



Corrosion Studies of CNT Reinforced Al Metal Matrix Composites

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Abstract

This work reports a study of the corrosive characteristics of nickel coated carbon nanotubes reinforced with Al metal matrix composites in acidic environment. The composites were prepared by the liquid metallurgy system and the weight reduction strategy was adopted to investigate the corrosion rate. The term of the tests gone from 30 to 90 hours in the means of 10 hours. Unreinforced matrix alloy and the composites were subjected to indistinguishable test conditions to study the impact of carbon nanotubes on corrosion behavior. The erosion rates of both the unreinforced matrix alloy and the composites decreased with the introduction time. Corrosion resistance was found to improve with increase in wt. % of carbon nanotubes. Scanning Electron Microscopy (SEM) was utilized to study the corroded surface of the specimens.

Keyword: Metal matrix composites, carbon nanotubes, corrosion rate.

1. INTRODUCTION

CNT reinforced metal matrix composites have been most popular among the automotive industries over last three decades due to its potential applications in

various high temperature environments, particularly in the car motor parts, such as drive shafts, cylinders, pistons, and brake rotors. [1, 2]. Greater research work has been carried out by various researchers on manufacturing methods and characterization of various mechanical properties of aluminium reinforced with fiber metal matrix composites [3- 7]. Very limited research work has been carried out on corrosion mechanisms of alumina-reinforced with fiber MMCs. for example consumption initiation spots and the part played by alumina in corrosion.[8-10]. Corrosive factors for metal matrix composite are its nature and the present environmental conditions. The parts in these applications are affected by corrosive media like salt water solutions, acidic and alkaline media. enhanced wear resistance and enhanced damping capacities and heat transfer property are important [1-6]. Reinforcement influences the corrosion rate and hence this affects the use of metal matrix composite. A protective oxide film provides corrosion resistance in aluminium alloy based composites. When a reinforcing phase is added, it makes the film more discontinues and increases the corrosive sites, [11]. Study of corrosion behaviour of such composites is very much necessary as they often come in contact with acid during cleaning, pickling, descaling, etc. Corrosion resistance of metal matrix composites depend largely on processing techniques, Contaminations in the alloys, and in homogeneity of the chemical composition adds to the corrosion damage. Chloride environment makes the aluminium alloys more prone to pitting corrosion and further inhibits the development of the compact protective layer. As a result, pitting centres are developed. As the number of pits increases, the alloy elements are more cathodic than pure aluminium, further accelerating the propagation of pits and promotes depassivation [12, 13].

Wider applications of metal matrix composites [14] makes the study of their corrosion behaviour in different aggressive environments an important research area. [15]. Corrosion characteristics of CNTs reinforced metal matrix composites are deeply studied the paper focuses on corrosion characteristics of Al 7075/carbon nanotubes metal matrix composites.

2. MATERIALS AND METHODS

2.1 Materials

In the present analysis, the base alloy used is Al 7075 and reinforcement is carbon fiber, obtained from commercial ingots with proper chemical composition. This has been confirmed by SEM/EDS spectra. Iron and carbon short fiber impurities are also highlighted in this spectrum.

The alloy is found to be pollution free in the foundry. The advantages of alloy are its low energy requirements and excellent machinability which increases the tool life and reduces the production time during its fabrication process. Here, Al 7075 is the matrix alloy with carbon short fiber reinforcement. The chemical composition of alloy shown in Table 1

Table 1. Chemical composition of Al alloy (wt.%)

Element	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
%	0.4	0.5	1.6	0.3	2.5	0.15	5.5	0.2	Bal

2.2 Reinforcement

Here, a prototype device is used to produce the nanotubes and a platinum-rhodium crucible is used to melt the basrock at $600 \pm 750^\circ \text{C}$. The graphite rods is extracted from the crucible and intermittently subjected to electric arc. The rotating nanotubes vapour are then condensed and using a constant-condenser are anodized tubes of uniform length about 100 to 150 μm . The CNTs is finally rinsed using deionised water and dried at 110°C .

