Research Article

Corrosion Behavior of Zinc-Graphite Metal Matrix Composite in 1 M of HCl

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This paper is aimed at investigating the corrosion behavior of Pure and Zinc-graphite particles with percentage of 1, 3, and 5%, respectively. The composites were fabricated by powder metallurgy method. Corrosion tests were performed according to ASTM standard. Corrosion rate was calculated and it is found that in all cases the corrosion rate was decreasing with the increase in exposure time. Meanwhile, the microstructure of composites was imaged and analyzed using optical microscope and scanning electron microscope. It is observed that the best corrosion resistance was zinc with 1% Graphite while Zinc with 3% and 5% Graphite composites did not enhance the corrosion resistance comparing to pure Zinc.

1. Introduction

Increasing use of advanced composites materials is being made especially in aircraft and aerospace vehicles. Metal matrix composites (MMCs) are currently being developed as possible structural materials, offering improved elastic modulus, strength, elevated temperature properties, and control over the coefficient of thermal expansion. The resulting high specific properties can provide significant weight saving in many components compared with conventional alloys [1].

The corrosion behavior of the composites in various environments that the material is likely to encounter is one important consideration in choosing a suitable material for a particular application. It follows from the literature that limited work has been done to study the corrosion behavior of MMCs. Though a few studies concerning the corrosion behavior of MMCs state that they suffer severer attack than the respective nonreinforced alloys [2]. It has been established that the corrosion behavior of MMCs is influenced by various factors like composition of the alloy used, the reinforcing particles used, its size and distribution in the matrix, the technique adopted for fabrication, and the nature of interface between the matrix and reinforcement. Even a very small change in any one of these factors can seriously affect the corrosion behavior of the material [3].

Corrosion behavior of zinc composites with nano-CeO₂, which were prepared by powder metallurgy method, was reported and it was shown that the corrosion has been improved significantly using mass fraction of 1% of CeO₂ [4]. Seah et al. have investigated the corrosion characteristics of cast ZA-27 alloy reinforced with graphite particles (1, 3, and 5% wt) which results in increasing corrosion rate [5].

In the investigation carried out by Seah et al., the effect of the graphite particles content on corrosion behavior of ZA-27 alloy in 1 M HCl solution was studied. Figure 1 shows the effect of graphite content with %wt loss of ZA composite, which is a noble conductor that can induce galvanic corrosion (see Figure 1). Several hypotheses were made, such as the presence of the graphite network hindering the reaction between HCl and the matrix [5]. Another possibility is that zinc ions in solution, acting as a cathode inhibitor [6], may have eventually precipitated as zinc hydroxide on the cathodic graphite particles if the local pH resided in the correct range. This would also explain the decreasing corrosion rates with time that was observed. Similar behavior was noticed in graphite-aluminum couples in solutions containing zinc chloride [7].

This phenomenon is surprising because graphite is very noble compared to zinc and these two elements form an excellent galvanic cell in the HCl solution. One would expect

that, as the graphite content is increased, the corrosion of the zinc should be aggravated instead of being reduced. Such a mechanism is commonly seen in grey cast iron in which the graphite present acts as a cathode, causing corrosion of the iron, even in relatively mild environments, as documented by Fontana [8].

Historically, galvanic corrosion has been reported to occur mostly in bimetallic couples. With the ever-increasing use of nonmetallic materials, galvanic corrosion is now being identified in many situations where a metal is in contact with a nonmetallic material (e.g., galvanic corrosion of metals occurs in metal-reinforced polymer matrix composites and graphite metal matrix composites [9, 10], in processing of semiconducting minerals [11], in contact with conducting polymers [12], with semiconducting metal oxides [13], and with conducting inorganic compounds [14]). It has been found that minerals, in general, exhibit potentials more noble than most metals and, therefore, may cause galvanic corrosion of metals used in processing equipment [11].

In view of this, we have produced Pure Zinc and Zinc based alloy with Graphite of mass fractions 1, 3, and 5 wt% and aimed to investigate the corrosion behavior of composites on 1 M HCL. The reinforcements have a size less than 4 μm . Zinc-Graphite MMCs were fabricated using conventional powder metallurgy (P/M) route. The effect of weight percent on the corrosion behavior of Zn-Graphite MMCs was extensively investigated.

