Influence of Sulphate and Chlorides Acidic Media on Mechanical and Corrosion Behavior of Fly Ash Particulate Reinforced 2024 Al/TiO₂ Composites

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Abstract. This research studied the corrosion behavior of 2024 Al/2%TiO₂ with different additions of fly ash in 0.1N H₂SO₄ and 0.1N HCl media. Using a liquid metallurgy route (stir casting technique) 0, 2, 4 and 6 wt.% of fly ash were added to 2024 Al/2%TiO₂ and the density and corrosion potential of the samples was evaluated by potentiodynamic polarization. The highest corrosion current density (7.437 x 10⁻⁷) was obtained in 0.1N HCl media while the corrosion current density in 0.1N H₂SO₄ media was 2.276 x 10⁻⁷. The corrosion current density values of 2024 Al/2%TiO₂ alloy rise with increase in the fly ash addition from 0.305 x 10⁻⁷ to 1.08 x 10⁻⁷ as a result of the micro galvanic coupling between the matrix alloy and the reinforcement or conducting interfacial products. Micro-Vickers hardness of the composite increased from 120 V to 160 V with increasing fly ash content. The values of yield strength increased from (231MPa) to (279 MPa) and the values of ultimate tensile strength (UTS) were increased from (136MPa) to (184MPa) with increase in the percentage of fly ash.

Keywords. 2024 Al alloy, TiO₂ particulates, Fly ash, corrosion current (Icorr).

1. Introduction

There are many significant applications of reinforced Al in areas such as structural avionics, automobiles and transport. This is because Al properties include high specific modulus, high specific strength and low thermal expansion coefficient [1]. The addition of SiC, B, Al₂O₃, TiC and ZrB₂ to aluminum alloys leads to decrease in the corrosion resistance for the composites, when compared to matrix alloys, as a result of galvanic corrosion [1, 2, 3, 4].

Many factors, such as the composition of alloy, preparation, and intermetallic precipitation, affect the corrosion resistance of composites [5, 6, 7, 8]. Emenike Raymond Obi investigated the corrosion behavior of cast Al-Mg alloy A535 and its composites containing 10 wt.% and 15 wt.% fly ash, and 10 wt.% hybrid reinforcement (5 wt.% fly ash + 5 wt.% SiC) using weight-loss and electrochemical corrosion tests, in fresh water and 3.5 wt.% NaCl solution at room temperature. The results of the weight-loss corrosion test showed that unreinforced A535 alloy had a lower corrosion rate in fresh water and seawater environments than the composites at all the tested pH values [9].

The objective of Y. Gouale et al. was to show the effects of the addition of tin to aluminum in a solution of sodium chloride (NaCl 3%) by weight, as well as the influence of the alloy’s immersion time on its corrosion resistance. Results showed that the addition of tin enhanced aluminum electrochemical activation, as well as the spontaneous formation of an oxide layer containing Al₂O₃, which then protected the metal from further corrosion [10].

The present research study explores the mechanical behavior and corrosion behaviors of aluminum alloys, reinforced by micro hard particles such as TiO₂ and fly ash, in two different electrolytes (0.1N H₂SO₄ and 0.1N HCl). We used a potenio-dynamic polarization technique to investigate the corrosion behavior and noted increasing resistance to corrosion of 2024 Al/2%TiO₂, with added fly ash particulate composites, in comparison to 2024 Al/TiO₂ alloy. Addition of 0, 2, 4, 6
% fly ash particulate into 2024 Al alloy matrix increased the hardness, yield strength and ultimate tensile strength (UTS), and reduced elongation.