2.3 Composite Preparation

The method employed for composite preparation here, is liquid metallurgy using vortex technique where the vortex is created using a mechanical stirrer. Ni coated carbon nanotubes is preheated and maintained to a temperature of 500°C in a muffle furnace till it was introduced into the Al alloying elements melt. Inorder to improve wetting between the molten metal and the basal short fiber and also reduce the temperature gradient, preheating is carried out. To remove the surface impurities, pickling of these metal ingots with known quantities in 10% NaOH solution at room temperature for ten minutes is done. Ingots are immersed in a mixture of 1 part nitric acid and 1 part water for one minute and then washed in methanol to remove the smut formed during pickling. The cleaned Ingots are then dried in air and loaded into different alumina crucibles. The crucibles were the setting metals kept in composites furnace under melting temperature. They are then super-heated and maintained to that

temperature. Chromel alumel thermocouple is used to record the temperature during the process. The degasification of molten metals was done utilizing filtered nitrogen gas. Filtration process with industrially pure nitrogen was bought about by allowing the gas through an gathering of chemicals organized consecutively in the form of rows (concentrated sulphuric acid and anhydrous calcium chloride, and so on.) at the rate of 1,000 cc/minute for around 8 minutes.

The liquid melt is blended using a stainless steel impeller to make a vortex. The centrifugal impeller with three cutting edges welded at half of 90° inclination and 120° separated is utilized for mixing. The stirrer was turned at a speed of 500 rpm and a vortex was formed in the melt. The impeller is submerged at a stature of 33% of the liquid metal from the crucible base. The preheated fiber is brought into the vortex at 125°C

gm/min.

Mixing was proceeded until interface cooperates between fiber and the matrix improving wettability. Degassing of the melt is accomplished within 3-4 minutes with unadulterated nitrogen and afterward warmed to super temperature (540 C) and filled into the pre warmed lower half die of the water powdered press. The composite is cemented with the help of top die by applying a weight of 100 kg/sq.cm. Before emptying the melt into the dies, both were preheated to 290 C. Pressure is applied to guarantee common dissemination of the fiber in the created composite.

2.4 Specimen Preparation

The specimens in the form of small cylindrical disks were obtained from the bar castings. Disks having diameter 20 mm and thickness 10 mm were used for study. Using an abrasive cutting wheel, the material was cut into 20 × 20 mm pieces as per ASTM standards. Using 240, 320, 400 and 600 SiC paper the samples were then ground and polished according to standard metallographic techniques and dipped in acetone and dried. Electronic balance and Vernier gauze are used to weigh (up to fourth decimal place) the samples and note the dimensions respectively.

2.5 Corrosion Test

Conventional weight reduction strategy was utilized to lead the erosion tests as per the ASTM standards of G1 at room temperature (28 C). The corrodent utilized was 1N, 2N & 3N HCl and afterwards the samples was gotten billets which were casted. Little round and hollow plates of measurement 20 mm and 20 mm length were utilized for study. So as to acquire a smooth and indistinguishable surface, the samples were cleaned with SiC emery paper of grade 450 to 650 coarseness. They are then washed with refined water, trailed by acetone, dried completely. They were at last weighed to an exactness of three decimal spots.

A similar cleaning technique is rehashed before each weighing during each erosion test phase. At first measured examples were submerged in the corrosive environments as shown in Fig. 1 and removed after 10 days intervals for testing to an aggregate of 90 days. A test condition was analysed on one specimen only and the eroded layers that were formed on the specimens were eliminated with an abound brush. These samples were dried and weight was calculated. The reduction in weight is measured and their percentage rate weight reduction were calculated with information as the first weight data of the non-eroded sample.

3. RESULTS AND DISCUSSION

3.1 Corrosion Behaviour

3.1.1 Effect of Corrosion Duration

The plots of mass loss of as cast Al7075 combination and Al7075/ fiber strengthened composites against various introduction times (in days) in 1N, 2N & 3N HCl solution using weight loss method is dictated in Fig. 2. The computed average value of corrosion loss were plotted against different exposure times (in days). Within the scope of this investigation, it has been studied that, the exposure time (in days) is directly proportional to the corrosion loss.

the variation of the corrosion loss against different exposure times (in hours) in 1N, 2N & 3N HCl solution for carbon nanotubes-reinforced composite as well as the cast Al7075 alloy. This shows as the term of introduction of the corrodent increases, corrosion loss also increases inferring that the erosion resistance of the material tested increments as the exposure time is extended. Here, we find in the initial state, corrosion loss increases appreciably and increases monotonically thereafter with increase in duration of the test. During 90 hours exposure time, both the weight loss and corrosion loss were maximum.

The phenomenon of gradually increasing corrosion loss and slope of the curve increasing with exposure time demonstrates a conceivable passivation of the matrix. When the specimen is exposed to HCl, a thin

protective layer is formed on its surface and protects the base metal from the aggressive environment. Henry et al. [16] clarified that the defensive film here is a hydrogen hydroxy chloride film which impedes the forward response. Moshier et al. [17] have called attention to the film comprises of aluminum hydroxide compound. Corrosive growth of the specimen in HCl solution is prevented by this layer, yet the correct compound nature of such defensive film is as yet obscure. This behaviour may be because of the solution being excessively concentrated by Al^{3+} ions and hence retarding the progress of forward reaction as explained by Mc. Cafferty [18]. The reaction further slows down due to depletion in hydrogen ions.

