

# Hard chromium electroplating reinforced by Nano zirconium oxide particles

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**Abstract** In this work hard chromium electroplating carried out on samples from steel 1037. Some parameters were changed like time of electroplating, concentration of nano zirconium oxide, and agitation velocity. The hardness investigated by micro hardness tester at load 200gr. The corrosion resistance tested by potentiostat using 35gr/liter NaCl solution. Thickness of co-deposit was investigated by ultrasonic thickness tester. The results indicate that the thickness of chromium deposit layer increases with increasing the electroplating time. However, this increment in thickness was higher when the Nano zirconium oxide added. The thickness of hard chromium layer was increased from 15 $\mu$ m to about 135 $\mu$ m by increasing the time to 45 minutes, agitation velocity to 250 rpm and 11gr/l Nano zirconium oxide particles. The  $I_{corr}$  of sample electroplated by hard chromium without (ZrO<sub>2</sub>) was (91.25nA) and  $E_{corr}$  also increases to (-200mV). The best corrosion resistance was  $I_{corr}$  and  $E_{corr}$  3.15 $\mu$ A and -590.5 mV respectively, on samples electroplated by co-deposit of chromium and (ZrO<sub>2</sub>) particles for 45 minutes and 4gr/l of (ZrO<sub>2</sub>). Microhardness reveals the highest hardness was 1036HV for sample electroplated with high thickness co-deposit layer.

**Keywords:** — Nano-composite; Trivalent chromium bath; ZrO<sub>2</sub> nano-particles; Hard chromium electrodeposition

## 1 INTRODUCTION

Chromium plating is used for two purposes, the first one is decorative and the second is engineering. Generally, the chromium plating improves the hardness, wear resistance of the metal surface, reduce frictions and in some cases improve corrosion resistance [1]. Electroplating is suitable method for co-deposition of metallic, nonmetallic fine particles into a metallic matrix to create wear resistance coatings [2, 3]. Chromium plating is electrolysis process applied on most metals and alloys.

Corrosion is a chemical or electrochemical reaction between a material, like a metal, and its environment to produce a deterioration of the material and its properties [4-6].

The high corrosion resistance of chromium belongs to the formation of a thin film of chromium oxide which protects it from corrosive environment. This passive oxide film impairs protection against numerous chemical influencers. Where chemical attack occurs as in some corrosive reagent like hydrochloric acid and diluted sulphuric and nitric acids, is a result from the cracks in the deposit.

To make certain an acceptable degree of protection, chromium deposited for use in a gaseous environment should at least 30  $\mu$ m thick and when the concentration of chemical attack solution increases the deposit thickness should be, about 50  $\mu$ m thick. In the case of weaker corrosive effects, thinner deposits of 15-20  $\mu$ m thickness provide adequate protection. For parts subject to light corrosive conditions in service, 8-10  $\mu$ m thick deposits are adequate [7].

In last decade, successful co-deposition of Nanoparticles such as hard ceramic oxides and carbides like (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, WC, TiO<sub>2</sub>, and SiC) have been practiced and their corresponding structures and properties extensively have been investigated. Many researchers were interested and carried out many researches in this field of electroplating [8-10]. Corrosion resistance Cr-SiO<sub>2</sub> nano-composition electrolytic coatings has used by Yar-Mukhamedova G et al, to improve the corrosion resistance of chromium deposit on construction steel 17T1C

[8]. Talib, also studied the Cr-Al<sub>2</sub>O<sub>3</sub> co-deposit on st.1037 from trivalent chromium baths containing Al<sub>2</sub>O<sub>3</sub> nanoparticles electroplating to improve surface properties such as hardness, wear resistance and corrosion resistance [9]. Moreover, the effects of pulse electrodeposition parameters on the micro-structure and properties of metals and alloys have been reported by Li Chen [10].