2. Experimental

2.1. Material. Pure Zn was used as a matrix material; the Zn powder has purity of about 99.5% (wt.-%). The Zn powders have size range between 1 and 15 μm . The Graphite particulates have a size less than 4 μm .

2.2. Preparation of Composites by Powder Metallurgy Method. The Zn MMCs were fabricated according to the following procedures: first, the reinforcement particles and Zn powders were mixed together by a mixer, where Paraffin oil was added by 3% weight percent of the charge to lubricate the surface of powders and reduce the heat generated from friction during mixing. The green powders were put into a cylindrical die made from H13 tool steel.

The green powders were then compacted under 100 MPa for 15 minutes using the hydraulic press shown in Figure 1. After that, the powders were heated to about 310°C in the die during compression. Heating the mould was conducted using electrical resistance heaters around the die. After reaching the desired temperature, the powders were again hot-pressed under 320 MPa for 15 minutes and then release the pressure and remove the product from the die. After releasing the samples from the die, they were cut to a thickness of 5 mm, making the dimensions of samples identical to 15 mm diameter and 5 mm thickness.

2.3. Corrosion Test. The corrosion test was conducted at room temperature (27°C) using conventional corrosion rate measurement according to ASTM G1-03 and ASTM G31-72 [15, 16].

FIGURE 1: The hydraulic press.

The area of the specimen, subjected to corrosion, was calculated before performing corrosion test using the following equation (according to ASTM G31-72):

$$A = \frac{\pi}{2(D^2 - d^2)} + t\pi D + t\pi d, \quad (1)$$

where t is thickness, D is diameter of the specimen, and d is diameter of the mounting hole.

The corroducts used for the tests were 1 M hydrochloric acid. Small cylindrical discs of diameter 15 mm and thickness 5 mm were polished using emery paper in order to obtain a smooth and identical surface finish on all specimens, then washed in distilled water, followed by acetone, and then allowed to dry thoroughly [3]. They were finally weighted accurately to an accuracy of three decimal digits.

The initially weighted specimens were immersed in the corrosive environment and taken out at 24 h intervals for testing up to 96 hr. To avoid crevice corrosion, the specimens were suspended in the solution with a plastic string. The specimens were exposed to the test solution for several hours up to 96 hr. The corroded surface was removed by immersing the specimen on 100 mg ammonium per sulphate for 5 min. The cleaned specimens were dried and weighed to an accuracy of three decimal digits. The corrosion rate was calculated and compared with other reinforcements.

The corrosion rate (CR), from the mass loss, was calculated (according to ASTM Standard [6, 7] using the following equation:

$$\text{CR} = \frac{(K \times W)}{(A \times T \times D)}, \quad (2)$$

where CR is corrosion rate (mm/year), K is a constant equal to 8.76×10^4 , T is time of exposure in hours to the nearest 0.01 hour, A is area in cm^2 , W is mass loss in grams, and D is density in g/cm^3 .

The microstructure was examined using CETI optical microscope and SEM Model Quanta FEG 250.

FIGURE 2: Microstructure of pure Zn matrix.

3. Results and Discussions

Figures 2 and 3 show micrographs of the microstructure of Pure Zn matrix as well as the Zn/Graphite composites before performing corrosion test.

As shown in figures, graphite ceramic particles were successfully dispersed into the Zn matrix. The micrographs indicated that the production of bulk MMCs using conventional P/M technique used in the current study is effective. The ceramic particulates distribution in the Zn matrix was fairly uniform. However, on increasing wt% of Graphite to 3 and 5% agglomerations start to appear in the microstructure.

