, E. R., Fahr, D., & Busch, R. (1967). The enhancement of ductility

In high-strength steels. ASM Trans Quart, 60(2), 252-259.

- Bode, R., Meurer, M., Schaumann, T. W., &Warnecke, W. (2004). Selection and use of Coated advanced high-strength steels for automotive applications. Revue de Métallurgie, 101 (7-8), 551-558.
- Mintz, B. (2001). Hot dip galvanising of transformation induced plasticity and other Intercritically annealed steels. International materials reviews, 46(4), 169-197.
- 8. Ball, A., Chauhan, Y., & Schaffer, G. B. (1987). Microstructure, phase equilibria, and

Transformations in corrosion resistant dual phase steel designated 3CR12. Materials

Science and technology, 3(3), 189-196.

- Llewellyn, D. T., &Hill's, D. J. (1996). Dual phase steels. Ironmaking& steelmaking, 23(6), 471-478.
- Verdeja, J. I., Pero-Sanz, J. A., & Asensio, J. (2005, August). Multiphase steels: Structure Mechanical properties relationships in the cold rolled and continuous annealed condition. In Materials Science Forum (Vol. 500, pp. 429-436).
- 11. Bleck, W., & Phiu-On, K. (2005, August). Micro alloying of cold-formable multi-phase Steel grades. In Materials Science Forum (Vol. 500, pp. 97-114).