Journal of Mechanical Engineering Research and Developments
ISSN: 1024-1752
CODEN: JERDFO
Vol. 44, No. 7, pp. 09-18
Published Year 2021

Ni/ Porcelanite-Alumina-Cow Bone, Coating to Protect Carbon Steel from Corrosion in seawater

Amel S Merzah[†], Heyam Razaq Atwan[‡], Rana Afif Anaee[†‡]

[†] Al Esraa University College, Baghdad – Iraq
[‡] Technical Engineering College- Baghdad – Iraq
[†‡] Department of Materials Eng., University of Technology, Baghdad, Iraq

*Corresponding Author Email: dr.rana_afif@yahoo.com; amelmerzah@gmail.com , dr.amal@esraa.edu.iq; heyamra80@gmail.com

ABSTRACT

Porcelanite stone powder and Cow bone were prepared and mixed with nano-Alumina. Nano Alumina was used with particle size20-30nm. Ni deposition was achieved on carbon steel specimens. The electrochemical corrosion performance of obtained coating was analyzed using potentio dynamic polarization test at four temperatures (30, 40, 50 and 60oC) The Ni/porcelanites-Al2O3-bone coating gets a new phase, which formed between Ni and other materials in XRD analysis. The coating has the highest efficiency compared with other coatings especially at 30 C^0. Ã£2.50% NCl.

KEYWORDS

Ni co-deposition; Electro deposition; Marine environment; electrochemical corrosion.

INTRODUCTION

Corrosion of steel is a normal spontaneous process, by which metal is changed into a steadier compound so that corrosion control is more realistic than corrosion prevention. Through the application of coatings, corrosion is prevented by one of the three main mechanisms or by combination of two of them [1]; *Barrier effect*, where any contact between the corrosive medium and the metallic material is prevented; *Cathodic protection*, where the coating material acts as a sacrificial anode; and *Inhibition/ passivation*, including cases of anodic protection. The selection of coating type depends on some properties, mode of action, fields of application, and coating methods. Without regard to the type of coating and the application method, a proper pretreatment of the material to be protected is necessary for obtaining a good result [2]. Much of the attempt to replicate the coatings of the ancients has been an effort to recapture the romantic notion of the craftsman using “Natural” materials, which are by definition in this arena to be “more beautiful” than modern synthetics. There is an almost indescribable visual quality (saturation, sheen, or even glow) to a coating of low-molecular weight natural resin as opposed to the “plasticky” appearance of modern high-molecular-weight synthetics [3].

A *bone* is a rigid organ that constitutes part of the vertebral skeleton. Bones preserve and support many organs of the body, produce red and white blood cells, store minerals and enable mobility. Bones come in a variety of sizes and shapes and have a composite interior and external structure. They are lightweight yet strong, hard, and assist multiple functions. Mineralized osseous tissue or bone tissue, is of two types – cortical and cancellous and gives it rigidity and a coral-like three-dimensional internal structure [3]. Many authors applied coating by ceramic materials using different methods such as deposition Nano- and micro- Al_2O_3–Y_2O_3 composite coatings on boiler steel substrates using sol–gel composite coating technology. The coating is mainly composed of α-Al_2O_3 and γ-Al_2O_3, and is relatively dense without cracking after drying and sintering treatments. The oxidation tests performed in air at 600℃ showed that the coatings possess much [4], electrolytic electrodeposition technique used to deposit Ni/Co–SiC composite coating on mild steel substrate and he corrosion protection potential of Ni–Co matrix embedded with finer size of SiC particles increases due to the presence of chromium [5], deposition of nickel–alumina (Ni/α–Al_2O_3) composite onto mild steel was done by electrodeposition as cathode at ambient temperature (27°C) with current density about 30 $mA.cm^{-2}$ under α-Al_2O_3 contents around of 2 g/L and several irritation speeds at 50, 100, 150, 200, and 250 rpms [6], preparation of Ni/Al_2O_3 composite coatings from a modified Watt's type electrolyte including alumina nanoparticles was done by (DC) electroplating process to enhance the hardness of coated metal and wear resistance of the nickel electrodeposited [7], sol-gel method also used to deposit alumina coating on mild steel surface [8], electrodeposition of particles (nano-Al_2O_3 oxide) has been carried out in a Watt's type bath at room temperature in a system with the steel rotating disk electrode [8], also the electrodeposition of zinc-nickel composite film on carbon steel surface was applied via adding tetraethylorthosilicate (TEOS) in electroplating solution [9], and alumina nanoparticles thin film deposited using hybrid sol-gel method to preserve carbon steel from high-temperature oxidation [10]. The objective of the present study is to provide a better coating ceramic composite material composed of the local abundant rock porcelanite and the cow bone with a small addition of alumina in a Nano scale particles size. The mixture of the three compounds gives a great adhesion and corrosion protection of carbon steel in a saline media, which used in a wide variety of applications.

