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Corrosion Behavior Studies of Al7075 Reinforced with Multiwalled Carbon Nanotubes Metal Matrix Composites in Acidic Medium

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Abstract

The attempts to use the Carbon nanotubes as the reinforcements in the Metal matrix composites is engulfing worldwide since it possess excellent material properties which improves the composites strength. The present work was carried out to test the corrosion behavior of the Al7075 Composites prepared with the carbon nanotubes as the potential reinforcements. The composites were added to the base material in 2wt%, 4wt%, and 6wt % via liquid metallurgy procedure the corrosional studies were conducted as per the Mass loss technique using HCl solution of varying Normalities of 1N, 2N and 3N the weight loss during the period of 10 weeks the observations were made in the gap of each week upto 10 weeks and obtained the mass loss data in each week later the corrosion rate was calculated. The corroded specimens were then analysed using SEM. The results revealed that as the wt% of the MWCNTs was increased the Corrosion rate was found to be decreased.

Keywords: Multiwalled Carbon nanotubes (MWCNTs), Metal Matrix Composites (MMC), Stir Casting, Weight reduction, Corrosion Resistance.

INTRODUCTION

The MWCNTs are the new class of functional materials which is the main theme of research in recent years. MWCNTs inherent capacity to improve the properties of the composites has increased its demand to be used as reinforcements. The Metal Matrix composites such as aluminium as the base material has become the point of interest for researchers in worldwide since the resulting composites have promised to be the sure replacements for the conventional materials. The aluminium composites are the prime materials for most of the aerospace components and the considerable amount of automotive parts are also based on the composites. Since the high weight to strength ratio of the composites offers the induced attraction towards the MWCNTs reinforced Aluminium MMCs its scope has been doubled in recent trends. MWCNTs reinforced MMCs offers the designers of materials to tailor the requirements such as high stiffness , temperature resistance, rigidity, structural stability and lightweight in addition to this the corrosion resistance of the material can also be enhanced. The basalt fiber when exposed to the corrosive environment showed the pitting which was observed in fiber clusters in crystallographic directions the inter porosity of the composites tends to increase the corrosion rates [1]. The inclusion of the second phase particles in the Al6061 matrix like Zirconium oxide changes the response to the corrosion in the MMCs the nanoscale light carbide materials like B_4C, TiC is suitable to be used as reinforcements the investigations on such MMCs has shown that these materials possess superior properties when characterized using the ultrasonic effects via acoustic streams to obtain uniform dispersion of the B_4C in the Al alloy [2]. When exposed to the corrosive environment the matrix alloy will be showing the passivity compared to the reinforcements this was examined when an alkaline medium like Nacl was used it gave rise to a thin protective layer over the surface of the base metal alloy which was acting like a protective shield to retard further chemical reaction over the surface this phenomenon was justified with the presence of small amount of Mg in the Al alloy while the corrosion of the fiber was not much [3]. The gradual increase of the corrosion loss was with the increase with the exposure time of the parts made up of composites affected by the corrosive medium like alkaline, acidic and salt nature solutions the unreinforced alloy would experience the severity of the corrosion in contrast with the Al based composites because of the diminished properties like thickness, damping capacities, heat transfer coefficients, wear resistance etc. the addition of the reinforcements pave the way for the increase in the corrosive sites which makes the alloy to prone to more corrosion compared to the unreinforced material [4]. The very limited works carried out in the field of corrosion of Al based reinforced with MWCNTs the information and interpretations will some times conflicts one another [5]. Ni coated MWCNTs appear like fiber with uniform dispersion the resulting MWCNTs were further used as the reinforcements in the Al7075 alloy via casting methods [6]. Due to the Compositions the composites are most of the times susceptible to corrosion it affects the structural integrity and stiffness of the parts since Al7075 is used widely in aircraft and automotive components those parts must be studied thoroughly about corrosion[7]. Though many researchers have worked on the corrosion characteristics of the MMCs the MWCNTs reinforced MMCs are no subjected to the core investigations which has created the platform for the further gathering the information of the MMCs behavior in the corrosive atmosphere the present paper discusses the techniques and the methods to study the Corrosion behavior of the MWCNTs reinforced Al7075 MMCs.

