Microstructural and Corrosion Aspects of Aluminum-Zirconia Metal Matrix Composites in Acidic Condition

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Abstract

Aluminum (Al6061) reinforced with ZrO_2 was fabricated using stir casting techniques. In the present study, this composite's corrosion behavior was investigated with 0, 5, 10, and 15 vol% of ZrO_2. This work investigates the corrosion rates of Al6061-ZrO_2 composites by weight loss and electrochemical polarization methods. In the weight-loss method, the base metal and its composites were immersed in 0.1M hydrochloric acid (HCl) solution for 480 hours, periodically measuring the losses in weight. The composite was immersed in a 0.1M HCl solution in the electrochemical polarization method, and its corrosion parameters such as corrosion potential (Ecorr) and corrosion current (Icorr) were evaluated. In both weight loss and polarization methods, the corrosion rate of Al6061 was found to be more than the composites, and the composite with 15 vol% of zirconia had the least corrosion rate. The surface morphology of Aluminum before and after corrosion was investigated using scanning electron microscopic images (SEM). Before corrosion, the results showed that ZrO_2 particles were finely distributed in the matrix with a little agglomeration in some areas. The microscopic images after corrosion revealed very deep pits in Al6061 alloy. The pits were seen as shallow as the volume % of reinforcement increased.

Keywords — metal matrix composite, stir casting, corrosion, weight-loss method, electrochemical polarization, microstructure.

I. INTRODUCTION

When exposed to an acidic environment, the corrosion resistance of Aluminum is determined by its chemical composition and microstructure. The alloying elements in Al6061 (Mg, Mn, Si, Zn, Cu) affect Aluminum's corrosion kinetics. Among these elements, Si and Mn produce very complex effects. The addition of Cr reduces the effects of corrosion to a certain extent [1]. The current research is focused on improving the corrosion resistance of Aluminum and its alloys.

Aluminum and its alloys have emerged as an alternate in many industries, especially in chemical processing industries. In these industries, they frequently contact acids, base, and salty environments [2]. When Aluminum has been exposed to these environments, a stable, protective film of Al_2O_3 is formed on the surface. This layer is amphoteric and dissolved in strong acidic or alkaline media, leading to corrosion [3]. Many methods have been adopted so far to control the rate of corrosion. Among them, corrosion inhibitors were considered to be the most effective alternative. An extensive study on literature reveals that most inhibitors contain nitrogen, oxygen, or sulfur in their molecular structure. These inhibitors act as a barrier and protect the metal from getting corroded [4,5]. The efficiency of these inhibitors increases when there is an increase in its concentration but decreases when the temperature rises [6]. Coating methods can protect metals from corrosion, but it is not a permanent solution [7]. Apart from reducing corrosion, a metal matrix composite also enhances other material's physical and mechanical properties [8].

In the present study, Aluminum (Al6061)-zirconia (ZrO_2) composite in various volume % has been investigated to observe the extent of corrosion resistance in the acidic medium. The composites of four different volume % (0, 5, 10, and 15) were prepared using stir casting techniques. Zirconia is chemically unreactive by nature. It may be slowly attacked by concentrated hydrofluoric acid and sulphuric acid [9, 10]. It forms a strong bond when added to Aluminum, thus resisting the Aluminum atoms from dissolved in chloride ions [11]. Since Al6061is widely used in many applications and zirconia is chemically unreactive, the two elements were chosen to prepare Aluminum metal matrix composites.

II. MATERIALS

Aluminum (Al6061) was used as matrix materials. ZrO_2 powder of size 2295 nm (Fig. 1a) was used as reinforcement. The composites of size 200mm × 200 mm × 200 mm and 0, 5 10, 15 vol) were used for chemical and electrochemical analysis. The samples were mechanically polished using different grades of sheets, washed with deionized water, and dried. The acid used in this study was from Analan grade. The chemical composition of Al6061 is given in Table 1. The scanning electron microscopic (SEM) image of ZrO_2 powder is shown in Fig.1b.

Table I
Chemical composition of Al6061

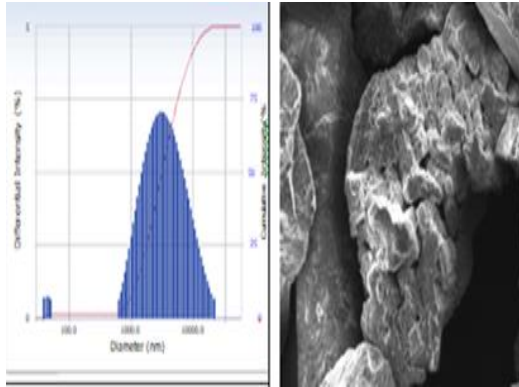| Element	Cr	Fe	Mg	Mn	Si	Zn	Ti	Cu	Al
Amount (wt %)	0.35	0.7	1.2	0.15	0.8	0.25	0.15	0.40	Bal

Fig. 1:(a) Intensity distribution. (b)SEM image of ZrO₂.

