

Engineering and Technology Journal

Journal homepage: https://etj.uotechnology.edu.iq



Improve the Corrosion Resistance of the Copper-Zinc Alloy by the Epoxy-WO₃ Nanocomposite Coating

Ban D. Abbass^{*}, Kadhum M. Shabeeb , Ayad K. Hassan 💿

Materials Engineering Dept., University of Technology-Iraq, Alsina'a street, 10066 Baghdad, Iraq. *Corresponding author Email: <u>mae.19.36@grad.uotechnology.edu.iq</u>

HIGHLIGHTS

- Brass samples were coated by Epoxy/ tungsten trioxide nanoparticles.
- Potentiodynamic polarization corrosion test was used to study the corrosion behavior of the coated samples.
- The epoxy nanocomposite coating improved the protection performance against corrosion.

ARTICLE INFO

Handling editor: Jawad K. Oleiwi Keywords: Composite coating; Copper-zinc alloy; Corrosion; Epoxy; Tungsten trioxide.

1. Introduction

A B S T R A C T

Metal corrosion is one of the most critical challenges in industrial processes. In this research, nanocomposite coating was synthesized by blending tungsten trioxide (WO₃) nanoparticles with Epoxy resin and applied on brass samples to evaluate the performance of corrosion protection under stressed environments. A dip-coating method was adopted to coat the brass sample's surface. Coated and uncoated brass samples have been subjected to corrosion tests to study the corrosion behavior when exposed to corrosive media. Obtained results indicated that the brass coated samples with mixed epoxy\tungsten trioxide (WO₃) exhibited reasonable corrosion resistance because of the ceramic protective barrier on the surface of the metal. Therefore, the proposed methodology could be considered as a promising surface coating that promotes corrosion resistance under stressed industrial conditions.

Corrosion is the process that involves the degradation of metals when they are exposed to a stressed natural or industrial environment. The anode is the corroding metal in the fluid, and the metal ions are released into the solution after the anodic oxidation reaction. Corrosion process is only possible if the cathodic reaction like dissolved oxygen reduction is consumed the electrons generated by this reaction. A path with electrically conductive must be present allowing the electrons to be able to pass between two locations between these locations [1]. Corrosion of metals is problematic causing significant economic losses worldwide. Economic losses due to the corrosion of metals could exceed USD 100 billion annually, and that may exceed the sum of economic losses of natural disasters like wildfires, river floods, and sea typhoons [2]. Additionally, corrosion of metals in industrial activities may lead to unprecedented accidents because of the failure of structural materials [3].

Copper alloys are highly corrosion resistant in a lot of aqueous and atmospheric environments. Brass is the most common copper alloy, and it is susceptible to dezincification, dealloying, and impingement attacks. Copper–Zinc alloys that include zinc more than 15% are susceptible to this type of corrosion. When Zinc is removed a weak and porous layer of copper and copper oxide is results [4].

Heavy ions of metals are released then diffused into the soil, water, and crops making serious pollution to the environment [5, 6]. Therefore, it is vital to decrease the dangers of corrosion of metals. There are a few different ways to prevent the corrosion of metals in various engineering fields. In the meantime, the main ways for the protection of metals involve alloying treatment [7,8], adding corrosion inhibitors [9], electroplating spraying [10,11], methods of electrochemical protection [12] and non-metallic coatings [13–15] etc.

A general method for metal protection from corrosion is to apply coatings or protective films, and they also enable the required properties of the metal to be coated by the chemical modification of these coatings for example optical appearance, mechanical strength, bioactivity, and so on [16]. The coating is considered as a barrier to reduce or prevent direct contact between the surface of the metal and the corrosive media [17]. Shen et al. are prepared a uniform coating of TiO_2 nanoparticles on steel by the sol-gel method. The electrochemical techniques demonstrated that the coatings exhibit excellent anti-corrosion performances [18]. Also, L. Fedrizzi et al. studied the barrier properties of electrophoretic coating (Epoxy resin) and polyurethane coating with metallic pigments. Optical microscopy was used to evaluate the capacity of these coatings to cover