2. Methodology

2.1 Material

The study was carried out on cast samples of 2024 Al alloy. In this study, the samples were analyzed by the Specialized Institution of Engineering Industries, Baghdad. The chemical composition of 2024 Al alloy is shown in Table 1. Table 2 shows the chemical composition of the fly ash particulate.

| Table 1. Chemical composition of the matrix alloy ingot. |
|---------------------------------------------------------|
| Element | Si | Pb | Cr | Mg | Zn | Mn | Cu | Fe | Al% |
|---------|----|----|----|----|----|----|----|----|-----|
|         | 0.42 | 0.04 | 0.08 | 1.44 | 0.21 | 0.47 | 4.31 | 0.47 |     |

| Table 2. Chemical composition of fly ash (weight percentage). |
|---------------------------------------------------------------|
| Al2O3 | Lo | Na2O | SiO2 | P2O5 | Mn3O4 | Fe2O3 | K2O | MgO | TiO2 | CaO | Element % |
|-------|----|------|------|------|-------|-------|-----|-----|------|-----|----------|
| 27.54 | 1.74 | 0.58 | 55.21 | 0.44 | 0.46 | 6.85 | 4.32 | 0.03 | 2.15 | 0.67 |         |

2.2 Casting Procedure

Using the liquid metallurgy technique, the composite specimens for this work were manufactured. In this work, the matrix alloy used was standard 2024 Al alloy. The alloy was melted in an electrical melting furnace. First, the alloy was heated beyond its melting temperature and, using a stainless-steel mechanical stirrer, a vortex was created in the melt. The die was heated in the electrical furnace before casting, to remove the moisture, improve melting and prevent adhesion to the die surface. The reinforcement particles were also heated before being adding into the melt. Composite materials samples were reinforced by TiO2 to have 2 wt. % with the addition of fly ash particles with particle size (82.484 µm) with selected weight percentage (0, 2, 4, 6 %). Also, 1 wt. % Mg was added during melting to improve the wettability of the matrix and improve the interfacial bonding between the reinforcement particles and matrix. The reinforcement particles were wrapped in very thin Al foils and heated to 250 °C for 1 hr in a heating furnace, then these heated reinforcement particles were added to the molten 2024 Al alloy for 15 minutes using an electrical stirrer at a speed of 590 rpm. The resulting molten product was put into the furnace at a temperature of 750 °C and then poured into the die, which was preheated at 300 °C for 30 min. The die was of height 250 mm and cavity diameter was 22 mm.

2.3 Specimen Preparation

The specimens of 22 mm diameter were cut from the specimens as cast (the fabricated composites). The samples prepared for tensile testing complied with standard ASTM E8 as shown in Figure 1. Using a Shimadzu Autograph 100 kN testing machine, the tensile tests were performed. A video-extensometer was used to measure the deformation.
2.4 Electrochemical Measurements of 2024 Al alloy

The deterioration of a material through reaction with its environment can be quantified by electrochemical testing, which consists of four parts: anode, cathode, electrolyte and glass path. In this study, the electrochemical test was conducted according to the ASTM G5. These four parts constitute what is called the “corrosion cell”. Potentiodynamic polarization studies were carried out in 0.1N H₂SO₄ solution and 0.1 N HCl media that achieved by a potentiostat device (Wenking LT87, Germany). The measurements were achieved at room temperature in stagnant electrolyte exposed to the atmosphere. In this study, the corrosion behavior of 2024 Al/TiO₂ reinforced in media was detected by calculating the potential of 2024 Al alloy reinforced, by using the potentiostat. The corrosion rate was calculated by using equation (1)[11]:

\[
\text{Corrosion rate (mpy)} = 0.13 \times \frac{I_{\text{corr}} \cdot e}{D}
\]

Where:
- \(I_{\text{corr}}\) : Corrosion current density \(\mu\text{A/cm}^2\).
- \(e\) :Equivalent weight (for 2024 Al = 4.3).
- \(D\) : Density of metal (for 2024 Al = 2.7 gm/cm³).

The hardness of the polished samples from reinforcing alloys was obtained using a digital Vickers micro hardness tester at a load of 0.5 kg for 5 sec, three measures were taken for each sample, then the average values were calculated. The micro hardness of the reinforcing alloys was calculated by equation (2):

\[
H_V = 1.8544 \times \frac{P}{(d_{av})^2}
\]

Where:
- \(P\) : The applied load (0.5 Kg).
- \(d_{av}\) : The average diameter of the rhombus indentation in (mm).
- \(H_V\) : Vickers hardness (Kg/mm²).

