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Effect of Al, Zn, and Fe on the corrosive behavior of (90Cu-10Ni) alloy used in electric power plants

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Abstract

It is well known that copper alloys are commonly used in heat exchangers and other marine industries. Although copper alloys (copper-nickel) have better properties than copper-zinc alloys in general, they are very expensive. The main alloy used in this research is the (copper-nickel) alloy used in the electric power plant (South Baghdad station). The current research aims to reduce the percentage of nickel in the base alloy and replace it with other alloying elements that give the manufactured alloy superior properties, in order to improve its performance and prolong its use in the most important parts of the heat exchangers (pipes). The nature of the oxides on the surface was also studied by scanning electron microscope(SEM), EDS and XRD. The results showed a significant increase in the corrosion resistance due to the significant improvement in the plasticity and adhesion of the oxide layer.

Keywords: Heat Exchanger, Copper-Nickel, Pipes, Copper, Zinc, Iron.

1.Introduction

Few of the metals of technological importance remain stable when exposed to ambient conditions, whether at high or low temperatures. As a result, most metals are subject to damage during use, either as a result of corrosion at normal temperatures or as a result of oxidation at high temperatures or due to exposure to wear or Corrosion is wear or as a result of the formation of gaps associated with turbulent flow. As for the amount of damage, it depends on the type of metal and the nature of the medium.

The resistance from the mineral to harmful media depends on the characteristics of the surface layer or layers [1] .The desire to reach high operating temperatures in power plants implies an increase in efficiency and a decrease in the spent fuel, although this is accompanied by a decrease in the resistance of the alloy and an increase in the rate of attack by hostile circles.

The corrosion of metals is considered a serious economic problem that causes heavy losses to industrial facilities. We have found that the heat exchangers and compressors used in power stations in Iraq also suffer from similar problems. As for the corrosion tests, they were carried out by three methods, namely simple immersion, corrosive wear and Tafel test.

Copper nickel alloys are very common in marine applications due to their high electrical and thermal conductivity, corrosion resistance and easy production[2]. The 90/10 nickel alloy is a favorite material for condensers, heat exchangers and desalination facilities [3, 4]. This alloy is ammonia and sulfide ion stress resistant and is resistant to biofouling through release of copper ion [5]. This alloy is also resistant to pitting and crevice corrosion in quiet seawater. The corrosion resistance of this alloy is linked to the performance of the passive foil, which is made mostly from Cu2O, after lengthy exposure, while the film also contains other copper compounds (II) such as atacamite and cupron oxide[6].

In the current research, the percentage of nickel in the alloy (90 Cu- 10Ni) was reduced and replaced by other alloying elements. As for the corrosion tests, they were carried out by three methods, namely simple immersion, corrosive wear and Tafel test.

2. Preparation of Specimens

The casting system has been prepared so that the casting system ensures a quick and somewhat directional solidification in order to soften the granules and reduce the shrinkage pores. Table (1) shows the chemical composition of the alloys used in the current research.

Table (1): Analyzed Chemical Composition of Alloys.

Sample	Cu	Ni	Al	Zn	Fe
A	Bal.	9.72	-	-	-
B	Bal.	8.21	10.66	-	-
C	Bal.	8.34	10.58	-	**2.36**
D	Bal.	8.53	-	9.55	-
E	Bal.	8.28	-	10.12	**2.52**

Metal molds were used, and appropriate precautions were taken during the melting process to avoid problems caused by melting an alloy whose components vary greatly in the degree of melting. The hardness values are shown in Figure (1).

To homogenize the cast structure, the ingots were annealed for 7 hours at 850°C. The cold rolled strips of all the test alloys were then annealed anwater quenched at 850° C for 1 hour.

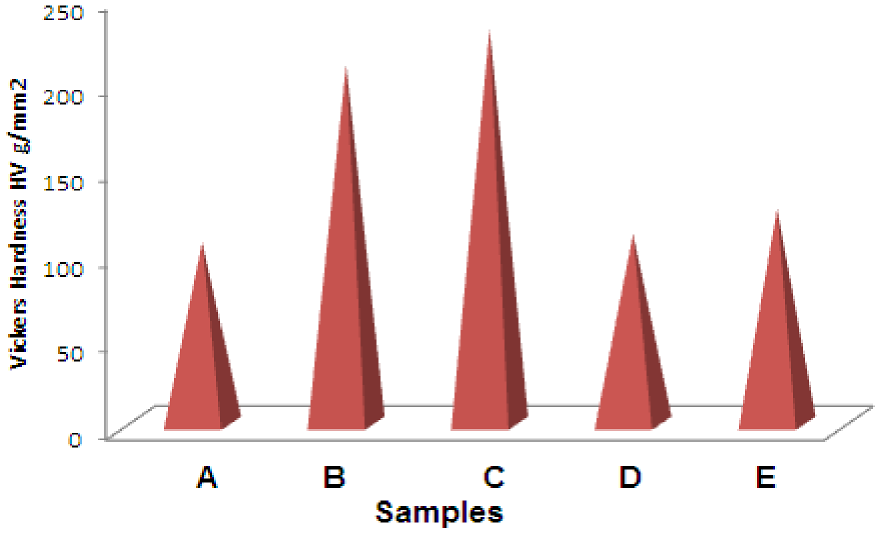


Fig. 1: Micro Hardness for Samples.

3.Simple Immersion Test:

The test was carried out by immersing the samples (A, B, C, D, and E) in salt water (sea water) (3.5% NaCl). Each of the weight changes has been cached (3 days). Prior to the immersion process, all samples were weighted with a sensitive weighting balance with an accuracy of 0.0001 g, and surface areas were determined for each sample. Samples were taken out after each immersion process to clean them by distilling water, drying with warm air, and then weighing them.

The change of weight was measured and reported for each experiment.

