

# Corrosion behavior of ZrC particles reinforcement with Al-12Si composites by weight loss method using acidic media

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**Abstract.** This paper aims to investigate the corrosion behavior of zirconium carbide (ZrC) reinforced Al – Si metal matrix composites (MMCs) in a mixture of acidic solution using weight loss method. The composites are prepared by powder metallurgy method. Al-12Si-xZrC composites containing 0, 5, and 10 weight percentage of ZrC particles are compacted in a die set assembly and sintered in an inert gas muffle furnace. The acidic solutions used for corrosion are 1 N HCl, 1 N H<sub>2</sub>SO<sub>4</sub> and 1 N HNO<sub>3</sub>. The corrosion characteristics of Al-12Si-xZrC composites and the pure 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 H<sub>2</sub>SO<sub>4</sub> and 1 N HNO<sub>3</sub> for different exposure time (i.e., 24 h, 72 h, 144 h and 216 h), 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 solutions used as corrodents. Al-12Si-xZrC 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 solution on the surface of the examined material.

**Key words:** Al-Si-ZrC composites, powder metallurgy, weight loss method, corrosion rate, SEM.

## 1. Introduction

Aluminium metal matrix composites, an important class of materials, 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, B<sub>4</sub>C, TiB<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, 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 widely used, often in acidic or alkaline environments exposed to corrosion [3]. Silicon in aluminium forms a eutectic mixture at 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 resistant to corrosion. The group IVA metal carbides are practically inert to attack by strong aqueous acids and aqueous bases even at 100°C. The

mechanical and wear characteristics of Al matrix composites have been extensively studied. Corrosion characteristics of specific components are factors advocating for the use of Al matrix composites subjected to corrosive media.

Generally, due to several reasons, the corrosion resistance of aluminium metal matrix composites is lower than that of aluminium alloys, which results from crevices at the matrix or strengthening interface, fabricating defects, interior stress, microstructural changes and galvanic properties due to linking of the matrix and the strengthening [4]. In chemical processing and aerospace industries, Al matrix composites have emerged as alternate materials. During pickling, de-scaling and 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 solution; electrolytic corrosion takes place if the two parts are detached. The progress of the corrosion reaction may be direct chemical or electrolytic and occurs according to the known laws of electrochemistry and thermodynamics [5]. Hydrogen gas evolution is often predominant in strong acid and alkaline solutions of metals by many conjugate cathodic processes in which corrosion occurs [6]. The corrosion studies on aluminium metal matrix com-

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posites have shown that more pits are formed on composites than on aluminium alloys. The corrosion is more destructive in acidic medium. Hydrochloric acid medium is used for pickling in chemical and process industries in which aluminium metal matrix composites are applied [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 H<sub>2</sub>SO<sub>4</sub> solution. It is perceived that Al (6063) – Al<sub>2</sub>O<sub>3</sub> composites show higher corrosion resistance in comparison with the Al alloy in H<sub>2</sub>SO<sub>4</sub> solution [8]. Al 7075/SiC metal matrix composite studies on corrosion resistance properties were conducted in acid medium. Weight loss methods were applied 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. An increase in number of days will augment 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 on the corrosion behavior of aluminium metal matrix composites in acidic media is insufficient. Consequently, the aim of the present research is to investigate the Al-12Si-xZrC composites containing different weight fractions of ZrC particle prepared using conventional powder metallurgy (P/M) route. The static immersion corrosion characteristics of Al-12Si-xZrC composites in 1 N HCl, 1 N H<sub>2</sub>SO<sub>4</sub> and 1 N HNO<sub>3</sub> acidic medium were discussed. The characterization behavior of the composites before and after immersion in acidic medium was studied using scanning electron microscope (SEM).