EXPERIMENTAL

Materials

MWCNTs used in this study were supplied by United Nanotech Innovations Pvt. Ltd., Bangalore the carbon nanotubes in the powder form. These are synthesized through catalyst assisted chemical vapour deposition method they have average diameter of 20-30 nm and length measured is about 16-20 µm, , yield stress of around 4.3 GPa and elastic modulus of 70 GPa the presence of the compound is verified by the EDS spectra. was pre-cleaned by cleansing with the Soap, then washing with Distilled water further rinsing with concentrated sulphuric acid to remove the impurities such as iron. The Al7075 alloy was prepared in the foundry with the ease of fabrication and pollution free environment. The below table shows the Al7075 chemical composition.

Table1. Chemical Composition of Al7075 in wt%

Element	% Composition
Fe	0.5
Cu	1.5
Cr	0.2
Mg	2.6
Mn	0.3
Si	0.3
Ti	0.2
Zn	5.8
Al	Bal

The Reinforcements was initially coated with the Nickel via electroless method in the presence of Sodium hypophospate and Nickel sulphate.

Table 2. Properties of Muliwalled Carbon nanotubes

Properties	**Values**
Diameter	20nm
Length	20µm
Purity	>98%
Density	0.2g/cm^3
Metal particles	<1%

The Nickel presence was confirmed using XRD the Phase of the component was also studied. The wt% of the nickel composition was analysed under EDS the percentage of Ni deposition over the surface of the MWCNTs was largely controlled by the increasing the activation sites. The palladium chloride addition will directly affects the proportion of the Ni deposition on the MWCNT. The Coated MWCNTs was stored in the Desiccators in the vacuum.

Fabrication of Composites:

The liquid metallurgy route was employed for composite preparation. The 2wt%, 4wt%, 6wt% the weight percentages of MWCNTs was added to the Al7075 alloy to prepare the composites. Initially the Ni coated MWCNTs were pre heated to about 5500C in a hot oven because there to remove any carbon compounds which might have been resulted due the reactivity with the environment the much care have taken to avoid the chemical reaction by storing the coated MWCNTs in a vacuum container. Also the molten metal will be at higher temperature of the order more than 8000C to reduce the temperature Gradient the pre heating is necessary which also adds to improve the interface bonding in the intermetallic structure. During casting the metal is characterized by forcing molten metal under high pressure into a mold cavity. The mold cavity is created using two hardened tool steel dies which have been machined into shape and work similarly to an injection mold during the process. Most die castings are made from non-ferrous metals, specifically zinc, copper, aluminium, magnesium, lead, pewter and tin-based alloys. The Nitrogen tablets was used as the Degassing reagent which release the nitrogen gas and form a compounds with the other gas within the Al7075.

Using sodium hydroxide the impurities in the ingots was removed by soaking the ingots in the solution for about 15mins. Then the surface is washed with the dilute nitric acid followed by washing with methanol and finally water. These cleaned ingots were then kept in the respective crucibles then melting process was initiated by switching on the furnace. The melting temperature was recorded with the electronic thermocouple at around 850^0 C the Ni coated MWCNTs were added into the melt with the help of Stainless steel impeller also used as a stirrer. The stirrer was coated with the Ni-Cr the stirrer speed was gradually increased from 100rpm to 500rpm in increments of 100rpm which created a whirl vortex so that the heavier particles was allowed at the bottom and the incremental increase of the stirrer speed made the MWCNTs to mix well with the alloy. The stirring continued for about 10 mins during each speed so that the better intermetallic bonding would be achieved. This process enables the uniforn distribution of the MWCNTs throughout the Composites.

Figure 1: The Die set after Pre Heating

Figure 2: Al7075 alloy Melt at desired Temperature

Preparation of the Specimens:

The cylindrical round specimens of the dimensions 15mm diameter and 10mm thickness was obtained by abrasive cutting as per the ASTM G1 standards the specimens were polished with the varying size SiC emery paper of the grades 240,320,400 and 600 the specimens were thoroughly washed with acetone and dried using drier the polishing was etched in the presence of keller's reagent later the Specimens were examined under the optical microscope. The digital electronic balance was used to verify the weight of the specimens and it was set to fourth decimal places. Utmost care was taken to prepare all the specimens in identical manner.