the surface of the substrate. Also, the electrochemical behavior of coated substrates is studied by electrochemical impedance spectroscopy in a 3.5% sodium chloride solution [19]. A similar explanation was presented by HaeRi Jeon et al. They prepared coating consisting of Epoxy and multi-walled carbon nanotubes. The impact of the multiwalled carbon nanotubes on corrosion resistance was examined. Coated steel surfaces show high protection against corrosion [20]. Xavier [21] analyzed the impact of introducing antimony oxide nanoparticles in epoxy coatings by scanning electrochemical microscopy in 3.5% sodium chloride. (3 mercaptopropyl) trimethoxysilane was added for nanoparticles modification to better disperse the nanoparticles and enable chemical interactions between nanoparticles and epoxy resin. the antimony oxide-grafted epoxy coating had better anticorrosion properties. The aim of this study is to development of an epoxy coating using tungsten trioxide nanoparticles as the additive material and to evaluate the barrier properties of the coating on brass samples and to study the corrosion behavior when it is exposed to seawater.

2. Experimental Work

2.1 Materials

2.1.1 Brass alloy (B-111) sample

Copper alloys are defined as metal alloys that have the copper element as the primary constituent. the most well-known tr Epoxy resin. Epoxy resin (made by Sikadure-52 and complies with ASTM C881-78 Type I, Grade 1 Class B+C) was used as the basic material for the preparation of the coating solution. It has many advantages such as high mechanical and adhesive strength, low viscosity, solvent-free, useable at low temperature, hard but not brittle, shrinkage-free hardening, and suitable in both dray and damp conditions. Epoxy resin is in the liquid state, so a hardener is added to it, where we notice after a certain period the epoxy turns into a viscous state and then solidifies. The hardener for epoxy is added in proportion 2:1 then it is subject to mixing.

2.1.2 Tungsten Trioxide

Nano Tungsten Trioxide (WO₃) (made by HONGWU NEW MATERIAL) with a purity of 99.9%, APS of 50 nm, and yellow color were used as an ingredient of the coating solution to strengthen the properties of the epoxy resin.

2.2 Preparation of samples

Brass tubes were cut into small samples of $2 \ge 2$ cm in dimensions. These samples are pressed using a hydraulic press to obtain a flat surface, then abrade the samples using silicon carbide papers to ensure the adhesion of the coating to the surface. Then clean these samples with distilled water and acetone to get rid of dirt, dust, and grease to achieve good adhesion of the coating to the surface of the sample.

2.3 Preparation of Epoxy coating

The epoxy coating solution was prepared by adding the hardener to the epoxy at a ratio of 1: 2 and subjected to continuous mixing for ten minutes by a magnetic stirrer (LabTech) until homogeneity is achieved between them.

2.4 Preparation of nanocomposite coating

The coating solution was prepared by mixing specific proportions of nanostructured tungsten trioxide (1% wt, 2% wt, and 3% wt) separately with epoxy resin by magnetic stirrer (LabTech) for three continuous hours, then this solution was subjected to an ultrasound device for thirty minutes to ensure the dispersion of the nanoparticles in epoxy resin. After that, a hardener is added to this solution and mixed with a magnetic mixer for ten minutes, then it is ready to be used in coating the samples.

2.5 Coating process

The process that is used in this work to coat the brass sample is the dip-coating method. Dip coating is one of the simplest and most effective techniques where it can be made in uniform films. The dip-coating method involves the Immersion of the brass sample in the coating solution at a constant speed then this sample remains in the coating solution to be fully coated. After that, the sample is withdrawn at a constant speed too. Finally, the coated sample was left at room temperature for 24 hours for drying. An additional kind of copper alloy is brass. Brass is a copper-zinc alloy with variable proportions of these elements to obtain different mechanical, chemical, and electrical properties. Brass may contain minor amounts of other elements as shown in Table 1.