The rate of corrosion was defined by the following relationship:

$$\mathbf{Corrosion\ Rate}\left(\frac{\mathbf{mg}}{\mathbf{mm^2 \cdot day}}\right) = \frac{\mathbf{change\ in\ weight}\ (\Delta \mathbf{w})}{\mathbf{surface\ area \times time}} \dots\dots (\mathbf{1})$$

According to fig.(4.26) which represents the corrosion rate of all specimens, sample C shows lower corrosion rate after more than 90 days, then sample A6,A8,and A9, this is due to ability of these alloys to build a protective layers such as (NiO3, AL_2O3,Fe2O3 & ZnO) which improving the corrosion rate for specimens B, C,D & E where (46.8, 46, & 31.2) respectively, with respect to reference sample A.

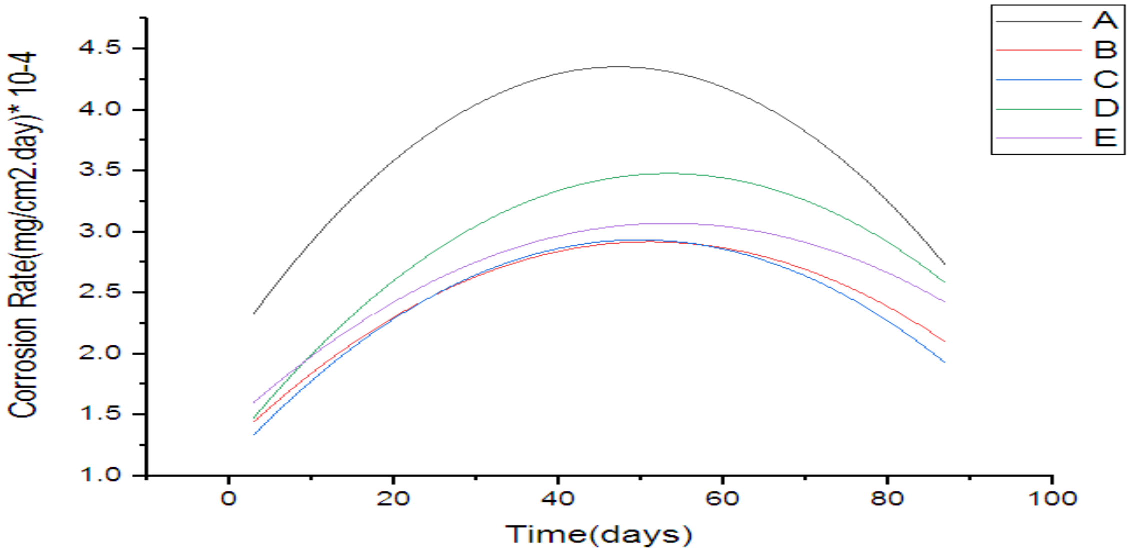


Figure 2: Fitting Curves of Simple Immersion Test for All Specimens in Salt Solution for Immersion Period (90 days).

4.Polarization Test

Tafel extrapolation, which is used to estimate corrosion current, was used to investigate the corrosion behavior of specimens. A saturated calomel electrode was used to test the potentials (SCE). As a counter-electrode, a platinum wire was used. The working electrodes are made up of cylindrical components. The open circuit potential (OCP) was measured for at least 30 minutes before each experiment.

At scan rates of 1 mVs-1, a linear potential sweep was performed at a (250) mV potential window around the observed OCP, from the cathodic to the anodic side, to obtain polarization curves potentiodinamically.

According to ASTM G 102, corrosion current values can be determined using galvanic cells and polarization measurements like Tafel extrapolations or polarization resistance measurements. The following is an example of an equation:

$$i_{cor} = \frac{I_{cor}}{A} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where:

i_{cor} = corrosion current density, $\mu A/cm^2$
I_{cor} = total anodic current, μA, and
A = exposed specimen area, cm^2

To calculate the alloy equivalent weight (E.W), the following approach may be used.

$$Q = \sum \frac{nifi}{wi} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where:

fi = the mass fraction of the i^{th} element in the alloy.
wi = the atomic weight of the i^{th} element in the alloy, and
ni = the valence of the i^{th} element of the alloy.

Therefore, the alloy equivalent weight, EW, is the reciprocal of this quantity:

$$EW = \frac{1}{\sum \frac{nifi}{wi}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

According to ASTM G 102, corrosion current values can be determined using galvanic cells and polarization measurements like Tafel extrapolations or polarization resistance measurements. The following is an example of an equation:

$$CR = \frac{K_1 \times i_{cor} \times EW}{\rho} \quad \ldots\ldots\ldots\ldots\ldots(5)$$

Where:

CR is given in mm/yr, i_{cor} in $\mu A/cm^2$,
$K_1 = 3.27\times 10^{-3}$, mm g/µA cm yr
ρ = density in g/cm^3

Fig.3: The Electrochemical System.

The improvement of the rate of corrosion in Table (4.6) was higher in sample D, in reference sample (99.3), Niand Zn seem to minimize the corroding rate of the alloy in conjunction with Cu. Generally, Ni, Zn oxides and other corrosion products are compactly bonded to the alloy substratum and enhance its resistance to corrosion.