3.1.2 The effect of short carbon fiber content on corrosion

Fig. 1 dictates the plot of the corrosion loss with a variety of carbon dispersed in MMC's in HCl solution. Here, the measured mean values of corrosion loss were plotted as a component of weight rate of fiber. Here, we can analyse that the increment in the content of the carbon short fiber, diminishes the corrosion loss. From the Fig. 1, we can conclude that, more the carbon nanotubes added more is the corrosion resistance of the composite. The interface formed between the fiber and the Al alloy matrix, generated during manufacturing might be the purpose behind the reduction in resistance for corrosion. Electron trade essential for oxygen diminishment becomes easier due to the more conductive stage at intermits driving the anodic reaction to higher level. Here, the corrosion loss decreases with test time lapse for both reinforced composite and unreinforced matrix alloy. The hydrogen bubbles are believed to be cleaned off since the samples were altogether cleaned and weighed at each time

This takes out the like hood of hydrogen air pockets sticking to the surface of the samples and forming changeless layer influencing the corrosion process. The results of continuous reduction in corrosion loss may be due to 'very steady defensive layer in neutral and numerous acid solutions' but influenced by alkalis.

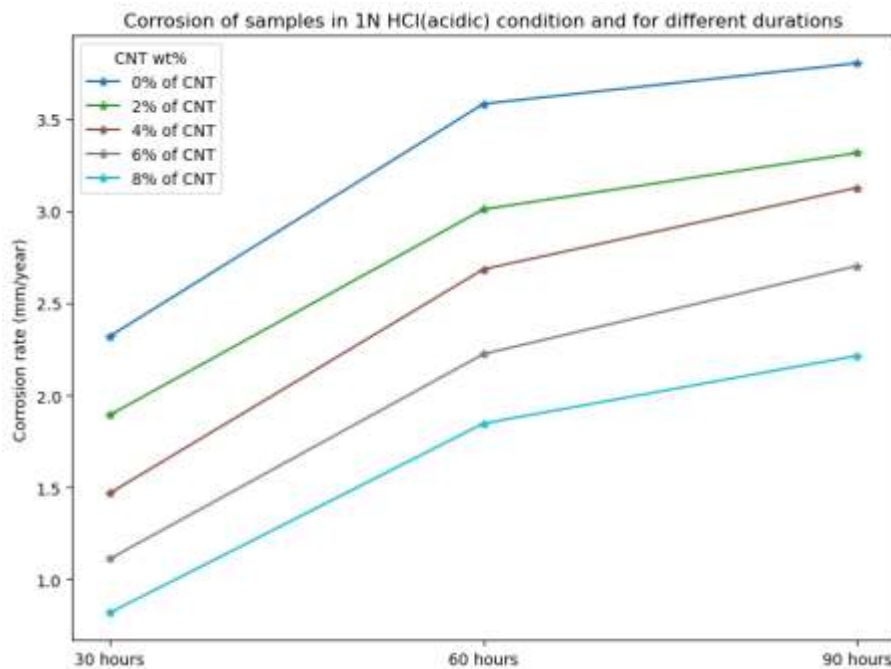