EXPERIMENTAL

Sample Preparations

Steel (ASTM A283 GC) with the dimensions of (20 mm ×20 mm × 2 mm) was used as the substrate, its chemical composition is listed in Table (1). Before the coating test, the substrate was in turn ground with SiC abrasive papers of 400,600, 800, and 1000 in water, rinsed with alcohol, dried in the air, and sandblasted with the alumina grit [11].

Table 1. Chemical composition of low carbon steel

Element	C%	Si%	Mn%	P%	S%	Cr%	Mo%	Ni%	Al%	Fe%
Wt.%	0.16	0.12	0.32	0.006	0.019	0.041	0.19	0.11	0.035	Bal

Characterization Methods

The phases were analyzed by X–ray diffraction (XRD). The coating roughness was measured using an image analysis from AFM. The electrochemical test was conducted using WINKINK MLab 200 Potentiostat/Galvanostat from Bank Company at 303 and 333 K. The classical three–electrode configuration was composed of platinum rod, saturated calomel electrode (SCE) and steel sample, which was used as the counter electrode, reference electrode and working electrode, respectively. The working electrode with the area of $1cm^2$ was immersed into the solution for 30 min to attain the stable state of open circuit potential (OCP), the potentio dynamic polarization test was conducted with the scanning rate of 10 mV/s by increasing and decreasing of (OCP) with $\pm$200mV.

Coating Process

Materials

Specimens of low carbon steel according ASTM A283 GC obtained from Iraqi refinery were used in this work to test the corrosion and protection in seawater**.** The composition as in table (1) below:

The coating materials used in this work were: ***Porcelanite stone*** with a chemical composition given below in Table (2)below. The stones were crushed by jaw crusher then milled to fine powder by planetary ball mill and then the powder was sintered at 1000℃ for 1 hour in order to eliminate the hydrated and crystalline water and to remove the impurities. The powder classified by sieve analyzer to particle size of less than 25µm.

Table 2. The chemical composition of the porcelanite.

Material	MgO	Fe_2O_3	Al_2O_3	SiO_2	CaO	Others
Wt%	7.2	0.87	2.71	62.02	11.55	15.65

Cow Bone was used as a binding material, which was dried in atmosphere for 4 weeks and firing at 250℃ for 1 hr. to remove the oils and calcined water in its composition, then crushed by jaw crusher, and washed with diluted acid and acetone and milled with coffee grinder. The resulted powder was sieved in a sieve analyzer to 45μm. The chemical composition of bone was shown in Table (3).

Alumina, nano Alumina was used with particle size 20-30 nm type (MTI, China, solid purity99%).

Table 3. Chemical composition of cow bone.

Material	Ca	P	Cl	Mg	Si	Loss of ignitation
Wt%	30.7	13.1	0.3	1.4	0.7	53.8

Ni Deposition

Ni deposition was achieved on carbon steel specimens by preparation of batches for coating materials with certain percentages as given in Table (4).The deposition was achieved using nickel (Purity 99.9%) as anode and carbon steel specimens as cathode at 46 ºC and current density equal to 2.5 Amp/dm^2. Dodecyl sodium sulfate ($C_{12}H_{25}NaO_4S$) was added to electrolyte bath with 0.1g/L at pH =4.3.

Table 4. Batches of Ni deposition materials.

Coating type	Chemical composition of bath	Composition of powders in batch
Ni	$NiCl_2$= 50 g/L $NiSO_4$= 300 g/L H_3BO_4=40 g/L	100%Ni
Porcelanite-Al_2O_3-Bone		50%Porcelanite+20%Al_2O_3+30%Bone

Electrodeposition Process

The electrodeposition process was carried out in plastic vessel. The power supply, which give current up to 6 Amp and voltage up to 20 Volt. Bath components were identified for one liter of solution by sensitive balance, then the coating materials were added as suspension materials. The coating solution must be prepared before 24 hr. and mixed for 1hr by magnetic stirrer (200 rpm, mode-220V, 50Hz -China) for suspension agitation. Carbon steel specimen was used as a cathode, which was holed with wire copper hook. Nickel plate was used as an anode and placed parallel to the substrate in the electrolyte, the distance between two electrodes was equal to 40 mm. The coating deposition was conducted at 46℃ for time of 45 minutes. Finally, the coated specimens were drawn out from the electrolyte then washed with distilled water and kept in desiccators [12].