Corrosion Test:

The corrosion test was conducted as per the ASTM G1 standards at the room temperature (26^0C). the formula used for the calculation of the area subjected to the corrosion was

$$\text{Area} = (\pi/2(D_s^2 - D_h^2) + t\,\pi\,D_s + t\,\pi\,D_h \quad (1)$$

Where D_s is the diameter of the specimen and D_h is the diameter of the mounting hole, t refers to thickness of the specimen. The HCl acid was used as the corrode solution in 1N, 2N and 3N. the identical specimens which was thoroughly washed with acetone and dried using drier was initially weighed to an accuracy using the digital electronic balance to three decimal places the weight loss was measured and converted into the corrosion rate using the equation

$$\text{Corrosion Rate} = (K_t \times M_L) /(A \times T \times d) \quad (2)$$

Where, K_t is the mathematical constant whose value is 8.76×10^4, M_L is the mass loss in grams weighed after the specified duration, A is the area in m^2 , T is the period of exposure in hours and d is the density in g/cm^3. The SEM analysis was carried out at R&D, BMSCE using VEGA3 TESCAN equipment.

The Corrodent used was HCl of 1N,2N,3N the cylindrical round specimens which polished and etched with the keller reagent was ready for corrosion test. The regular weight reduction method was employed to conduct the Corrosion studies in the present work, at first the measured samples were immersed in the corrosive environment. The corrosion studies were carried out for a period of 10 weeks in the interval of one week. The mass loss was calculated for each week when the specimen under test was taken the visual examination revealed the formation of the dark grey layer of the eroded surface which was cleaned with a brush then the specimen was dried and weight was recorded afterwards the mass loss for the week was noted down. Later specimen was placed back into the same corrosion environment for the next week.

RESULTS AND DISCUSSIONS

The Corrosion behavior

The specimens were subjected to the corrosion environment i.e. in HCl solution of 1N, 2N, 3N for the duration of 10 weeks. The specimens were observed in the regular intervals of each week and the weight loss data was recorded using a digital electronic balance as shown in the Table3 for 1N, Table 4 for 2N and table 5 for 3N. The time of exposure is directly proportional to the corrosion loss. When the specimens were exposed to the corrosive environment its surface was observed to be corroded and due to the erosion of the material the corrosion loss was found. As the exposed time increases the corrosion loss was also found to be increased. Also as the normality of the HCl increases the mass loss also increased which is evident from table $ and table 5. The another observation was the formation of the thin protective layer of hydroxyl Chloride which acted as a shield against the erosion of the material which retarded the corrosion. The ionic activity between the hydroden atoms in the presence of Aluminium ions could be the reason for the formation of such protective sheathing. As the exposure time was longer the ionic activity was found to become less and with the exposure of the time duration the mass loss was increased as shown in the tables.

Table 3: Mass loss for 1N HCl

wt% of MWCNT	Mass loss during Corrosion Period in grams									
	week 1	week 2	week 3	week 4	week 5	week 6	week 7	week 8	week 9	week 10
0	2.213	2.785	2.882	2.973	2.995	3.005	3.123	3.228	3.306	3.311
2	2.106	2.632	2.736	2.912	2.991	2.886	2.832	2.805	2.791	2.788
4	1.832	2.261	2.701	2.845	2.864	2.864	2.976	2.846	2.842	2.321
6	1.352	2.202	2.562	2.631	2.761	2.812	2.823	2.802	2.111	1.991

Table 4: Mass loss for 2N HCl

wt% of MWCNT	Mass loss during Corrosion Period in grams									
	week 1	week 2	week 3	week 4	week 5	week 6	week 7	week 8	week 9	week 10
0	2.455	2.561	2.763	2.891	2.972	2.998	3.063	3.126	3.231	3.438
2	2.221	2.312	2.471	2.634	2.835	2.902	2.999	3.01	3.112	3.261
4	1.981	1.983	1.997	2.112	2.331	2.564	2.872	2.978	3.001	2.982
6	1.465	1.632	1.735	1.892	1.923	2.006	2.112	2.118	2.321	2.413

