

# EFFECTS OF MICROSTRUCTURE ON THE CORROSION BEHAVIOUR OF MEDIUM CARBON STEEL

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## ABSTRACT

The effects of microstructural changes achieved through different types of heat treatments on the corrosion resistance of a medium carbon steel (0.40% C, 0.25% Si, 1.20% Mn, 0.04%P, 0.04%S, 0.25%Cu, 0.10%Cr, 0.10%Ni, 0.011%N) in different media was undertaken in this research. Four types of heat treatment: annealing, normalizing, hardening and tempering were carried out, after which the heat treated samples were exposed to fresh water, sea water, 0.1M H<sub>2</sub>SO<sub>4</sub> and 0.1M HCl environments and were allowed to stay in these media for 70 days. Weight loss measurements were taken at intervals of 14 days. Metallographic study of the different samples was also done. The results obtained showed that the different microconstituents obtained via the heat treatments are environment sensitive. Also the microgalvanic effect which is a consequence of the presence of secondary phases tend to have a more negative effect on corrosion resistance than the effect of residual stresses and lattice distortions found in martensitic structures.

**KEYWORDS:** microstructure, microgalvanic, microconstituent, residual stresses, lattice distortions.

## INTRODUCTION

Steels are by far the most widely used engineering materials, primarily because they can be manufactured relatively cheaper in large quantities to very precise specifications. More over, they provide an extensive range of mechanical properties from moderate strength levels (200 – 300 MNm<sup>-2</sup>) with excellent ductility and toughness, to very high strengths (5500MNm<sup>-2</sup>) with adequate ductility (Honeycombe and Bhadeshia, 1995). In order to have maximum advantage, the mechanical properties can be changed by varying the structure and relative proportions of the microconstituents. This change is achieved chiefly through the use of alloying elements and heat treatments (Honeycombe and Bhadeshia, 1995; Smallman, 1995).

With the possible variations in the properties of steels, there can be no question as to why they are used extensively in different applications. Steels are however prone to drastic changes in their corrosion behaviour in different environments, especially when they have undergone certain heat treatments (Ovri and Ofeke, 1998; Fontana and Greene, 1995). Their response however differ from material to material and also depends on the type of heat treatment they are subjected to. The effects of microstructural changes achieved through different heat treatment processes on the corrosion resistance of a medium carbon steel in different environments is the subject of this paper. The chemical composition of the steel is given in Table 1.

## MATERIALS AND METHODS

### Samples Preparation

The steel samples used for this investigation were obtained from Delta Steel Company, Ovwian – Aladja, Delta State, in the form of ribbed bars of about 16mm diameter. The samples were machined to remove the ribbed surface of the bar in order to prevent crevice corrosion. They were then cut into suitable lengths using a hacksaw.

### Heat Treatment

The samples were grouped into 6 sets, labeled A to F according to the type of heat treatment they were given. The heat treatment was carried out using a Nabertherm box type furnace. Microscopic examination and study of the heat treated samples was done in the Metallography Laboratory of the Federal University of Technology, Owerri, Imo State. The observed microscopic features of the heat treated samples were noted, after which the dimensions (diameter and length) and weight were then taken using a Vernier caliper and a top loading digital electronic balance respectively. The heat treatment involved holding of all samples at 925°C for 20 minutes followed by:

- (i) SET A: slow cooling in the furnace (annealing)
- (ii) SET B: slow cooling in air (normalizing)
- (iii) SET C: quenching in 17 litres of engine oil.
- (iv) SET D: quenching in 25 litres of water.
- (v) SET E: quenching in 25 litres of water followed by tempering at 460°C for 2 hours.
- (vi) SET F: control (as-received material).

### Environment Preparation

The sea water used in this investigation was collected from an estuary of about 300m from the Atlantic Ocean, near the operation base of Texaco Overseas Petroleum Company of Nigeria (TOPCON) in Warri, Delta State, while fresh water was collected from the Otamiri River in Owerri, Imo State. The chemical analysis of the water samples are shown in Table 2. The acid solutions were prepared in the Metallurgical Engineering laboratory of Federal University of Technology Owerri, Imo State. The weight losses of the samples were determined at intervals of 14 days for a period of 3 months.