ANALYSES AND DISCUSSION

Characterization of Ni-co coating

Figures (1) and (2) show the XRD of coated carbon steel surfaces by Ni and Ni/porcelanite-alumina-bone respectively. These figures indicate the peaks for nickel and iron phases (Ni_3Fe) according to JCPDS-International Center for Diffraction Data with No. of card 38-0419, the three main peaks appear at 2θ values equal to 44.8, 52.5 and 77.14. The presence of ceramic materials (porcelanite, alumina and bone) in Ni deposition bath and magnesium element addition of the coating appear as Mg_2Ni phase in XRD analysis according to card No. 1-1268 in addition to some components in coating composition. The phases between nickel and aluminum appear at 2 Theta from 34 to 45. AFM was performed on the coatings to reveal the surface characteristics of the coated specimen in addition to the statically determining the particles size distribution. Figures (3) to (5) show the AFM images of uncoated and coated carbon steel with Ni co-deposition coatings. Figure (3) displays the surface topography of uncoated carbon steel surface, which indicates no particles must be deposited on the surface. Only some scratches can be seen due to grinding and polishing processes. Table (5) shows the roughness and particle size values which were obtained from AFM inspection. The presence of nano alumina (20-30 nm particle size) with porcelanite (< 25 µm particle size) in Ni co-deposition gave the higher roughness than Ni coating. The highest average diameter was observed for Ni/porcelanite-alumina-bone coating which is equal to (102.80 nm).

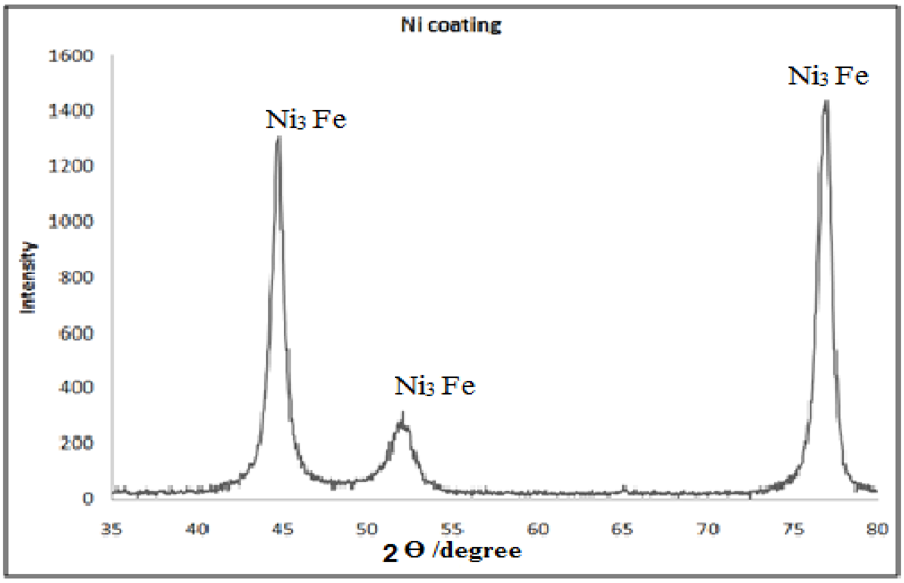


Figure 1. XRD pattern of coated low carbon steel with Ni.