III. METHODS

A. Fabrication of Composite

From the literature survey, a double stir casting process was carried out to fabricate the composites [17]. Calculated quantities of Aluminum and 0, 5, 10, and 15 vol% of ZrO_2were used to prepare the composite.

The ZrO_2 particles were initially preheated at a temperature of 300 °C. From the SEM image of ZrO_2, it can be seen that the ZrO_2 powders are found in clusters. The clusters were removed by preheating the powder. Preheating was also done to eliminate dampness and improve wettability with the molten Al6061 alloy.

The Al ingots were placed in the electric furnace and heated up to 800 °C to ensure that the alloy melted completely [13]. The temperature was brought down to 600 °C before adding the preheated ZrO_2. The slurry was stirred using an electric stirrer at 300 rpm for 2 minutes. The composite slurry was then superheated to 700° C, and a second stirring process at 350 rpm was performed for another 3 minutes. The second stirring process helped in the distribution of the ZrO_2 particles in the Aluminum alloy. The liquid was then poured into sand molds, which were inserted with metallic chills to increase the composite's solidification rate [14]. A similar procedure was adopted for the manufacture of all the composites of various volume %. The details of the composites prepared are mentioned in Table 2.

Table 2:
Various compositions of AMC prepared for the corrosion test.

Specimen name	Composition
A0	Al6061 + 0% ZrO_2
A1	Al6061 + 5% ZrO_2
A2	Al6061 + 10% ZrO_2
A3	Al6061 + 15% ZrO_2

B. Microstructure examination

The initial microstructures of all the composites were examined by optical microscope and SEM. For these examinations, the composites of size 5× 5 × 2 mm were grounded using 600–2000 grit SiC paper and polished with a diamond polisher. After etching with Keller's reagent solution, the surface of the composite was examined.

C. Corrosion resistance testing
a). Weight loss measurements

Static immersion corrosion tests were carried out at room temperature. The Aluminum composites of size 20 × 20 ×10 mm were used as the test piece for weight loss measurement. They were scrubbed with 600–2000 grit SiC papers and then polished by diamond grit suspension to remove decarburization layers and surface scratches, washed with deionized water, and dried for 24 hours. The initial weight of all the specimens was noted. The specimens were then immersed in 0.1M HCl+ 500ml deionized water for 48 hours and stirred vigorously to remove the corroded products as outlined in the ASTM G1-03 standard. It was then cleaned, dried, and weighed. This procedure was repeated until the variation of mass loss was gradually decreasing. The final weight was then determined, and the weight difference between the final and initial weight was obtained for each specimen. The corresponding weight loss (Δm) was calculated for the entire specimens. To find the microstructure after corrosion, SEM analysis was performed.

b) Electrochemical testing

For electrochemical testing, the specimens were sized to 10 × 10 × 2 mm. They were polished using the same procedure adopted for the weight loss method. Both anodic and cathodic polarization curves were recorded potentio dynamically using a corrosion measurement system (BAS model 100 kHz to 10 kHz). Three electrode cell system was used in this experiment, in which the tested sample was considered as the working electrode with a surface area of 1.5 cm². A platinum plate with a surface area of 1.5 cm² acted as the counter electrode, while a saturated calomel electrode (SCE) was used as the third electrode. All potentials were measured,

keeping the SCE as reference. Potentiodynamic polarization curves were recorded at a potential scan rate of 1.0 mV/s.

IV. RESULTS AND DISCUSSION

A. *Surface morphology of the composites before corrosion*

The optical micrograph of Al6061 and its composites are shown in Fig. 2. The microstructure consists of α-Al grains and uniform distribution of fine particles of ZrO_2 in the matrix. The SEM images (Fig. 3) also reveal good bonding between the matrix and ZrO_2 particles. This is due to Mg's presence in Al6061, which improves the matrix's wettability of reinforced particles. The images also show some amount of agglomeration of ZrO_2 particles. These regions act as a barrier and prevent Aluminum atoms from getting dissolved in the chloride ions.
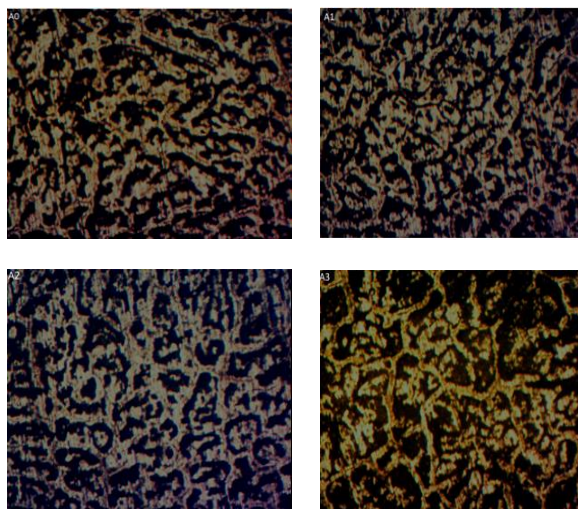
B. *Corrosion behavior of the Al-ZrO₂ composites*
a) *Weight loss method*

