

Effect of Saline Medium on Corrosion and Erosion-Corrosion of Surface Treated Low Carbon Steel

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Abstract: The research investigates the effect of the surface treatment carbonization, nitriding and carbonitriding on the corrosion and erosion-corrosion of low carbon steel in saline medium. Micro-hardness testing using the Vickers hardness method was applied to all samples before and after surface treatment of carbonization, nitriding and carbonitriding. Steel samples were immersed once in a saline bath as a medium for the corrosion, and once in saline with 1% wt. SiO_2 as a medium for the erosion-corrosion. The immersions took place for different periods of time for 120, 240, 360 and 480 hr. The results of the corrosion and erosion-corrosion testing showed occurrence of corrosion and erosion-corrosion on the surface of the tested samples evident by weight loss as measured expressed as g/cm^2 . Comparison between the results of the corrosion and the erosion-corrosion testing, was carried out by analyzing weight loss results. Results show that the surface carbonitriding treatment offers the best resistance to corrosion and erosion-corrosion.

Keywords: Corrosion, Erosion, saline, Ringer Saline, carbonization, nitriding, carbonitriding, Surface Treatment

1. Introduction

One of the main problems facing petrochemical projects and factories is corrosion and the erosion-corrosion. This corrosion causes damage to parts of the industrial structure. Therefore when planning for the creation of industrial units, corrosion reduction methods have to be taken into consideration to reduce the damage to those parts. This can be done by manufacturing those parts using metals that show high resistance to corrosion and the erosion-corrosion. Low carbon steel is distinctive of the most suitable metals for this particular purpose, as its mechanical properties can be improved, and its corrosion resistance can be increased, by applying surface treatments such as carbonization and nitriding, in preparation for use as parts in industrial structures [1]. Studies regarding parts made of low carbon steel show that it has a weak resistance to corrosion in highly effective environments, thus noting the need of providing an effective protection for such parts in those environments by applying a dual surface treatment such as carbonitriding [2]. Different techniques have been used to protect these parts from corrosion and the erosion-corrosion, such as the surface treatment (carbonization, nitriding, carbonitriding and part of the spreading paint process) [3]. Testing the parts after treatment in such environments, they showed improved resistance to corrosion, thus the economic benefits were convincing

enough to warrant a study of those techniques, in terms of which is best when it comes to quality and ease of application. Treatment is done by painting metal parts with non-metal materials which can be spread on the surface [4]. Most of the effective ways of offering protection from the two types of corrosion depend on the diffusion process, where the materials are applied to the metal, at the solid state, via carbonization, nitriding and carbonitriding, using standard laboratory methods. This way was accepted by the factories, thus leading to an increase in the research efforts in the field of applying dual paint to increase resistance to corrosion and the erosion-corrosion [5]. This research investigates the effect of the surface treatment carbonization, nitriding and carbonitriding on the corrosion and erosion-corrosion of low carbon steel C10E. Surface treatment has been applied to samples of the steel used by means of immersion, while monitoring the effects of saline and erosion environments on their weight loss. Steel samples were immersed once in a saline bath as an environment for the corrosion, and once in saline with SiO_2 as a medium for the erosion-corrosion.

2. Experiment & Materials

A steel of a low commercial carbon was used. It has a square cross section (10x10x55) mm. Table (1) shows its chemical composition. Analysis was done using the spectral analysis device.

Table 1: Chemical Structure of the Steel Used

Element	C	Si	Mn	P	S	Cr	Ni	Fe
Concentration	0.17- 0.2	0.5- 0.35	0.4-0.7	0.035	0.045	0.55- 0.95	2.25- 2.75	Rem.

The Ringer's saline solution used was supplied by Haidylen for advanced medical industries Egypt. Table (2)

shows its chemical contents as provided by the supplying company.

Table 2: Chemical content of the Ringer Saline Solution as provided by the supplier

Chemical component	100 ml contain	Equivalent to approx.	Na+	147.5 mmol/l
Sodium chloride	0.860 gm		K+	4 mmol/l
Potassium chloride	0.03 gm		Ca++	4.5 mmol/l
Calcium chloride $2\text{H}_2\text{O}$	0.033 gm		Cl-	156 mmol/l

3. Surface Treatment

Surface treatment by carbonization, nitriding and carbonitriding was applied to samples of the steel used as revealed below.