**Table 1:** Chemical Analysis of the Medium Carbon

Element	C	Si	Mn	P	S	Cu	Cr	Ni	N	Fe
% Composition	0.40	0.25	1.20	0.04	0.04	0.25	0.10	0.10	0.011	balance

Table 2: Chemical Analysis of Water Samples

	Ca <sup>2+</sup>	Mg <sup>2+</sup>	CO <sub>2</sub>	Fe <sup>2+</sup>	Cl <sup>-</sup>	O <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	HCO <sub>3</sub>	NO <sub>3</sub>
Sea water	3.43	3.12	0.31	0.0014	54.36	0.55	2.99	30.10	5.23	0.001
Fresh water	1.38	3.34	4.25	0.01	14.47	5.50	0.40	1.50	42.12	0.006

**EXPERIMENTAL RESULTS**

The corrosion rates were calculated using weight loss measurements got over the period of the investigation. The relationship used for the calculation was:

$$mmy^{-1} = \frac{36.52 \times Mdd}{D} \quad (\text{Wranglen, 1972})$$

Where:

$mmy^{-1}$  = millimeters penetration per year

$Mdd$  = mg per  $md^2$  per day =  $10 \times g \times m^{-2} \times d^{-1}$

$D$  = density of the metal in  $Kgm^{-3}$

$d$  = time in days

$m^2$  = cross sectional area in metre square

$g$  = weight loss in grammes.

The graphs of corrosion rates versus days are shown in Figs. 1 - 9.