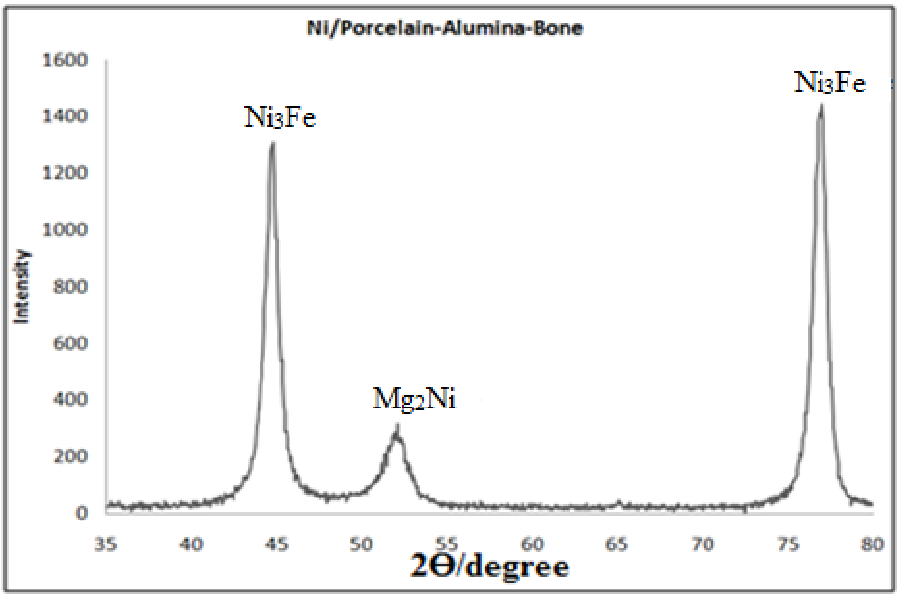
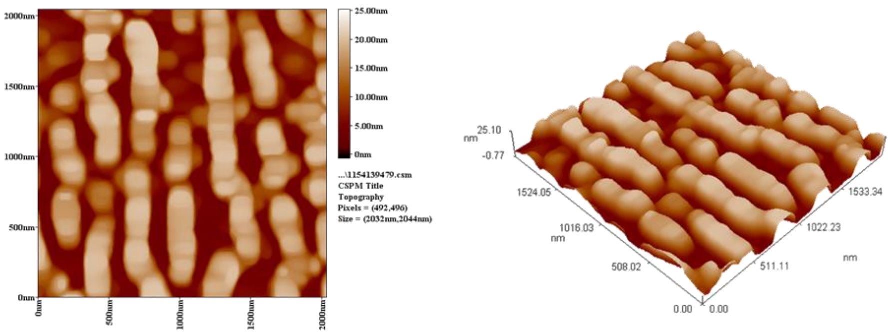
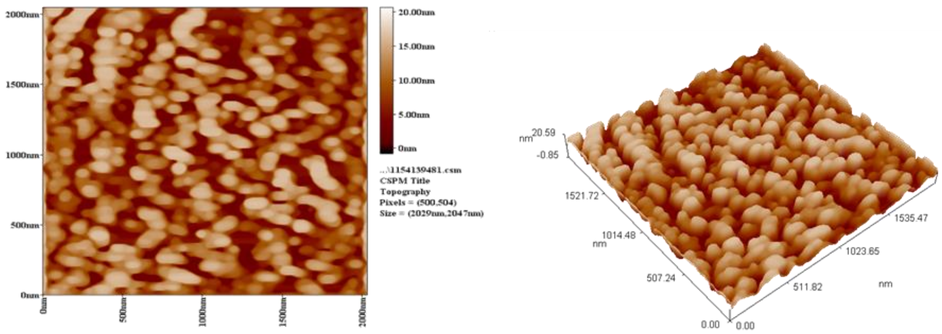


Figure 2. XRD pattern of coated low carbon steel with Ni/porcelanite-alumina-bone.



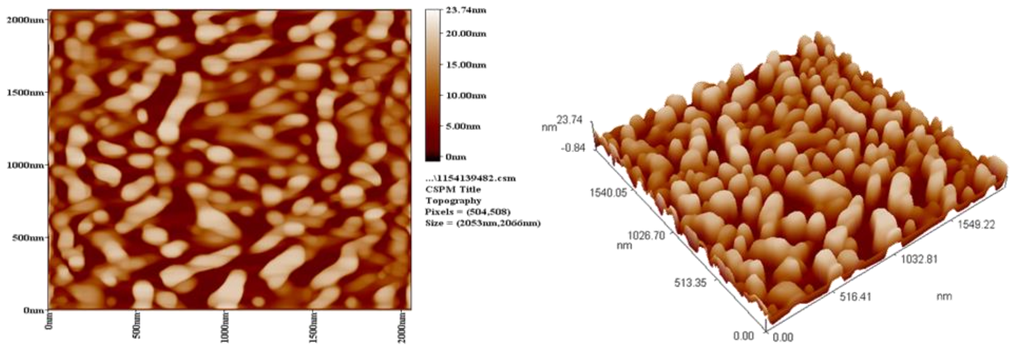
2D 3D

Figure 3. AFM images of uncoated low carbon steel.



