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Improving the Corrosion Resistance of Bronze (G-CUSN10) by Coating It with Graphene Oxide and Reduced Graphene Oxide Using Electrochemical Deposition Technology

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

This research aims to deposit a coating layer of Graphene oxide and reduced Graphene oxide on a substrate of bronze metal (G-CUSN10), which is one of the most widely used bronze alloys in the manufacture of centrifugal water pump impellers.

The deposition process was carried out using electrophoretic deposition technique by applying a constant voltage of 10 volts for 15 minutes. The carrier medium was distilled water, 0.03%

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Graphene oxide, and the same percentage of reduced Graphene oxide manufactured using the modified Hummer's method.
The coating layer was verified using different techniques: (scanning electron microscope, X-ray diffraction device, and Raman spectrometer), These tests confirmed that the coating layer conforms to the reference properties of Graphene oxide.
Then the corrosion of a sample coated with Graphene oxide, another coated with reduced Graphene oxide, and another without covering, was studied using a Tafel device in an aqueous solution containing 3.5% sodium hypochloride at a temperature of 25 degrees Celsius, where the corrosion voltage value for the open circuit of the bare sample was (-291 mv). The value of the corrosion current was (12.552 μA/cm^2), and the voltage for the sample covered with Graphene oxide was (-250 mv) and the corrosion current was (1.990μA/cm^2). As for the sample covered with reduced Graphene oxide, the voltage was(-210 mv) and the corrosion current was
(0.125 μA. /cm^2).
From these values it is clear that Graphene oxide has significantly reduced the corrosion current, which reduced the corrosion rate by (84.1%). The same is true for the sample covered with reduced Graphene oxide, which reduced corrosion by (99%).
This research showed the importance of covering with Graphene oxide in increasing the corrosion resistance of bronze (CUSN10) in a medium containing sodium hypochloride used in sterilizing drinking water. This increase in corrosion resistance will increase the life of the impellers used in drinking water pumps, which maintains their work efficiency.

Keywords: Grapheme oxide; reduced graphene; electrophoretic deposition; bronze; general corrosion.

1. INTRODUCTION

Copper and all its alloys are considered one of the most widely used metals in various industrial fields, due to their distinctive mechanical and electrical properties.

Bronze type (G-CUSN10) is widely used in the manufacture of water pump impellers, due to its good resistance to the conditions of the pumping process.

Due to the sterilization process carried out on drinking water using chlorine compounds, corrosion was observed in the bronze impellers, and this corrosion caused a decline in the efficiency of the pumps due to the decrease in their abundance.

In order to resist corrosion, the coating method was adopted as a process to help reduce the corrosion occurring in the equipment. Covering does not only mean adding materials to the surface of the metal to be protected from corrosion, but also extends to the process of deposition and penetration of the additives into the substrate metal [1].

Previously, paint based on inorganic materials was used as some types of corrosion-resistant paints, but it did not have a long life and was not even safe for human health [2].

Therefore, work has been done to use coatings that are more stable and less harmful to human health, especially when the equipment to be protected from corrosion produces a product for direct human consumption, such as food and beverage factories [3].

Since the discovery of nanomaterials, especially Graphene, scientists have been actively searching to invest in this revolutionary material in the field of corrosion protection, due to the excellent laboratory results it has given compared to other approved methods of corrosion resistance.

As a result of the distinctive characteristics of Graphene, scientists have devised different methods to perform the deposition process on metal substrates. Among these methods are Chemical vapor deposition [4], Physical vapor deposition [5], Dip coating [6], and Electrodeposition, which is considered one of the easiest and least expensive methods [7]. Other methods help deposit Graphene and its compounds on metal substrates to be protected from corrosion.