Table 5: Mass loss for 3N HCl

wt% of MWCNT	Mass loss during Corrosion Period in grams									
	week 1	week 2	week 3	week 4	week 5	week 6	week 7	week 8	week 9	week 10
0	2.325	2.854	2.921	2.975	2.998	3.007	3.131	3.145	3.265	3.333
2	2.311	2.478	2.587	2.598	2.601	2.876	3.026	3.113	3.127	3.216
4	2.267	2.198	2.323	2.413	2.493	2.673	2.897	3.005	3.009	3.167
6	1.987	2.107	2.11	2.121	2.223	2.365	2.422	2.514	2.697	2.791

The Effect of MWCNT Reinforcements

The average values of the corrosion loss for the week 1, week 5 and week 10 is depicted in the Fig 3, Fig 4 and Fig 5 , the corrosion loss tends to increase as and when the duration of exposure increased. But with the increase in the wt% of MWCNTs the corrosion loss was diminished table 3,4,5 gives the data regarding the corrosion loss. The addition of more MWCNTs increases the corrosion resistance of the composites. The strong intermetallic bonding must be the reason to the improved resistance to corrosion whereas in the unreinforced alloy the hydrogen reacts with the anions and loss is more. The corrosion loss will be even more reduced if the more percentage of Ni coating is deposited over the MWCNTs which enhances the interfacial bonding.