In this study, the electrolytic codeposition of Nano-ZrO<sub>2</sub> with particle size (20 nm) from CrO<sub>3</sub> bath to disperse into a chromium matrix is investigated. The parameters effect on hardness, thickness and corrosion resistance of the electrodeposited chromium composite was studied. These parameters are; concentration of zirconia Nanoparticles, time of electroplating and mixing velocity. Pure chromium deposits were produced under the same parameters for comparison.

## 2 EXPERIMENTAL WORK

The work pieces to be plated were cathode (negative terminal) made of st.37 steel. The sample dimensions were 1cm diameter and 1.5cm length. The permanent anodes made of lead-tin (Pb-7Sn).

The electroplating was carried out by electroplating system provided with four cells, two heaters with thermocouple and thermostat, voltage and current adjustment options. Also magnetic stirrer was provided to the system.

The samples were prepared according to standard of sample preparation by alkaline and acidic cleaning processes. The parameters of electroplating illustrates in tables 1-4.

TABLE 1

Electroplating parameters without Nano-particles

	Sample 1	Sample 2	Sample 3
CrO <sub>3</sub> (gr /l	350	350	350
H <sub>2</sub> SO <sub>4</sub> / CrO	1:100	1:100	1:100
Voltage (V	3.7	3.7	3.7
Current (amp)	7	7	7
Time (min.)	15	30	45
Mixing velocity (rpm)	170	170	170
Temperature (°C	42	42	42

TABLE 3

ELECTROPLATING PARAMETERS WITH 4GR/L ZICONIA NANO-PARTICLES

	Sample 1	Sample 2	Sample 3
CrO <sub>3</sub> (gr /l	350	350	350
H <sub>2</sub> SO <sub>4</sub> / CrO	1:100	1:100	1:100
Voltage (V	3.7	3.7	3.7
Current (amp)	7	7	7
Time (min.)	15	30	45
Mixing velocity	170	170	170
Temperature (°C	42	42	42
Nano (ZrO <sub>2</sub> )(gr/l)	4	4	4

TABLE 2

ELECTROPLATING PARAMETERS WITH 2GR/L ZIRCONIA NANOPARTICLES

	Sample 1	Sample 2	Sample 3
CrO <sub>3</sub> (gr /l	350	350	350
H <sub>2</sub> SO <sub>4</sub> / CrO	1:100	1:100	1:100
Voltage (V	3.7	3.7	3.7
Current (amp)	7	7	7
Time (min.)	15	30	45
Mixing velocity (rpm)	170	170	170
Temperature (°C	42	42	42
Nano (ZrO <sub>2</sub> )(gr/l)	2	2	2

TABLE 4

ELECTROPLATING PARAMETERS WITH 11GR/L ZIRCONIA NANO-PARTICLES

	Sample 1	Sample 2	Sample 3
CrO <sub>3</sub> (gr /l	350	350	350
H <sub>2</sub> SO <sub>4</sub> / CrO	1:100	1:100	1:100
Voltage (V	3.7	3.7	3.7
Current (amp)	7	7	7
Time (min.)	15	30	45
Mixing velocity (rpm)	250	250	250
Temperature (°C	42	42	42
Nano (ZrO <sub>2</sub> )(gr/l)	11	11	11

The chromium oxide CrO<sub>3</sub> dissolved in distilled water to prepare two liters of solution then, the sulfuric acid added carefully to the solution. After that, the Nano particles of zirconia (ZrO<sub>2</sub>) with (20 nm particle size) added carefully with mixing using ultrasonic cell crusher type SJIA-1200w.

The hardness of all samples were tested by micro hardness tester with 200gr load. The thickness of co-deposit layer was measured by ultrasonic tester type (TT260). The corrosion resistance of co-deposit layers was investigated by potentiostat type (Wenking M-Lab).

### 3 RESULTS AND DISCUSSION

In this work the effect of time, temperature, current density, mixing velocity and the addition of Nano zirconium oxide on the thickness and properties of chromium electroplating layer on steel samples were studied.

#### 3.1 Effect of time of electro plating and mixing velocity on the chromium layer

Fig. 5 shows the relation between time and chromium layer as in illustrate in tables1 and 5.