Graphene is known to be the most transparent, hardest, lightest, and most electrically conductive material in the world [8]. In 2004, two Russian scientists worked on extracting Graphene, which is one of the allotropic forms of carbon (graphite, diamonds, fullerenes, carbon tubes, and

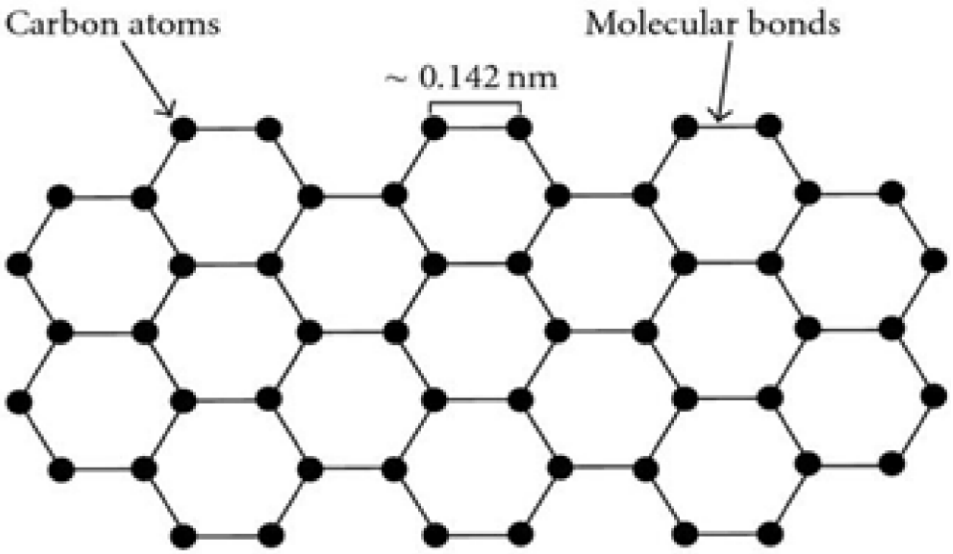

Fig. 1. The hexagonal structure of Graphene, where the distance between carbon atoms is 0.142 nm

Graphene flakes). At the end of a series of experiments, they were able to extract Graphene flakes with a thickness equivalent to the diameter of one atom, by using a tape. An ordinary peel-off adhesive of graphite used in pencils. Although it is a form of carbon, it has a two-dimensional hexagonal crystal structure, resembling a slice of a beehive, as shown in Fig. 1. [9].

Graphene has a strong structural structure that makes a thin slice of it with the thickness of one atom 300 times stronger than steel with the same thickness (this is if we theoretically assume that a steel slice of the same dimensions can be manufactured). This is what one of the tests conducted in 2009 showed, which called for Graphene to be classified as the strongest materials known to date. In addition, it is an excellent conductor of electricity, Graphene is almost completely transparent, which allows it to be used in the manufacture of touch screens and photocells [10].In this research, work will be done on the deposition of Graphene oxide manufactured using the improved Hummer's method [11], and reduced Graphene oxide, by The electrophoretic deposition technique on bronze substrates (G-CU SN10), In order to improve its resistance to corrosion in a water medium containing 3.5% of sodium hypochloride used in sterilizing drinking water, we will compare the results between the coated and uncoated sample.

2. MATERIALS AND METHODS

Graphene oxide was prepared using the modified Hummer method, and Graphene oxide was reduced using the thermal method.

The resulting oxides were checked using an X-ray diffraction device with a model device (PHILIPS-PW3850-X-Ray-Difractometer).

The electrodeposition process was then carried out on the bronze substrates after they were cleaned, polished, and placed in the deposition cell. The aqueous medium saturated with Graphene and reduced Graphene oxide was prepared. The amount of effort and time required to complete the deposition process was also controlled.

Then the coated samples were studied using Raman spectroscopy in order to verify the presence of the covering material on the surface of the substrates. A Raman type device was used (Raman Spectrometer -CNI- 200-1100nm) made in China.

The corrosion test was also conducted using a Tafel device, where the test was conducted for the three samples, and the polarization curves resulting from the test were obtained after adjusting the experimental values of the temperature and concentration of the corrosive substance.

The three samples were then examined after the corrosion test under a scanning microscope to clarify the form of corrosion occurring in the three samples.