Cu	ZN	Pb	Р	Sn	Mn	Ti	Fe
73.32	25.08	0.0084	0.0017	0.001	0.006	0.0042	0.09
Sb	Mg	Al	Si	Cd	V	Zr	Ni
0.001	0.032	0.057	0.0026	0.003	0.0021	0.02	0.097
Nb	Mo	W	Cr	Co	As	Ag	S
0.0021	0.175	0.021	0.0579	0.045	0.0005	0.0011	0.002

Table 1: The chemical composition of the brass alloy (B-111) using the examination of X-ray fluorescence

3. Results and Discussion

3.1 Measurement of corrosion rate

There are a variety of methods used for corrosion tests. Some methods have acquired specific recognition. The potentiodynamic polarization corrosion test is one of these methods where this type of corrosion test is broadly used. So in this

work, the potentiodynamic test was used to study the characteristics of corrosion behavior of coated and uncoated brass samples when they were exposed to corrosive media. The corrosion experiments were carried out by methods of electrochemical polarization tests done with a solution of 3.5% of sodium chloride at room temperature for a certain period.

In this test, the test electrode is exposed to a wide variety of potentials, which causes a dominating oxidation or reduction process on the surface of the metal (depending on the polarization direction) and, as a result, an appropriate current to be created. The polarization curve is obtained by plotting the potential as a function of current density (I) (or log I) for each measured point. the value of the corrosion voltage and corrosion current is determined. The intersection point of both the tangents of the anode curve and the cathode curve, which represents the point of equilibrium for the potential, represents the corrosion current value. The x-coordinate indicates the logarithmic values of the corrosion rate and corrosion potential). The polarization curve can be used to calculate the corrosion rate and corrosion potential of the metal sample. The benefit of this method is evident in the ability to detect localized corrosion, the ease and speed with which the corrosion rate may be determined, the effectiveness of corrosion protection, and so on.

Figures (1 - 5) show the polarization curves of the coated and uncoated brass samples. Where it can be noted that the uncoated brass sample has the highest corrosion rate compared to the other coated brass samples, and where both the corrosion rate and the corrosion current have the highest values, but the corrosion potential has the lowest value. Also, it can be noted that the values of the corrosion rate and the corrosion current start to decrease gradually beginning with the brass sample coated with neat epoxy, where there is a considerable drop in both the corrosion rate and the corrosion current, as well as an increase in the value of the corrosion potential. When varying amounts of WO₃ nanoparticles were added to the epoxy resin, both the corrosion rates and corrosion current dropped dramatically, while the corrosion potential began to increase to levels much beyond those of the uncoated brass sample. This is due to adding the nanoparticles to the epoxy resin that leads to reducing the number of micro-defects that may present in the coating layer which would accelerate corrosion. As a result of the nanoparticles, the structure of the coating layer was changed, became more uniform and cohesive, and limiting flaws that increase the corrosion rate, as evidenced by the drop in corrosion current and rise in corrosion potential. With the increase in the weight ratio of the nanoparticles, the material seeks to approach the behavior of noble metals. Also, it can be noted from these results the corrosion rates values decrease as the weight ratio of WO₃ nanoparticles added to the epoxy resin increases as shown in Table 2. So, the presence of WO₃ nanoparticles is very necessary to act as a strong barrier against corrosion products. The current density of corrosion current I_{corr} is used to calculate the corrosion rate from the Faraday equation:

$$Corrosion rate (mm/year) = K. EW. I_{corr} / p$$
(1)

K = 3272 mm / Amp.cm.year, EW: Equivalent weight of corroding species (gm), I_{corr}: The current corrosion density of the samples in Amp / cm². (It can be obtained from Table 2), p: The density of the metal in (gm/cm³),

Equation values for the brass metal used:

EW: Equivalent weight of brass = 31.91 gm, p: The density of brass = 8.75 gm/cm^3 . For example: The uncoated brass sample: Corrosion rate = $(3272 * 31.91 * 690.2 \times 10-6) / 8.75 = 8.23 \text{ mm} / \text{year}$