The agglomeration of the particles in MMCs was reported by many workers [17–20]. For example, Xiandong et al. [17] have different observations; all pores are filled by graphite and the graphite flakes are uniformly distributed throughout the matrices and the interfaces are well integrated. The pores found on the microstructure may be result of inadequate mixing of graphite powder. Similar observations by Martinez-Flores et al. [18] have been reported; it was observed that the reason for reduction of grain growth with increasing Al_2O_3 is its accommodated around the big metal particles, producing some sort of thermal insulation for the metal grains on higher amounts of Al_2O_3 ; the effect of insulation is bigger, resulting in a retardation of grain growth inside the metal particles. Božić et al. [19] worked on Zn–Al–Cu alloy reinforced with Al_2O_3 particles produced by powder metallurgy method; it was observed that Al_2O_3 particles agglomerate around Zn grains, and the presence of the agglomeration has detrimental effect on the mechanical properties of composite. Seyed Reihani [20] states that, as the reinforcement of SiC is increased in volume, porosity and agglomeration of SiC particles become more evident. Gnjdic et al. [21] have similar observations, by using adequate mixing method; agglomeration of SiC is found and the bond between the particles within the agglomeration is weak and the rearrangement that occurred during hot pressing resulted in the formation of large pores. Wang et al. [22], who study characterization of a powder metallurgy SiC/Cu–Al composite, find that SiC grains disperse homogeneously in the boundary region or inside the grown Al grains and the relatively homogeneous microstructure leads to the highest hardness and as a result the composite is inhomogeneous.

TABLE 1: The average corrosion rates of pure Zinc.

Exposure duration (hr)	Average corrosion rate (mm/year)
24	80
48	44
72	28
96	20

TABLE 2: The average corrosion rate of Zn/Gr MMCs.

Gr (wt.%)	Exposure duration (hr)	Average corrosion rate (mm/year)
1	24	53
	48	36
	72	20
	96	15
3	24	92
	48	42
	72	36
	96	27
5	24	130
	48	60
	72	40
	96	31

Tables 1 and 2 list the average corrosion rates of pure Zn as well as Zn/Graphite MMCs; the average is of 10 samples.

3.1. Effect of Exposure Time. It is clear from Figure 4 that corrosion rates of the Zn/Graphite MMCs as well as the pure Zn were decreased with increasing exposure duration. This may be attributed to the formation of passive layer on the surface of the samples and reduction of chlorides content in the acidic solution [23]. Sharma et al. [24] studied corrosion of ZA-27/Zircon particulate composites in 1M HCl. They reported that corrosion rate of ZA-27/Zircon particulate composites was decreased with increasing the exposure time.

The same observation was observed by the same authors in another investigation when they studied the corrosion of ZA-27/Glass fiber composites [25] and Bobić et al. on working on Corrosion of Aluminium and Zinc-Aluminium Alloys Based Metal-Matrix Composites [26].

Different observations were found by Yildiz and Kaplan [27] on studying corrosion of Zn–Al alloy. They found that corrosion rate revealed an altering property by showing sometimes an increase and sometimes a decrease in time as a result of presence of Al content.

3.2. Effect of Reinforcement Weight Percent. In Zn/Graphite MMCs, it has been found that increasing the weight percent of Graphite particulates tends to increase the corrosion rates of the Zn/Graphite MMCs. It was found also that Zn/1% Graphite MMC improved the corrosion resistance to 1M HCL in comparison to Zinc/3% Graphite and Zinc/5% Graphite and even better than Pure Zinc. Fontana [28]

FIGURE 3: The microstructure of Zn/Gr composites containing (a) 1 wt.-%, (b) 3 wt.-%, and (b) 5 wt.-% of Graphite particulates.

reported that relatively large amount of Al_2O_3 present in the Zn alloy matrix confers a certain amount of corrosion resistance because the oxide layer is quite stable in neutral and many acid solutions. The effect of Graphite reinforcement in ZA-27 magnesium alloy was reported by Seah et al. [5]; it was observed that, with increasing graphite content, corrosion rate decreases. This phenomenon was surprising because graphite is very noble compared to zinc and these two elements form an excellent galvanic cell in the HCl solution [28]. Figure 4 shows that, with increasing graphite content, the corrosion rate increases as a result of galvanic coupling.