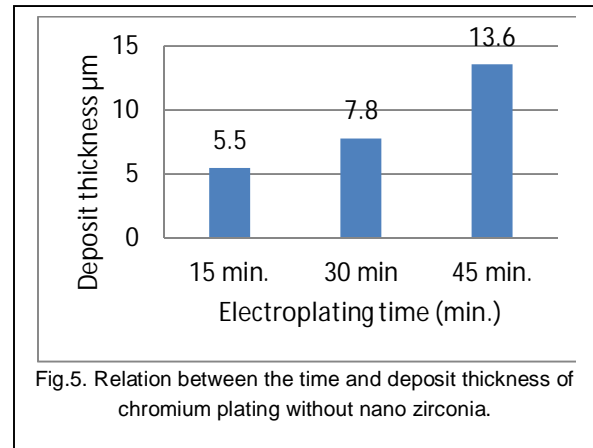


Fig.5. Relation between the time and deposit thickness of chromium plating without nano zirconia.

The rate of deposit decreases with time. The rate of deposit precipitation increased proportionally with the time in the beginning of electroplating during 45 minutes and the rate of deposit increased more higher. This increasing in the rate of

TABLE 5

THICKNESS OF DEPOSIT WITHOUT NANOPARTICLES

Sample No.	electroPlating Time	Chromium Deposit thickness
1	15 min	5.5μm
2	30 min	7.8 μm
3	45 min	13.6 μm

The chromium oxide, sulphate, current density and temperature are fixed but only time of plating was changed. It clearly evidence that, the chromium layer increased with time.

TABLE 6.

THICKNESS OF DEPOSITS WITH 2 GR/L NANO-PARTICLES

Sample No.	Plating Time	Chromium Deposit thickness
4	15 min	15 μm
5	30 min	22.3μm
6	45 min	33 μm

deposit may be because the mixing which prevents the polarization.

Fig. 6 shows the relation between time and chromium deposit layer with fixing each of current density, temperature, and magnetic stirrer and only two grams of aluminum oxide was added to the bath as illustrate in table 2 and 6

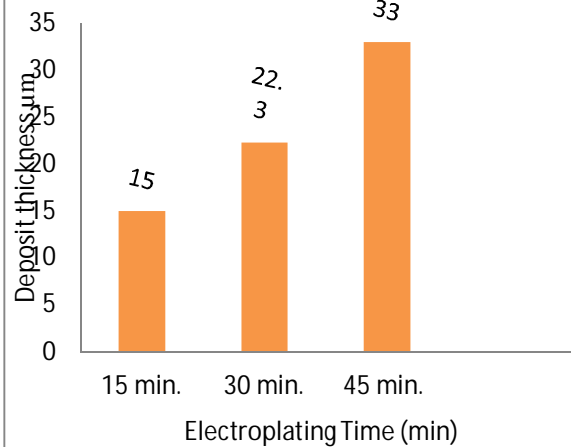


Fig.6. Thickness Relation between the time and deposit thickness of chromium plating with 2gr of nano zirconia

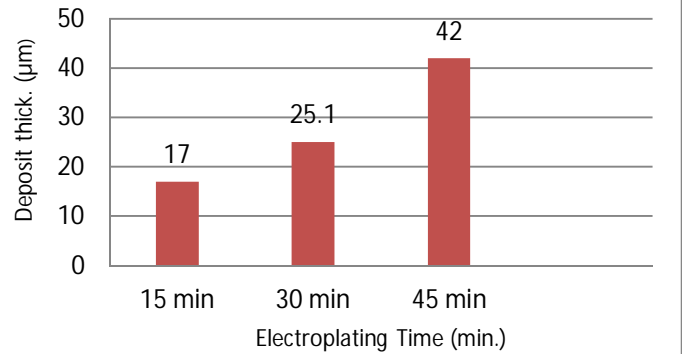


Fig. 7 Relation between the time and deposit thickness of chromium plating with 4gr of nano zirconia

The thickness increased to 42 μm at 45 min. This high rate of thickness is belonging to the increasing in zirconia particles precipitation with chromium.