3. RESULTS AND DISCUSSION

3.1 Preparation of Graphene Oxide and Reduced Graphene Oxide

Graphene oxide was prepared using improved Hummer's method, which is one of the most common chemical methods in preparing Graphene oxide, according to the following:

0.2g of 99% pure graphite was mixed with 1.2g of potassium permanganate, and then concentrated sulfuric acid was slowly added with (2.7ml/24ml) phosphorous acid at 15C^{o} degrees for 24 hours.

To stop the reaction, 3% hydrogen peroxide was added. After that, the mixture was sonicated for one hour, then the mixture was purified and dried at room temperature(25C^{o}). Fig. 2 shows the resulting Graphene oxide.

Fig. 2. Graphene oxide produced by Hummer's improved method

In order to obtain reduced Graphene oxide, the thermal method was used, which is the simplest and safest. Part of the previous oxide was placed in a closed oven saturated with inert gas (argon) at a temperature of 180C^{o} for 6 hours. When sufficient time had elapsed to complete the process, the oxide was taken out. It appeared in the form of granules and crusts, as heating helped to eliminate the hydroxyl and epoxide functions [12].

The following figure shows the reduced Graphene oxide.

Fig. 3. Shows the reduced Graphene oxide by the thermal method

3.2 Analyzing the Resulting Oxide

In order to verify the resulting nano-oxide, Graphene oxide and the reduced were examined using an X-ray diffraction device, and the results were as shown in the following figure:

From the previous figure, we notice the appearance of a high-intensity peak for GO at the angle range (15^{o}-18^{o}). This is due to the entry of oxygen functions between the graphite layers due to the oxidation process during the manufacture of the oxide using the modified Hummer's method.

We also notice the appearance of a less intense peak for RGO at the range (25^{o}-30^{o}) due to the decrease in the oxygen functional groups between the oxide layers.

Accordingly, by comparing these results with a reference study**[13]**, it becomes clear that the resulting oxides are nano-oxides traced to Graphene, which indicates the success of the manufacturing process using the modified Hummer's method.

3.3 Electrophoretic Deposition

To perform electrochemical deposition, we did the following:

1- Prepare two sheets of bronze metal (G-CU SN10), which has the following chemical composition:

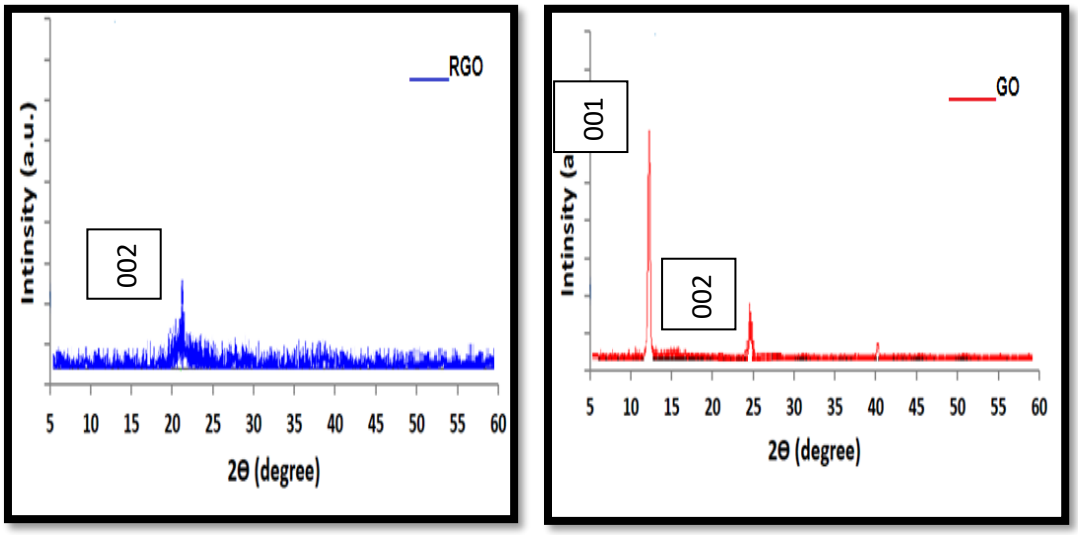

Fig. 4. Shows XRD for GO, RGO

Table 1. Chemical composition of the studied mineral [14]