Carbonization: Carbonization was applied by using a controlled electric oven (manufactured by Nabertherm of Germany). The maximum temperature of this oven is 1100 °C. Samples were placed in an environment comprised of 80% vegetarian grinded coal, and 20% stimulant chemical material as an energizer, Barium Carbonate BaCO_3 , inside a metal mold designed and manufactured for this particular purpose. Samples were heated at 930 °C for 6 hours. As a result of the chemical interaction, carbon dioxide was produced, and it combined with the carbon atoms, leading to the generation of the carbon monoxide gas. Carbon monoxide gas combines with carbon at a high temperature, generating carbon dioxide and atomic carbon, which in turn spreads through the metal surface at a specific depth, towards the core of the metal. The surface carbonization process helps enriching the surface with atomic carbon, which in turn reacts with iron, forming deposited iron carbide Fe_3C . This resulting cementite, with a low resistance against corrosion, is highly brittle, presenting the danger of desquamation in the grain boundary while cooling down the steel slowly from its carbonization temperature. Due to that, it is necessary to achieve hardening to get to the martensite state, and then the tempering process would be carried to improve the mechanical properties of the metal [6,7]. As carbonization needs a long time at the carbonization temperature, overheating may occur, which leads to a growth in the size of granules on the surface (outer case) and inside the core. In order to develop the mechanical properties of the steel, and because of the difference in the amount carbon content between the core and surface, and in order to break the carbide network in the carburized case, there is a need to apply thermal treatment in proportion to the amount of carbon content in the core and the surface [6]. As the first step, the core was treated by heating the samples slightly higher than the degree of the upper critical higher temperature, 880 °C, for 15 minutes, until the core structure turns to very small grains of Austenite, which are then quenched in oil, in order to form a structure inside the core of ferrite particles, in an environment of martensite. But this process leads to the forming of a hard and brittle structure on the surface, in the form of big grains of martensite particles. Heating to the high temperature of 880 °C, which is much higher than the temperature required for the normal hardness of the surface,

causes the forming of a thick Austenite, and when extinguishing, these grains turn to a thick martensite. Thus it is necessary to remove this structure on the surface, by applying another thermal treatment, in order to have a new surface formed which consists of very small grains of martensite. As the last step, samples were heated to a temperature slightly higher than the highest critical temperature of the surface, 760 °C, to create very small grains of Austenite, and when quenching in oil, very small grains of martensite forms, and these are hard but less brittle than the thick martensite. When heating the samples to the degree of 760 °C, the core would consist of very small grains of Austenite, obscured in a base of ferrite, and with quenching they transform to Austenite particles in the base of ferrite, and these show a high resistance to corrosion, and also created is Trostite Pearlite. To improve the toughness of the core, samples were rapidly heated to the degree of 650 °C, and quenched in oil instantly, without sustaining this temperature for any period of time, and such treatment helps reduce the amount of martensite and increase the hardness of the core. Tempering was done at the temperature of 150 °C to remove the internal stresses [7].

Nitriding: Samples of the steel used were placed in a nitriding medium of ammonia gas NH_3 , which decays by heating to nitrogen and hydrogen, using a furnace, at a temperature of 550 °C, for 6 hours, and then the samples were allowed to cool in the box outside the furnace.

Carbonitriding: This process was done in a nitriding oven, at a temperature of 800 °C, for 6 hours, using a mixture of 5% methane CH_4 and 15% ammonia NH_3 gases. Methane, carbon, and Al-ammonia would provide the metal surface with nitrogen. After carbonitriding, quenching in oil is carried out to avoid cracking [8].

Metallographic Preparation

The samples of the steel used were cut, and metallographic preparation was done using graded granular size smoothing paper (Emery paper), and polishing was done using sand paper and diamond paste, with a graded granular size of 3, 6 and 15 μm . Low napped polishing cloths were used to produce a scratch-free mirror finish. Etching was done using Nital Alcohol 98% as the etching solution. Afterwards the thickness and micro-hardness of the surface layer was measured before and after applying the surface treatment, by using the Innovatest mechanical testing device for micro-hardness.

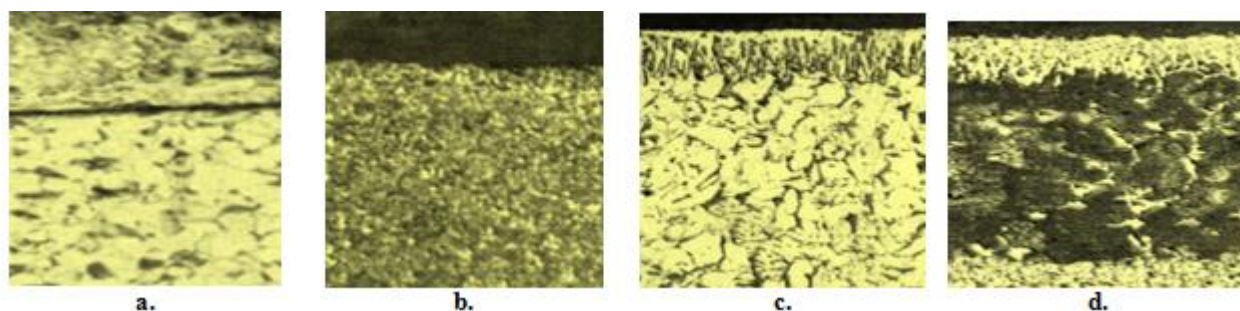


Figure 6: The Microscopic Structures of the Tested Samples 200x(a-The metal in its untreated original form, b- The metal after carbonization, c- The metal after nitriding, d- The metal after the carbonitriding treatment.)