Sample No.	Coating materials	E _{corr} (mV)	I _{corr} (Amp/cm ²)	Corrosion Rates (mm/y)
1	Without coating	-1186.6 mv	690.21 µA/cm ²	8.23 mm/yaer
2	Epoxy	-383.5 mv	3.06 µA/cm ²	3.6×10^{-2} mm/yaer
3	Epoxy $+ 1\%$ wt of WO ₃	-218.2 mv	167.83 nA/cm ²	2×10^{-3} mm/year
4	Epoxy $+ 2\%$ wt of WO ₃	-241.2 mv	47.2 nA/cm ²	5.6 × 10 ⁻ 4 mm/year
5	Epoxy + 3% wt of WO_3	152 mv	41.28 nA/cm ²	4.92×10^{-4} mm/year

Table 2: The values of corrosion rates and corrosion currents of the coated and uncoated brass samples



Figure 1: The polarization curve of the uncoated



Figure 2: The polarization curve of the brass sample coated with the neat epoxy



Figure 3: The polarization curve of the brass sample coated with epoxy and 1% wt of WO3 nanoparticles



Figure 4: The polarization curve of the brass sample coated with epoxy and 2% wt of WO3 nanoparticles



Figure 5: The polarization curve of the brass sample coated with epoxy and 3% wt of WO₃ nanoparticles

4. Conclusions

The consequence of mixing WO_3 nanoparticles with Epoxy resin was evaluated by electrochemical polarization tests. The presence of WO_3 nanoparticles enhances the capacity of Epoxy to prevent the entering of corrosion products into the epoxy matrix. So, the samples coated with Epoxy and WO_3 nanoparticles exhibit higher corrosion resistance than that of the sample coated with Epoxy only. The epoxy nanocomposite coating improved the protection performance against corrosion and the corrosion resistance increases when the weight ratio of WO_3 nanoparticles increases.

Acknowledgment

Acknowledgments may be directed to individuals or institutions that have contributed to the research or a government agency.

Author contribution

All authors contributed equally to this work.

Funding

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors. **Data availability statement**