Fig. 8 shows relation between the time and deposit thickness of chromium plating with 11gr of nano zirconia and increasing the mixing velocity to 250r/min as shown in tables 4 and 8. The deposit thickness increases to 135 μm at 90 minutes.

Generally, there is increment in the chromium deposit layer in comparison with Fig. 5. The chromium layer increased from 5.5μm to 15μm at 15 min. time. In addition, the layer's thickness increased from 18.5 μm to 7.5μm. at time 30 min., and the chromium layer thickness increased to 33μm at 45 min. The reason for this increment returned to the addition of Nano zirconium oxide to the bath of chromium plating. Also, the rate of precipitation increased proportionally. From Fig.7 which represents the relation between time and thickness of co-deposit with addition of 4gr/l Nano zirconia as in tables 3 and 7

TABLE 7. THICKNESS OF DEPOSITS WITH 4 GR/L NANO-PARTICLES

Sample No.	Time min.	Deposit thickness
7	15	17 μm
8	30	25.1μm
9	45	42 μm

TABLE 8  
THICKNESS OF DEPOSITS WITH 11 GR/L NANO-PARTICLES

Sample No.	Time min	Deposit thickness
10	15	43,5 μm
11	30	75μm
12	45	135 μm

It is clearly appear that, there are more increasing in the thickness of chromium layer.

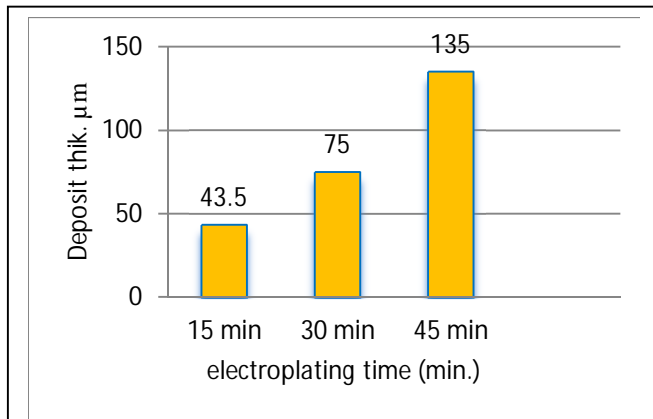


Fig.8. Relation between the time and deposit thickness of chromium plating with 11gr of nano zirconia and increasing the mixing velocity to 250 rpm

This increasing in nano zirconia and velocity increases the dispersion of Nano particles and then increasing of zirconium oxide Nano particles to be in the way of chromium ions that move to cathode and precipitate on the steel surface.

### 3.2 Corrosion resistance

Corrosion test carried out for 12 samples by using potentiostat tester. The undesirable surfaces of samples were covered by colored Nitrocellulose layer which resist to corrosion bath. The curves of tafel tests are in fig.9 to fig. 20. The corrosion test were carried out in bath 3%NaCl water solution.

Fig. 9-11 shows the corrosion resistance of samples 1, 2, and 3 with chromium deposit only. From these curves the corrosion resistance of sample 2 is the best because the  $I_{\text{corr}}$  and  $E_{\text{corr}}$  are low. The  $I_{\text{corr}}$  and  $E_{\text{corr}}$  were 91nA and (-200 mV) respectively.