Weight%	Cu	Sn	Pb	Zn	Fe	Ni	P	AL	Mn	Si	Sb	S
	88	8.2	0.5	0.5	0.2	2	0.2	0.03	0.1	0.02	0.2	0.05

According to the following dimensions (50mm×30mm×4mm), the plates were cleaned well using ethanol in order to remove any dirt on the surface. We will use these plates as an anode (positive electrode) in the electrochemical deposition cell.

2- An aluminum plate with dimensions identical to those of the bronze plate was prepared, and it will be used as a negative electrode in the cell, after cleaning it with ethanol.
3- The carrier medium within the cell is GO for the first plate, and the RGO for the second plate, where 20mg of Graphene oxide is mixed with 250ml of distilled water, and the same proportion is for the reduced Graphene oxide.
4- A constant voltage source (model 1502DD-YAOGONG) was used to provide the current necessary to complete the deposition process.

The stages of deposition were as follows:

The plates were suspended vertically in a glass container filled with oxide, and we connected the two bronze plates as a positive electrode in the cell and the aluminum plate as a negative electrode. The distance between the two electrodes was 10 mm. Then we applied a continuous voltage of 10 V for 15 minutes, according to a reference study [15].

After completing the deposition process, the two bronze plates were taken out and dried at room temperature for 12 hours.

The following figure shows the three samples of bronze sheets:

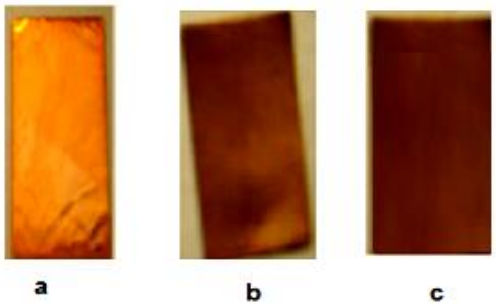

Fig. 5. a- Bronze plate without coating, b - Bronze plate coated with GO, c - Bronze plate coated with RGO

3.4 Examination of Coated Samples using Raman Spectroscopy

Raman spectroscopy was used to examine samples coated with Graphene oxide and reduced Graphene oxide with the

aim of characterizing the crystalline structure and defects in the coating layer. Fig. 6 shows the results of Raman spectroscopy.

The previous figure shows the appearance of a peak (D) at 1345 cm^{-1} for RGO and 1350 cm^{-1} for GO, which expresses disturbances in the coating layer.

We also notice the appearance of a peak (G) at 1590 cm^{-1} for RGO and 1600 for GO, and the appearance of this peak expresses the expansion occurring in the Graphene layers.

The previous figure shows the appearance of a double peak (2D) clearly in the low-intensity RGO at 2680cm^{-1} , which indicates that the coating layer consists of a small number of Graphene layers, while we notice a decrease in the intensity of this peak that appeared at 2700cm^{-1} for GO, and this indicates that the graphite has been semi-oxidized. complete.

These three peaks are considered the most important indicators that describe the covering layer, and they are close to experimental values in a reference study [16].

3.5 Corrosion Test

The corrosion test was carried out using the Tafel inductive method, where bronze sheets (coated with GO, coated with RGO and not coated) were placed sequentially at the working electrode of the corrosion cell of the device. The working electrode was immersed in a sodium hypochloride solution 3.5% for 10 minutes in order Open circuit potencial (OCP) so that the flowing current is zero to achieve stability in the OCP reading, after which the device data is stabilized.

Range = (-350 mv -150 mv), Interval = 1mv,
Slope = 1mv/s

The following figure shows the Tafel device used in the corrosion testing process.