Within ternary alloys, a further passivation process is carried out in neutral solutions where the surface dissolution of Al produces a layer of al-oxide [7] as follows:

$Al + 4Cl^- \rightarrow AlCl_4^- + 3e^-$ (5)

$AlCl_4^- + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 8Cl$ (6)

Al_2O_3 is subject to continual dissolving in chloride solutions and the process of corrosion takes place as follows[8]:

$Al^{3+}(in Al_2O_3.nH_2O crystal lattice) + Cl^- \rightarrow Al(OH)_2Cl + 2H^+$ (7)

or

$Al^{3+}(in Al_2O_3.nH_2O crystal lattice) + 2Cl^- \rightarrow Al(OH)_2Cl_2^- + 2H^+$ (8)

Progress of these processes in some places leads to barrier film dilution. The process of hydrolysis creates acidity at local levels and rapid corrosion of recession [8].In the Zn containing alloys an additional passivationprocess is taking place due to the formation of Zn-oxide film duringa dezincification process according to [9,10]:

$Zn + H_2O \rightarrow ZnO + 2H^+ + 2e^-$ (9)

The dissolved nickel ions from the alloy dissolution are integrated into the crystal mesh of Cu_2O which has been already made up as a barrier layer in the presence of Ni . Solid State reaction and mobile vacancy interacts with the segregation of Ni into the Cu_2O layer, leading to a decrease in theionic conductivity and an increased electronic conductivity, and therefore an increase in alloy corrosion resistance[11].

Table 2: Corrosion Parameters for Polarization of Specimens in Salt Solution environment.

Specimens	**Density (g/cm^3)**	**Exposed Surface Area (cm^2)**	**Equivalent Weight (E.W.)**	**E_{cor} (mV)**	**Current Density, i_{cor} (μA/cm^2)**	**Corrosion Rate (CR) mm/yr**	**Improving (%)**
A (Cu-Ni)	8.77	4.15		-710.7	29.87	0.1869	-
B(Cu-Ni-Al)	7.2	4.15		-982	24.07	1.258×10-3	99.3
C(Cu-Ni-Al-Fe)	7.099	4.13		-1046.7	23.35	4.05×10-6	99.99
D(Cu-Ni-Zn	8.6	4.15		-897.5	30.79	3.0607×10-4	99.83
E(Cu-Ni-Zn-Fe)	8.3	4.15		-925.4	29.62	5.8191×10-3	96.8

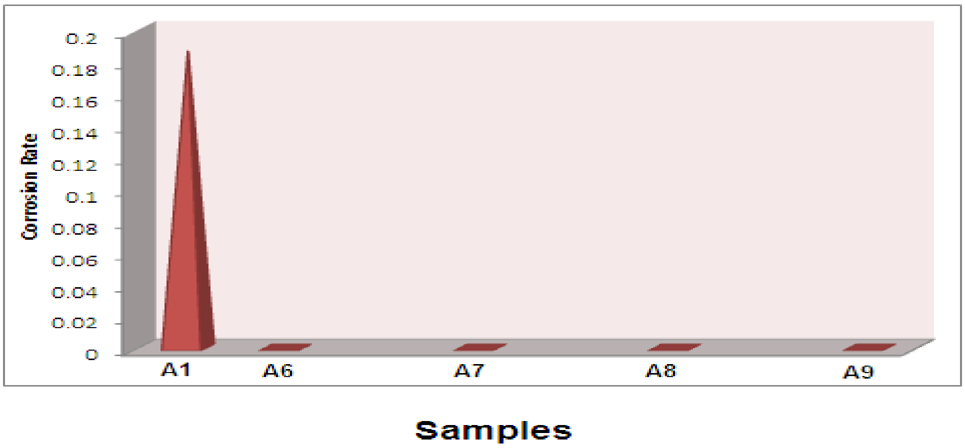


Fig.4: Comparative in Corrosion Rate with Respect to Base Alloy(A).

5.Erosion/Corrosion Test

Because of the collision or gases and liquid impact, erosion is a mechanical mechanism such as removing part of the material from the surfaces. During this study, the erosion-corrosion apparatus was designed to rely on ASTM (G 73), as shown in Fig (3.13). The erosion-corrosion system consists of the motor (Q max 53 l/min, H max = 38m, HP = 1hp, 2850 rpm, scale 1in-1in), the granite tank, the tubes on the specimen to drop the water by nozzle.Temperature (25-30oC) tested by all alloys, anywhere salt solution (sea water) induces erosion-corrosion and falls from the nozzle at angle=90 ° (the impact angle between the line of water and surface of specimen).

The nozzle has a diameter of (2mm) and is mounted at a fixed distance of (10 mm) from the specimen. The change in weight can be determined and then the erosion rate according to the equation (3.3) is obtained as follows.

$$Change\ in\ weight(\Delta w) = original\ weight(w_o) - weight\ after\ a\ fixed\ time\big(w_{1,2,....}\big)$$

$$\boldsymbol{Erosion\ rate\ (gm/hr)} = \frac{\boldsymbol{\Delta w}}{\boldsymbol{time\ of\ exposure}} \dots\dots\dots\dots..(\mathbf{10})$$

Fig. 5: erosion-Corrosion Apparatus Depend on (G73) ASTM.

while Fig. (4.28) represent erosion rate of the specimens with nickel, there are a great improving in erosion- corrosion behavior, there are an enhancement in weight lose per unit hour improving reach to (82.14, 92.85, 21.42 & 50) for B, C,D & E specimens respectively, with respect to base alloy Tables 3 & Fig.6, this is due to two factors: first, high hardness; second, protective oxide layers formed on the surface; XRD and EDS show the presence of oxides with high properties capable of protecting the surface from corrosion and oxidation.

Table 3: Shows Improving in Erosive Rate at Steady State for with nickel alloys.

