Oxidation of Steel by Electrochemical Technique

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Abstract

Electro-oxidation of steel in a suitable solution has been done rather the chemical one which operates with a strict conditions (T~140°C and very high concentration of main components). For temperature values of 60C and above and with the starting concentration of the solution of 10% good results were obtained, meaning that the black oxide is formed by dissolution of steel electrode (anodically) and hence transforming to FeO Fe2O3 (Fe3O4) or black oxide. Some useful inspection procedures were qualified to inspect the quality of such oxide and the result was good.

الخلاصة

تمت دراسة اكسدة الفولاذ في محاليل معينة بطريقة كهروكيمياوية عوضا عن الطريقة الكيمياوية والتي تعمل تحت ظروف قاسية (درجة الحرارة~140م وتراكيز عالية للمواد الاساسية). لقيم درجات حرارية مبتداة ب 60م وتراكيز دنيا 10% للمحلول المستخدم وتم الحصول على نتائج جيدة, بمعنى الحصول على طبقة الاوكسيد الاسود المتكون عن طريق تحلل الحديد انوديا ومن ثم تحوله ال FeO Fe2O3 (Fe3O4) الاوكسيد الاسود. بعض الفحوصات الضرورية رشحت لفحص طبقة الاوكسيد وكانت النتائج جيدة.

Introduction

Corrosion is a deterioration of metal mainly by electrochemical reaction (Philippe Marcus et al, 2006). In order to reduce or to slow down its effect, many strategies could be used, viz inhibition of the corroding solution, painting of surfaces, electroplating and others.

One of the famous techniques or types of coating is conversion coating, where as the term implies that the metal is transformed to one of its product by reacting with its surrounding (solution) (Lowenheim 1978), examples are, phosphating of ferrous metals, chromating, coloring of some metals, bluing or blackening of steel ..etc and in general this type of coating is used mainly as a key for painting, varnishing or sealing and could be not used alone for its short term protection.

Blackening (bluing) is a passivation process in which steel is partially protected against rust, and is named after the blue-black appearance of the resulting protective finish. True gun bluing is an electrochemical conversion coating resulting from an oxidizing chemical reaction with iron on the surface selectively forming magnetite (Fe_3O_4) which is coming from FeO Fe_2O_3 (Greenwood et al 1997), the black oxide of iron, which occupies the same volume as metallic iron. Black oxide coatings should be of the following classes as specified in (MIL-DTL-13924D, 1999):

Class 1 Alkaline oxidizing process (for wrought iron, cast and malleable irons, plain carbon, and low alloy steels).

Class 2 Alkaline chromate oxidizing process (for use on certain corrosion resistant steel alloys which are tempered at less than 482°C.

Class 3 Fused salt oxidizing process (for corrosion resistant steel alloys which are tempered at 482°C or higher).

Black oxide is not used as permanent coating without further treatment, i.e., painting, oiling or varnishing and the baths used for oxidation working at higher temperatures and using high concentrations of materials in question.

In this paper a trial was done to carry on the oxidation process in presence of external current with a diluted solution at lower values of temperatures than that of chemically obtained. The difference between this work and the usual oxidizing technique lies in that the former depends on electricity to dissolve metal and hence deposition of oxidation compound while the later depends on the action of an oxidizing agent such as nitrate to sustain the oxidation process, generally there is a scant literature about the oxidation of steel.

Experimental Work

Steel specimens having the composition **C** 0.1977, **Mn**, 0.152, **Si** 0.155, **Ni** 0.064, **S** 0.0265, **Cr** 0.021, Fe 0.9938 and of a rectangular shape with dimensions 50*30*1 mm^3 were used. Before use, the specimen was thoroughly cleaned with coarse and fine sand paper to remove scales and oxides or tarnishes and then dipped in 10%HCl solution for 30 sec, after that with a soft tissue the specimen was dried and weighed to get w1. Now the specimen connected to the positive pole (working) of the d.c.(direct current) supplier and another specimen (auxiliary) to the negative pole and the circuit is switched on for a specified voltage, after a specified period the working specimen was dried by soft tissue and weighed to get w2. The cell is shown in figure 1 below. The electrolyte was prepared by using 10-20% **Durum** (proprietary) solution and the total volume was adjusted to 400 ml. Before each run the temperature was fixed at either 60 or 80±2°C by using Gosonic Heater and these values were chosen hypothetically, since as it was deduced (by trial) primarily that no oxidation was obtained under reduced values of temperatures.