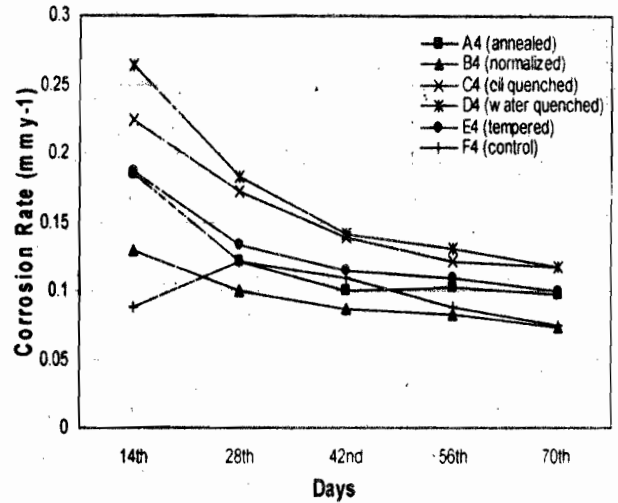


FIG. 2: CORROSION RATE VERSUS DAYS IN FRESH WATER

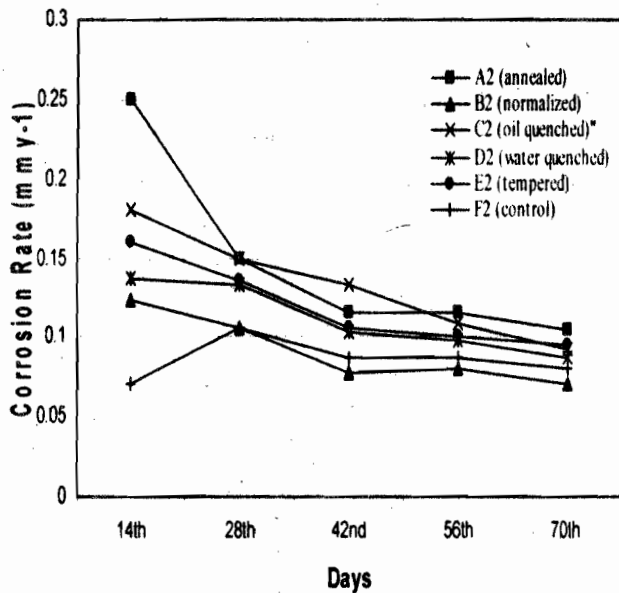


FIG. 1: CORROSION RATE VERSUS DAYS IN SEA WATER

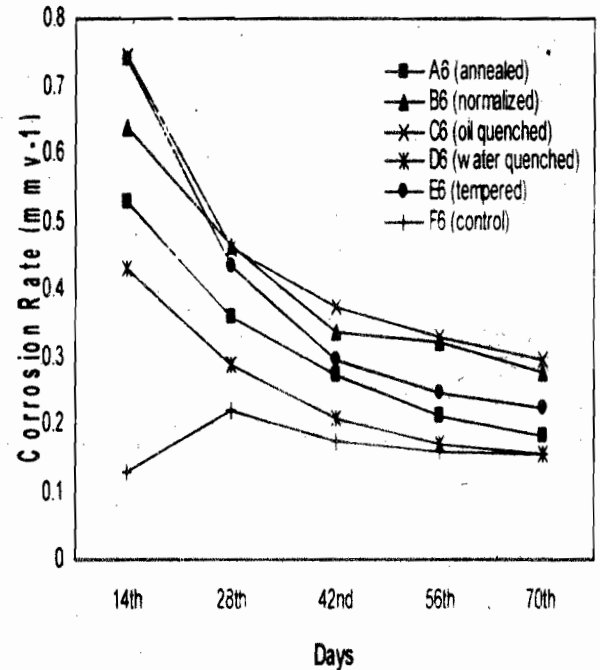


FIG. 3: CORROSION RATE VERSUS DAYS IN 0.1M H2SO4

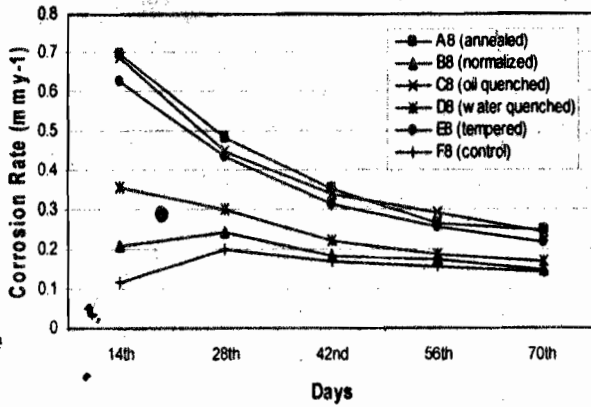


FIG. 4: CORROSION RATE VERSUS DAYS IN HCl

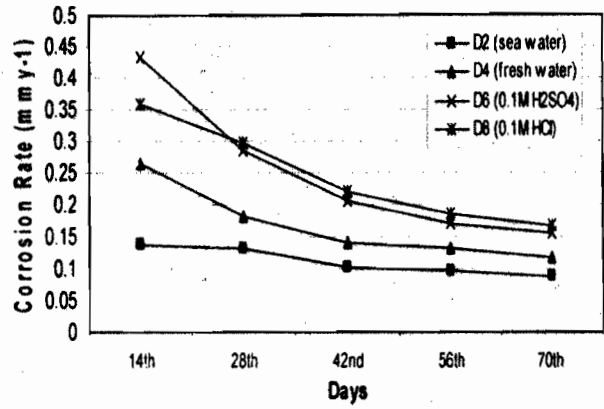


FIG. 8: CORROSION RATE OF WATER QUENCHED SAMPLES IN DIFFERENT MEDIA

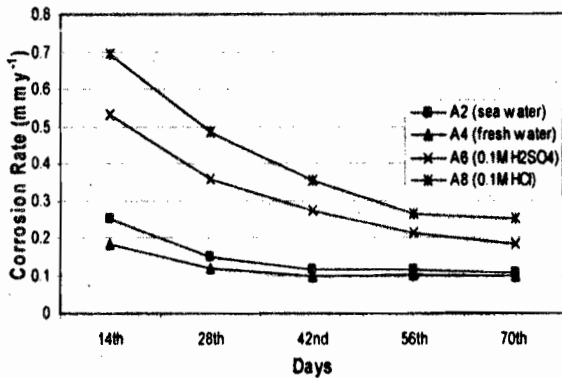


FIG. 5: CORROSION RATE OF ANNEALED SAMPLES IN DIFFERENT MEDIA

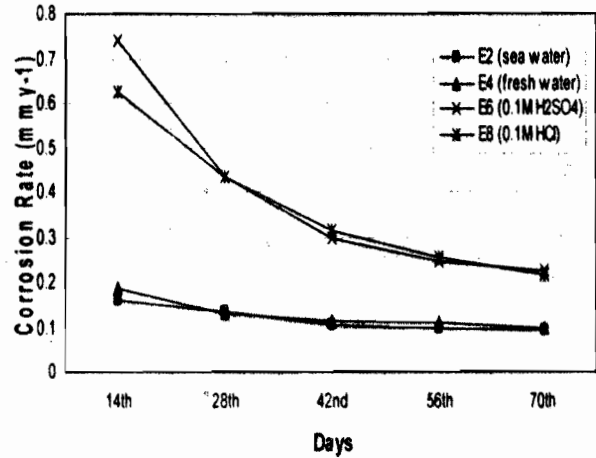


FIG. 9: CORROSION RATE OF TEMPERED SAMPLES IN DIFFERENT MEDIA

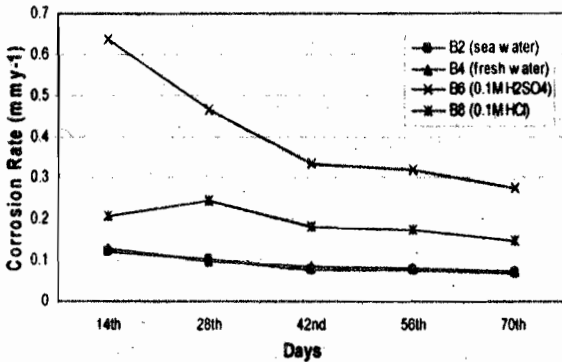


FIG. 6: CORROSION RATE OF NORMALIZED SAMPLES IN DIFFERENT MEDIA

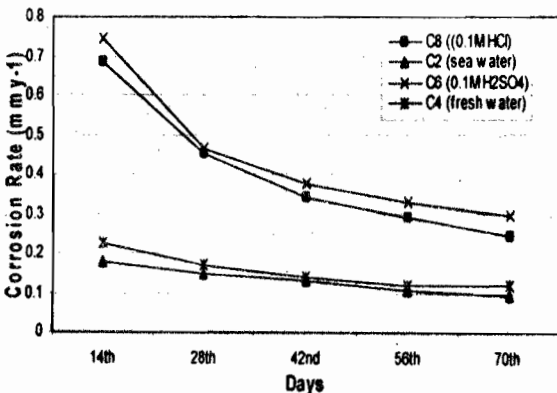


FIG. 7: CORROSION RATE OF OIL QUENCHED SAMPLES IN DIFFERENT MEDIA

## DISCUSSION OF RESULTS

It can be seen from Figs 1 – 4 that there was a gradual drop in the corrosion rate of all the heat treated samples with exposure time (days). Exceptions are however seen in the as – received samples in the different environments where there was a sharp rise in the corrosion rate during the first 28 days, followed by a gradual drop during the remaining period of the investigation. This trend may be as a result of the non – homogeneity and non – uniformity in composition that is often associated with metallic materials in the as – cast condition. These are known to increase corrosion rate (Davies and Oelmann, 1983; Fontana and Greene, 1986; Wranglen, 1972). On the other hand, the gradual drop may be as a result of the formation of corrosion product on the surface of the steel and decrease in the concentration of the corrosion media with time (Ovri and Ofeke, 1998).

Examination of the annealed and normalized samples under the microscope at a magnification of x200 revealed that they had a microstructure consisting of proeutectoid ferrite with small regions of lamellar pearlite. The grain sizes of the annealed samples were however larger than those of the normalized samples; due to the very slow cooling rate obtainable in the former. The rather slow cooling rates of these treatments are known to also encourage the precipitation of carbides (Rajan, Sharma and Sharma, 1988; Davies and Oelmann, 1983). The presence of these secondary phases have been found to lead to the setting up of microgalvanic cells within the microstructure, with the new phases becoming cathodic to the rest of the matrix (Ovri and Ofeke, 1998; NACE Group Committee, 1979). The result is that corrosion of the annealed and normalized samples was

accelerated in all of the four media. An interesting trend was however noticed in the behaviour of the annealed/normalized samples in the different media. The corrosion rates of the annealed samples were higher than those of the normalized samples in fresh water, sea water and  $H_2SO_4$ , but the reverse was the case in the HCl media. This suggests that the microconstituents are environment sensitive. The samples quenched in oil and water also showed significant losses in corrosion resistance. However, the water quenched samples exhibited relatively lower corrosion rates than the oil quenched samples in the different media except fresh water where the reverse was the case.

