Improvement the Corrosion Resistance of Aluminum Bronze Alloy (Cu-7.7wt%Al) Reinforced by Al₂O₃ and TiO₂ Nanoparticles

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Abstract. This work involves study of corrosion behavior of Aluminum bronze alloy (Cu-7.7wt%Al) reinforced by both nanoparticles of Al₂O₃ and TiO₂ with different percentage (0.6, 1.1, 1.5 and 3 weight percent). Composite materials are prepared by stir casting method with mechanical stirring and magnetic field from induction furnace that used in this work. The copper base alloy reinforced samples were tested to investigate corrosion behavior, by using Tafel extrapolation technique. The Scanning Electron Microscope was used to study the effect of Al₂O₃ and TiO₂ nanoparticles on the topography of surfaces. The results showed that the microstructure of reinforced alloy is composed of a fine dendritic structure of αCu phase and CuAl₂ as intermetallic compound. The samples reinforced with 3wt% of Al₂O₃ and TiO₂ have a lower corrosion rate compared to nano-composites reinforced with 1.5wt% of Al₂O₃ and TiO₂. While the nano-composites reinforced with 1.5wt% of Al₂O₃ and TiO₂ has lower corrosion rate compared to the Cu-Al matrix in 3.5%NaCl solution at ambient temperature.

1. Introduction
Recently, copper-based alloys have great interest due to their excellent chemical and physical properties, casting property, good wear resistance and corrosion resistance in addition to low material cost [1, 2]. Copper-based alloys such as bronzes have been desired for the applications in industry such as railway, connectors, contact wires, lead frame, automobile radiators, pipes, valves and heat exchangers, because of their excellent electrical and thermal conductivity in addition to the ease of fabrication and ability to resist corrosion [3, 4]. The corrosion behavior of copper in aqueous solutions are changed with pH and associated with the morphology of the surface films formed. However, copper alloys are sensitive to high attack in ammonia (NH₃), NH₃ compounds and sulfur, and acids oxide. The aluminum oxide (Al₂O₃) is an important constituent of corrosion film on copper alloys surface [5, 6]. The study of corrosion resistance of copper alloys with nano particles addition is very rare. However, this section sheds lights on the corrosion behavior of Cu-Al alloy. Adeline et al. (2009) [7] studied potentiodynamic polarization methods in a 25 ppm chloride solution with pH 6 of Cu, Al, Cu-Al₂, Cu-Al and Cu₉-Al₄. Corrosion current densities for the alloys were observed in the order sequence of Al > Cu₉-Al₄ > Cu-Al₂ > Cu-Al > Cu. With an increase in Al content, the corrosion current density shift to higher value. This is in conformity with the reducing current density with high Al content. Moreover, Bukola et al. (2013) [8] investigated the corrosion behavior of Al bronze alloy in four selected aggressive media. These media are HCl, H₂SO₄, NaOH and NaCl. Aluminum bronze alloy by sand casting process was prepared. However, there is increased in the rate of corrosion with an increase in the concentration of NaCl and H₂SO₄ media. In NaOH and H₂SO₄ media, aluminum bronze samples show gradual discoloration. The environment of NaCl shows high corrosion resistance
and discoloration slight effect until at concentration increase. Finally, Oluwayomi et al. (2014) [9] pointed out the corrosion behavior of (8 wt %) aluminum bronze alloys prepared in alkaline, acidic, and marine environments by sand casting. It was observed that, on the protective film, an intense chloride attack is formed. It indicates that no corrosion observed for aluminum bronze according to the comparative studies in selected environments. The alloys have a highest tendency to marine applicable, alkaline, and sulphuric acid environments. The aim of this study is to investigate the corrosion resistance of Aluminum bronze alloy (Cu-7.7wt%Al) reinforced by Al₂O₃ and TiO₂ nanoparticles in 3.5%NaCl solution by the potentiostat polarization that produced by stir casting methods.

2. Experimental Procedures

2.1. Material
In this study, Aluminum bronze alloy and nanoparticles as received were used. The raw alloy was cut to the small pieces with dimensions of 20x20x20 mm in order to easy melting process in stir casting. These materials were analysed by X-Ray fluorescent in Baghdad Central Laboratory, Ministry of Construction and Housing. This analysis was done to identify chemical compositions as indicated in Table 1. Scanning electron microscopy (SEM) with EDS type (TESCAN) available in the scanner (Tscan) available at the Ministry of Science and technology was used to identify the particle size and shape of Al₂O₃ and TiO₂, the as shown in Figure 1.