## 2. Materials and methods

**2.1. Materials.** Aluminium and silicon powder with the purity of 99.5%, particle size of 44 μm were purchased from Metal Powder Company Limited, Thirumangalam, Tamilnadu, India, and ZrC powder with the purity of 99.9%, particle size of 400 nm was purchased from US Research Nanomaterials Inc., USA. Scanning electron microscope images were used for the analysis of mixed powder particles. Fig. 1 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, different weight proportions of Al-12wt. % Si-xZrC (x = 0, 5 and 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

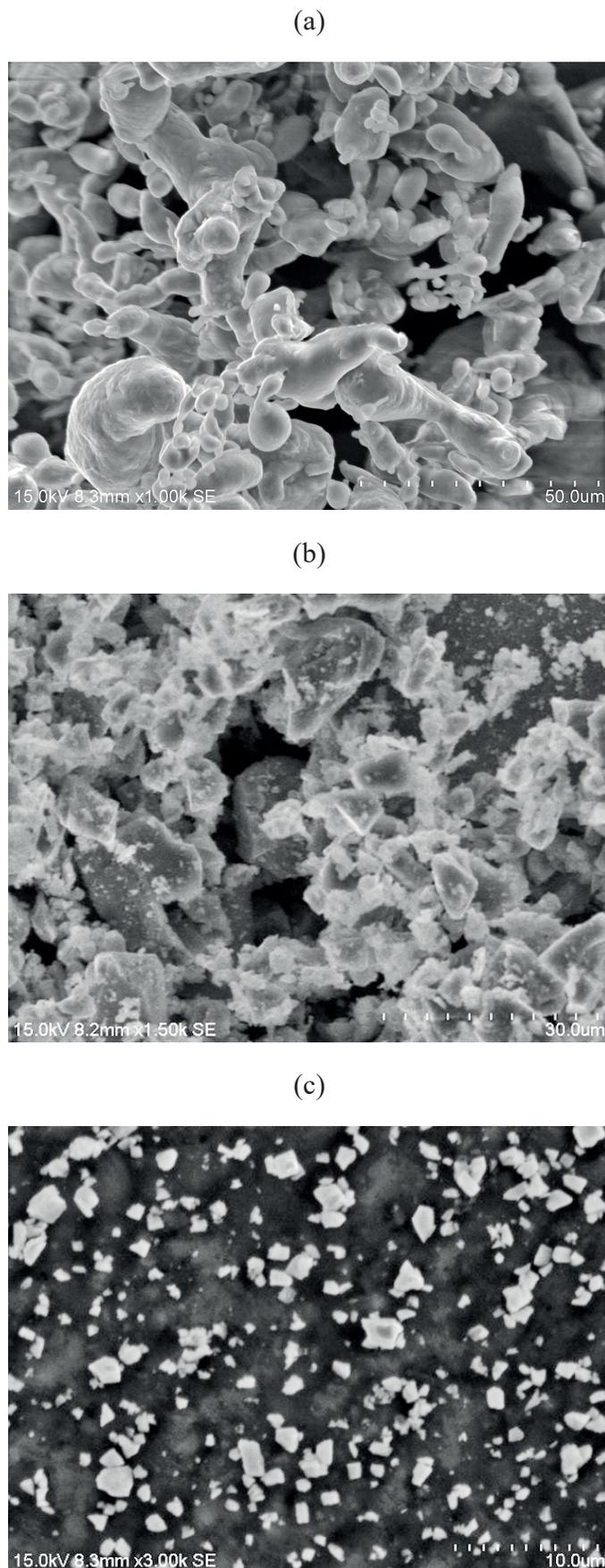


Fig. 1. SEM micrograph of received powders (a) Al, (b) Si, (c) ZrC

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 1.1 GPa for all samples [11]. Table 1 shows the compositions of prepared green compact are shown below.

Table 1  
The composition of prepared specimens

No	Combinations of specimens
1	100 wt. % Al
2	88wt. % Al-12 wt. % Si-0 wt. % ZrC
3	83wt. % Al-12 wt. % Si-5 wt. % ZrC
4	78wt. % Al-12 wt. % Si-10 wt. % ZrC

Molybdenum disulphide was used to lubricate the die set assembly. Next, 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 till 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, 5 mm width and 5 mm thickness for corrosion test. SEM micrograph also reveals that the sharp flattened structure of aluminium was broken, and because of that the ZrC nanoparticles were 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 visible 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 immersion 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 studied by SEM. The concentration of the acid was chosen as 0.1N HCL, 0.1N H<sub>2</sub>SO<sub>4</sub> and 0.1N HNO<sub>3</sub> acidic solution. The corrosion tests were conducted using weight loss technique similar to ASTM-G67-80 test standards. The tests were conducted on all