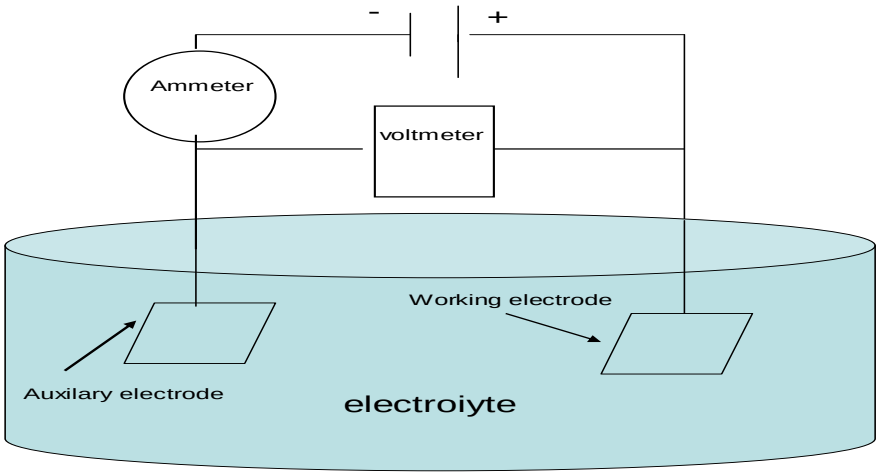


Figure 1; The used cell

Results and Discussion

The results will be classified to the following, depending on concentration of solution used:

Time of	Δw (w1-w2), g

1- The following obtained for variation values of voltages (2 and two values temperatures).

	2V		5V	
	60C	80C	60 C	80C
5	0.0015	0.0029	0.0048	0.0019
10	0.0017	0.0028	-	-
15	-0.0027	0.0037	.0014*	0.0006
20	-0.0022	-	-0.002	-
		0.0006	-	0.0073
			0.0042	-
				0.0142

10%solution. table was the weight under two applied and 5 volt) of (60 and 80° C

Table 1: Values of weight variation with voltage and temperature at 10% solution Durum

*minus value means that W2 is less than W1, i.e., dissolution is controlling.
From these data, figure 2 was graphed.

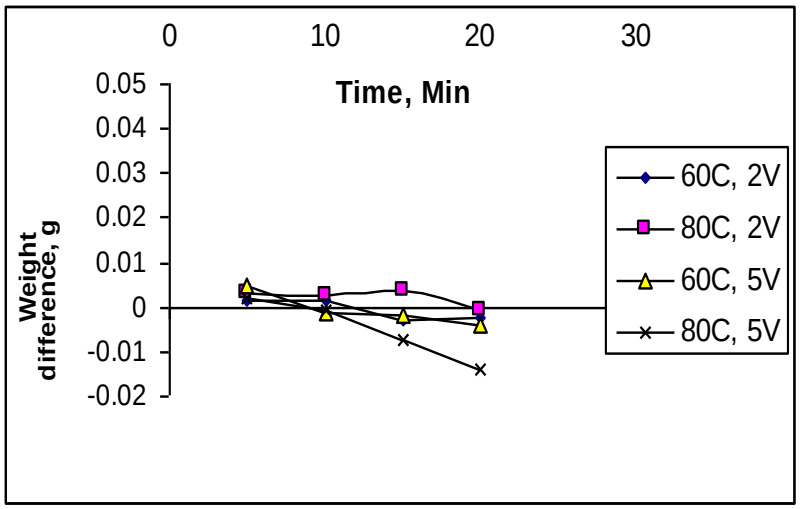


Figure 2: Effect of potential, temperature and time on oxidation process of steel