| Table1. Shows the chemical composition analysis of raw materials used (as received). |
|------------------|------------------|------------------|------------------|------------------|
|                  |                  |                  |                  |                  |
|                  |                  |                  |                  |                  |
| Alloy            | Cu               | Al              | Fe              | Si              | Mn              | P               | Ag              |
| CuAl             | 92.217           | 7.7             | 0.0             | 0.0             | 0.00            |                  |                  |
| Cu powder        | 99.721           | --              | 0.0             | 0.0             | 0.01            | 0.1             | 0.0             |
|                  |                  | 82              | --              | 82              | 04              | 82              |
| Nano powder      |                  | α-Al₂O₃         | TiO₂            | CuO             |
| α-Al₂O₃          | 99.777           | --              | 0.001           |                  |
| RutileTiO₂       | --               | 99.929          | 0.008           |

Figure 1. The SEM micrographs of a,b. Al₂O₃ and c,d. TiO₂.
2.2. Preparation of samples by stir casting

The system of stir casting consisted of induction furnace, graphite crucible, mixer with speed about 600 RPM by graphite impellers, and cast-iron mold with two holes diameter 10mm and 16 mm were carried out as shown in Figure 2. Optical Microscope type (Kruss Mbi3300 Germany) connected with a digital camera and computer was used. XRD is used also a Shimadzu 6000 X-ray diffraction target CuKα1 radiation with 2θ angle covered from 15 to 120 degree.

![Figure 2. Shows stir casting system.](image)

2.3. Casting and Molding

Copper powder with particle size of 75 µm and 40 nm for nanoparticles of Al₂O₃ and 80 nm TiO₂ were used in this study. These mixtures were placed in a ball mill at 300 rpm for 2 h, containing 138 g of tungsten carbide balls (20 numbers). The powder that milled were pressed or compacted to a pellet with a size of 15mm in diameter and 5mm thick to facilitate their addition to the melt and enhance wettability of the reinforcements with the matrix as shown in Figure 3(a and b). The system of stir casting methods is used to produce CuAl alloy reinforced by nanoparticles. The process is started with the preparation of the charge containing required quantities of different elements Al₂O₃, and TiO₂. Stir casting method with argon atmosphere was adopted for producing the samples in this experimental study.

![Figure 3. shows the SEM and EDS Mapping of pre-distribution of copper aluminum alloy reinforcement by nanoparticles.](image)

The melting and pouring temperatures of CuAl alloy are 1120 °C and 1080 °C, respectively. Preheat of casting molds for about (100–150) °C before pouring because very important [11]. Then weighed amount of nanoparticles (0.6, 1.1, 1.5, and 3) wt% of Al₂O₃, and TiO₂ were added to the CuAl alloy melt. After five minutes, the alloy is dissolved, the nanoparticles are added, and the melt is stirred vigorously. The melt surface covered with fluxes is usually based on borax, due to the ability to dissolve and collect objectionable oxide and makes it possible to obtain a structure free from
inclusions [12]. These alloys were poured in a steel mold to produce rods casts. The chemical analysis of these casts was tabulated as shown in Table 2. The obtained analyses are agreed with aluminium bronze alloy standard C95600 [13].

Table 2. Indicates chemical analysis of casts alloys after and before the casting of the alloys

| Samples No. | Additive before casting Wt% | Additive after casting Wt.% |
|-------------|-----------------------------|-----------------------------|
| 1           | Cu8 Al                      | Cu7.7 Al                    |
| 2A          | Cu8Al+0.8Al2O3+ 0.8 TiO2    | Cu7.7Al+0.6 Al2O3+ 0.6 TiO2|
| 2B          | Cu8Al+ 1.3 Al2O3+ 1.3 TiO2  | Cu7.7Al+ 1.1 Al2O3+ 1.1 TiO2|
| 2C          | Cu8Al+ 1.8 Al2O3+ 1.8 TiO2  | Cu7.7Al+ 1.5 Al2O3+ 1.5 TiO2|
| 2D          | Cu8Al+3.5 Al2O3+ 3.5 TiO2   | Cu7.7Al+3 Al2O3+ 3 TiO2     |

Table 3. Design and production capacity of the water treatment plants available in the Balad city

| WTP/Project        | Design Capacity m³/day | Production Capacity m³/day | Status     |
|--------------------|------------------------|----------------------------|------------|
| Yathreb            | 22000                  | 18000                      | Operating  |
| Balad old WTP      | 6000                   | 2000                       | Out of service |
| Balad new WTP      | 10080                  | 4000                       | Out of service |
| AlHussain project  | 200                    | 200                        | Operating  |
| Al-Furat project   | 200                    | 200                        | Operating  |

2.4. Sample Preparation
The cast diameter of 16 mm and a length of 120 mm cast as rods are shown in Figure 4 (a). These materials are cut to prepare specimens with dimensions of 5 mm length and 16 mm diameter for corrosion test as shown in Figure 4 (b). These samples are ground, polished and etched by Keller reagent (5 g FeCl3, 95% methanol, 5 mL HCl) in order to reveal the microstructure [13].

