Corrosion resistance on Al-12Si-xZrC composites using acid mediums

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Abstract-- This paper is to investigate the corrosion behavior of Zirconium Carbide (ZrC) reinforced Al - Si metal matrix composites (MMC) in a mixture of acidic medium using weight loss method. The composites are prepared by powder metallurgy method. Al – 12Si – x ZrC composites containing 0, 5, 10 and 15 weight percentage of ZrC particles are compacted in a die set assembly and sintered in an inert gas muffle furnace. The acidic mediums used for corrosion is 1 N HCl, 1 N H₂SO₄ and 1 N HNO₃. The corrosion characteristics of Al – 12Si – x ZrC composites and the Al were experimentally evaluated. The corrosion test was carried out at different weight proportions of the samples in various concentrations of the acid such as 1 N HCl, 1 N H₂SO₄ and 1 N HNO₃ for different exposure time (i.e., 24h, 72h, 144h and 216h) respectively. The results specified that corrosion rate of composites was lower than that of base metal Al under the corrosive atmosphere regardless of exposure time and acidic mediums used as corrodent. Al – 12Si – x ZrC composites become more corrosion resistant as the ZrC content is increased. This is because of the development of stable oxide layer above the specimens. Scanning Electron Microscopy (SEM) confirms the degree of attack of acidic medium on the surface of the examined material.

Index Term-- Al-Si-ZrC composites; Powder metallurgy; weight loss method; corrosion rate; SEM

1.0 INTRODUCTION

Aluminium metal matrix composites are important classes of materials, which contain metal or alloy as matrix and ceramic particles as reinforcements. Aluminium based composites exhibit improved corrosion resistance, wear and mechanical properties. Ceramic particles such as (SiC, B₄C, TiB₂, Al₂O₃, WC, TiC and ZrC) offer significantly improved properties over metals and alloys [1]. Aluminium based composites are used for the applications in aircraft parts, utility in electrical power systems, automobile parts, and military sectors [2]. Al matrix composites are wide spread and the usages of these light-weight materials were exposed to acidic or alkaline environments exposed to corrosion [3]. Silicon in aluminium forms a eutectic mixture at about a fraction (12 %) which solidifies with very little thermal contraction, thereby improving the hardness and wear resistance of aluminium. Zirconium carbide (ZrC) is an extremely hard ceramic material and is highly corrosion resistant. The group IVA metal carbides are practically inert to attack by strong aqueous acids and aqueous bases even at 100 °C. Al matrix composites have been extensively studied the mechanical and wear characteristics, however increasing importance in corrosion characteristics of specific components become candidates for use in Al matrix composites subjected to corrosive media.

Generally, due to several reasons the corrosion resistance of Aluminium metal matrix composites is less than the Aluminium alloys, such as the crevices at the matrix/strengthening interface, fabricating defects, interior stress, microstructural changes and galvanic properties due to link of the matrix and strengthening [4]. Some chemical processing and aerospace industries, Al matrix composites have emerged as alternate materials. During pickling, descaling, electrochemical etching Al matrix composites have been extensively used in many chemical process industries, where they frequently come in contact with acids or bases, owing to their wide applications. Direct chemical corrosion reactions take place without detachment of metal and medium and electrolytic corrosion takes place if the two parts are detached. The progress of the corrosion reaction may be direct chemical or electrolytic must be in conformity with the known laws of electrochemistry and thermodynamics [5]. Hydrogen gas evolution is often predominant in strong acid and alkaline mediums of metals by many conjugate cathodic processes in which corrosion is accompanied [6]. The corrosion studies on aluminium metal matrix composites have shown that more pit are formed on composites than on aluminium alloys. The corrosion is more destructive in acidic medium. Hydrochloric acid medium was used for pickling, chemical and process industries wherein aluminium metal matrix composites are used [7].