Fig.4 shows the weight losses (Δm) measured for the Al-ZrO_2 composites as a function of the immersion time (t in hours). At the beginning of the immersion, it can be seen that the loss in weight is negligible, but its magnitude starts to increase after 96 hours. About 192 hours later, the rate of weight loss gradually decrease. In Fig.4, four stages (a1–a4) corresponding to the corrosion rate differences are shown. In the initial stage (before point a1), an oxidation film formed on the surface acts as a protective layer of the composites. This leads to a reduction in the corrosion rate. After a few hours, the chloride ions' oxidation layer is destroyed, and the composites' surface is exposed to the solution directly (the section between a1and a2). So a sharp increase in the rate of corrosion can be observed, leading to the quick formation of corrosion products until it reaches the maximum value a2. After that, a reverse phenomenon can be observed in the corrosion rate. This may be attributed to the fact that a dynamic balance may have been created between the chloride ions and corrosion products [15]. This behavior can be observed until it reaches the a3 region. After that, the corrosion rate starts decreasing gradually. This may be because the corrosion products gradually decrease the diffusion rate of the chloride ions that dissolves the specimen's surface. The same process takes place for all the composites with various volumes %. From Fig. 5, it may also be observed that the corrosion rate of Aluminum is very much higher than the composites. This may be because the reinforced material may act as a protective coat on the grain boundaries.

Fig. 2:Optical microscope images of Al6061, Al6061+5vol%ZrO_2, Al6061 +10vol%ZrO_2 and Al6061 +15vol%ZrO_2.

b) *Electrochemical characteristics*

The electrochemical characteristics of the base alloy and its composites were examined using potentiodynamic polarization measurements. The graphs (Fig.5) show that the cathodic and anodic polarization curves are similar in both composites' corrosion behavior. Still, the difference can be seen in the corrosion current density and corrosion potential of the composites. This is because of the difference in volume % of ZrO_2 in the matrix. The polarization curve of Al6061 and its composites increases corrosion current density, indicating inclination towards pitting corrosion. From the graph, it can be analyzed that the corrosion rate of the base metal is higher than the composites. This is because the corrosion behavior of Aluminum is sensitive to small amounts of impurities in the metal, and all these impurities are cathodic to Aluminum and tend to increase the pitting corrosion [16]. It can also be observed that the composite with 10 vol% has low corrosion current density and negative potential than the composite with 5 vol% composite. This is due to the residual stresses in the matrix, which arises due to the difference in the composites' mechanical and thermal properties. Since the 10 vol% reinforced composite's mechanical and thermal properties are higher than the composite with 5 vol%, the 10 vol% residual stresses are comparatively lesser than the composite with 5vol%. These regions under residual stresses are the regions that are considered to be the preferred sites for dissolution and pitting.
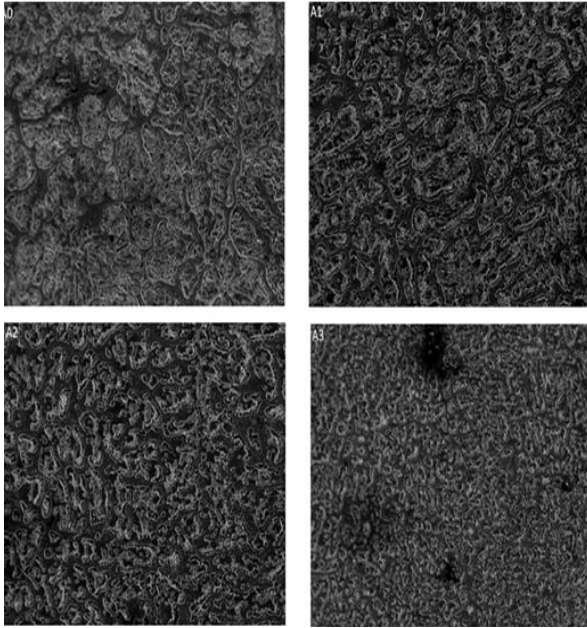
Fig.3: SEM images of Al6061, Al6061+5vol%ZrO$_2$, Al6061 +10vol%ZrO$_2$ and Al6061 +15vol%ZrO$_2$.
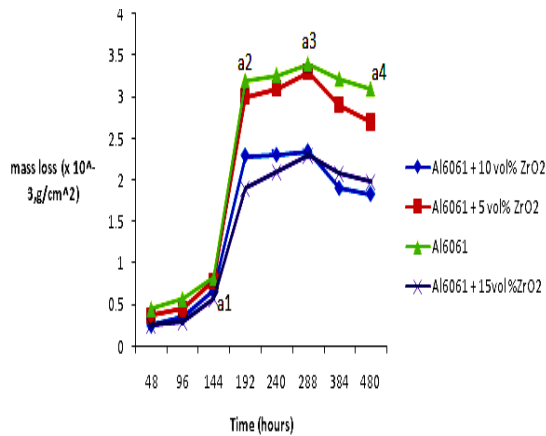