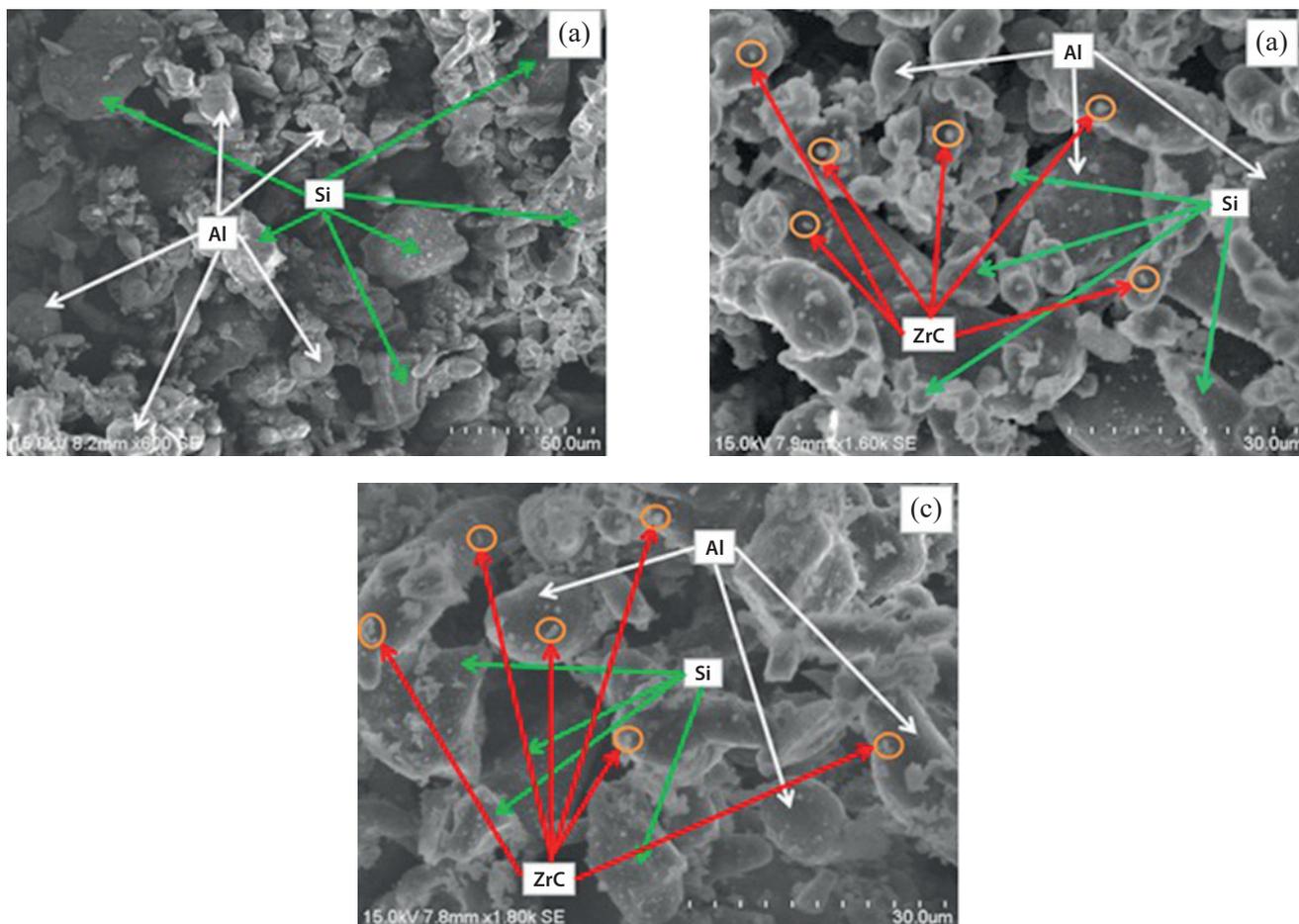


Fig. 2. SEM micrograph of the various wt. % of powder after mixing (a) Al-12Si, (b) Al-12Si-5ZrC, (c) Al-12Si-10ZrC



The change in initial and final weights was used to measure the weight loss through the interval period. The weight loss measurements were studied at the intervals of 24 h, 72 h, 144 h and 216 h for the complete period of immersion and the results were presented in the form of weight loss of the composites. Table 2 shows the weight loss in specimens before and after dipping in concentration of acids.