2D 3D

Figure 4. AFM images of Ni coated low carbon steel.



2D 3D

Figure 5. AFM images of Ni/porcelanite-alumina-bone coated low carbon steel.

Table 5. Roughness values of uncoated and coated low carbon steel surfaces.

Coating type	***Roughness average (nm)***	***Average diameter (nm)***
Uncoated	5.32	90.20
Ni coating	3.57	80.40
Ni/Porcelanite-Al_2O_3-Bone	4.88	**102.80**

Electrochemical Examination

Steel corrodes in 3.5% NaCl to form ferrous ions at anode and hydroxyl ions at cathode as follows:

$$Fe \rightarrow Fe^{2+} + 2e \quad (1)$$

$$O_2 + 4e + 2H_2O \rightarrow 4OH^- \quad (2)$$

Corrosion includes the destructive attack of metallic by chemical or electrochemical reaction with its environment. Generally, corrosion involves collection of redox reactions that are electrochemical in nature. Corrosion test has been carried out to estimate the behavior of uncoated and coated carbon steel with nickel and Ni co-deposition using porcelain, nano alumina and cow bone. Figure (6) shows the polarization curve of uncoated carbon steel in seawater solution (3.5% NaCl) at four temperatures in the range of 30 – 60ºC. This figure indicates the two main regions; cathodic region, where the reduction of oxygen can occur, while at anodic region, oxidation of metals was takes place. Figures (7) and (8) show the polarization curves of coated carbon steel. From these figures it can be seen that the coatings affect both cathodic and anodic regions. This means that the coatings control cathodic and anodic reactions. The data of corrosion were measured by Tafel extrapolation method and are listed in Table (6). These data indicate the coatings shift the corrosion potential (E_{corr}) either to active or to noble direction according to the nature of reduction and oxidation reactions which can occur at electrodes. In general, the coated specimen's exhibit lower corrosion current density (i_{corr}) compared with uncoated specimen due to the role of coating in acting barrier effect, where any contact between the corrosive medium and the metallic material is reduced. The values of cathodic and anodic Tafel slopes (b_c&b_a) are decreased for coated specimens compared with uncoated specimen; this means that the polarization was reduced at cathodic and anodic sites. Generally, increasing the temperature leads to shifting corrosion potentials toward more active values and corrosion current density to higher values. This is due to increasing the kinetic energy of particles (ions and molecules) and then increasing the rate of reaction.

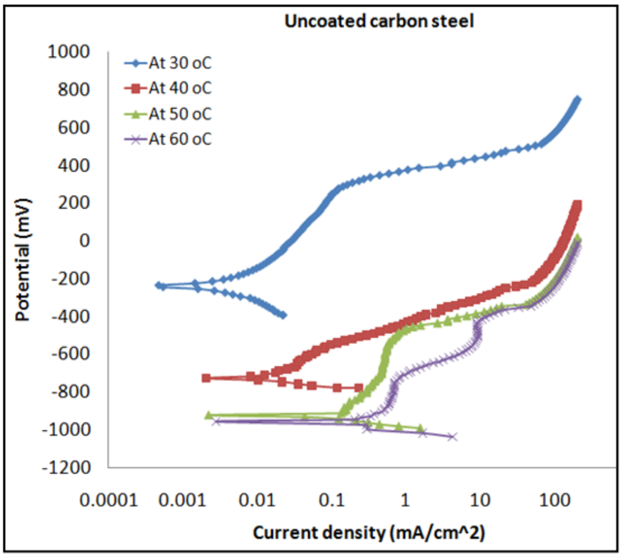


Figure 6. Polarization curve of uncoated low carbon steel in seawater at four temperatures.