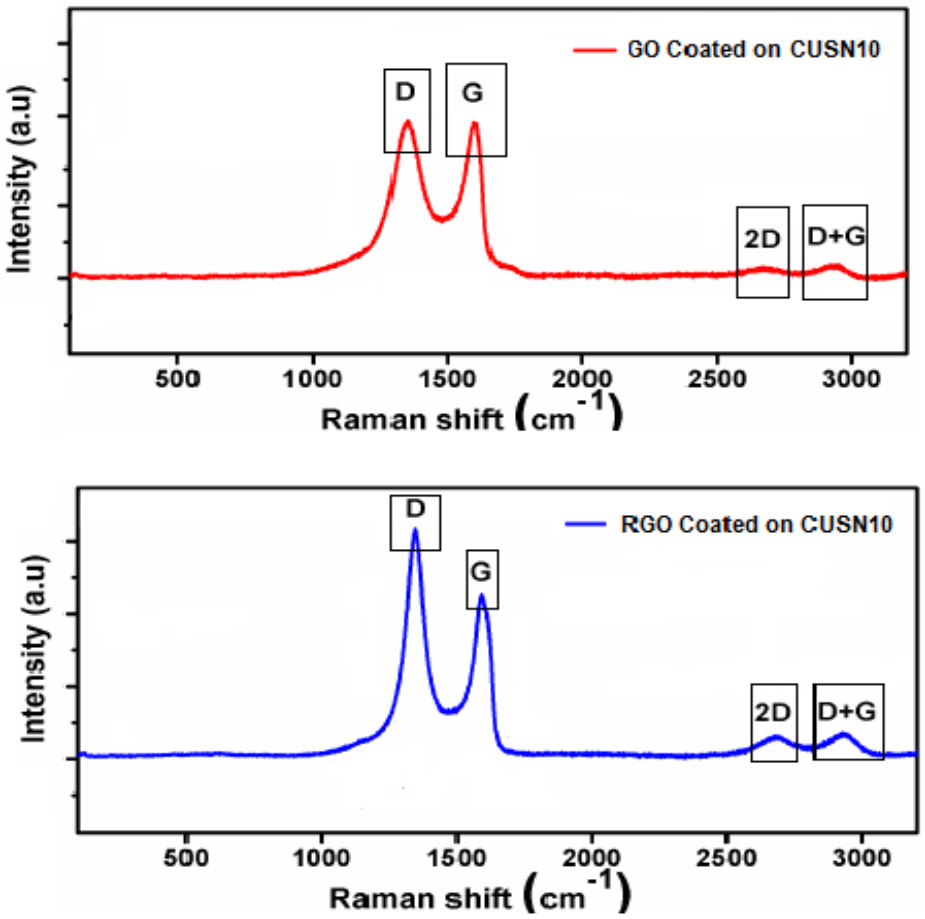

Fig. 6. Shows the results of raman spectroscopy

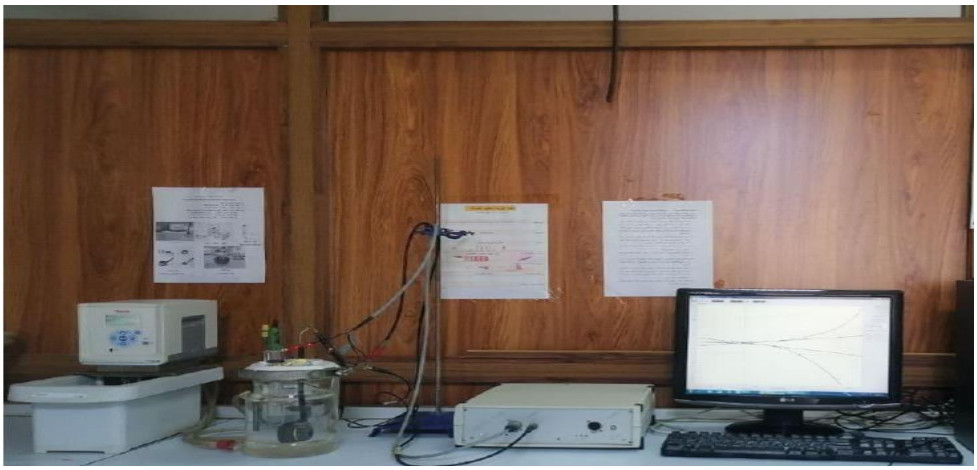

Fig. 7. Shows Tafel device

3.5.1 The electrodes that used

A- **Working Electrode:**Use a PVC disk fix electrode fixture to place the bronze sheets onThe disc is closed with a circular, toothed, tightly sealed cover, and the exposure area is 1 cm^2 The factor consists of a circular base with a diameter of 3cm connected to an arm with a length of 20 cm, where it is made of a special polymer that can withstand high temperatures.

Made of a special polymer that can withstand high temperatures.

B- Reference electrode: It is an electrode (Ag/AgCl).

C-Auxiliary electrode: Made of platinum, 6 mm in diameter and 50 mm long.

The following figure shows the electrodes that used.

After completing the corrosion test, which was conducted at room temperature (25 C^O). The test was conducted three times for each sample in order to confirm the results, the Tafel device showed the graph shown in the following figure.