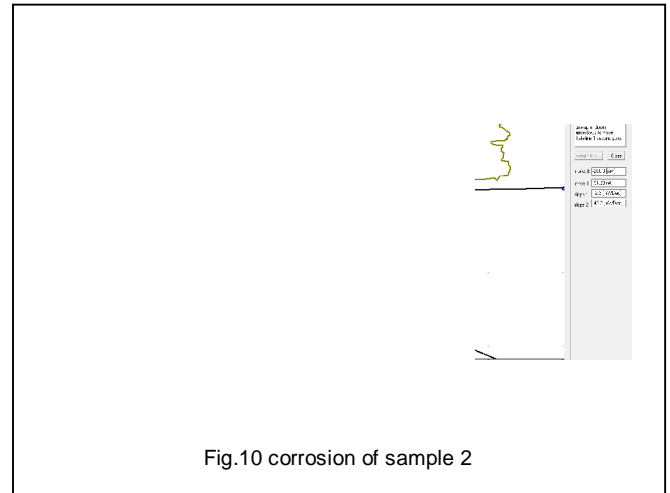


Fig.10 corrosion of sample 2

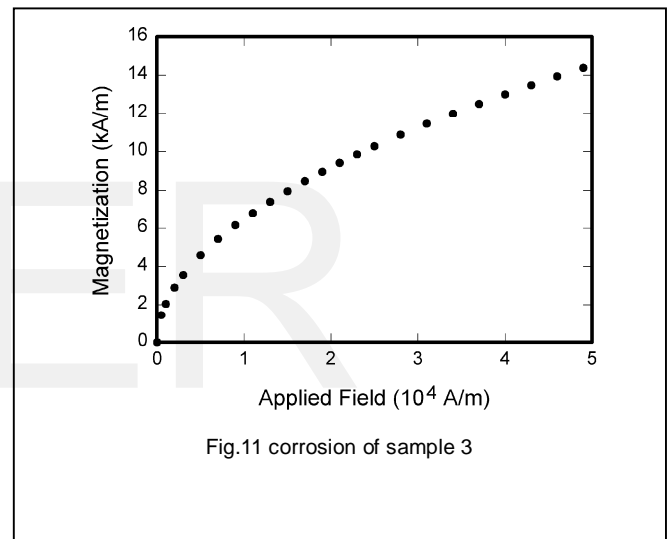


Fig.11 corrosion of sample 3

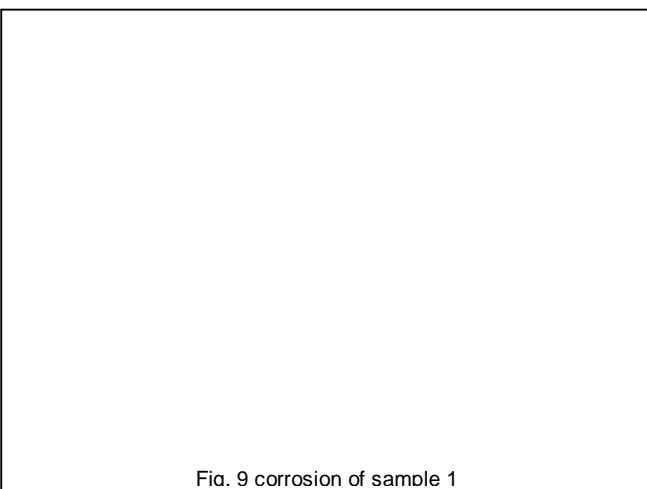


Fig. 9 corrosion of sample 1

The  $E_{\text{corr}}$  were (-625.7, -590.5, -627.5mV for samples 7, 8, and 9) respectively. The best one was -590.5 mV is the best nobility for sample 8 but the  $I_{\text{corr}}$  for those samples were 25.24, 3.15, and 21.58 $\mu\text{A}$  respectively.

The corrosion resistance of samples 4, 5, and 6 reveals in fig. 12 to 14. From these curves the  $E_{\text{corr}}$  decreases with increasing the percent the nano zirconium oxide precipitate on sample. The reason for that maybe belongs to the roughness of electroplating co-deposit of chromium-ZrO<sub>2</sub> composite. The best one is for sample 4 (-535.4 mV). Mean that the nobility of corrosion increased. More over the  $I_{\text{corr}}$  of sample 5 was 20 $\mu\text{A}$  and  $E_{\text{corr}}$  was (-536.7mV). These results indicate that sample 5 is the best corrosion resistance.

Fig. 15 to 17 shows the corrosion resistance of samples 7 to 9. The  $E_{\text{corr}}$  were (-625.7, -590.5, -627.5mV for samples 7, 8, and 9) respectively. The best one was -590.5 mV is the best nobility for sample 8 but the  $I_{\text{corr}}$  for those samples were 25.24, 3.15,

and 21.58 $\mu$ A respectively.