Table 2  
Weight loss before and after dipping in concentration of acids

Composition	Weight of specimens before dipping (g)			Weight of specimens after dipped in conc. acids for 216 h (g)		
	H <sub>2</sub> SO <sub>4</sub>	HCL	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCL	HNO <sub>3</sub>
Pure Al	1.182	1.066	1.109	1.127	1.004	1.035
Al-12Si	0.978	0.885	0.892	0.931	0.835	0.826
Al-12Si-5ZrC	0.832	0.685	0.637	0.797	0.642	0.586
Al-12Si-10ZrC	0.933	0.870	0.745	0.903	0.836	0.696

Figure 4 shows the variation of the weight loss of Al-12Si-xZrC composites with exposure time under the static immersion technique of the concentrations of the acid such as 0.1N HCL, 0.1N H<sub>2</sub>SO<sub>4</sub> and 0.1N HNO<sub>3</sub> at ambient temperature. The corrosion behavior of Al-12Si-xZrC composites depends on the compaction, size and weight fraction of the reinforcements. The weight losses were determined for nine days in acidic medium for all the compositions. The results showed that the weight loss of the Al-12Si-xZrC composites decreased with increasing in reinforcement of ZrC particles content. This is due to 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. ZrC particles are ceramic materials and they remain inert. It is expected that they are not affected by the acid medium throughout the corrosion tests. A similar observation was made 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