Examination of the samples under the microscope revealed that the oil quenched samples were basically made up of pearlite in a martensite matrix. The microgalvanic effect induced by the presence of these two phases must have had preeminence over the effect of internal stresses and lattice distortions inherent in the nearly 100% martensitic structure of the water quenched samples. However, the environment appeared to have played the major role in case of fresh water. Generally, it has been found that although tempering relieves residual stresses and removes the lattice distortions in the martensitic structure of the quenched samples, it results in the precipitation of carbide particles (Rajan, Sharma and Sharma, 1988; Davies and Oelmann, 1983). These new phases tend to increase the corrosion rates of steels especially in acid media (Ovri and Ofeke, 1998). The behaviour exhibited by the water quenched samples in the fresh water environment, where it was found to have higher corrosion rates than the oil quenched samples and the tempered samples (the converse was the case in the other three media), suggest that the martensitic structure of the water quenched sample is very sensitive to the presence of some ionic species in the fresh water environment.

The plots in Figs. 5 - 9 further show that the microconstituents are environment sensitive. The annealed samples had the least corrosion resistance in HCl, followed by  $H_2SO_4$ , sea water and the fresh water. This may be connected with the fact that acidic environments are generally more aggressive than other water media. The normalized and the oil quenched samples showed similar behaviour. They had the least resistance in  $H_2SO_4$ , followed by HCl, fresh water and then sea water. The water quenched samples had the least resistance in HCl, followed by  $H_2SO_4$ , fresh water and sea water. The acids (HCl and  $H_2SO_4$ ) had very similar corrosion inducing effects on the tempered samples; however they had a slightly lower corrosion resistance in fresh water than in sea water. On the whole, although the acid media were more aggressive than the water media, it is obvious that the microconstituents obtained via the different heat treatment processes are environment sensitive.

## CONCLUSION

It can be concluded from this investigation that the microconstituents of medium carbon steel obtained via different heat treatment processes are environment sensitive. More so, the presence of secondary phases as obtained in the annealed, normalized and tempered samples have been found to lead to the setting up of microgalvanic cells within the microstructure, with the new phases becoming cathodic to the rest of the matrix. Further more, the microgalvanic effect which is a consequence of the presence of secondary phases tend to have amore negative effect on corrosion resistance that the effect of residual stresses and lattice distortions inherent in martensitic structures in all the media investigated except in the fresh water medium.

## REFERENCES

- Honeycombe, R. W. K. and Bhadeshia, H. K. D., 1995. Steels: Microstructure and Properties, 2<sup>nd</sup> ed., Edward Arnold, London.
- Shreir, L. L., Jarman, R. and Burstein, T., 1994. Corrosion, v. 1, Metal/Environment Reactions, 3rd ed., Butterworth Heinemann, Oxford.
- NACE Group Committee T - 1 (1979). Corrosion Control in Petroleum Production, NACE, Houston.
- Rajan, T. V., Sharma, C. P., Sharma, A., 1988. Heat Treatment - Principles and Techniques, 1<sup>st</sup> ed., prentice-Hall, New Delhi.
- Davies, D. J. and Oelmann, L. A., 1983. The structure, Properties and Heat Treatment of Metals, 1<sup>st</sup> edition, Pitman Book Ltd, London.
- Ovri, J. E. O and Ofeke, B. G., 1998. The Corrosion Behaviour of Mild Steel in a Marine Environment; J.Sci Engr. Tech. 5 (2): 1117-1129.
- Smallman, R. E., 1995. Modern physical Metallurgy, 9<sup>th</sup> edition, Butterworth Heinemann Ltd, Oxford.
- Wranglen, G., 1972. An Introduction to Corrosion and Protection of Metals. IFM Publishers. Stockholm.
- Fontana, M. G. and Greene, N. D., 1986. Corrosion Engineering, McGraw Hill Higher Education, 3rd ed. Singapore.