![Figure 4](image)

2.5. Corrosion Test
There are three types of corrosion tests which have been obtained in this work; the first one is the open circuit potential- time measurements, the second is Tafel extrapolation used as the techniques for evaluating corrosion parameters of the samples. The last one is reversion anodic polarization (cyclic) in order to indicate the probability of pitting corrosion. The specimens for corrosion test are prepared by machining to dimensions of 16 mm diameter and 3 mm thick. The exposed surface area of the specimen was 1.0 cm². Corrosion test is carried out in the corrosion laboratory in Ministry of Science and Technology.
The electrochemical cell consists of a container holding the 3.5% NaCl solution of 1000 ml capacity to immerse the three electrodes. The electrochemical cell is composed of a reference, working, and counters (auxiliary) electrodes. The Calomel Standard Electrode (saturated calomel electrode) is referred to the reference electrode. The working electrode is related to the materials need to be examined. The Platinum rod with size (100 mm × 10 mm) is used as a counter electrode. The current in the circuit is specifically carried by the electrode. The counter electrode used to measure the voltage between the electrolyte and W.E. is respected to the reference electrode, as shown in Figure 5. The connection of these electrodes was done via the potentiostat type (M Lab 200, Germany), and the experiments were carried out at ambient temperature at a scanning rate of 2 mV/s within the prepared solution. During the electrochemical reaction, the following equation is used to determine the rate of corrosion via the current density in the solution [13]:

\[
CR \text{ (mpy)} = 0.13 \times \frac{i_{corr} \times e}{\rho} \quad \text{...(1)}
\]

CR: Corrosion rate (mpy)

\(i_{corr}\): Corrosion current density (µA/cm\(^2\)).

e: Equivalent weight (atomic weight / valance).

\(\rho\): Density of metal (g/cm\(^3\)).

3. Results and Discussions

3.1. XRD of Cu-Al Alloy Reinforced by Nanoparticles

Figure 6 elucidates that the CuAl\(_2\) phase as intermetallic compound is identified by the XRD analysis using CuK\(\alpha1\) radiation. The 2\(\theta\) angle covered is from 15 to 100 degrees. That is indicated depending on the standard cards in Tables 4. The TiO\(_2\) and Al\(_2\)O\(_3\) nanoparticles percentage in the matrix is less than 5%. Therefore, it is not diagnosed.

![Figure 6. Shown the XRD of copper aluminum alloy reinforcement by nanoparticles.](image-url)
Table 4. The XRD data results of copper aluminum alloy reinforcement by nanoparticles.

| peak | Phase    | 2θ (Deg) | d measured (Å) | d standard (Å) | Intensity (Counts ) |
|------|----------|----------|----------------|----------------|---------------------|
| 1    | Cu       | 42.7483  | 2.1135         | 2.1171         | 100                 |
| 2    | Cu       | 49.7283  | 1.8320         | 1.8335         | 28                  |
| 3    | CuAl2    | 73.5603  | 1.2865         | 1.2880         | 9                   |
| 4    | CuAl2    | 77.3959  | 1.2320         | 1.2840         | 18                  |

3.2. Microstructure of alloy

Figure 7 indicates the dendrite of α-phase, and CuAl2 as intermetallic compounds appeared in the matrix. The microstructure of aluminum bronze alloys with 3 % Al2O3 and 3 % TiO2 show finer dendrite compared with the 1.5 % Al2O3 and 1.5 % TiO2. While the alloys with 1.5 % Al2O3 and 1.5 % TiO2 finer dendrite than of the matrix as shown in Figure 7 (a to f). Hence, the α-Cu dendrite is decreased as a content of nano-Al2O3 and TiO2 particles increases. These nanoparticles act as nucleation sites during solidification as proposed by Iman et al [14].

![Figure 7. Optical microscope of Cu-Al alloys](image)

3.3. Corrosion Test

The corrosion behavior of the Cu-Al alloys reinforced by nanoparticles samples is studied in 3.5% NaCl solution by open circuit potential, Tafel extrapolation and reversion anodic polarization (cyclic).

3.3.1 Open Circuit Potential

Figure 8(a and b) shows the open circuit potential for Cu-Al alloy and reinforced alloy. In general, the open circuit potential for both cases initially rapid increases to noble direction until reaches roughly steady state approximately (-242) mV for the matrix and (-100) for the reinforced alloy. The increase in potential to noble direction is due to the presence of aluminum in the alloy which passivate to aluminum oxide on the alloy surface. This passivation behavior also increases in the presence of Al2O3 and TiO2 nanoparticles. This value refers to an equilibrium condition between the specimen and the surrounding solution of 3.5% NaCl. The variation in open circuit potential with time depends on many parameters such as elements addition and surface treatments. This value indicates that the presence of nanoparticles improves its potential to more noble value.
3.3.2 Polarization

Figure 9 demonstrate the polarization curve of the matrix copper alloy in 3.5 wt% NaCl solution. The curve AB represents cathodic polarization curve and curve BC represents the anodic polarization curve. The Tafel extrapolation method was used in the electrochemical corrosion test of all specimens within pH of 7.4. The corrosion parameters $i_{\text{corr}}$ and $E_{\text{corr}}$ were obtained by using this method.