The weight loss and corrosion rate were used for evaluating the corrosion behavior of Al (6063) alloy composites reinforced with alumina in 0.3M H₂SO₄ medium. It is perceived that Al (6063) – Al₂O₃ composites showed
higher corrosion resistance in comparison with the Al alloy in H₂SO₄ medium [8]. Al 7075/SiC metal matrix composites studies on corrosion resistance properties were conducted on acid medium. Weight loss methods were conducted for corrosion tests at different exposure time with 1N HCl as corrodent. The corrosion rate of Al 7075/SiC metal matrix composites was lower than that of Al 7075 alloy under the corrosive medium [9]. Al 4032 alloy undergoes corrosion in both nitric and citric acid medium. The corrosion rate increases with an increase in the concentration of nitric as well as citric acid medium. Increase in number of days will increases the corrosion rate of the Al 4032 alloy. The corrosion of Al 4032 alloy is more severe in nitric than in citric acid medium [10]. Literature about the corrosion behavior of aluminium metal matrix composites in acidic media is inadequate. Consequently, the aim of the present research is to investigate the Al-12i- xZrC composites containing different weight fractions of ZrC particle were prepared using conventional powder metallurgy (P/M) route. The static dipping corrosion characteristics of Al-12i-xZrC composites in 1 N HCl, 1 N H₂SO₄ and 1 N HNO₃ acidic medium were discussed. The characterization behavior of the composites before and after dipping in acidic medium was studied using Scanning Electron Microscope (SEM).

2.0 MATERIALS AND METHODS

2.1 Materials

Aluminium and silicon powder with the purity of 99.5 %, particle size of 44µm were purchased from Metal Powder Company Limited, Thirumangalam, Tamilnadu, India, and ZrC powder with the purity of 99.9 %, particle size of 400 nm and was purchased from US Research Nanomaterial’s, Inc. USA. Scanning electron microscope images were used for the analysis of mixed powder particles. Figure1 shows the received powders of aluminium, silicon and zirconium carbide. From the SEM image it can be visualized that aluminium was irregular in shape, silicon was flattened in shape and nano zirconium carbide had a cubic crystal shape.

2.2 Preparation of Aluminium metal matrix composites

By using the rule of mixtures, the different weight proportions of Al-12wt. % Si-xZrC (x= 0, 5 & 10 wt. %) were calculated. Mechanical alloying was carried out for the individual composition using a ball mill with tungsten carbide vial and balls of 10 mm diameter in argon atmosphere. The ball-to-powder weight ratio of 20: 1 was used for mechanical alloying the powders for 1 h. Milling was done at a constant speed of 300 rpm in inert and wet medium in the presence of toluene to avoid oxidation. Cylindrical preforms of 50 mm diameter and 5 mm thickness were prepared using suitable die set assembly on a compression testing machine having 1000 kN capacity. Compacting pressure was applied steadily, with 1.1GPa for all samples [11].

Molybdenum disulphide was used to lubricate the die set assembly. Successively, the green preforms were immediately taken out from the die and kept in the inert gas muffle furnace for sintering. To prevent oxidation, the green preforms were sintered in the argon gas atmosphere at 550°C, for a holding period of 1 h. Subsequently, the preforms were cooled in the furnace itself till the room temperature was attained. Further the sintered preforms were cleaned by various emery papers. Further the sintered preforms were cut into rectangular samples of 30 mm length and 5 mm wide and 5 mm thick for corrosion test. SEM micrograph also reveals that the sharp flattened structure of Aluminium has been broken, and
because of that the ZrC nanoparticles have been easily joined with the Al-12Si alloy. To increase the strength of the soft aluminium material regardless of different wt. % ZrC particles were reinforced into the matrix. It is obviously shown in the SEM micrographs in Fig. 2 (a–c).

2.3 Corrosion test

The corrosion test was carried out on Al-12Si-xZrC composites using static dipping weight loss method as per standards. However, the specimen surfaces were ground with silicon carbide paper of 1200 grit size and polished in steps of 1 to 2 micron diamond paste to obtain a mirror surface finish. After subsequent rinsing with water and acetone the specimens were weighed accurately before starting the test by the weight loss method [1]. The corrosion procedures as per ASTM were conceded out with all fractions of specimens and the uniform dispersion of reinforcements was studied by SEM.

The concentration of the acid was chosen as 0.1N HCL, 0.1N H₂SO₄ and 0.1N HNO₃ acidic medium. The corrosion tests were conducted using weight loss technique similar to ASTM-G67-80 test standards. The tests were conducted on all types of compositions in various acidic medium for 72 h. The cradles containing the measured specimens were kept inside the flask, which contains the corrodat. After the corrosion test, the specimens were immersed in acetone medium for 10 min and softly dressed with a soft brush to eliminate adhered scales. After drying thoroughly the specimens were weighed to determine the percentage weight loss. After the corrosion test, the corroded surface of the specimens was studied under the SEM. Weight of the corroded specimens was evaluated, weight loss is determined and the corrosion rate is communicated in mpy [11].