From figure 2 above it can be seen that the Δw is pronounced as the temperature varies, this is to be expected since all chemical reactions are sensitive to variation of temperature depending on activation energy, this is firstly, and secondly it can be seen

also that as the applied voltage increases, the Δw is increased negatively, i.e., w2 is less than w1 and this is an expected case since according to Faradays laws (Kelly et al, 2002) that the current is proportional to the weight deposited or dissolved and by increase the applied voltage the current is increased too according to ohms law.
The mechanism by which oxidation occurs in our opinion is as follows;
1-dissolution at anode due to anodic current;

$Fe=Fe^{+2}+2e$ ……..1
2-reduction of oxygen at cathode due to cathodic current:
$O_2+2H_2O+4e=4OH^-$ ……...2
The final product which covers the steel surface is $Fe(OH)_2$ (Shreier et al. 1994) and by further oxidation it is transformed to Fe_3O_4 (black oxide) or a mixture of FeO-Fe_2O_3 .
Figure 3 shows the obtained black oxide coating.

Figure 3: The specimen divided into coated (black appearance) and uncoated (light appearance) with black oxide

Accordingly and due to reaction 1 above, there is no need to use nitrate or any other oxidizing agent which extends the cost as well as the environmental treatments.
2- 20%solution. Table 2 below shows the difference in weight Δw with applied voltages and temperatures .

Table 2: values of weight variation with voltage and temperature at 20%solution

Time of electrolysis, minute	Δw (w1-w2), g			
	2V		5V	
	60C	80C	60 C	80C
5	0.0071	0.0031	-0.0255	-0.029
10	0.0048	0.0029	-0.003	0.005
15	0.0051	0.0041	-0.0021	0.085
20	0.0165	0.0017	-0.0087	-0.051

From this table figure 4 is graphed.

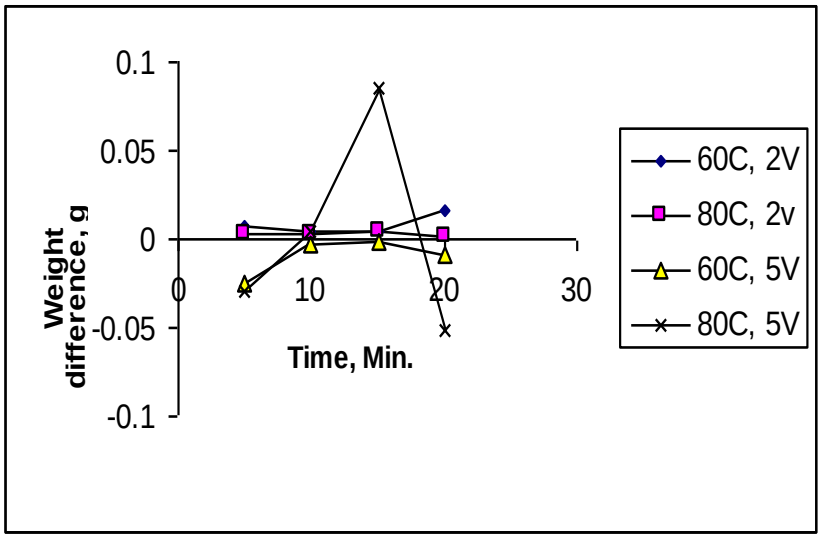


Figure 4: Effect of potential, temperature and time on oxidation process of steel

It can be deduced that Δw is increased (in positive or negative value) in case of 20% solution at the other fixed parameters and the deviation is larger that that was obtained at 10% solution.

If we assume that reaction of Fe^{+2} with OH ions according to (Greenwood et al, 1997)

$2\ Fe + 3/2\ O_2 + H_2O \rightarrow 2\ FeO(OH)$ ……3a

$2\ FeO(OH) \rightarrow Fe_2O_3 + H_2O$ …….3b

or

$Fe^{+2}+2OH^{-}=Fe(OH)_2$.....4

This product $Fe(OH)_2$ is formed due to satisfaction of solubility product and hence precipitation, therefore, we thought that the rate of $Fe(OH)_2$ formation is:

$d\ Fe(OH)_2\ /dt=K_f C^{\ m}_{\ fe+2}\ f(x)$ ……5

is the rate determining step in Fe^{+2} formation.

where:

$d\ Fe(OH)_2\ /dt$ is the formation rate of iron hydroxide.