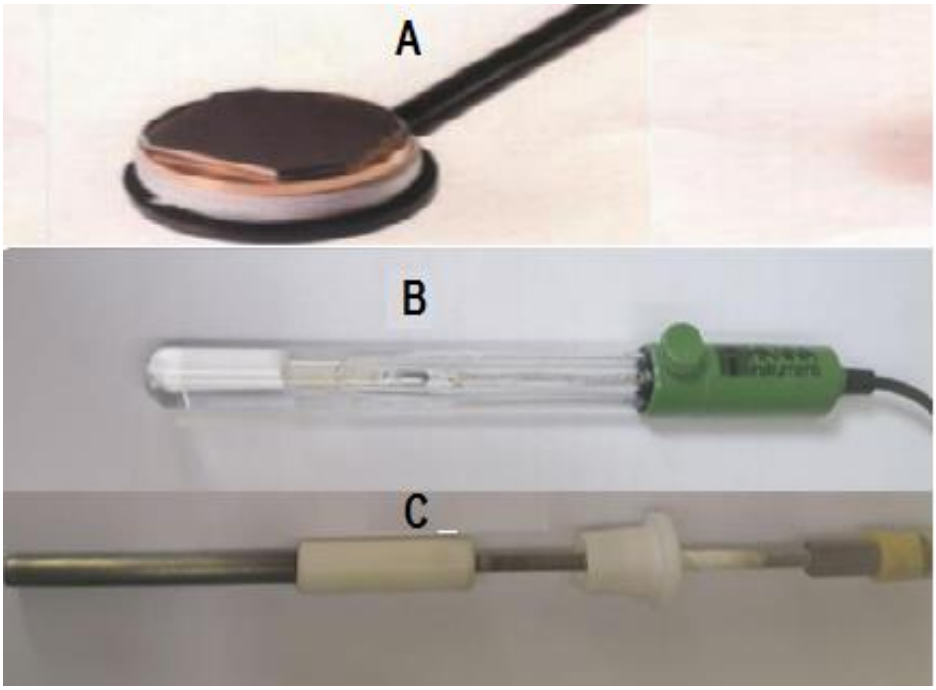

Fig. 8. Shows the electrodes

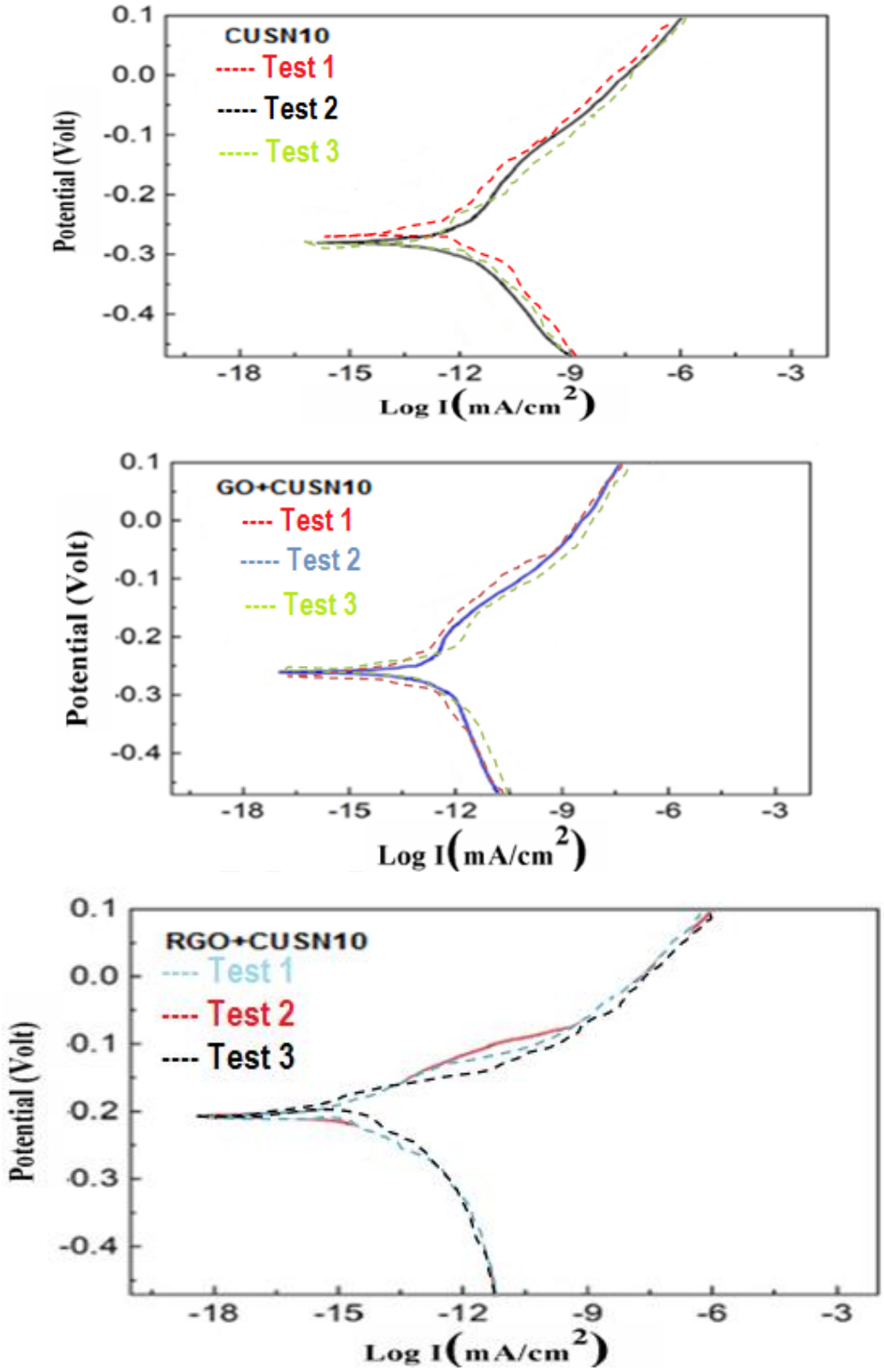

Fig. 9. Shows a Tafel diagram of the relationship between current density and potential difference for the samples studied at a temperature of 25C^{O} degrees

From the previous figure, the Tafel test results for the three samples are as shown in Table (2).

From the previous table, we notice that the corrosion current density for the sample covered with the reduced Graphene oxide has decreased significantly from what it was in the case of the uncoated sample, and better than the sample covered with Graphene oxide. Graphene oxide also increased the corrosion resistance of the studied bronze by 84.1%, and improved it in the case of reduced Graphene oxide reaches 99%, which confirms the effectiveness of this layer in reducing the corrosion of bronze.