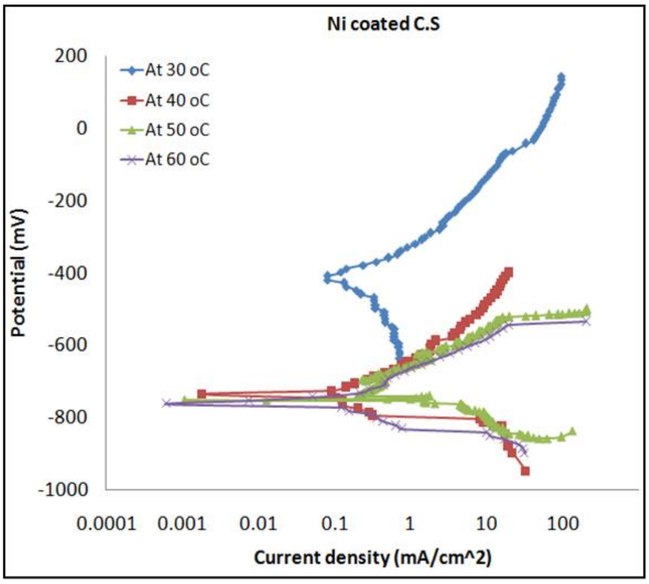


Figure 7. Polarization curve of Ni coated low carbon steel in seawater at four temperatures

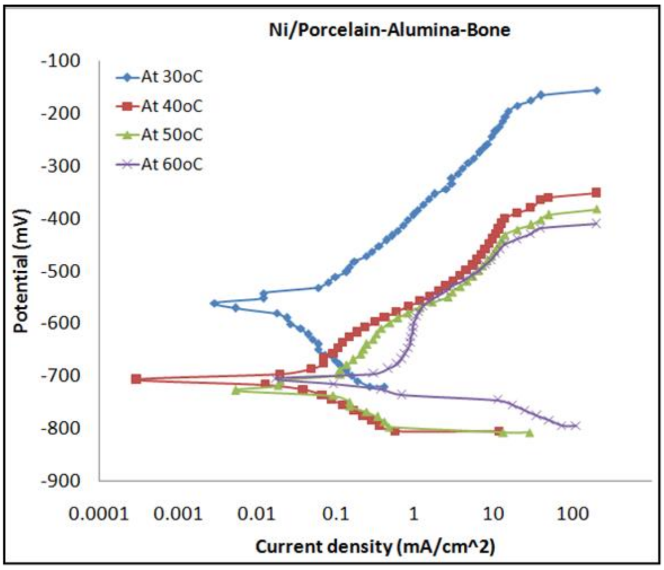


Figure 8. Polarization curve of Ni/porcelanite-alumina-bone coated low carbon steel in seawater at four temperatures.

Table 6. Corrosion parameters from polarization curves of uncoated and coated low carbon steel in seawater (3.5% NaCl) at four temperatures.

Coating	***Temp. °C***	***E_{corr} mV***	***i_{corr} $\mu A.cm^{-2}$***	***$-b_c$ $mV.dec^{-1}$***	***$+b_a$ $mV.dec^{-1}$***
Uncoated	30	-243.0	75.6	194.7	235.4
	40	-724.5	86.7	163.0	269.1
	50	-926.6	100.3	133.4	646.6
	60	-965.9	111.7	52.0	588.2
Ni	30	-411.6	66.8	144.1	86.3
	40	-739.0	75.03	87.2	78.4
	50	-744.8	81.56	74.6	88.4
	60	-765.2	99.26	68.2	93.5
Ni/Porcelanite-Al_2O_3-Bone	30	-560.8	12.57	113.5	29.8
	40	-710.5	21.46	57.7	90.7
	50	-722.5	60.16	78.3	125.5
	60	-723.9	75.4	16.1	136.7

The values of corrosion current densities for coated specimen ($i_{corr,\ coated}$) and uncoated specimen ($i_{corr,\ uncoated}$) can be used to calculate protection efficiency (PE %) using the following formula [64]:

$$PE\% = \left[1 - \frac{i_{corr,coated}}{i_{corr,uncoated}}\right] \times 100 \quad (3)$$

The results of PE % are listed in Table (7), the data indicate that the best protection efficiencies are obtained for Ni/Porcelanite-Al_2O_3-Bone coating with the highest value equal to 83.37% at 30ºC. This coating also had the highest average diameter [14].

Table 7. Total protection efficiency for coated low carbon steel in seawater (3.5% NaCl) at four temperatures.