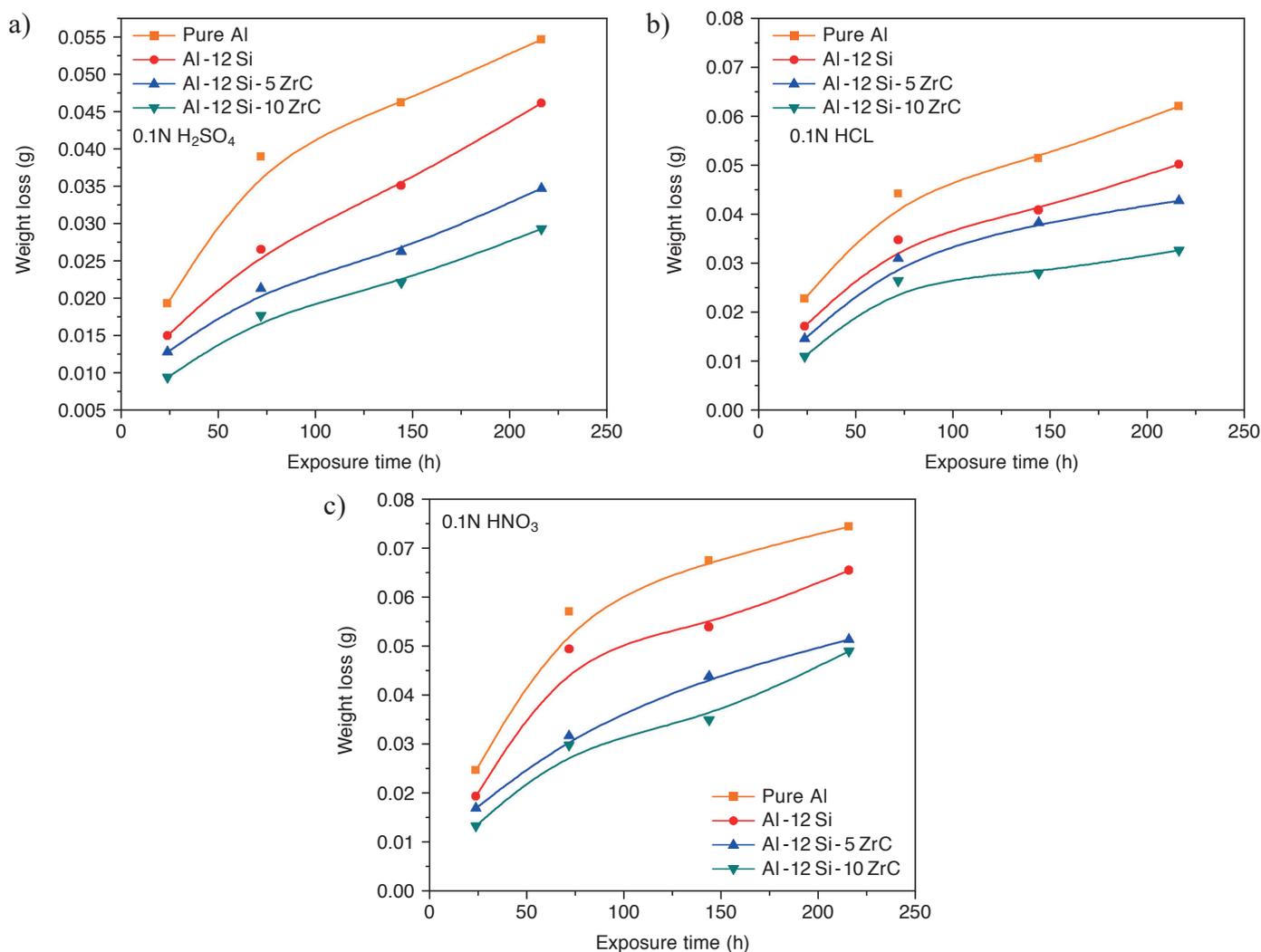


Fig. 4. Variation of weight loss on exposure time with different compositions and concentrations of the acid