3.0 RESULTS AND DISCUSSION

3.1 XRD analysis

Figure 3 shows the XRD pattern of the Al-Si composite reinforced with different wt. % of ZrC particles. Al, Si and ZrC peaks were indexed using JCPDS files (file numbers 851327 [14], 800018 [14], and 730477 [15] respectively). Figure 3 with Al-12Si composite powders shows the highest peak that indicates the presence of Al and the lowest peak indicates Si. Figure 3 with Al-12Si-5ZrC, Al-12Si-10ZrC and

![Fig. 2. SEM micrograph of the various wt. % of powder after mixing (a) Al-12Si, (b) Al-12Si-5ZrC, and (C) Al-12Si-10ZrC](image-url)
Al-12Si-15ZrC composites shows that the different wt. % of ZrC particles is present in the composite powders and it also consist of Al and Si.

XRD analysis for the prepared Al-12Si-xZrC composites powders are presented in Fig. 3. In general, ZrC reinforcing particles were homogenously dispersed in the matrix. These results specify the existence of Al as the major peaks; Si and ZrC were specified by minor peaks. The ZrC peak was clearly visible and can be identified in the Al-12Si-xZrC composites.

There is an evidence for the increase in the intensity of the ZrC peaks with the increase in wt. % content of the Al-12Si-xZrC composites. A steady marginal shift of the pure Al peaks to greater angles with an increase in the wt. % of the ZrC content was also noticed.

![XRD pattern](image)

Fig. 3. shows the XRD pattern of the Al-Si composite reinforced with different wt. % of ZrC particles.

### 3.2 Corrosion loss on acidic medium of Al – 12Si – xZrC composites

Weight loss method has been recognized as preferably good as other techniques for corrosion evaluation of metals in an dipping test. In this exploration, the weight loss method was used to evaluate the corrosion of Al-12Si-xZrC composites samples in acidic medium. The weight of the each samples were measured before dipping and then measured after 24h, 72h, 144h and 216h dipping in the acidic medium to obtain the corrosion loss. The change in initial and final weights was used to measure the weight loss through the interval period. The corrosion loss measurements were studied at the intervals of 24h, 72h, 144h and 216h for the complete period of dipping and the results were presented in the form of corrosion loss of the composites.

Figure 4 shows the variation of the corrosion loss of Al-12Si-xZrC composites with dipping time under the static dipping technique of the concentrations of the acid such as 0.1N HCl, 0.1N H2SO4 and 0.1N HNO3 at ambient temperature. The corrosion behavior of Al-12Si-xZrC composites depends on the compaction, size and weight fraction of the reinforcements. The corrosion losses were determined for nine days in acidic medium for all the compositions. The results showed that the corrosion loss of the Al-12Si-xZrC composites decreased with increasing in
reinforcement of ZrC particles content. This is due the presence of ZrC particles in the surface of the specimen that will protect the surface layer in acidic medium. For all the investigated composites, there is a trend of decreasing of the weight loss with the increase of the ZrC particles content. The pure Al exhibit higher weight loss compared to that of the Al-12Si-10ZrC composites. Since, ZrC particles are ceramic materials and they remain inert. It is expected that they are unpretentious by the acid medium throughout the corrosion tests. Similar, observation was noticed for the entire acidic medium that reacts with the composites. From the aforementioned results, it can be concluded that Al-12Si-xZrC composites offer reduced weight loss and thereby increasing weight loss for 0.1N HCl compared to 0.1N H$_2$SO$_4$. Similarly, the results shows that the corrosion loss was increased for 0.1N HNO$_3$ medium than the other two acidic medium of the composites corroded [1-4].