In contrast, the observations noticed in the current investigation, in which increasing the amount of the ceramic particulates tends to increase the corrosion behavior of the MMCs, were reported by Hihara and Latanision [29]. It was observed when studying the galvanic corrosion of Al MMCs that, with increasing SiC content, a galvanic coupling between Al and SiC occurred which reduces the corrosion resistance of the MMCs.

It is believed that the contrary results reported by the investigators may be result of the difference in the fabrication methods, the nature, amount, shape, and size of the reinforcements and the matrix material. Several investigations showed that the aforementioned factors play an important role in determining the characteristics of MMCs [4, 24].

3.3. Examination of the Corroded Surfaces of MMCs. The surface of the pure Zn matrix underwent degradation, especially along the grain boundaries. These grain boundaries provide

FIGURE 4: The variation of the corrosion rate of Zn/Gr MMCs with the exposure duration.

preferential corrosion initiation sites because of the discontinuity in the surface oxide film due to the changed substrate structure. Such a discontinuity would facilitate the passage of the hydrogen ions to the metal, which when contacted by ions would suffer localized corrosion (Figure 5).

Figures 6, 7, and 8 show optical micrographs of the corroded surfaces of Zn/Graphite MMCs containing 1, 3, and

FIGURE 5: Optical micrographs of the corroded surfaces of unreinforced Zn matrix after immersion in 1 M HCl solution for (a) 24 hr, (b) 48 hr, (c) 72 hr, and (d) 96 hr.

FIGURE 6: Optical micrographs of the corroded surfaces of Zn/Graphite (1 wt.-%) MMCs after immersion in 1 M HCl solution for (a) 24 hr, (b) 48 hr, (c) 72 hr, and (d) 96 hr.

FIGURE 7: Optical micrographs of the corroded surfaces of Zn/Graphite (3 wt.-%) MMCs after immersion in 1 M HCl solution for (a) 24 hr, (b) 48 hr, (c) 72 hr, and (d) 96 hr.

FIGURE 8: Optical micrographs of the corroded surfaces of Zn/Graphite (5 wt.-%) MMCs after immersion in 1 M HCl solution for (a) 24 hr, (b) 48 hr, (c) 72 hr, and (d) 96 hr.

FIGURE 9: SEM of Zinc/3% Graphite showing galvanic corrosion performed between grains.

5 wt.-%, respectively, after exposure in 1 M HCl solution for 24, 48, 72, and 96 hours. It is clear from the micrographs that galvanic corrosion took place at the corroded surface of Zn/Graphite containing 3 and 5%. It has been reported that the graphite particles make graphite network interfering with the reaction between the acid and metallic matrix [5], and so, graphite protects zinc grains from corrosion and, on increasing graphite content, a galvanic coupling occurs.

It is clear from corrosion surface images and corrosion rate results that Zn/Graphite (1 wt.-%) MMC has the best corrosion resistance, when compared to Zn and Zn/Graphite (3 and 5 wt.-%) MMC. Figure 3(a) shows the microstructure of Zn/Gr (2 wt.-%) MMC, where graphite particles were successfully dispersed into the Zn matrix and as a result, when exposed to the corrosive medium, Graphite particles isolate Zn grains from the exposure to HCl solution protecting the composite from corrosion and enhancing the corrosion resistance. Fontana describes a possible mechanism by which graphite present in a metal can actually protect it from corrosion, as in the case of cast iron in strong acids. The better resistance is probably due to the graphite network interfering with the reaction between the acid and the metallic matrix [30].

Figures 7 and 8 show the corroded surface of Zn/Graphite (3 wt.-%) and Zn/Graphite (5 wt.-%) where deep pits and gaps are found causing an increase in the mass loss and corrosion rate. Moreover, Figure 9 shows that gaps were found as a result of the galvanic action between Zinc and Graphite by using SEM under $\times 2000$; this is because, on increasing the weight percentage, the agglomeration was increased and as a result galvanic coupling occurs. Similar observations were found when working on higher weight percentage of graphite like Hihara and Latanision [29] when studying the galvanic corrosion of Aluminum matrix composites. A galvanic action between Al and Graphite was found and pitting was found on the corroded surface. Similar observations were obtained [31, 32]; Payan et al. [31] studied galvanic coupling between Al and Graphite fibers and found poor resistance to corrosion in aqueous environments (chloride solution) and found galvanic action between Al and Graphite; Buonanno et al.