Sample	Erosive Rate(mg/hr.) **at steady state**	**Improving (%)**
A1(Cu-Ni)	2.8	-
A6(Cu-Ni-Al)	0.5	82.14
A7(Cu-Ni-Al-Fe)	0.2	92.85
A8(Cu-Ni-Zn	2.2	21.42
A9(Cu-Ni-Zn-Fe)	1.4	50

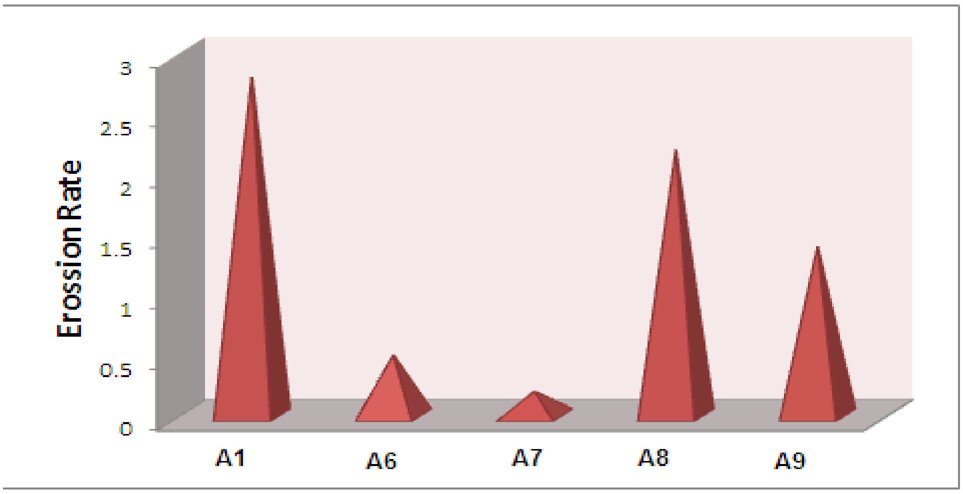


Fig. 6: Comparative in Corrosion Rate for with nickel alloys with Respect to Base Alloy.

6.X-Ray Diffraction Analysis For all Samples (After Erosion-Corrosion Test.

The compositions of erosion-corrosion product films on samples (A6&A7) appear to be similar**,** some characteristic peaks in sample A6 are marked to indicate the existence of Cu2O, α-Cu, NiO, Al2O3 while diffraction pattern characterized the corrosion products formed on the surface of sample A7. It shows the characteristic peaks and Fe2O3of Cu2O, α-Cu, Al2O3 and Fe_2O_3. Although there is a difference in the erosion-corrosion rate of the samples used, they all have good resistance to erosion-corrosion because the formation of Al2O3 greatly protects the surface against corrosion.

The diffraction pattern belongs to the corrosion products formed on the surface of samples A8 & A9 as a result of exposure to sea water which reveals the presence of Cu2O, α-Cu, NiO, ZnO, and Fe_2O_3.

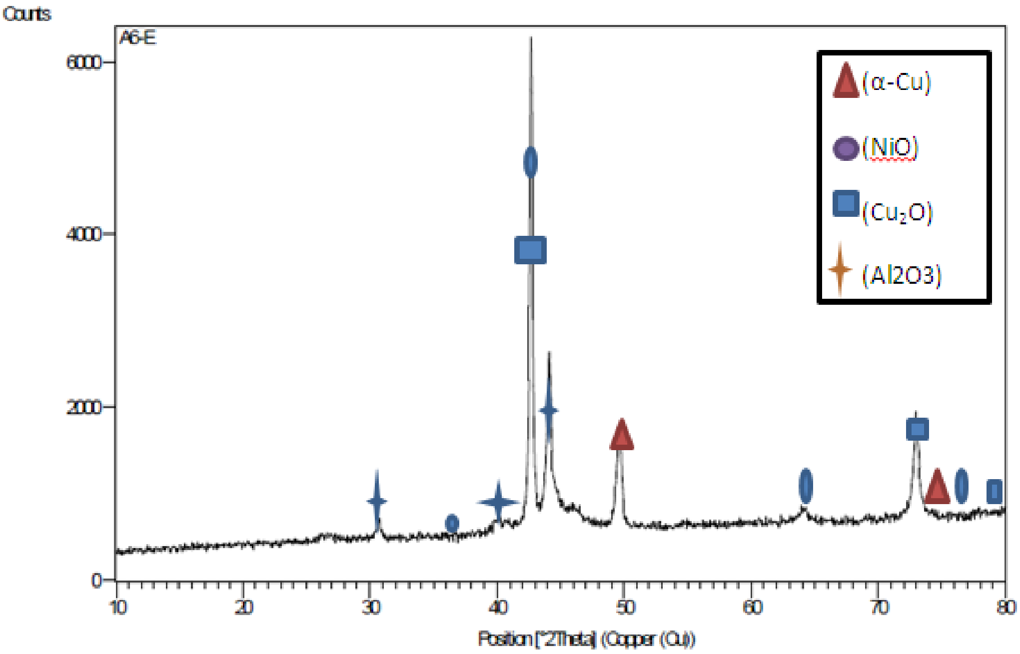


Figure (4.60): X-Ray Diffraction Analysis for Sample A6.