Fig. 4. Variation of corrosion loss on dipping time with different compositions and the concentrations of the acid

3.3 Corrosion rate of Al-12Si-xZrC composites

The corrosion rate was measured as a function of corrosion loss of the Al-12Si-xZrC composites in the static dipping test as shown in above Figure 5. Figure 5 shows the variation of the corrosion rate of Al-12Si-xZrC composites with dipping time under the static dipping
Fig. 5. Variation of corrosion rate on exposure time with different compositions and acidic medium

The technique of acidic medium such as 0.1N HCL, 0.1N H$_2$SO$_4$ and 0.1N HNO$_3$ at ambient temperature. From the figures it can be clearly observed that for Al-12Si-xZrC composites, corrosion rate decreases strictly with increase in the strengthening content. The corrosion rate of the Al-12Si-xZrC composites is mainly due to the formation of pits, cracks on the surface. Al has the severity of the acid used that was induced cracks development on the surface, which finally indicates the development of pits, thereby initiating the loss of material. The existence of cracks and pits on the pure Al surface was observed clearly since there is no strengthening fails to offer any sort of confrontation to the acidic medium. Therefore, the corrosion loss in the case of pure Al is higher.

The strengthening of ceramic relics inert and is barely affected by the acidic medium during the test. As the ZrC are inert, they are not likely to affect the corrosion mechanism of composites [2]. The corrosion results specify an enhancement in corrosion resistance as the weight percentage of ZrC content increased in the composites. This shows that the ZrC directly or indirectly influence the corrosion property of the composites. Thus strengthening act as a reasonably inert physical barrier to the beginning and development of corrosion pits and also transforms the microstructure of the composites and hence reduces the rate of corrosion. Some more reason for diminution in the corrosion rate is the inter-metallic area, which is the spot of corrosion starting crevice around each particle [3]. In all the cases it is observed that the corrosion rate increases in the beginning with increase in test duration and remains constant towards the end due to passivation. It is clear from the figure that the corrosion rate decreases as the exposure time increases. The initial increase in potential is due to the corrosion process which takes place on the surface of the composites. Also, it is clear from the figure that the percentage variation of strengthening lead to the decrease in current density. For evidence, the addition of ZrC particles will diminish the corrosion resistance of the composites [5-8].

3.4 Microstructural Characterization of corroded surfaces

The SEM microstructural analysis of the samples was also examined before and after dipping in acidic medium for 9 days to study the corrosion resistance of these samples in the corrosive medium. SEM of the Al and Al - 12Si – xZrC composites are exploited after subjecting to the corrosion test and shown in Fig. 6. The scanning electron micrographs of corroded samples of base metal reveal more severe pitting and cracks growth in unreinforced matrix than in strengthened composites. Greater degree of surface deterioration in base matrix as observed from SEM images indicates the higher corrosion rates for matrix than for composites. The SEM micrographs show a complete deterioration of the smoothness of the surface of composites, suggesting the penetration of chloride ions into the material surface forming corrosion spots.

Figure 6 (a-d) shows the SEM micrograph of Al before dipping and after dipping in acidic medium. Figure 6 (a, e, i, m and q) shows the microstructure of Al and the Al-12Si-xZrC composites after sintering. Figure 6 (b-c) shows the SEM images of pure Al sample after dipping in H$_2$SO$_4$, HCl and HNO$_3$ for 9 days. From the Figure, it can be seen that the specimens after the corrosion experiment showed rare deep pits, flakes and cracks on the surface. The pits, flakes and cracks are more in nitric acid medium than HCl and H$_2$SO$_4$. Figure 6 (f-h) shows the SEM images of Al-12Si sample after dipping in H$_2$SO$_4$, HCl and HNO$_3$ for 9 days. Figure 6 (j-l, n-p and r-t) shows the SEM images of Al-12Si-xZrC composites with x=5, 10 and 15 weight percentage ZrC content of sample after dipping in H$_2$SO$_4$, HCl and HNO$_3$ for 9 days. The development of pits and cracks on the surface of the composites decreased with increasing in ZrC particles content.
4.0 CONCLUSIONS
In the present study, Al-12Si-xZrC composites were fabricated by mixing aluminium, silicon and the various weight percentages of ZrC particles by powder metallurgy technique and the corrosion resistance was studied using weight loss method.

- Al-12Si-xZrC composites were prepared by powder metallurgy method and subjected to corrosion test in acidic mediums.
- Corrosion rate decreased with the increase in dipping time and weight percentage.
- The extent of corrosion damage decreased with increase in ZrC strengthening which may be due to increase in bonding strength.
- Corrosion loss was significantly high in the base Al matrix with respect to composites.
- Microstructural studies show that the corrosion in acidic medium caused more pits and cracks in the base metal and it is reduced in the Al-12Si-xZrC composites. This is due to the addition of ZrC particles into the matrix reduces the pits and crack formation into the composites.

REFERENCES
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