[32] obtained similar observations when studying corrosion of Graphite-Al MMCs.

In sum, it is found that corrosion resistance was improved on using Zinc/1% Graphite in comparison to Pure Zinc and Zinc/3% Graphite and Zinc/5% Graphite under static corrosion on 1 M HCl medium for all periods till 96 Hr.

4. Conclusions

- (1) Zn/Gr MMCs were successfully fabricated using powder metallurgy (PM) method.
- (2) Increasing the weight percent of the ceramic particulates in the fabricated MMCs increased the particles clusters volume fraction (agglomeration percent).
- (3) The corrosion rates of Zn/Graphite MMCs as well as the pure Zn were decreased with increasing exposure duration. However, increasing the weight percent of the Graphite particles tends to increase the corrosion rate of the composite materials.
- (4) Zn/Graphite MMCs containing 1 wt.-% of Graphite particulates exhibited the best corrosion resistance comparing to Zinc, Zinc/3% Graphite, and Zinc/5% Graphite as a result of graphite network phenomena.

Conflict of Interests

There is no conflict of interests or any financial support.

References

- [1] A. Brown, "How to deposit DLC successfully," *Materials World*, vol. 1, pp. 20–26, 1993.
- [2] S. L. Pohlman, "Corrosion and electrochemical behavior of boron/aluminum composites," *Corrosion*, vol. 34, pp. 156–162, 1987.
- [3] D. M. Aylor and P. J. Moran, "Effect of reinforcement on the pitting behavior of aluminum-base metal matrix composites," *Journal of the Electrochemical Society*, vol. 132, no. 6, pp. 1277–1281, 1985.
- [4] Q. Wang, "Preparation and properties of nano-CeO₂/Zn composites," *Transactions of Nonferrous Metals Society of China*, p. 623, 2007.
- [5] K. H. W. Seah, F. S. C. Sharma, and B. M. Girish, "Corrosion characteristics of ZA-27-graphite particulate composites," *Corrosion Science*, vol. 39, no. 1, pp. 1–7, 1997.
- [6] B. P. Bofardi, "Control of environmental variables in water reticulating systems," in *Metals Handbook*, vol. 13 of *Corrosion*, p. 487, ASM International, Materials Park, Ohio, USA, 9th edition, 1987.
- [7] L. H. Hihara and R. M. Latanision, "Suppressing galvanic corrosion in graphite/aluminum metal-matrix composites," *Corrosion Science*, vol. 34, no. 4, pp. 655–665, 1993.
- [8] M. G. Fontana, in *Corrosion Engineering*, p. 89, McGraw-Hill, New York, NY, USA, 3rd edition, 1987.
- [9] F. Bellucci, "Galvanic corrosion between nonmetallic composites and metals I. Effect of metal and of temperature," *Corrosion*, vol. 47, no. 10, pp. 808–819, 1991.