K_f is the standard constant its unit depends on concentration.

m is the reaction order, dimensionless.

C is the concentration of Fe^{+2}, mol/unit volume

f(x) is a function that depends on the availability of steel surface for solution interaction.

R is the gas constant kJ/mol.K

T is the temperature in K

The rate of steel dissolution (equation 1) is amenable to the following:

$i_d=zfK_dC^{\ n}_{\ Fe}$ ……..…….6

where

i_d is the dissolution current in amper/unit area

$K_d=K_{0d}e(\eta\alpha nf/RT)$

K_{0d} is standard constant of dissolution.

n is the reaction order, dimensionless.

α is the symmetry factor, dimensioless.

C_{fe} is the steel concentration at the surface, mol/unit volume.

η is the overpotential, in volt
f is the Faraday constant, Amper.sec/mol
z is the number of electron involved in the reaction, dimensionless

Therefore, the link point between equation 5 and equation 6 is the concentration of Fe^{+2} with an important notice that not all the formed Fe ions(equation 6) are converted into oxide (equation 5), noting that the formed Fe^{+2} from equation 1 is estimated by formula 6 via Faradays laws of electrolysis (Kelly et al. 2002), this could be detected or assured by solution analysis, indeed the color change was seen during electrolysis which reflects the availability of iron ions.

From the above relations, some explanation should be dealt with, that is at higher potential, higher dissolution rates obtained, i.e., Fe^{+2} concentration is high or W_2 is less than W_1 and this explain the appearance of negative value of Δw especially for a long periods of exposure, also due to this higher applied potential, the rate of OH ions migration (figure 5) is increased further to the direction of anode where they react with generated Fe^{+2} to form $Fe(OH)_2$ (equation 4). For the case of increasing temperature from 60-80C the variation is increased further due to increases in the diffusion coefficients of Fe^{+2} and OH ions and hence mobility's of these ions which reflected by the transfer mechanisms , therefore, the possibility of Fe_3O_4 formation is increased (at the expense of weight loss) and this is really the case was (by visual inspection), so for the purpose of keeping article dimension care should be taken not to hurt the outer dimensions, but one more thing to say is that the effect increasing applied voltage is clearer on the production of oxide than that of increasing temperature at constant potential and this could be attributed to the effect of potential on electrolysis (Faradays laws) . In a low potential value, the availability of Fe^{+2} is low (equation 6) and the rate of formation of oxide is too low as in equation 4 above. It is clear that at high temperature values, the rate of diffusion of hydroxyl ions is intensified due to concentration gradient near the steel electrode and this enhances the oxide formation (reduction of time of appearance).

There are some deviations that could be seen in table 2 column 5 from left, the values at 10 and 15 minutes (i.e., W2›W1), the interpretation for this phenomena in our opinion lies in that at higher potential and higher OH ions (20%), the feasibility for equation 4 is enhanced to the direction of $Fe(OH)_2$ formation and hence hindrance of anode dissolution (or blocking it) and here W2 is › W1, but why there is a difference between these values and others in the same column? The answer could be attributed to the absence of agitation, the mechanism by which the rate of product formation and removal is enhanced and gave a better distribution of deposits. Figure 5 explains the suggested mechanism of species transfer.

The formed oxide film was examined visually; no smut by rubbing, no spot, homogeneity, no smear.. etc while the oxalic acid test (5% solution) was held according to the specification MIL-DTL-13924D, 1999 , accordingly good results were seen from this test as can be seen from figure 6.