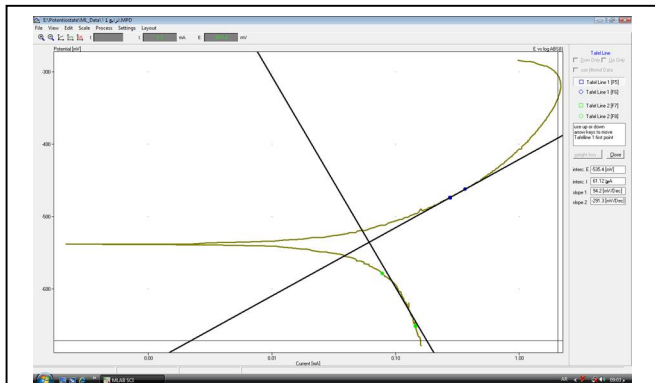


Fig. 12 corrosion of sample 4

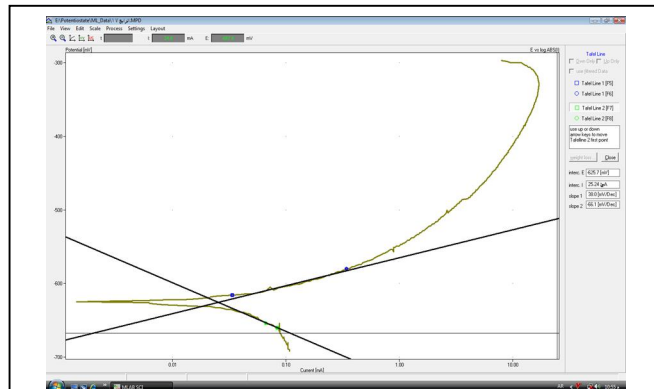


Fig. 15 corrosion of sample7

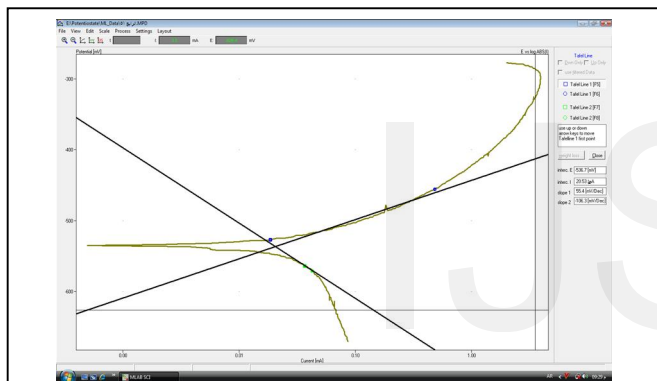


Fig. 13 corrosion of sample 5

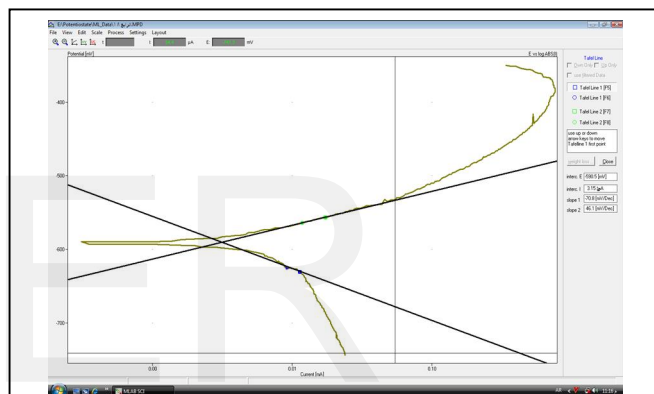