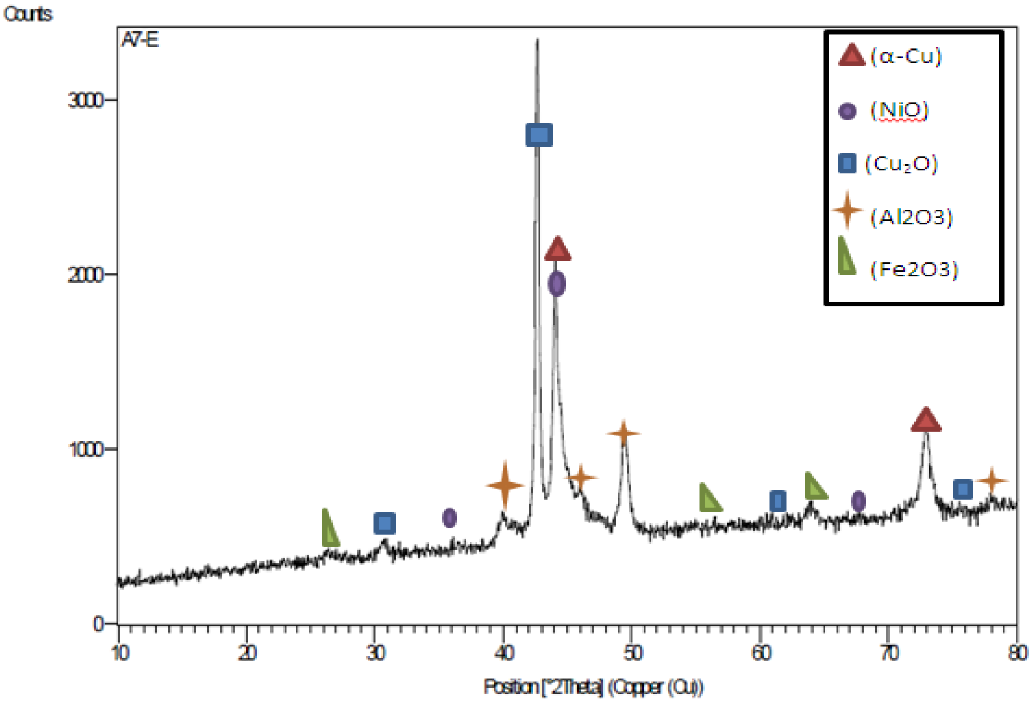


Figure (4.61): X-Ray Diffraction Analysis for Sample A7.

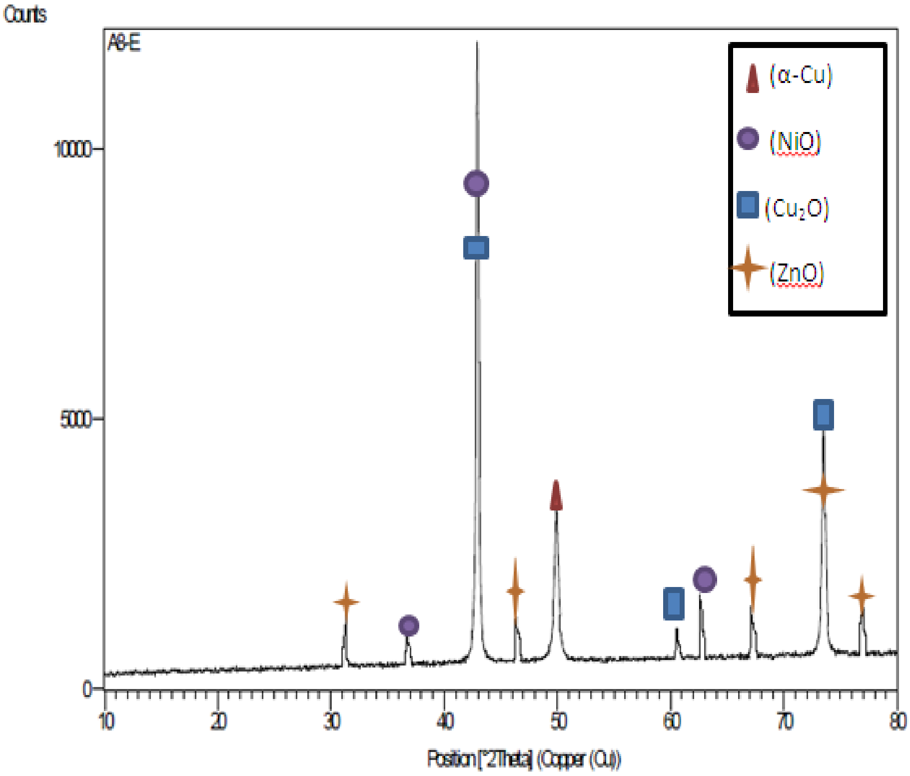


Figure (4.62): X-Ray Diffraction Analysis for Sample A8.