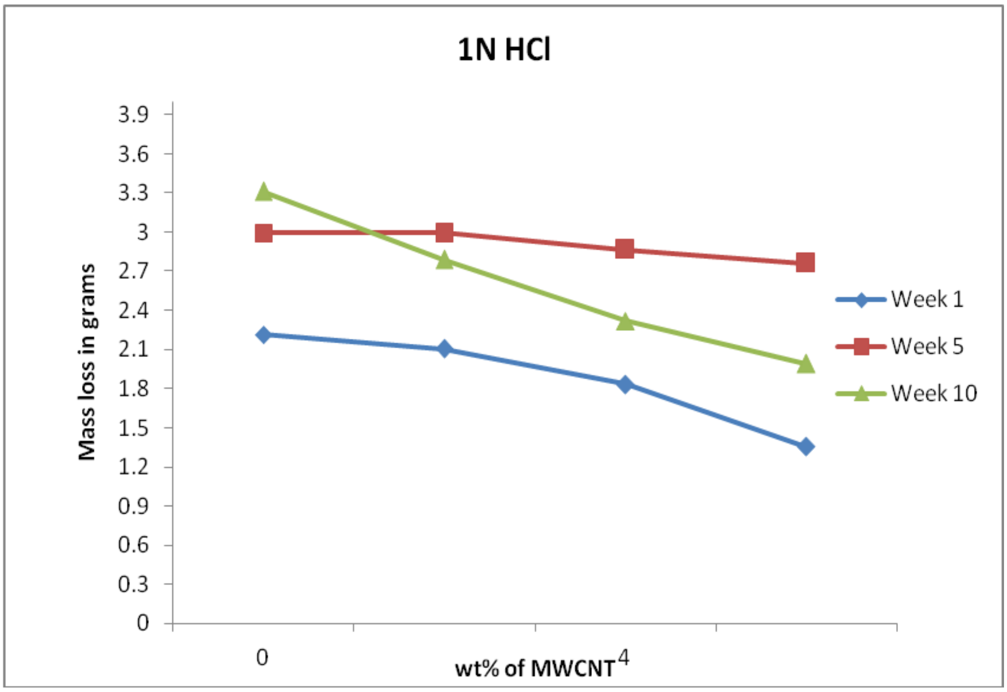

Figure 3: Mass loss vs wt% of MWCNTs for 1N HCl

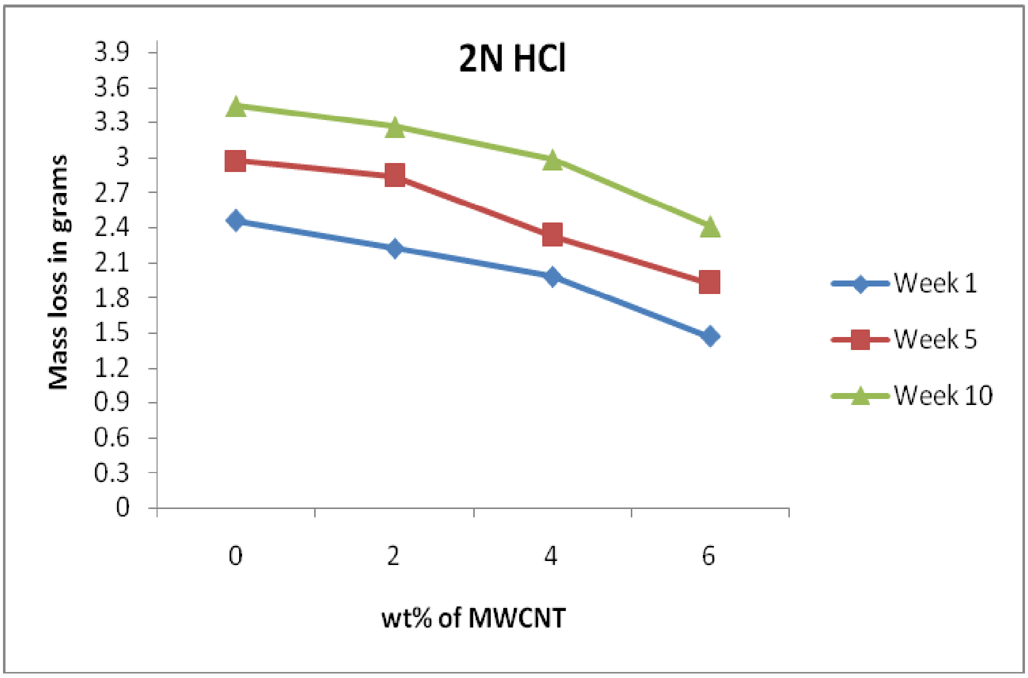

Figure 4: Mass loss vs wt% of MWCNTs for 2N HCl

The increase in the corrosion rate was also observed along with the increased Normality Fig 4, Fig 5. This is because the more acidic nature favors the deterioration of the material this influence can be retarded by the addition of the MWCNTs for 6wt% the trend was decrease in the Corrosion rate Fig 5. The MWCNTs plays a significant role in reducing the Corrosion.

Fig. 6 shows the plot of Corrosion rate vs wt% of MWCNTs we can see clearly as the reinforcements increases the corrosion rates have been considerably decreased for the long duration.