Fig 1: Corrosion rate v/s % CNT reinforced MMC for 1N HCl solution

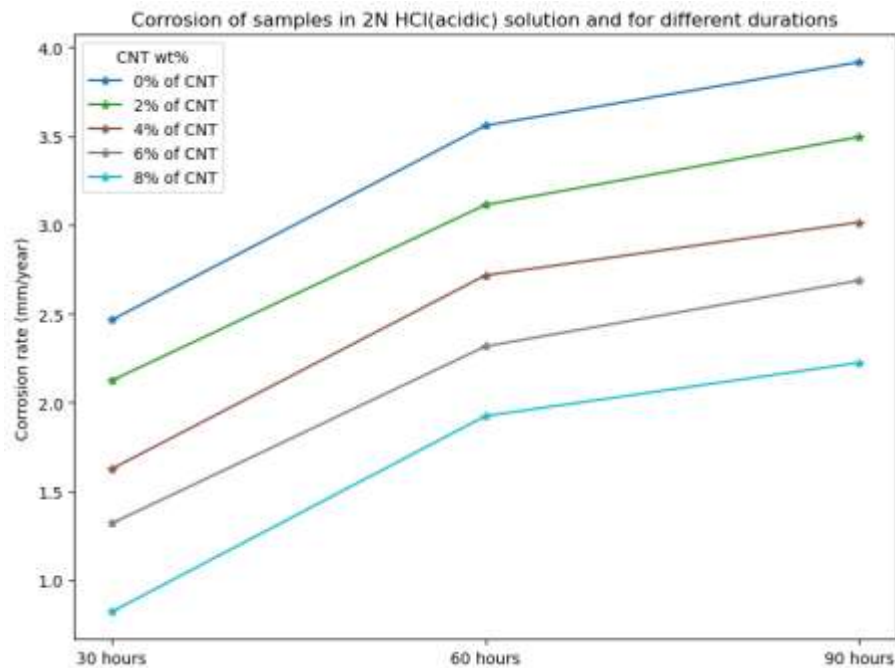


Fig 2: Corrosion rate v/s % CNT reinforced MMC for 2N HCl solution

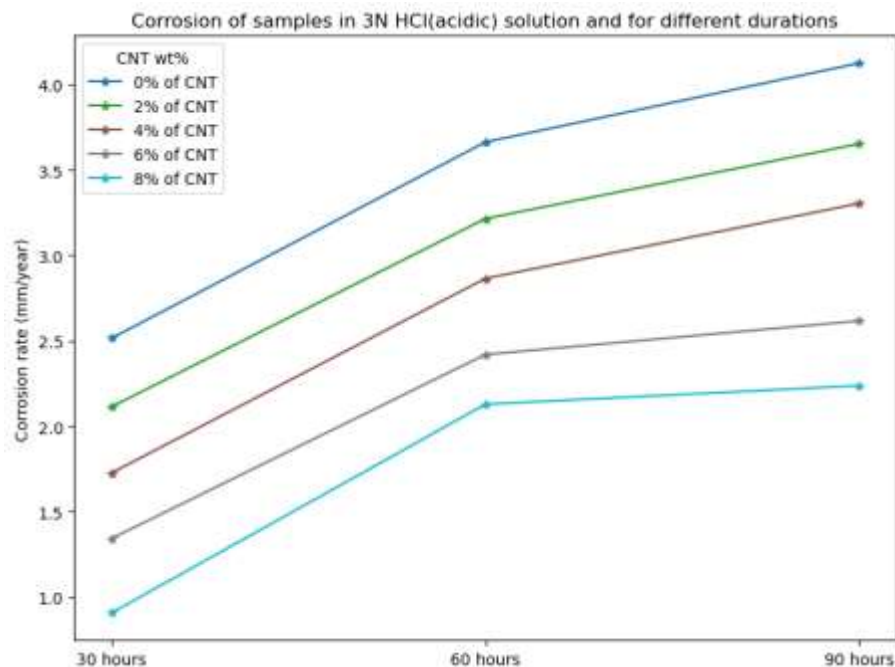


Fig 3: Corrosion rate v/s % CNT reinforced MMC for 3N HCl solution

3.2 Corrosion Morphology

Fig. 4 shows corroded surface of a) as cast, b) 4 wt. % carbon fiber and c) 6 wt. % carbon fiber exposed at 90 hours in HCl at 1 N solution. All the corroded specimen surfaces were observed in Scanning Electron Microscope (SEM). Fig 4a shows the unreinforced matrix alloy, revealing the presence of cracks on the surface. The surface of the unreinforced matrix experienced extreme degradation, particularly along the boundary. In case of the 4 % and 8% by weight CNTs showed round pits distributed all over the surface. In case of 4 wt. % carbon nanotubes composites, intense localized attacks were seen at the fiber matrix interface as shown in the Fig. 4b. In the neighbourhoods of the pits, the matrix did not show a generalized attack like that observed on the remaining surfaces as shown in the Fig.4c. Pitting occurred preferentially in correspondence with carbon nanotubes clusters. It gave rise to a few wide pits, which were distributed on the surface of the specimen. This was particularly evident by volcano-shaped pits appeared to be covered with white, thick, flaky corrosion product as was in the case for MMCs.