![Figure 9: Polarization curves of cast CuAl alloy matrix.](image)

The interaction of these two polarization curves is represented by $i_{\text{corr}}$ and $E_{\text{corr}}$. The values of $i_{\text{corr}}$ and $E_{\text{corr}}$ for Cu-Al alloy without nanoparticles are 47.25 mA/cm$^2$ and -257.3 mV, respectively as shown in Figure 9. While the sample that casted and reinforced by nanoparticles, there are some improvements in corrosion resistance parameters, $i_{\text{corr}}$, which is equal to 7.7 mA/cm$^2$ and $E_{\text{corr}}$ equal to -365.9 mV, as shown in Figure 10.
Figure 10. Shows the polarization curves of casts CuAl reinforced alloy.

Table 5 shows the current density of specimens decreased from $47.25 \times 10^{-3} \text{mA/cm}^2$ to $7.7 \times 10^{-3} \text{mA/cm}^2$ with addition of nanoparticles increased from 0.6 to 3 wt % of Al$_2$O$_3$ and TiO$_2$ in Cu-Al matrix. This cause improved in corrosion resistance or reduced in corrosion rate to $6.98 \times 10^{-3} \text{mpy}$, as shown in Figure 11, due to increase passive behaviour of nanoparticles addition.

| Samples No. | I$_{corr}$ mA/cm$^2$ | E mV | Equivalent Weight g | Density of alloy g/cm$^3$ | Corrosion rate mpy |
|-------------|---------------------|------|---------------------|--------------------------|-------------------|
| 1           | 47.35 $\times 10^{-3}$ | -257.3 | 59.18 | 8.46 | 43.06 $\times 10^{-3}$ |
| 2A          | 11.4 $\times 10^{-3}$ | -267.1 | 58.65 | 8.39 | 10.36 $\times 10^{-3}$ |
| 2B          | 10.77 $\times 10^{-3}$ | -446.1 | 58.65 | 8.4 | 9.78 $\times 10^{-3}$ |
| 2C          | 10.36 $\times 10^{-3}$ | -267.1 | 58.12 | 8.31 | 9.42 $\times 10^{-3}$ |
| 2D          | 7.7 $\times 10^{-3}$ | -365.9 | 57.75 | 8.28 | 6.98 $\times 10^{-3}$ |

Figure 11. Shows the shifted curves to the lift by addition of Al$_2$O$_3$ and TiO$_2$ to Cu-Al alloy.

The decrease in corrosion current density was observed with the presence of nanoparticles such as alumina and titania in the matrix. This is due to that nanoparticles improve the stability of surface oxide films formed on the material surface. It seems that the dissolution of copper to cuprous soluble as complex chloride ion CuCl$^-$ dominates the polarization behavior of Cu alloys in chloride solutions. It is controllable by the rate of diffusion CuCl$^-$ ions from the electrode surface through diffusion layer. Additionally, the variation in corrosion behavior occurs because of the difference in the microstructure.
3.3.3 Cyclic Polarization

Cyclic polarization allows for studying the relative susceptibility to localized corrosion or pitting corrosion phenomena in metals according to ASTM standard G61. The results indicate that there is intersection with the passivation region in the polarization curve in lower potential where the pitting corrosion occurred of Cu-Al matrix alloy as shown in Figure 12.

![Figure 12](image1.png)

**Figure 12.** Shows the cyclic polarization of Cu-Al alloy matrix.

Figure 13 shows that there is also intersected of passive region at higher potential ($E_{pit}=1814.3$ mV) and ($i_{pit}=32.1$). This means that alloys needed high potential to breakdown passive layer. Figure 14 shows that the alloys with equal amounts of 3%wt $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ that give high resistance to pitting corrosion because the layer polarization curve does not intersect the passive region.
4. Conclusions
The following conclusions can be drawn:

1. A fine dendritic structure of α Cu microstructure of reinforced alloy is composed compare to the matrix and CuAl2 as intermetallic compound.
2. It is found that the reinforced alloys have a lower rate of corrosion in 3.5% NaCl solution at ambient temperature in pH equal to 7.4.
3. The reinforced alloys with 3wt% of Al2O3 and TiO2 have a lower corrosion rate compared to reinforced alloys reinforced with 1.5wt% of Al2O3 and TiO2. While the reinforced alloys with 1.5wt% of Al2O3 and TiO2 has lower corrosion rate compared to the Cu-Al matrix

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