3. Results and Discussion

3.1 The Corrosion Results

From the electrochemical method using a potentiodynamic polarization method, we found the corrosion current density, corrosion potential and corrosion rate in saline solution (0.1N H₂SO₄ and 0.1N HCl media) for all samples. Figure 2 shows the relationship between corrosion potential and corrosion current density for 2024 Al/2% TiO₂ alloy reinforced with 0, 2, 4, 6 wt.% of fly ash in 0.1 N HCl media. Figure 2 reveals rising corrosion current density with increasing fly ash addition from 2-6%. That led to reduce corrosion resistance with increasing the addition for these alloys [1].

Table 3 shows the electrochemical corrosion parameters of 2024 Al/2% TiO₂ reinforced with 0, 2, 4, 6 wt. % of fly ash in 0.1 N HCl solution. The results show that the corrosion current density increased with increasing fly ash additions in the 2024 Al/2% TiO₂, which confirms the huge influence of fly ash addition on the corrosion rate of the 2024 Al/2% TiO₂ alloy.
Table 3. Electrochemical corrosion parameters of 2024 Al/TiO$_2$ reinforced and composites with fly ash in 0.1 N HCl solution.

| composites of fly ash | 0.1 N HCl |  |
|-----------------------|-----------|--|
|                       | Corrosion current density I$_{corr}$ $\mu$A/cm$^2$ | Corrosion potential E$_{corr}$/mV | Corrosion rate (mpy) |
| 0% ash and 2% TiO$_2$  | $2.414 \times 10^{-1}$ | -680.0 | $0.48 \times 10^{-1}$ |
| 2% ash and 2% TiO$_2$  | $3.585 \times 10^{-1}$ | -684.4 | $0.97 \times 10^{-1}$ |
| 4% ash and 2% TiO$_2$  | $3.979 \times 10^{-1}$ | -662.9 | $1.17 \times 10^{-1}$ |
| 6% ash and 2% TiO$_2$  | $4.037 \times 10^{-1}$ | -652.4 | $1.48 \times 10^{-1}$ |

Figure 2. Tafel plots of 2024 Al/TiO$_2$ and its fly ash composites (0%, 2%, 4%, and 6%) in 0.1 N HCl medium.

Table 4 shows the estimated electrochemical corrosion parameters for the 2024 Al/2%TiO$_2$ alloy reinforced with (0,2,4,6) wt. % of fly ash in 0.1 N H$_2$SO$_4$ solution. Taking into account the Tafel plots which are shown in Figure 3, it can be noticed that values of corrosion rate and corrosion current density (I$_{corr}$) increased with increase in fly ash particles in the 2024Al/2% TiO$_2$ alloy.

Table 4. Electrochemical corrosion parameters of 2024 Al/TiO$_2$ composites in 0.1 N H$_2$SO$_4$ solution.

| composites of fly ash | 0.1 N H$_2$SO$_4$ |  |
|-----------------------|------------------|--|
|                       | Corrosion current density I$_{corr}$ $\mu$A/cm$^2$ | Corrosion potential E$_{corr}$/mV | Corrosion rate / (mils per year) mpy |
| 0% ash and 2% TiO$_2$  | $0.679 \times 10^{-3}$ | -835.0 | $0.305 \times 10^{-2}$ |
| 2% ash and 2% TiO$_2$  | $1.148 \times 10^{-3}$ | -865.2 | $0.631 \times 10^{-2}$ |
| 4% ash and 2% TiO$_2$  | $1.373 \times 10^{-3}$ | -850.1 | $0.81 \times 10^{-2}$ |
| 6% ash and 2% TiO$_2$  | $2.276 \times 10^{-3}$ | -835.1 | $1.08 \times 10^{-2}$ |
These results show that in chloride medium, the 2024 Al/2% TiO$_2$ reinforced with 0, 2, 4, 6 wt.% of fly ash had lower corrosion resistance compared with the alloy without added ash and this is because the composite reduces the corrosion resistance, owing to galvanic corrosion [10,12]. Table 3 and Table 4 show the $I_{corr}$ values of 2024 Al/2% TiO$_2$ alloy without ash and with 0, 2, 4, 6 wt. % of fly ash in HCl media and H$_2$SO$_4$ media, so it revealed increase in the corrosion rate in acidic chloride medium compared with salt chloride medium; this too is due to galvanic corrosion. The high corrosion current densities and corrosion rates of 2024 Al/TiO$_2$ reinforced in 0.1 N HCl media compared with the values in sulphate media because of the superior penetration and combination abilities of chloride ions entering anion vacancies inside the passive Al$_2$O$_3$ film [12]. The adsorption ability of chloride ions on the passive layer was more aggressive in terms of pitting than sulphate and nitrate ions [12, 13, 14]. The protective oxide film will break down because of the adsorption of chloride [14, 15, 16].