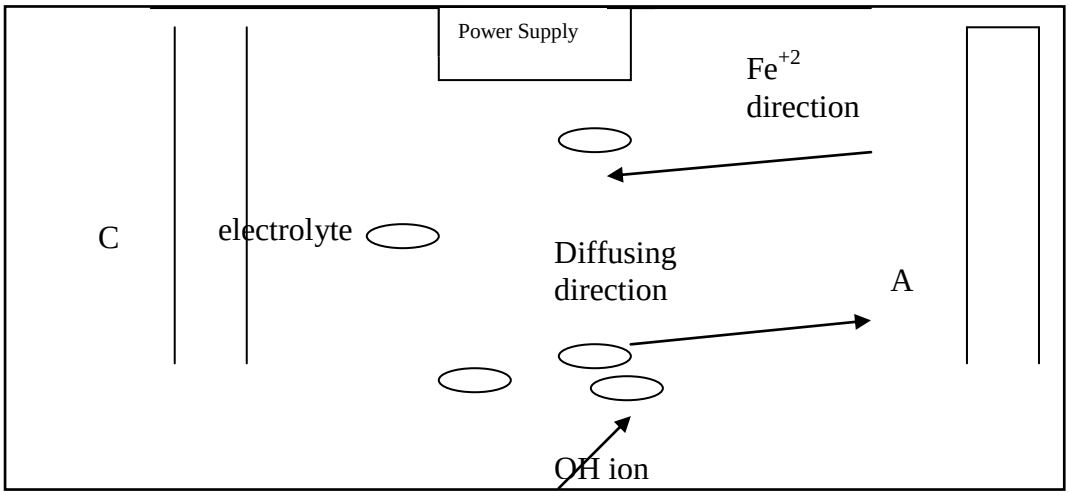
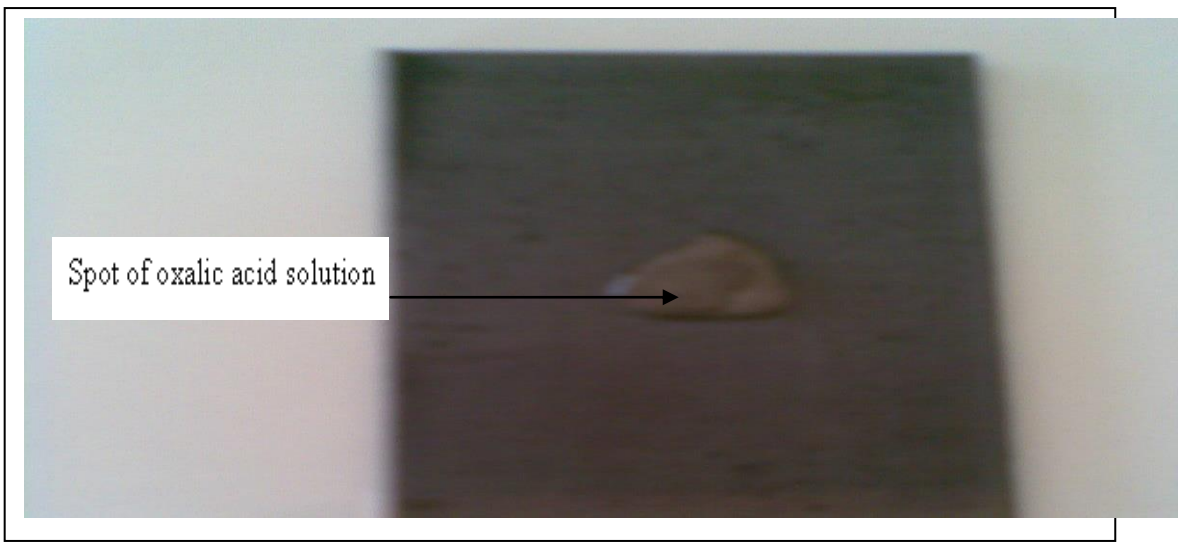


Figure 5: Suggested mechanism of OH^- and Fe^{+2} diffusing near the anode (steel surface), A is anode and C is cathode



Conclusions

1-oxidation of steel could be obtained by electrolysis (by application of direct current) in a suitable solution.

2-the formation of black oxide is function of applied voltage and temperature and the effect of increasing potential at constant temperature is more pronounced than that of the reverse.

3-the oxide formation is enhanced by increasing the electrolyte concentration.

4-the formed black oxide was inspected visually and chemically and good results were obtained according to the appropriate standards.

References

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