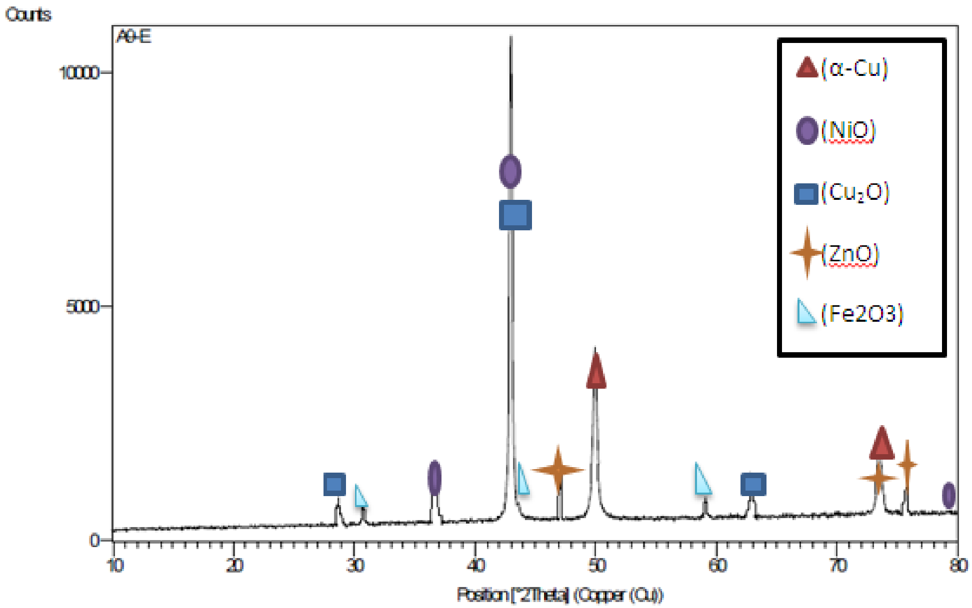
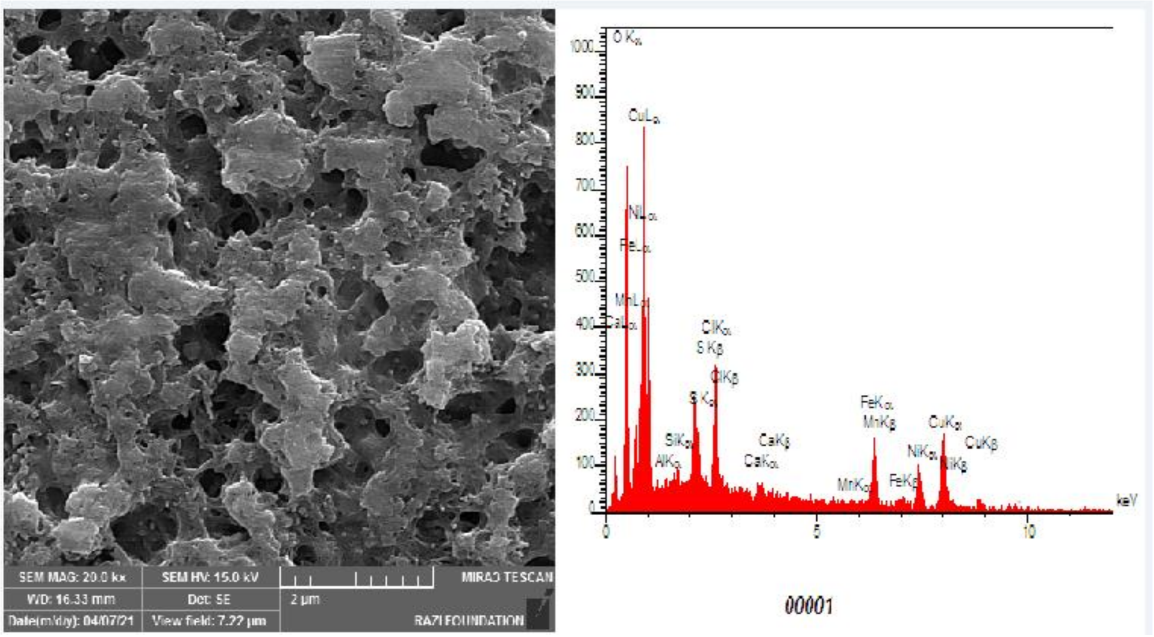
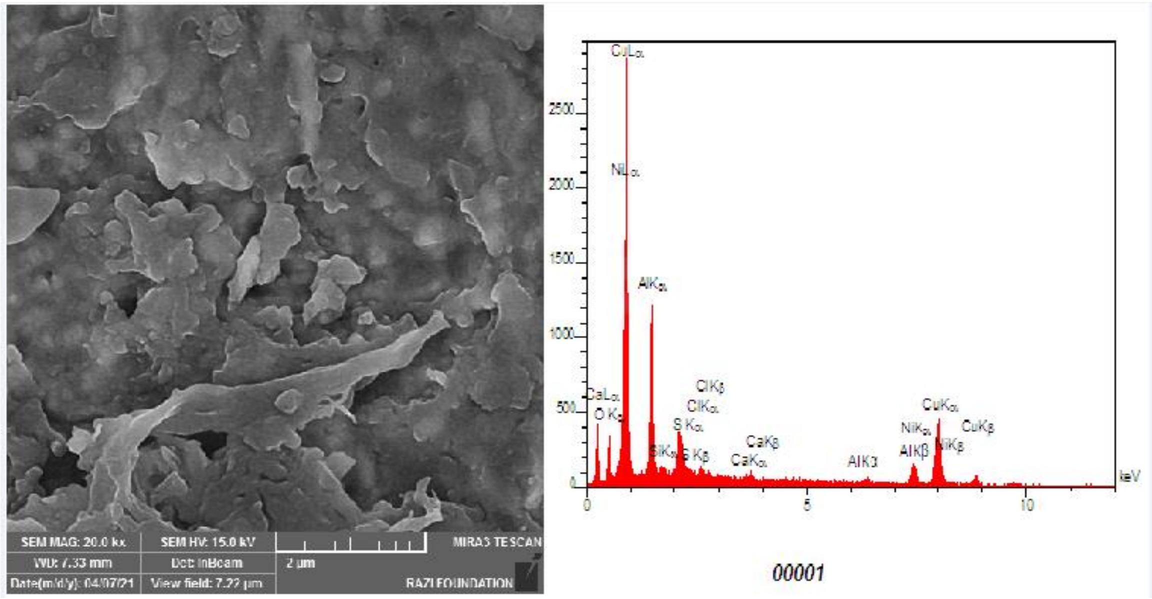


Figure (4.63): X-Ray Diffraction Analysis for Sample A9.

8.Scanning Electron Microscope for Alloys after Erosion-Corrosion Test.

Scanning electron microscope (SEM) has been employed to observe the corroded surfaces of alloys. The morphology of the all alloys specimens are shown in Fig.(4.81) to fig.(4.84) show, the surface of alloy appeared d corrosion products, which is analyzed by EDS microanalyses shown in Fig.(4.85) to fig.(4.88). The corrosion behaviors have obtained by the erosion-corrosion (salt solution) test have revealed the corrosion mechanism that chloride ions attacked the surface of alloy to enhance dissolubility, thus hindering the formation of protective films and leading to the corrosion process.