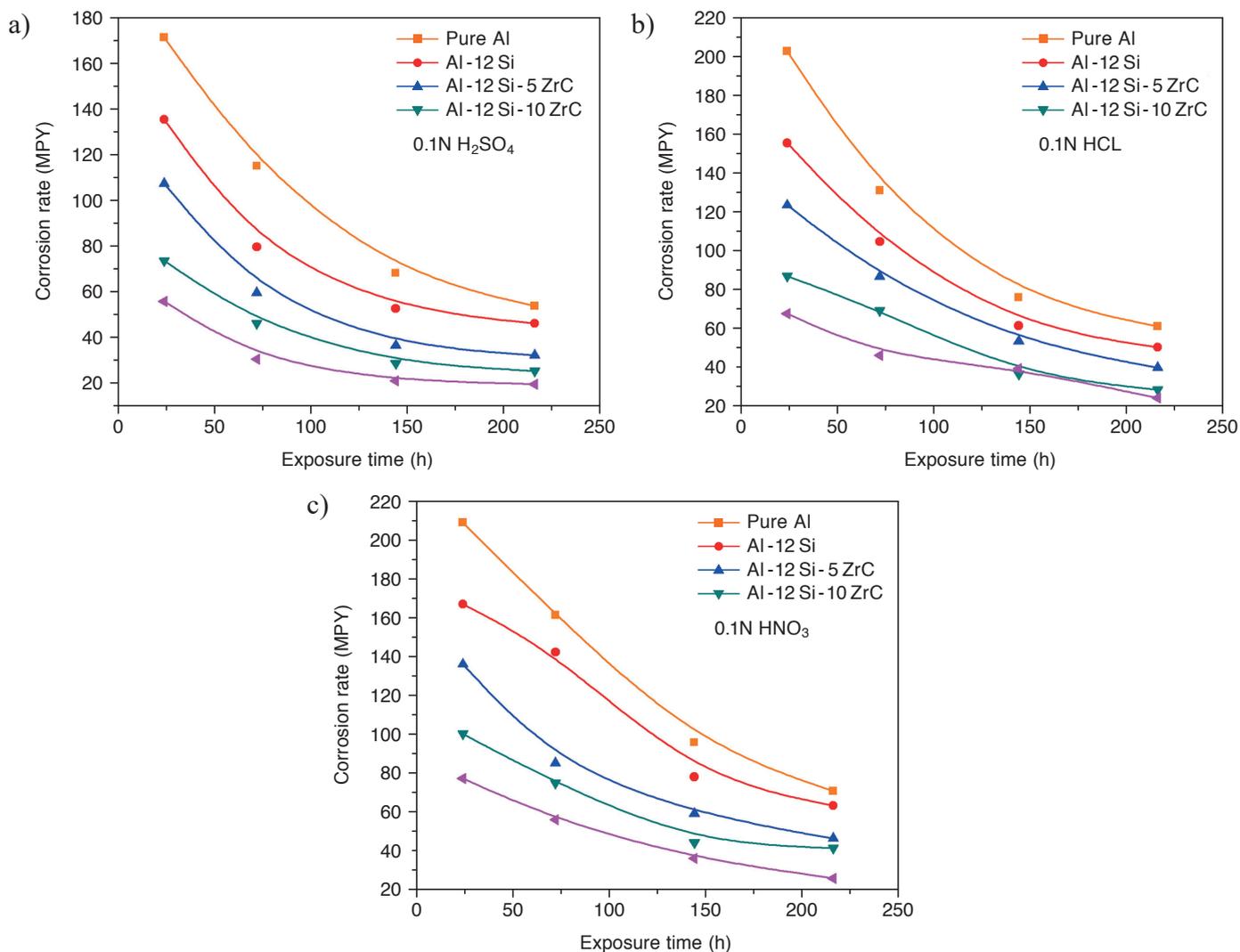


Fig. 5. Variation of corrosion rate on exposure time with different compositions and acidic medium

loss. Weight loss for 0.1N HCl is increased as compared to 0.1N H<sub>2</sub>SO<sub>4</sub>. Similarly, the results show that weight loss was increased for 0.1N HNO<sub>3</sub> medium as compared to the other two acidic medium of the composites corroded [1–4].

**3.3. Corrosion rate of Al-12Si-xZrC composites.** The corrosion rate was measured as a function of weight loss of the Al-12Si-xZrC composites in the static immersion test as shown in Fig. 5, which shows the variation of the corrosion rate of Al-12Si-xZrC composites with exposure time under the static immersion technique of acidic medium such as 0.1N HCl, 0.1N H<sub>2</sub>SO<sub>4</sub> and 0.1N HNO<sub>3</sub> 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. Pure Al has the severity of the acid, which induces the development of cracks on the surface, finally leading to the development of pits and initiating the loss of material. Therefore, the weight loss in the case of pure Al is higher.

The strengthening of ceramic remains 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 increases in the composites. This shows that the ZrC directly or indirectly influence the corrosion properties of the composites. Thus, strengthening act is a reasonably inert physical barrier to the beginning and development of corrosion pits, also transforming the micro structure of the composites and reducing the rate of corrosion. Another cause of decrease in the corrosion rate may be the inter-metallic area, which is the spot where corrosion starts in crevices 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 figures 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 figures that the percentage variation of strengthening leads to the

decrease in current density. Thus, 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 performed before and after immersion in acidic solution for 9 days to study the dissolution or resistance of these samples in the corrosive medium. SEM of the Al and Al-12Si-xZrC composites were used after subjecting to the corrosion test as shown in Fig. 6. The scanning electron micrographs of corroded samples of base metal revealed more severe pitting and cracks growing in unreinforced matrix as compared to strengthened composites. A greater degree of surface deterioration in base matrix 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 pure Al before immersion and after immersion in acidic solution.

Figure 6(a, e, i, m) shows the microstructure of pure Al and the Al-12Si-xZrC composites after sintering. Figure 6 (b, c) shows the SEM images of pure Al sample after immersion in H<sub>2</sub>SO<sub>4</sub>, HCl and HNO<sub>3</sub> for 9 days. It can be seen that the specimens after the corrosion experiment rarely showed deep pits, flakes and cracks on the surface. The pits, flakes and cracks are more frequent in nitric acid medium than HCl and H<sub>2</sub>SO<sub>4</sub>. Figure 6(f-h) shows the SEM images of Al-12Si sample after immersion in H<sub>2</sub>SO<sub>4</sub>, HCl and HNO<sub>3</sub> for 9 days. Figure 6(j-l, n-p) shows the SEM images of Al-12Si-xZrC composites with x = 5, and 10 weight percentage ZrC content of sample after immersion in H<sub>2</sub>SO<sub>4</sub>, HCl and HNO<sub>3</sub> for 9 days. The development of pits and cracks on the surface of the composites decreased with increasing ZrC particles content.