Fig. 16 corrosion of sample8

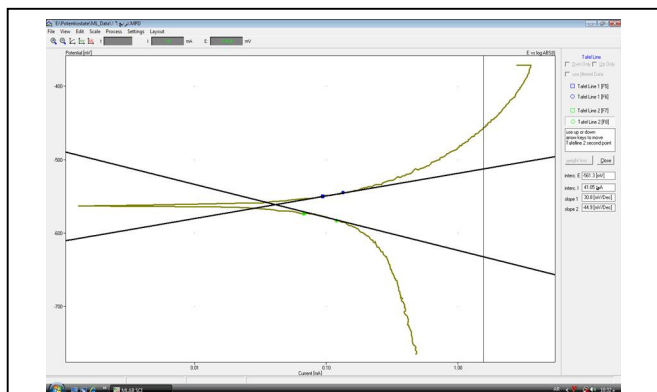


Fig. 14 corrosion of sample 6

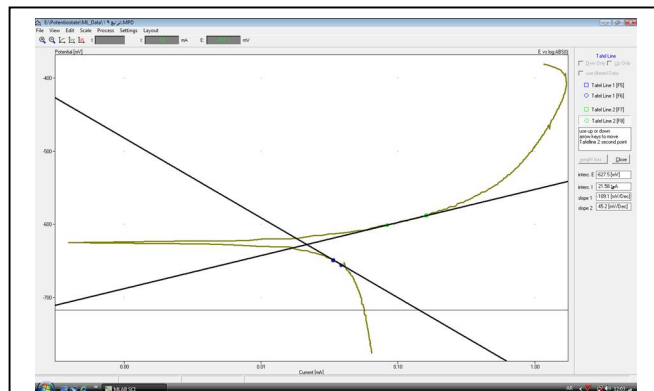
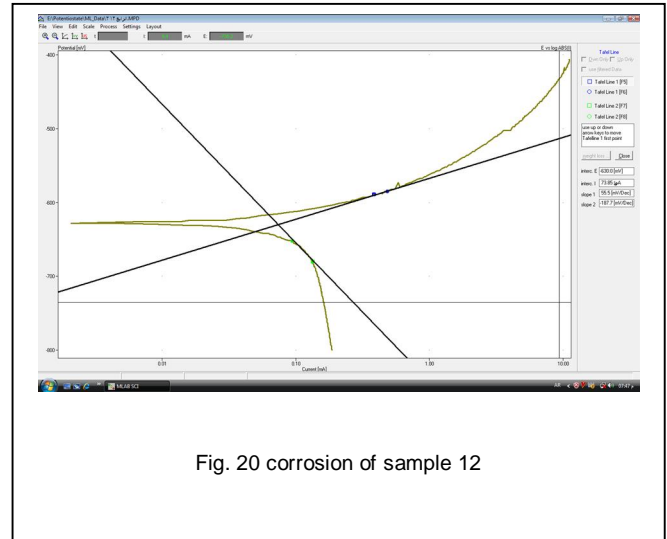
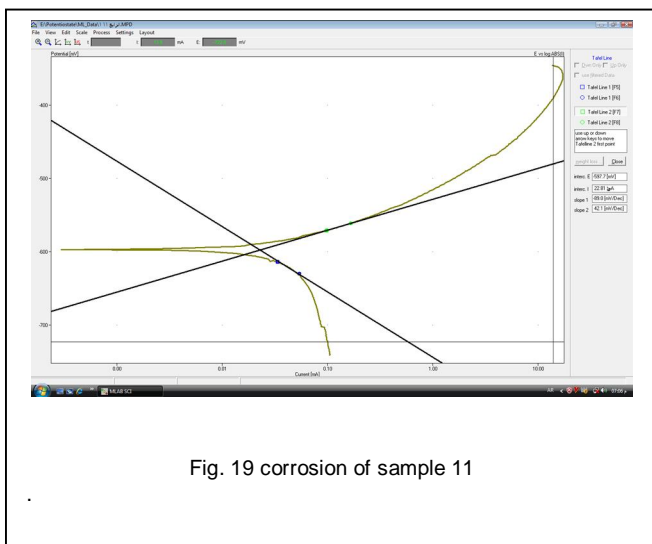
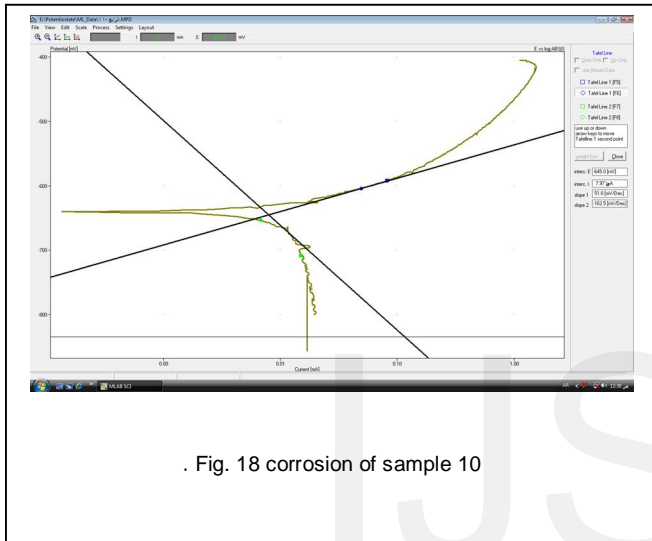