Coating	***Temp./ºC***	***PE%***
Ni	30	11.64
	40	13.46
	50	18.68
	60	11.14
Ni/Porcelanite-Al_2O_3-Bone	30	**83.37**
	40	**75.25**
	50	40.02
	60	32.50

CONCLUSIONS

In this particular batch, the finished coating has been applied on low carbon steel for protection from corrosion in seawater. Ni/ceramic coating does not work well on low carbon steel; the coatings are non-adhesive, bumpy, and they reduce the mechanical and thermal characteristics of the metal. The AFM examination also demonstrates that composite coatings have non-uniform particle size distributions. Composite coatings have lower heat conductivity and greater insulation than metallic coatings. Pure nickel specimens and other coating types have a higher micro hardness measurement. Applying ceramic materials to Ni co-deposition allows the protective efficacy of low carbon steel to be improved to (83%) in seawater.

REFERENCES

[1] E. Bradel, "Corrosion and Protection", Engineering Materials and process, Springer Verlag London limited, 2004.

[2] S. Mathur, H. Shen and J. Altmayer, "NanoStructured Functional Coatings By Molecule-Based Chemical Vapor Deposition", Department of Chemistry,Wuerzburg University, Germany, 2007.

[3] D.C. Williams, "Natural Resins as Coating Materials in Conservation", Conservation Analytical Laboratory, Washington Dc 20560.

[4] M. Yao, Y. He, W. Zhang and W. Gao, "Oxidation Resistance of Boiler Steels with (Al_2O_3-Y_2O_3) Nano- and Micro-Composite Coatings Produced by Sol–Gel Process", Materials Transactions, Vol. 46, No. 9, Pp. 2089 – 2092, Japan Institute of Metals, 2005.

[5] G. Sharma, R.K Yadava and V.K Sharma, "Characteristics of electrodeposited Ni–Co–SiC composite coating", Indian Academy of Sciences, Vol. 29, No.5, Pp. 491-496, 2006.

[6] N.A. Badarulzaman, S. Purwadaria, A.A. Mohamad, Z.A. Ahmad, "The Production of Nickel–Alumina Composite Coating via Electroplating", Springer-Verlag, Vol. 15, Pp. 603-607, 2008.

[7] H. Gül, F. Kılıc, S. Aslan, A. Alp, H. Akbulut, "Characteristics of Electrodeposited Ni-Al_2O_3 Nano-particle Reinforced Metal Matrix Composite (MMC) Coatings", International Journal Science, Pp. 976-990, 2009.

[8] E. Beltowska-Lehman, A. Goral, P. Indika, "Electrodeposition and Characterization of Ni/Al_2O_3 Nanocomposite Coatings", Archives of Metallurgy and Materials, Vol. 56, No. 4, 2011.

[9] Z. Lin, X. Li, and L. Xu, "Electrodeposition and Corrosion Behavior of Zinc-Nickel Films Obtained from Acid Solutions: Effects of TEOS as Additive", International Journal of Chemical Science, Vol. 7, Pp. 12507-12517, 2012.

[10] M.H.J. Al –Atia, "Developing the Alumina Hybrid Sol-gel Coating for Steel Oxidation Protection at High Temperatures", Engineering & Technology Journal, Vol. 32, Part (B), No.4, 2014.

[11] E.A. Yaqo, R.A. Anaee, M.H. Abdulmajeed, I.H.R. Tomi, and M.M. Kadhim, "Electrochemical, morphological and theoretical studies of an oxadiazole derivative as an anti-corrosive agent for kerosene reservoirs in Iraqi refineries", Chemcal papers. 2019.

[12] R.A. Anaee, I.H.R. Tomi, M.H. Abdulmajeed, S.A. Naser, M.M. Kathem, "Expired Etoricoxib as a corrosion inhibitor for steel in acidic solution", J. Mol. Liq., Vol. 279, Pp. 594–602, 2019.

[13] C. Verma, L.O. Olasunkanmi, E.E. Ebenso, M.A. Quraishi, and I.B. Obot, "Adsorption Behavior of Glucosamine-Based, Pyrimidine-Fused Heterocycles as Green Corrosion Inhibitors for Mild Steel: Experimental and Theoretical Studies", J. Phys. Chem. C., Vol. 120, Pp. 11598–11611, 2016.

[14] E.A. Yaqo, R.A. Annee, M.H. Abdulmajeed, I.H. Tomi,and M.M. Kadhim, "Aminotriazole Derivative as Anti-Corrosion Material for Iraqi Kerosene Tanks: Electrochemical", Computational, and the Surface Study Chemistry Select, Vol. 4, No. 34, Pp. 9883- 9892, 2019.

.