SEM MAG: 20.0 kx
SEM HV: 15.0 kV
WD: 7.33 mm
Det: InBeam
Date(m/d/y): 04/07/21
View field: 7.22 μm
2 μm
MIRA3 TESCAN
RAZI FOUNDATION
CuLα
NiLα
AlKα
CaLα
O Kα
ClKβ
ClKα
S Kα
SiKα
S Kβ
CaKβ
CaKα
AlK3
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2500
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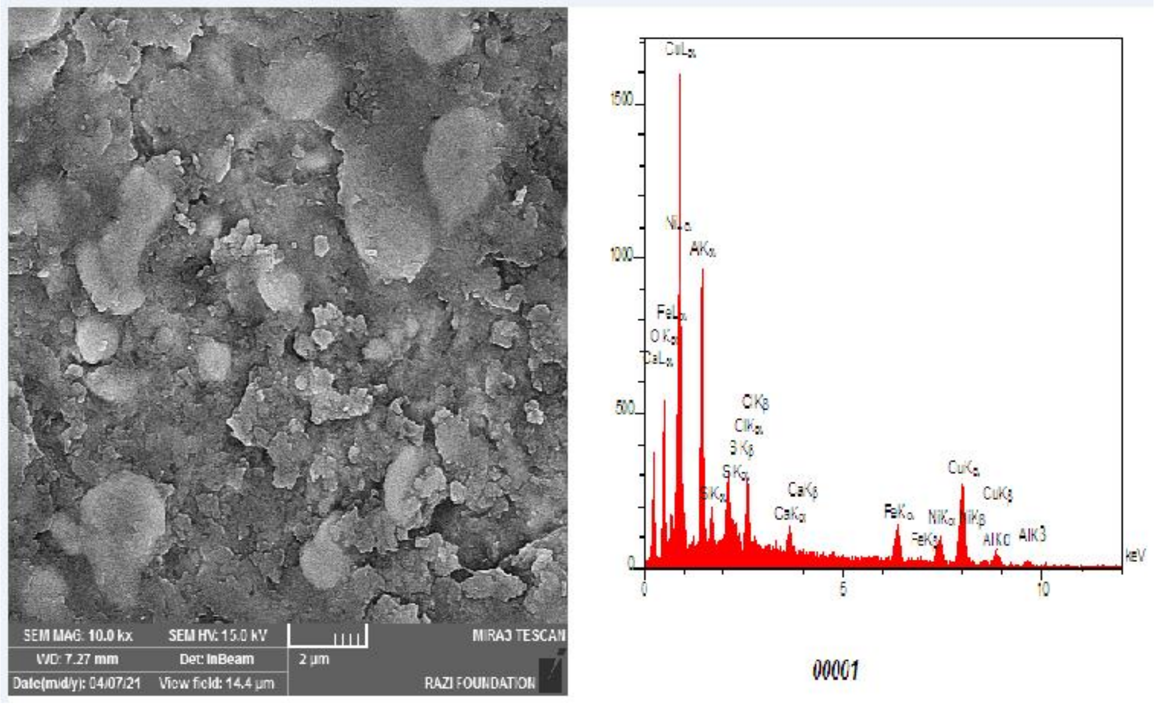
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SEM HV: 15.0 kV
WD: 7.27 mm
Det: InBeam
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View field: 14.4 μm
2 μm
MIRA3 TESCAN
RAZI FOUNDATION
CuLα
NiLα
AlKα
FeLα
O Kα
CaLα
ClKβ
ClKα
S Kβ
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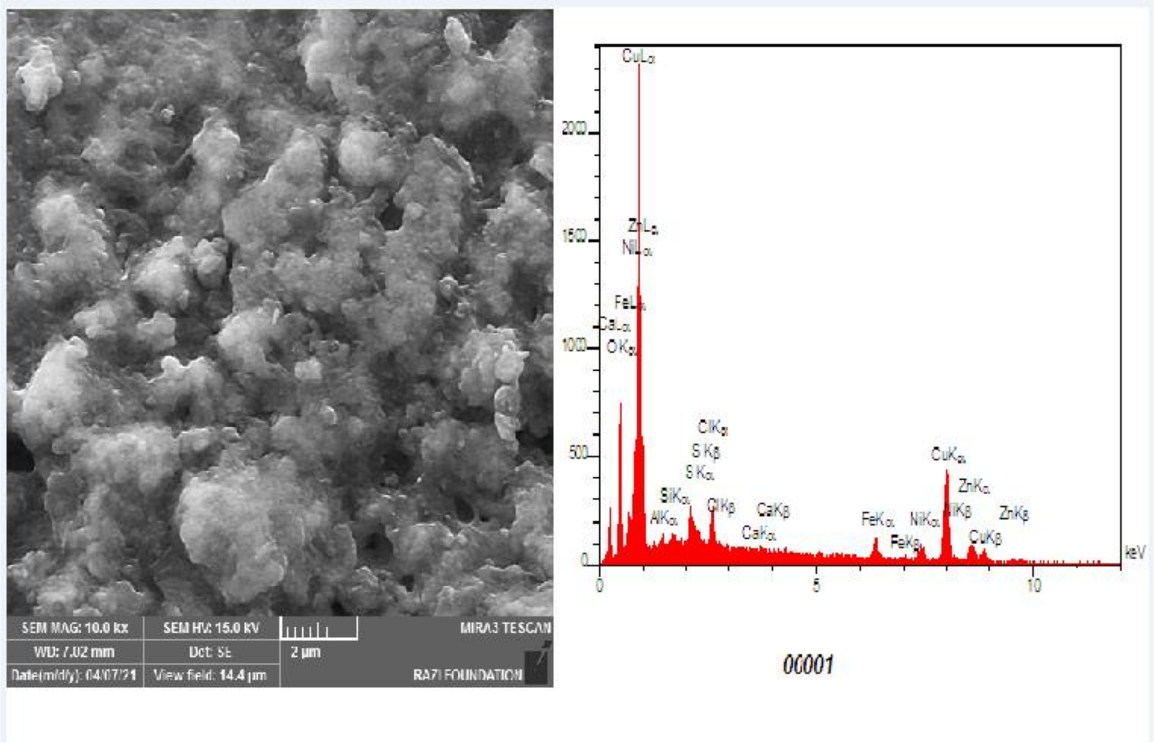