- [10] L. H. Hihara and R. M. Latanision, "Galvanic corrosion of aluminum-matrix composites," *Corrosion*, vol. 48, no. 7, pp. 546–552, 1992.
- [11] D. A. Jones and A. J. P. Paul, "Galvanic interactions between alloys and minerals in sulfuric acid," *Corrosion*, vol. 50, no. 7, pp. 516–521, 1994.
- [12] G. Schick, "Avoiding galvanic corrosion problems in the telephone cable plant," in *Galvanic Corrosion*, H. P. Hack, Ed., ASTM STP 978, pp. 283–290, American Society for Testing and Materials, Philadelphia, Pa, USA, 1988.
- [13] S. M. Wilhelm, "Galvanic corrosion caused by corrosion products," in *Galvanic Corrosion*, H. P. Hack, Ed., ASTM STP 978, pp. 23–34, American Society for Testing and Materials, Philadelphia, Pa, USA, 1988.
- [14] V. Brusic, M. Russak, R. Schad et al., "Corrosion of thin film magnetic disk: galvanic effects of the carbon overcoat," *Journal of the Electrochemical Society*, vol. 136, no. 1, pp. 42–46, 1989.
- [15] ASTM Standard, "Standard practice for laboratory immersion corrosion testing of metals," American Society for Testing and Materials G31-72, 2004.
- [16] ASTM Standard, "Standard practice for preparing, cleaning, and evaluating corrosion test specimens," American Society for Testing and Materials G1-03, 2004.
- [17] S. Xiandong, L. Chengping, L. Zhuoxuan, and O. Liuzhang, "The fabrication and properties of particle reinforced cast metal matrix composites," *Journal of Materials Processing Technology*, vol. 63, no. 1–3, pp. 426–431, 1997.
- [18] E. Martinez-Flores, J. Negrete, and G. Torres Villaseñor, "Structure and properties of Zn-Al-Cu alloy reinforced with alumina particles," *Materials & Design*, vol. 24, no. 4, pp. 281–286, 2003.
- [19] D. Božić, J. Stašić, and V. Rajković, "Microstructures and mechanical properties of ZA27-Al₂O₃ composites obtained by powder metallurgy process," *Science of Sintering*, vol. 43, no. 1, pp. 63–70, 2011.
- [20] S. M. Seyed Reihani, "Processing of squeeze cast Al6061–30vol% SiC composites and their characterization," *Materials & Design*, vol. 27, no. 3, pp. 216–222, 2006.
- [21] Z. Gnjjidic, D. Bozic, and M. Mitkov, "The influence of SiC particles on the compressive properties of metal matrix composites," *Materials Characterization*, vol. 47, no. 2, pp. 129–138, 2001.
- [22] H. Wang, R. Zhang, X. Hu, C.-A. Wang, and Y. Huang, "Characterization of a powder metallurgy SiC/Cu-Al composite," *Journal of Materials Processing Technology*, vol. 197, no. 1–3, pp. 43–48, 2008.
- [23] W. Feitknecht, "Studies on the influence of chemical factors on the corrosion of metals," *Chemistry & Industry*, vol. 36, pp. 1102–1109, 1959.
- [24] S. C. Sharma, D. R. Somashekar, and B. M. Satish, "A note on the corrosion characterisation of ZA-27/zircon particulate composites in acidic medium," *Journal of Materials Processing Technology*, vol. 118, no. 1–3, pp. 62–64, 2001.
- [25] S. C. Sharma, K. H. W. Seah, B. M. Satish, and B. M. Girish, "corrosion characteristics of ZA-27/glass-fibre composites," *Corrosion Science*, vol. 39, no. 12, pp. 2143–2150, 1997.
- [26] B. Bobić, S. Mitrovic, M. Babic, and I. Bobić, "Corrosion of aluminium and zinc-aluminium alloys based metal-matrix composites," *Tribology in Industry*, vol. 31, no. 3–4, pp. 44–53, 2009.
- [27] A. K. Yildiz and M. Kaplan, "Corrosion behaviour, microstructure and phase transitions of Zn-based alloys," *Bulletin of Materials Science*, vol. 27, no. 4, pp. 341–345, 2004.
- [28] M. G. Fontana, in *Corrosion Engineering*, p. 236, McGraw-Hill, New York, NY, USA, 3rd edition, 1987.
- [29] L. H. Hihara and R. M. Latanision, "Galvanic corrosion of aluminum-matrix composites," Tech. Rep., Office of Naval Research, Arlington, Va, USA, 1991.
- [30] M. G. Fontana, in *Corrosion Engineering*, p. 320, McGraw-Hill, New York, NY, USA, 3rd edition, 1987.
- [31] S. Payan, Y. le Petitcorps, J.-M. Olive, and H. Saadaoui, "Experimental procedure to analyze the corrosion mechanisms at the carbon/aluminum interface in composite materials," *Composites A*, vol. 32, no. 3–4, pp. 585–589, 2001.
- [32] M. A. Buonanno, R. M. Latanision, L. H. Hihara, and J. F. Chiang, "Corrosion of graphite aluminum metal matrix composites," Tech. Rep., Office of Naval Research, Arlington, Va, USA, 1991.