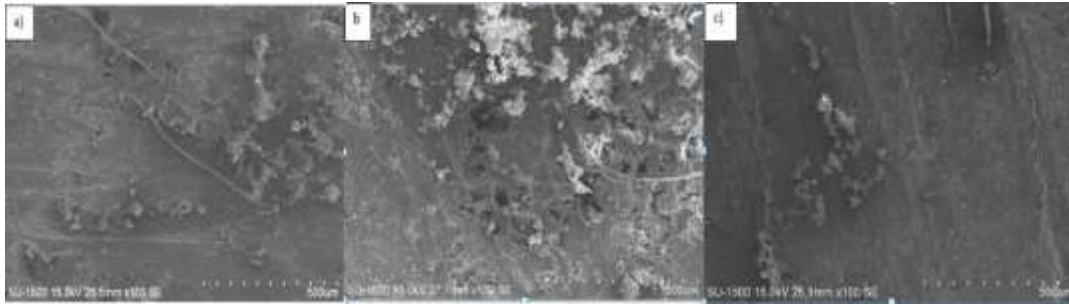


Fig. 4 shows corroded surface of a) as cast, b) 4 % wt. % carbon fiber and c) 6 % wt. % CNTs exposed at 90 hours in HCl at 1 N solution

4. CONCLUSION

In the view consequences of present investigation, following conclusions have been drawn.

1. Al reinforced with short carbon fiber MMCs were found to corrode in 1N, 2N & 3N HCl solutions.
2. The corrosion rate in HCl solution diminishes with time, likely on the account of the development of stable oxide layer over the samples. The rate of consumption of mass in case of both the alloy and composite diminished with increment in time lapse.
3. As the CNTs is increased, the composite become more corrosion prone due to increase in electrochemical reactions between the matrix alloy and the CNTs .
4. Scanning electron micrographs of the CNTs reinforced composite reveal numerous shallow pits in the tested sample.

REFERENCES

- [1] Popov, V.V.; Pismenny, A.; Larianovsky, N.; Lapteva, A.; Safranchik, D. Corrosion Resistance of Al–CNT Metal Matrix Composites. *Materials* 2021, 14, 3530. <https://doi.org/10.3390/ma14133530>.
- [2] Tsai, Y.-H.; Wang, J.; Chien, W.-T.; Wei, C.-Y.; Wang, X.; Hsieh, S.-H. A BIM-based approach for predicting corrosion under insulation. *Autom. Constr.* 2019, 107, 102923.
- [3] Sun, L.; Li, C.; Zhang, C.; Su, Z.; Chen, C. Early Monitoring of Rebar Corrosion Evolution Based on FBG Sensor. *Int. J. Struct. Stab. Dyn.* 2017, 18, 1840001.
- [6] Srinivasan, V.; Kunjiappan, S.; Palanisamy, P. A brief review of carbon nanotube reinforced metal matrix composites for aerospace and defense applications. *Int. Nano Lett.* 2021.
- [7] Brett, C.M.A., “On the electrochemical behaviour of aluminum in acidic chloride solution”. *Corros. Sci.* Vol. 33 (1992), pp. 203–210.
- [8] Candan, S., Biligic, E., “Corrosion behavior of Al–60 vol.% SiCp composites in NaCl solution”. *Mater. Lett.* Vol.58 (2004), pp. 2787–2790.
- [9] Daniela Alina Necşulescu “The effects of corrosion on the mechanical Properties of aluminium alloy 7075-T6, U.P.B. Sci. Bull., Series B, Vol. 73, Iss. 1, 2011.
- [10] T. Rajmohan, K. Palanikumar, S. Ranganathan, Evaluation of mechanical and wear properties of hybrid aluminium matrix composites, *Transactions of Nonferrous Metals Society of China*, Volume 23, Issue 9, 2013, [https://doi.org/10.1016/S1003-6326\(13\)62762-4](https://doi.org/10.1016/S1003-6326(13)62762-4).
- [11] Sharma, R.; Singh, A.K.; Arora, A.; Pati, S.; De, P.S. Effect of friction stir processing on corrosion of Al–TiB₂ based composite in 3.5 wt.% sodium chloride solution. *Trans. Nonferrous Met. Soc. China* 2019, 29, 1383–1392.
- [12] Lekatou, A.; Karantzalis, A.E.; Evangelou, A.; Gousia, V.; Kaptay, G.; Gácsi, Z.; Baumli, P.;

Simon, A. Aluminium reinforced by WC and TiC nanoparticles (ex-situ) and aluminide particles (in-situ): Microstructure, wear and corrosion behavior. *Mater. Des.* 2015.

[13] Noguchi, T.; Magario, A.; Fukazawa, S.; Shimizu, S.; Beppu, J.; Seki, M. Carbon Nanotube/Aluminium Composites with Uniform Dispersion. *Mater. Trans.* 2004, 45, 602–604.

[14] 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 (1985), No. 6, pp. 1277–1281.

[15] ASTM International. G5 Standard Reference Test Method for Making Potentiodynamic Anodic Polarization Measurements; ASTM International: West Conshohocken, PA, USA, 2014.