Fig.4: Weight loss measurement of Al6061 and its composite
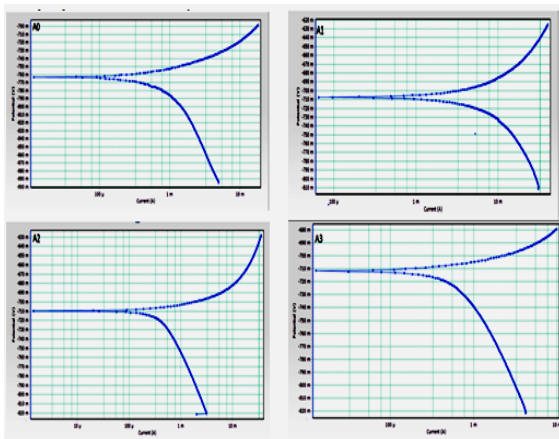

Fig. 5: Electrochemical analysis of Al6061 and its composite.

c) Surface morphology of the composites after corrosion

Fig.6 shows the surface topography of the composites after electrochemical corrosion in 0.1 M HCl solution. It can be seen that Al6061 has very deep pits, and its density is higher when compared to the composites. This is because aluminum oxide acts as a protective layer on the surface in the initial stage. Later, this layer dissolves in chloride ions and propagates very deep pits on the base metal's surface. In composites, the hard ceramic particles in the grain boundaries offer resistance against getting dissolved in the chloride ions. As a result, the pits' initiation sites occur only in the regions where pores, impurities, and residual stresses are found.
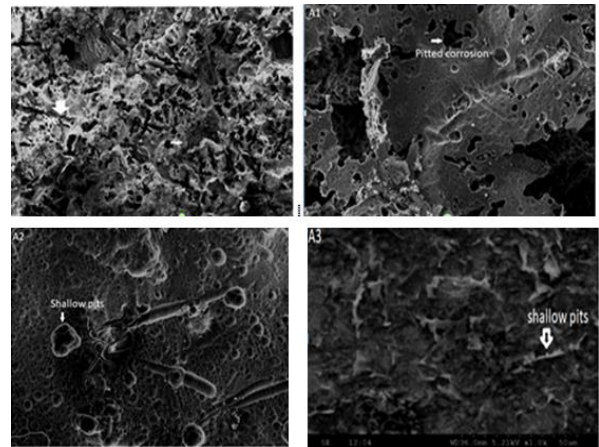

Fig. 6: SEM analysis of Al6061 and its composites after corrosion.

V. CONCLUSION

Microstructure and corrosion aspects of Al6061and its composites reinforced with ZrO$_2$ were analyzed. Stir casting technique was adopted to fabricate Al6061 and its composites. The composites were fabricated in 4 different volumes (0, 5, 10, and 15). The specimens were tested in an acidic medium (0.1M HCl). The following aspects were analyzed after testing the specimens.

1.Surface morphology of the composite material before the corrosion test revealed uniform distribution of the base alloy reinforcement. In some places, agglomeration was found in the composite.

2. Surface morphology of the composite after the corrosion test revealed deep pits in Al6061. The pits were getting shallower as the volume % of the reinforcement increased.

3. Two methods were adopted for testing corrosion - weight-loss method and electrochemical polarization methodology.

4. In the first method, corrosion was initially negligible, but it started increasing very sharply after a certain time period, finally adopting a reverse phenomenon. The corrosion rate was observed more in the base alloy.

5. Electrochemical corrosion testing also showed a high corrosion rate in the base metal compared to its composite.

It can be concluded that the composites prepared showed better corrosion resistance than the base alloy. Hence Al6061 reinforced with ZrO_2 can be better corrosive material and can be applied in various corrosive environments.

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