## 4. Conclusions

In the present study, Al-12Si-xZrC composites were fabricated by mixing aluminium, silicon and various weight percentages of

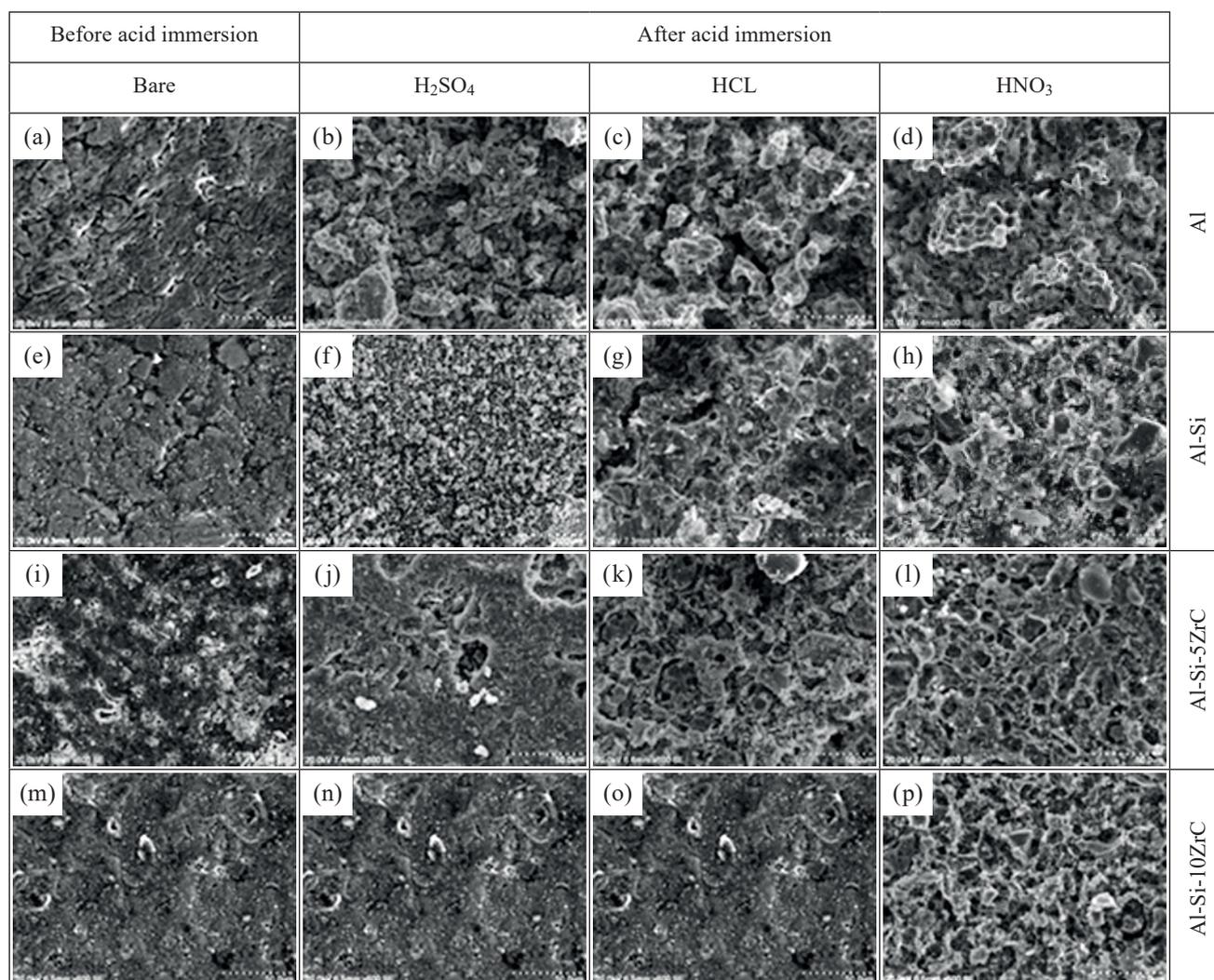


Fig.6. SEM images of different compositions before immersion and corrodant after acidic immersion

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 weight loss corrosion test in acidic solutions.
- Corrosion rate decreased with the increase in exposure time and weight percentage.
- The extent of corrosion damage decreased with increase in ZrC strengthening, which may be due to an increase in bonding strength.
- Weight loss from corrosion was significantly increased in the base Al matrix as compared to composites.
- Microstructural studies show that the corrosion by acidic medium causes 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, which reduces the pits and crack formation into the composites.