3.2 Mechanical Properties

3.2.1 Hardness

The reinforcement particle (ash particles) were hard compared with the matrix alloy (2024 Al/2%TiO$_2$ ) with is much softer than ash particles and that increased the hardness of composite from 120 V to 160 V with rising the amount of fly ash from 0% to 6%, as shown in Figure 4. Also, the dispersion of fly ash particles contributed positively by increasing the hardness of the composites [6].

3.2.2 Stress-Strain Curves

Figure 3. Tafel plots of 2024 Al/TiO$_2$ and its fly ash composites (0%, 2%, 4%, and 6%) in 0.1 N H$_2$SO$_4$ medium.

Figure 4. Variation of hardness with the weight fraction of fly ash.
Figure 5 shows the stress–strain curves. From this figure it can be noted that the yield stress and ultimate tensile strength increased rapidly with increased fly ash on 2024 Al/TiO$_2$, reinforced.

![Figure 5](image)

**Figure 5.** True stress - strain curves for 2024 Al/TiO$_2$ reinforced at (0,2,4 and 6) wt.% of fly ash particulates

Differences of ultimate tensile strength (UTS) and yield strength with the weight percentage of fly ash are shown in Figures 6 and 7. The values of yield strength of the 2024 Al/TiO$_2$ reinforced respectively from 231MPa to 279 MPa with increasing percentage of fly ash from 0% to 6%. Also, the values of ultimate tensile strength (UTS) increased from 136MPa to 184MPa with rising percentages of fly ash. The rising strength could be attributed to the mechanism of assisted diffusion, and effects of impurity atoms (as foreign particles of second phase) which led to a hindrance of dislocation. Also, the tensile strength of 2024 Al/2% TiO$_2$ rose with increasing additions of fly ash from 2-6%.

![Figure 6](image)

**Figure 6.** Yield strengths vs. various fly ash curve for 2024 Al/TiO$_2$ reinforced.
**Figure 7.** Ultimate tensile strengths vs. various fly ash curve for 2024 Al/TiO$_2$ reinforced.

Figure 8 shows elongation as a function of artificial various fly ash percentages for the samples. The elongation of the 2024 Al/TiO$_2$ reinforced at different fly ash percentages is 10.2 and 5.2. The reduction in elongation is caused by dislocation hindrance arising from impurity atoms, and the assisted diffusion mechanism hindrance [6, 17, 18]. From Figure 8 it can be noted an increasing value of elongation as the percentage of fly ash dropped, due to the hardness and clustering of fly ash particles. The elongation of the composites is affected by several factors including particle size and weight percentage of adding particles, even in the case of composites without defect [13, 18].

**Figure 8.** Elongation values of 2024 Al/TiO$_2$ reinforced, at (0, 2, 4 and 6) wt.% of fly ash particulates.

4. **Conclusions**

Using a potentiodynamic polarization technique, the corrosion behavior of 2024 Al/TiO$_2$ reinforced and fly ash particulate-reinforced composites (0, 2, 4 and 6% wt.) in different media (0.1 N H$_2$SO$_4$ and 0.1 N HCl) was investigated and the results show the following:

1. Increasing the fly ash adding in the composites up to 6% by weight led to increased corrosion current values ($I_{corr}$), owing to the possible micro galvanic corrosion coupling between the matrix alloys and added interfacial products.

2. Comparison of the corrosion rate of composites without added ash, and those with added ash of different weights (2, 4, 6%), in acid media and salts media revealed that the corrosion rate in chloride media is higher than the corrosion rate in the sulphate medium.

3. Addition of 0, 2, 4, 6% fly ash particulate into 2024 Al alloy matrix increased the hardness but this did not increase the corrosion rate.
5. References

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