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

References

- [1] W. Faes, S. Lecompte, Z. Y. Ahmed, J. V. Bael, R. Salenbien, K. Verbeken, M. D. Paepe, Corrosion and corrosion prevention in heat exchangers, Corros. Rev., 37 (2019) 131–155. <u>https://doi.org/10.1515/corrrev-2018-0054</u>
- [2] D. S. Chauhana, M.A. Quraishia, K.R. Ansaria, T. A. Saleh, Graphene and graphene oxide as new class of materials for corrosion control and protection: Present status and future scenario, Prog. Org. Coat., 147 (2020) 1-23. <u>https://doi.org/10.1016/j.porgcoat.2020.105741</u>
- [3] P. Sun, Z. Wang, Y. Lu, S. Shen, R. Yang, A. Xue, T.Parker, J. Wang, Q. Wang, Analysis of the corrosion failure of a semiconductor polycrystalline distillation column, Process. Saf. Environ. Prot., 135 (2020) 244-256. <u>https://doi.org/10.1016/j.psep.2020.01.007</u>
- [4] K. Ranjbar, Effect of flow-induced corrosion and erosion on failure of a tubular heat exchanger, Mater. Des., 31 (2010) 613–619. <u>https://doi.org/10.1016/j.matdes.2009.06.025</u>
- [5] H. B. Bradl, Adsorption of heavy metal ions on soils and soils constituents, J. Colloid. Interface. Sci., 277 (2004) 1–18. <u>https://doi.org/10.1016/j.jcis.2004.04.005</u>
- [6] E. Chajduk, A. Bojanowska-Czajka, Corrosion mitigation in coolant systems in nuclear power plants, Prog. Nucl. Energy., 88 (2016) 1–9. <u>https://doi.org/10.1016/j.pnucene.2015.11.011</u>
- [7] M. Li, P. Hu, Y. Zhang, Y. Chang, Enhancing performance of the CuCrZrTiV alloys through increasing recrystallization resistance and two-step thermomechanical treatments, J. Nucl. Mater., 543 (2020) 1-10. <u>https://doi.org</u> <u>10.1016/j.jnucmat.2020.152482</u>
- [8] J. Zhang, J. Liu, H. Liao, M. Zeng, S. Ma, A review on relationship between morphology of boride of Fe-B alloys and the wear/corrosion resistant properties and mechanisms, J. Mater. Res. Technol., 8 (2019) 6308-6320. https://doi.org/10.1016/j.jmrt.2019.09.004
- [9] Z. Tang, A review of corrosion inhibitors for rust preventative fluids, Cur. Opin. Solid. State. Mater. Sci., 23 (2019) 1–16. <u>https://doi.org/10.1016/j.cossms.2019.06.003</u>
- [10] P. Fallah, S. Rajagopalan, A. McDonald ,S. Yue, Development of hybrid metallic coatings on carbon fiber-reinforced polymers (CFRPs) by cold spray deposition of copper-assisted copper electroplating process, Surf. Coat. Technol., 400 (2020) 1-10. https://doi.org/10.1016/j.surfcoat.2020.126231
- [11] J. Lim, C. Lee, The rf-power dependences of the deposition rate, the hardness and the corrosion-resistance of the chromium nitride film deposited by using a dual ion beam sputtering system, Mater. Chem. Phys., 95 (2006) 164–168. <u>https://doi.org/10.1016/j.matchemphys.2005.05.039</u>
- [12] G. Grundmeier, W. Schmidt, M. Stratmann, Corrosion protection by organic coatings: Electrochemical mechanism and novel methods of investigation, Electrochimica Acta, 45 (2000) 2515–2533. <u>https://doi.org/10.1016/S0013-4686(00)00348-0</u>
- [13] A. A. Olajire, Recent advances on organic coating system technologies for corrosion protection of offshore metallic structures, J. Mol. Liq., 269 (2018) 572–606. <u>https://doi.org/10.1016/j.molliq.2018.08.053</u>
- [14] E. Chajduk, A. Bojanowska-Czajka, Corrosion mitigation in coolant systems in nuclear power plants, Prog. Nucl. Energy., 88 (2016) 1–9. <u>https://doi.org/10.1016/j.pnucene.2015.11.011</u>
- [15] J. Deering, A. Clifford, A. D'Elia, I. Zhitomirsky, K. Grandfield, Composite dip coating improves biocompatibility of porous metallic scaffolds, Mater. Lett., 274 (2020) 1-8. <u>https://doi.org/10.1016/j.matlet.2020.128057</u>
- [16] D. Wang, G. P. Bierwagen, Sol-gel coatings on metals for corrosion protection, Prog. Org. Coat., 64 (2009) 327–338. <u>https://doi.org/10.1016/j.porgcoat.2008.08.010</u>
- [17] M. H. Abdulmajeed, H. A. Abdullah, S. I. Ibrahim, G. Z. Alsandooq, Investigation of corrosion protection for steel by eco-friendly coating, Eng. Technol. J., 37 (2019) 52-59. <u>https://doi.org/10.30684/etj.37.2a.3</u>
- [18] G.X. Shen, Y.C. Chen, C.J. Lin, Corrosion protection of 316 L stainless steel by a TiO₂ nanoparticle coating prepared by sol-gel method, Thin Solid Films, 489 (2005) 130–136. <u>https://doi.org/10.1016/j.tsf.2005.05.016</u>
- [19] L. Fedrizzi, F. Andreatta, L. Paussa, F. Deflorian, S. Maschio, Heat exchangers corrosion protection by using organic coatings, Prog. Org. Coat., 63 (2008) 299–306. <u>https://doi.org/10.1016/j.porgcoat.2008.01.009</u>
- [20] H. Jeon, J. Park, M. Shon, Corrosion protection by epoxy coating containing multi-walled carbon nanotubes, J. Ind. Eng. Chem., 19 (2013) 849–853. <u>https://doi.org/10.1016/j.jiec.2012.10.030</u>
- [21] J. R. Xavier, Enhanced adhesion and corrosion protection properties of surface modified Sb₂O₃-epoxy nanocomposite coatings on mild steel, J. Fail. Anal. Prev., 20 (2020) 523–531. <u>https://doi.org/10.1007/s11668-020-00847-4</u>