Corrosion Test

In order to examine the effect of the surface treatment applied on the erosion-corrosion resistance, a set of samples were weighed. Samples were weighed in their untreated original form, after carbonization, after nitriding and after the carbonitriding treatment. Samples were immersed once in a saline solution, and in second solutions saline with 1% wt. SiO₂ suspension medium. The particle size of the sand (SiO₂) is < 75µm, and that size was limited by using a set of graduated sieves. The immersion of the samples took place for different periods of time for 120, 240, 360 and 480 hr, and the mixture was rotated by using waterspread to move the grains of sand. Afterwards, the samples were washed with distal water to remove the lingering impurities, then they were dried and weighed. Calculating the amount of weight loss was then carried out using the following equation:

$$W = \frac{m_g - m_i}{A}$$

Where:

w: weight loss expressed as g/cm²

m_g= the sample weight before immersion in the corrosion environment

m_i= the sample weight after immersion in corrosion environment

A= total surface area of the sample in cm²

4. Results and Discussion

Structures in figure (2) show that the thickness of the nitridized layer was in the range of 0.02-0.04 mm, and that the nitrogen in the surface caused a high level of hardness of the nitridized surface at 911 Hv, compared to the hardness of the carbonized surface at 788 Hv, and the compactness of the nitridized layer 0.02-0.04 mm.

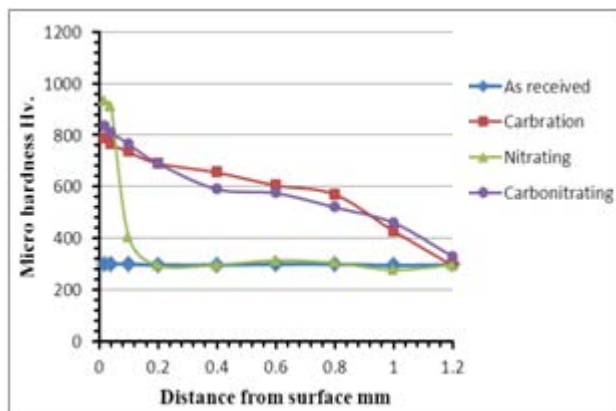


Figure (2) : shows the relationship between the micro-hardness (Hv) and the distance from the surface (mm) of the steel surface before and after the surface treatment (Carbonization, Nitriding, and Carbonitriding)

Figure (2) shows clearly that the values of the hardness of the carbonized samples are between 428-788 Hv. These values are low comparing to the hardness value of the nitridized samples. But the depth of the carbonized layer is 1 mm, which is more than the nitridized layer at 0.04 mm, due to the diffusion and penetration of atomic carbon inside the surface layers of the steel, and because its spreading is higher than that of nitrogen. Also the practical results show the

poor state of the surface layer treated by nitriding, because of the vast difference in the hardness values between the nitriding layer at 932 Hv and the original layer of the metal at 298-301 Hv, causing the occurrence of the Glassing Phenomenon.

This difference in hardness can be related to the formation of iron nitrides, which results from nitriding, thus making the surface shell brittle, causing cracking and leading to its damage and the corrosion of the original metal. Such a difference causes damage and reduces the resistance against erosion corrosion of the steel used. In fact this problem can be solved by applying the surface carbonitriding treatment, that practically results in a surface layer with a high level of hardness at 833 Hv, with a little depth of 0.02 mm at first, and then hardness is lowered gradually to the 810 - 430 Hv range, with an increase in the depth to 1 mm. The main objective of the dual surface carbonitriding treatment is to make the hardness at the surface and at the nearby layers convergent, which leads to getting rid of the Glassing Phenomenon on the surface [9,10].