## REFERENCES

- [1] G. Nataraj, A. Sudhakar, R.D. Pruthviraj, and S. Ramesh, "Weight loss corrosion studies of aluminium-7075 alloy reinforced with silicon carbide particulates composites in acid chloride medium", *International Journal of Engineering Sciences & Research Technology*, 4, 538–541 (2015).
- [2] K.K. Alanemea, T.M. Adewale, and P. A. Olubambi, "Corrosion and wear behaviour of Al–Mg–Si alloy matrix hybrid composites reinforced with rice husk ash and silicon carbide", *Journal of Materials Research and Technology*, 3, 9–16 (2014).
- [3] K. Zhou, B. Wang, Y. Zhao, and J. Liu, "Corrosion and electrochemical behaviors of 7A09 Al–Zn–Mg–Cu alloy in chloride aqueous solution", *Trans. Nonferrous Met. Soc. China*, 25, 2509–2515 (2015).
- [4] T. S. Mahmoud, E.-S.Y. El-Kady, and A.S.M. Al-Shihiri, "Corrosion behaviour of Al/SiC and Al/Al<sub>2</sub>O<sub>3</sub> nanocomposites", *Materials Research*, 15, 903–910 (2012).
- [5] P.B. Madakson, I.A. Malik, S.K. Laminu, and I.G. Bashir, "Effect of anodization on the corrosion behavior of aluminium alloy in HCl acid and NaOH", *International Journal of Materials Engineering*, 2, 38–42 (2012).
- [6] K.K. Alaneme, T.M. Adewale, and P.A. Olubambi, "Corrosion and wear behaviour of Al-Mg-Si alloy matrix hybrid composites reinforced with rice husk ash and silicon carbide", *Journal of Materials Research Technology*, 3, 9–16 (2014).
- [7] I. Boukerche, S. Djerad, L. Benmansour, L. Tifouti, and K. Saleh, "Degradability of aluminum in acidic and alkaline solutions", *CORROSION SCIENCE* 78, 343–352 (2014).
- [8] K.K. Alaneme and M.O. Bodunrin, "Corrosion behavior of alumina reinforced aluminium (6063) metal matrix composites", *Journal of Minerals & Materials Characterization & Engineering*, 10, 1153–1165 (2011).
- [9] W.R. Osório, C.M. Freire, R. Caram, and A. Garcia, "The role of Cu-based intermetallics on the pitting corrosion behavior of Sn-Cu, Ti-Cu and Al-Cu alloys", *Electrochimica Acta*, 77, 189–197 (2012).
- [10] T. Akhil, A. Khurshid, and K. Manikanta, "Corrosion behavior of A4032 in citric acid and nitric acid medium", *International Journal of Innovations in Engineering and Technology*, 6, 17–21 (2016).
- [11] F.A. Ovat, F.O. David, and A.J. Anyandi, "Corrosion behaviour of Al (6063) alloy (as-cast and age hardened) in H<sub>2</sub>SO<sub>4</sub> solution", *Journal of Materials Science Research*, 1, 35–40 (2012).
- [12] T.S. Mahmoud, E.-S.Y. El-Kady, and A.S.M. Al-Shihiri, "Corrosion behaviour of Al/SiC and Al/Al<sub>2</sub>O<sub>3</sub> nanocomposites", *Materials Research* 15, 903–910 (2012).
- [13] H.C. Ananda Murthy and S.K. Singh, "Influence of TiC particulate reinforcement on the corrosion behaviour of Al 6061 metal matrix composites", *Advanced Materials Letters* 6, 633–640 (2015).
- [14] A. H. Paksoy, O. Deprem, O. Tazegul, and H. Cimenoglu, "Tribology of SiC<sub>p</sub> reinforced Al-12Si matrix composite coatings in water", <http://dx.doi.org/10.1016/j.triboint.2016.10.037>.
- [15] C.F. John, R.C. Paul, S.C.E. Singh, and T. Ramkumar, "Tribological behavior, mechanical properties and microstructure of Al-12Si-ZrC composite prepared by powder metallurgy", *Bull. Pol. Ac.: Tech.* 65(2), 149–154 (2017).