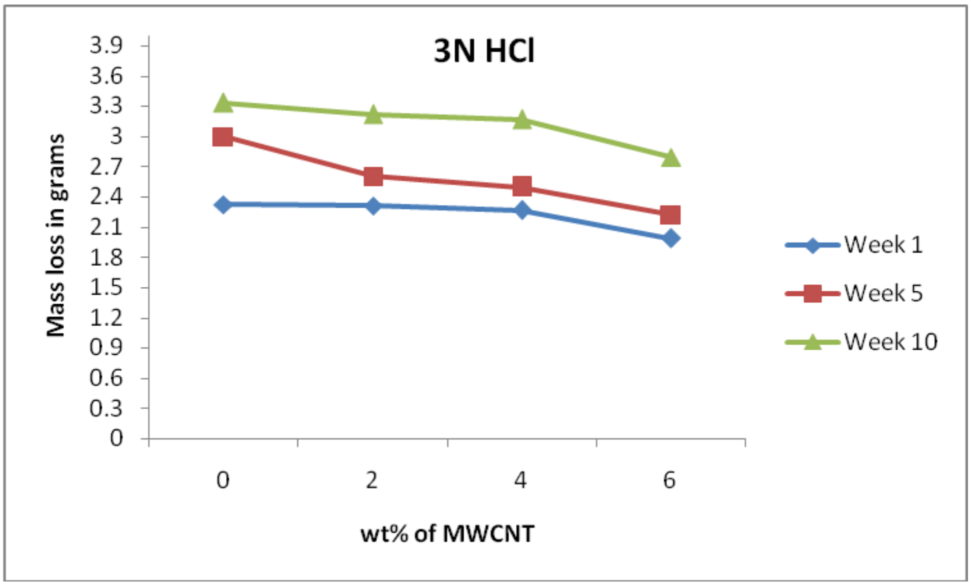

Figure 5: Mass loss vs wt% of MWCNTs for 2N HCl

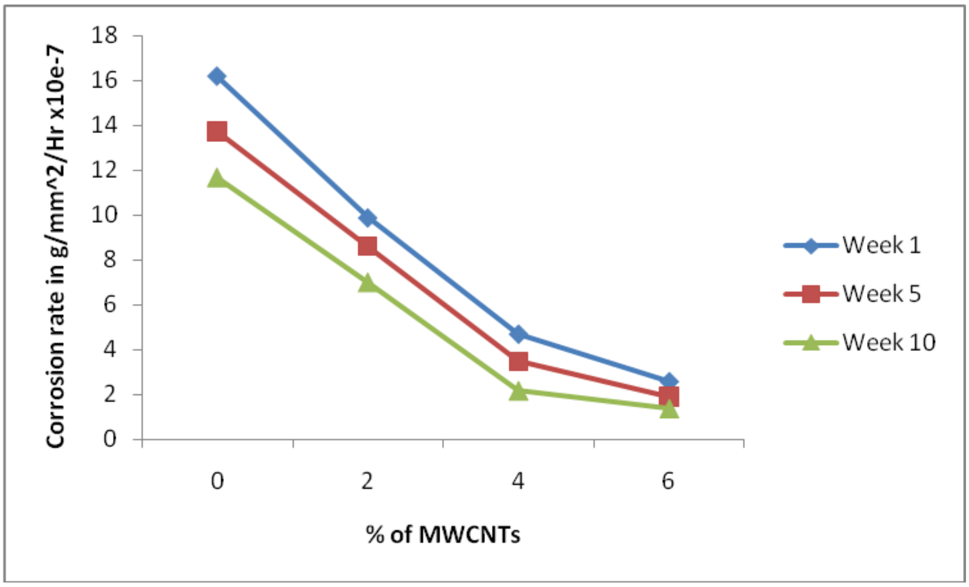

Figure 6: Corrosion rate vs wt% of MWCNTs

The Microstructural Studies of Corroded Specimens

Fig. 7 shows the SEM image of the unreinforced Al7075 matrix before test which confirms the uniform distribution of the MWCNTs in the matrix. The Stir casting founds to be effective in the dispersion of the reinforcements. Fig. 8 shows the after corrosion test result for the duration of 10 weeks it is evident from then SEM image that the piiting has occurred along the grain boundary giving rise to white corrosive flakes in crystallographic orientations. The agglomerations of the MWCNTs in the Al matrix is still present this can be minimized by the precise stirring speed so that the uniform dispersion of the reinforcements takes place. The microstructure also supports the Stir casting technique is effective to prepare nanocomposites. The severity in corrosion was decreased as the percentage of MWCNTs was increased upto 6% but it was found for increasing duration for 5th week and 10th week as the duration increased the corrosion was also found increasing drastically Fig. 9 and Fig. 10.