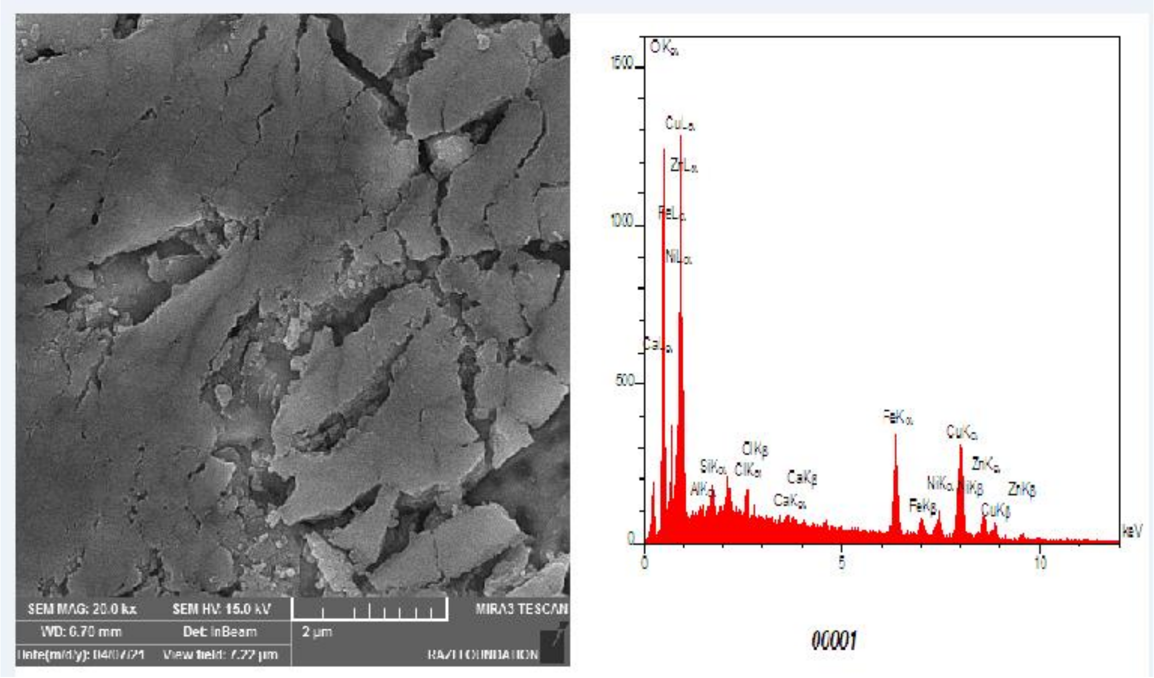

9. CONCLUSIONS

The results showed an increase in the corrosion resistance of the prepared alloys compared to the copper-nickel alloy used in electric power plants, and this is due to the addition of elements such as aluminum, zinc and iron, this is due to protective oxide layers formed on the surface; XRD and EDS show the presence of oxides with high properties capable of protecting the surface from corrosion and oxidation.

References

1- H. Nady, M. M. El-Rabiei, M. Samy, W. A. Badawy. "The Influence of Alloying Elements (Al, Ni and Zn) on the Corrosion Resistance of
Some Cu-Ternary Alloys in Na2SO4 Solutions", Journal of Bio- and Tribo-Corrosion, 2020.

2- S. Cere and M. Va□que□, “Properties of the passive films present on copper and copper-nickel alloys in slightly alkaline solutions,” *Journal of Materials Science Letters*, vol. 21, no. 6, pp. 493–495, 2002.
3-S. M. Sayed, E. A. Ashour, and G. I. Youssef, “Effect of sulfide ions on the corrosion behaviour of Al-brass and Cu10Ni alloys in salt water,” *Materials Chemistry and Physics*, vol. 78, no. 3, pp. 825–834, 2003.
4-Y. S. Tan, M. P. Srinivasan, S. O. Pehkonen, and S. Y. M. Chooi, “Effects of ring substituents on the protective properties of selfassembled benzenethiols on copper,” *Corrosion Science*, vol. 48, no. 4, pp. 840–862, 2006.
5-Boyapati, Venkata Appa Rao, and Chaitanya Kumar Kanukula. "Corrosion inhibition of Cu-Ni (90/10) alloy in seawater and sulphide-polluted seawater environments by 1, 2, 3-Benzotriazole." *International Scholarly Research Notices* 2013 (2013)
6- Leygraf, C.; Odnevall Wallinder, I.; Tidblad, J.; Graedel, T. Atmospheric Corrosion, 2nd ed.; Wiley Blackwell: Hoboken, NJ, USA, 2016; pp. 1–374.
7-W.A. Badawy, M.M. El-Rabiee, N.H. Hilal, H. Nady, Effect of nickel content on theelectrochemical behavior of Cu–Al–Ni alloys in chloride free neutral solutions,Electrochim. Acta 56 (2010) 913–918.
8- J.A. Wharton, R.C. Barik, G. Kear, R.J.K. Wood, K.R. Stokes, F.C. Walsh, The corro-sion of nickel–aluminium bronze in seawater, Corros. Sci. 47 (2005) 3336–3367.
9- R. Procaccini, D.J. Schiffrin, Oxygen reduction on Cu-Zn alloys, J. Appl. Elec-trochem. 39 (2009) 177–184.
10- B. Chen, C. Liang, D. Fu, D. Ren, Corrosion behavior of Cu and the Cu–Zn–Al shapememory alloy in simulated uterine fluid, Contraception 72 (2005) 221–224.
11- M. Metikˇos-Hukovi_c, R. Babi_c, I. Škugor, Z. Grubˇac, Copper–nickel alloys mod-ified with thin surface films: Corrosion behavior in the presence of chlorideions, Corr. Sci. 53 (2011) 347–352.