3.6 Microstructure Examination

The metallographic study was carried out using a scanning electron microscope (FESEM). (Tescanvega-II XMU5336).

This is with the aim of showing the change in the microstructure of bronze after covering it with a layer of Graphene oxide and after a corrosion test, with the aim of observing the differences in the surface structure of the three samples and the form of corrosion occurring, as the figure shows the microstructure of the studied samples.

We notice from the previous microscopic image that the uncoated sample(a) showed clear cracks on its entire surface. It was also observed that a layer of oxides had formed resulting from the chemical reaction between the bronze and the corrosive medium.

In the case of the second sample covered with Graphene oxide(b), we notice the beginning of the appearance of limited pitting corrosion points, forming a light layer of oxides compared to the bare sample. We also notice the smoothness of the surface of the sample, which indicates the stability of the covering layer and its protection of the surface of the sample from corrosion. In the case of the sample (c), we notice the absence of the oxidation layer. There are no obvious cracks, and the surface of the sample is more smooth, which explains the reason for the decline in corrosion parameters and their reduction by 99%.

Table 2. Tafel test results for the studied samples

Sample	Test	I_{corr} (μA/cm^2)	E_{corr} (mV)	Inhibition Efficiency (%)
CUSN10	1	12.435	-291	____
	2	12.632	-289	
	3	12.562	-293	
	Avg	12.552	-291	
GO+CUSN10	1	1.995	-250	84.1
	2	1.985	-248	
	3	1.990	-252	
	Avg	1.99	-250	
RGO+CUSN10	1	0.125	-210	99
	2	0.120	-220	
	3	0.131	-200	
	Avg	0.125	-210	

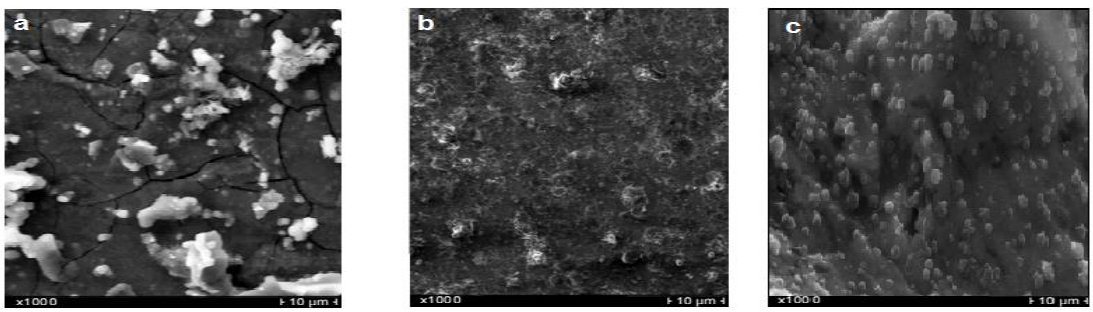

Fig. 10. FESEM images of (a) Bare bronze, (b) GO coated bronze, and (c) RGO coated on bronze

4. CONCLUSIONS

It is clear from the above that covering bronze with Graphene oxide or reduced Graphene oxide greatly improves its resistance to corrosion, due to the nature of the covering layer that it forms on the metal, as it forms a protective layer that covers the entire surface, which prevents the chemical reaction between the surface of the metal and the corrosive medium, thanks to the nanostructure. For Graphene oxide.

Also, the shape of the Graphene oxide layer was less regular than the reduced Graphene oxide, and this reduced the ability of Graphene oxide to protect the metal surface from corrosion compared to the reduced Graphene oxide, which was more homogeneous in terms of the shape of the crystals and the regularity of the spaces between them.

Therefore, it can be said that the adoption of Graphene oxide and the reduced Graphene oxide significantly improves the protection of (CUSN10) bronze from corrosion.

This research recommends studying the stability of the covering layer when testing corrosion at high temperatures, and whether the behavior of this layer will change when the temperature is raised.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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