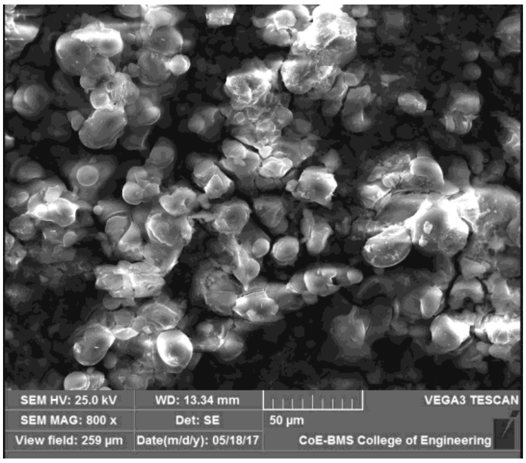

Figure 7: Unreinforced Al7075 before Corrosion Test

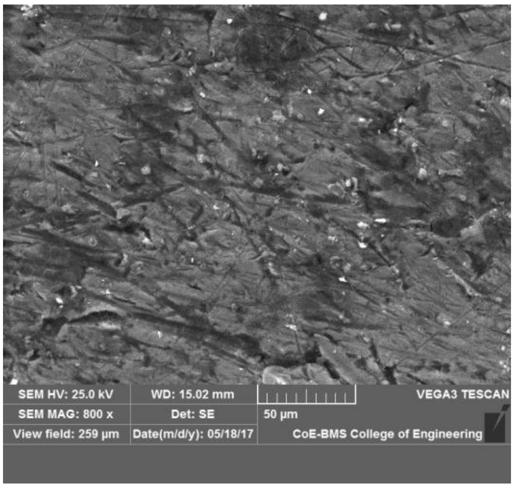

Figure 8: Unreinforced Al7075 after Corrosion Test

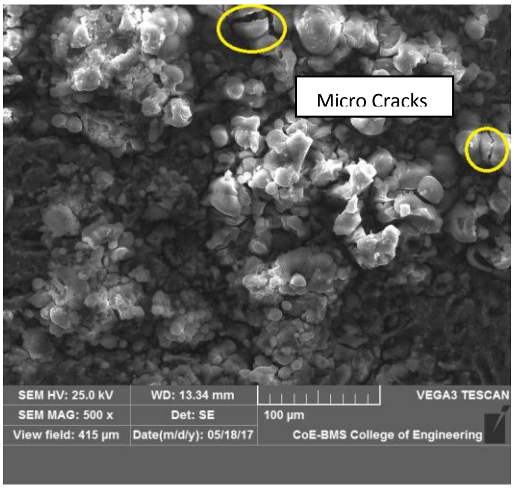

Figure 9: Corroded surface of the 6wt% MWCNTs in 5th week Corrosion Test

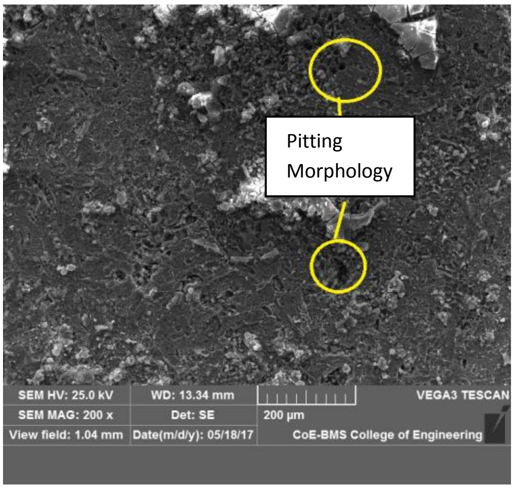

Figure 10: Corroded surface of the 6wt% MWCNTs in 10th week Corrosion Test

The micro cracks observed along the grain boundaries Fig. 8 shows the corroded in the 5th week duration this crack progression continues with in increase in normality of the HCl solution since the environment becomes more acidic. Tiny pits which is not visible through the visual inspection is observed by the SEM micrograph these pits are volcanic in shape Fig. 10 clearly depicts the degradation of the material with long exposure to the Corrodent and that too for increased normality. When compared to the wt% of the reinforcements the Pits was observed less in 6wt% of MWCNTs possibly due the increased corrosion that was achieved by the Composites.

CONCLUSION

Based on the results of the investigation the we can conclude that the Al7075 reinforced with MWCNTs for the weight percents of 2wt%, 4wt% and 6wt% was successfully prepared by the Stir casting method. The resulting MMCs were found to corrode in the presence of a acidic medium of normalities 1N, 2N, 3N solutions. The corrosion rate was found to decrease with long duration might be due to the formation of the strong oxide layer over the surface. The corrosion rate in the unreinforced Al7075 alloy was more compared to the nanocomposites prepared. When compared to the different weight percentage of MWCNTs 2wt% of MWCNTs suffered more corrosion loss with respect to 6wt% MWCNTs because the reinforcements retarded the Corrosion loss by forming a oxide layer. The SEM micrographs revealed the presence of the volcanic shape pits along the grain boundary of the reinforcements which gave rise to micro cracks. The SEM images showed the uniform distribution of the MWCNTs in the Al7075 matrix. The SEM images also showed the Corrosive surfaces for the periodic degradation of the specimens in the acidic medium. With the MWCNTs reinforcements into the Al7075 matrix the corrosion rate found to be decreased.

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