By analyzing the results of the microscopic testing for the samples, it is evident that the erosion corrosion on the surface layers (the diffusion layer) for some of the samples was more than what is expected, as shown in figure 3, 4 and figure 1

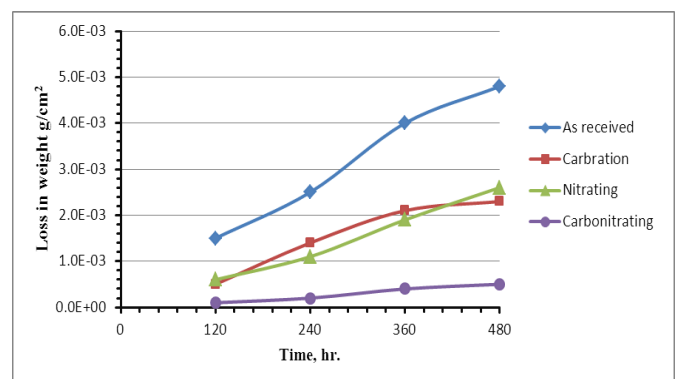


Figure 3: Amount of Weight Loss/cm² in Samples of Steel Immersed in the Saline Solution

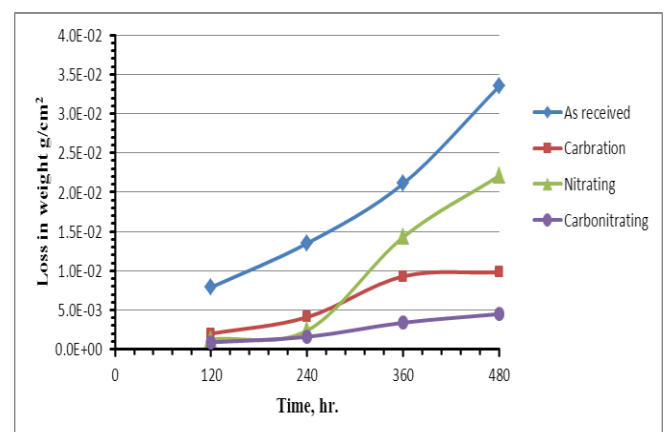


Figure 4: Amount of Weight Loss/cm² in Samples of Steel Immersed in the Saline Solution with SiO₂

Practical results show that in general, the resistance to erosion corrosion for the steel used is increased when applying the surface treatments (carbonization, nitriding and carbonitriding). The rate of weight loss, when comparing it

with the metal in its untreated original form, was lowered from 0.0335 g/cm² for untreated to 0.0098 g/cm² in the case of carbonization, and to 0.0221 g/cm² in the case of nitriding, and to 0.0045 g/cm² in the case of carbonitriding treatment, for a period of 480 hr. in a saline solution with SiO₂. The same occurred in case of the saline environment, where range of weight loss, when comparing it with the metal in its untreated original form, was lowered from 0.0048 g/cm² to 0.0023 g/cm² after carbonization, and to 0.0026 g/cm² after the nitriding, and to 0.0005 g/cm² after the carbonitriding treatment, for the same period of 480 hr.

In the carbonization, results occurred due to the forming of very small grains of austenite, which after being quenched turns to very small grains of martensite, which has a high level of hardness and is highly resistant to corrosion, comparing with the original structure of the metal composed of ferrite and pearlite. In case of nitriding, iron nitrate was formed on the surface, which is distinguished by a high level of hardness and a low thickness (crustal), and the occurrence of the undesired Glassing Phenomenon, which leads to quick corrosion under the surface.

In the case of carbonitriding treatment, a higher resistance is evident when compared to the above cases, due to the forming of iron nitrate on the surface, and followed by a cementite layer at the grain boundaries which forms a thick surface protection layer with a gradient hardness [11].

Results also show that the immersion period has an effect on the metal corrosion rate. This relation is directly proportional, as an increase in the immersion period leads to an increase in weight loss. This resistance against corrosion is reduced for both environments, as shown in figures 3 and 4 due to the increased corrosion of the treated surfaces when the immersion period is increased.

It is clear that the surface with applied carbonitriding treatment shows a higher resistance to the corrosion and erosion-corrosion when compared to the untreated sample, the carbonization samples and the nitridation samples for the same immersion period [12]. In addition, the results show an increase in the resistance against corrosion in the saline solution in the case of carbonitriding treatment as compared to carbonization or nitriding [13]. The erosion-corrosion of the steel in an effective suspension of environment saline and SiO₂ is lower when compared to the metal in its untreated original form, or when treated by carbonization or nitridation, due to the forming of an external layer of iron nitrides with a higher level of hardness and a high resistance to corrosion, followed by the carbonization layer which is highly resistant against corrosion [13,14] as shown in figure 1.

5. Conclusion

Based on this research it is concluded that a high level of hardness can be reached by the process of thermal diffusion of carbonization or nitridation. The highest depth of the diffusion for nitriding that gives the highest resistance to the corrosion and erosion-corrosion, lies between the range of 0.02- 0.6 mm. Resistance against corrosion and erosion-corrosion in the case of carbonitriding is better than that of

carbonization or nitridation. The steel was treated using carbonitriding in a highly effective environment suspended of saline and SiO₂. In general, the range of the corrosion and erosion-corrosion for the surface of the treated steel is less than that of the steel in its untreated original form. The best performance of the treated samples was obtained when the dual surface treatment of carbonitriding was applied.

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