Fig. 17 corrosion of sample9

Fig. 18 to 20 shows the corrosion resistance of samples 10 to 12. The lowest  $I_{corr}$  was for sample 8. Mean that the best corrosion resistance is sample 8 which has low current for corrosion and high nobility. Samples 10, 11, and 12 have  $E_{corr}$  (-645, -597.7, and 630mV) and  $I_{corr}$  (7.97, 22.81, and 73.85) respectively. The best nobility was sample no. 11 and the most corrosion resistance was sample no. 10 because the low corrosion current  $I_{corr}$  is 7.97  $\mu A$ . The results indicate that the best corrosion resistance was sample no. 2 which has  $E_{corr}$  (-200mV) and  $I_{corr}$  is 91.23nA. The reason for that may be the more homogeneity of coating layer but with increasing the chromium coating thickness may be increases the cracks in coating layer.



### 3.3 Hardness test

The micro hardness test was done for five samples; the first one was the steel without electroplating and its hardness was 267HV0.2, the hardness of sample 3 was 687 HV0.2, this sample was electroplated by chromium only without Nano particles. The samples number 6, 9, and 12 have hardness 907, 1017 to 1036 HV0.2 respectively. The hardness test carried out by using micro hardness test because the thin layer of chromium electro plating. The load used in this test was 200g.

These results indicate that, the hardness of the chromium – zirconium oxide composite layer has higher hardness than only chromium layer and increases with zirconia concentration increasing

Table 10 shows the microhardness of steel 37 coated by chromium deposit and co-deposit of chromium-zirconium oxide .

TABLE 9

HARDNESS VALUES

Sample no.	Hardness N/mm <sup>2</sup>
0	267
3	687
6	907
9	1017
12	1036

The reason for that is the higher thickness of chromium-zirconium oxide layer and homogeneity of precipitation. This homogeneity detected from the higher hardness. If there is no homogeneity the micro hardness may be lower.

## 4 CONCLUSIONS

It is concluded from the above results and discussion the following:

It is useful using zirconium oxide as Nano particles to improve the hard chromium electroplating on steel 37 surfaces. Corrosion resistances of samples which are electroplated by hard chromium only have best corrosion resistance.

With increasing chromium deposit's thickness the corrosion resistance decreases.

Also with increasing the Nano zirconium oxide percentage the corrosion resistance increases with limited increment.

The  $I_{\text{corr}}$  is decreases and  $E_{\text{corr}}$  increases in samples that have homogenous deposit layer.

The hardness of chromium-zirconium oxide co-deposit layer was higher than the hardness of chromium layer only.

Increasing the zirconia concentration in chromium electroplating bath and the agitation by increasing mixing velocity increases the precipitation rate of chromium-Nano zirconium oxide layer and then increases the hard chromium layer.

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