Electrochemical studies of Al 7075/zircon metal matrix composites in natural sea water

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Abstract

Metal matrix composites (MMCs) are engineering combinations of two or more materials of which the base material being a metal or its alloy, where tailored properties are achieved by systematic combination of different constituents. These are heterogeneous materials consisting of two or more phases which are in intimate contact with each other on a microscopic scale. These composite materials can be made by the dispersion of fibers, whiskers or particles as dispersoids in a metal matrix and exhibit combinations of properties which are difficult to achieve in monolithic materials. Out of the different forms of composite materials, particle reinforced composites are promising because of their isotropic properties and low cost. New aluminium based composites have been developed and they are being viewed as potential industrial products particularly in defense and automotive sectors. In particulate reinforced composites, investigations have been carried out with less expensive dispersoids to attain desirable thermal, mechanical and corrosion resistance properties to suit various applications, where cost effectiveness along with performance matters. These materials have a lot of potential to be used in marine, mining and mineral processing industries also, on account of their excellent characteristics like thermal conductivity, wear resistance and corrosion resistance. In order to use these materials in such industries, they are required to withstand high corrosive environments. Thus, there is a need to study the corrosion behaviors of AMCs reinforced with ceramic dispersoids. In order to extend the use of AMCs into other industries, it is also essential to investigate their corrosion behavior in different environments like acidic, basic, neutral and marine conditions. The present work has been carried out to evaluate the corrosion behavior of AMCs reinforced with ceramic dispersoids in various environments, since not much research work has

been done on AMCs; the present work was taken up. Stress corrosion studies were conducted by using natural sea water as a corrodent. Both composites and corresponding base alloys were subjected to identical test conditions to understand the influence of the reinforcement on alloy, corrosion behavior and effective corrosion control. Composites became less prone to corrosion and pit formation than that of matrix alloy, which may be due to inert zircon particles present in the metal matrix composites. Corrosion of alloys can be effectively controlled by converting them in to composites by the addition of inert materials like zircon particulates.

Key words: Composite, Stress corrosion, Zircon.

Introduction

Metal matrix composites (MMCs) are gaining considerable importance for their use in a variety of structural applications, which can cover a wide range, starting from components in high temperature gas turbines to wear resistant parts of various complex designs[1]. These materials maintain good strength at high temperature, good structural rigidity, dimensional stability and light weight[2-5]. These properties of MMCs enhance their use in automobile engine parts such as drive shafts, cylinders, pistons and brake rotors, which work particularly at high temperature and pressure environments[6,7]. Ceramic particle reinforced Al matrix composites are emerging out as potential materials to replace conventional alloys/metals. MMCs used at high temperature should have good mechanical properties and resistance to chemical degradation in air and acidic environment. For high temperature applications, it is essential to have a thorough understanding of the corrosion behavior of the aluminum composites. Some authors[8,9] have pointed out that the addition of SiC, Albite particles does not give rise to significant corrosion on aluminum alloys. The

objective of the present work is to study stress corrosion property at high temperature using natural sea water as corrodant with varying normality's. High temperature and pressure method is an excellent test for stress corrosion, which reflects actual service conditions and hence used to evaluate corrosion behavior of materials[10]. The microstructure of the corroded surface was studied with SEM and EDAX tests to predict the formation of compounds of corroded surface of the specimen.

Materials and Methods

Material selection

The matrix selected is Al 7075, which exhibits excellent casting properties and reasonable strength. This alloy is best suited for mass production of lightweight metal castings. The chemical composition of the Al 7075 alloy is given in table 1.

Zircon ($ZrSiO_4$) is used for reinforcement in the form of particulates. Zircon is a very hard material, its hardness is 7.5 on Mohr's scale and specific gravity is 4.1. The principal structural unit of zircon is a chain of alternating

edge-sharing SiO_4 tetrahedron and ZrO_8 triangular decahedra. The composition of zircon is given in table 2.

Composite preparation :

The liquid-metallurgy Vortex method was employed to prepare the composites. The reinforcement material (Zircon) used is of size 40-50mm. The composites containing 2, 4 and 6 weight percentage of Zircon were prepared. The matrix alloy was also cast under identical processing condition for comparison. The uncoated but preheated zircon was added into the molten Al 7075 alloy melt by creating a vortex using a stirrer. The composite melt was thoroughly stirred and subsequently degassed and poured into preheated split-type permanent moulds[11]. Samples for microscopic examinations were prepared by standard metallographic procedures, etched with Keller's agent and examined under optical microscope.

Specimen preparation :

Three-point loaded specimens, typically flat strips of 8mm thickness, 40mm wide and 150 mm long specimens were prepared from the composite and the matrix alloy for the stress corrosion testing. Before testing, the specimen surfaces were ground with silicon carbide paper of 1000grit and then polished in steps of 15 to 3 μm diamond paste to obtain a fine surface finish. After subsequent rinsing with water and acetone, the specimens were weighed precisely to a four-decimal place using electronic balance.

Corrosion studies :

Autoclaves are often used for testing at high temperature and pressure. The Teflon coating protects the autoclave from severe aggressive environments. Fig. 1 shows a bracket used to load corrosion specimen placed in the autoclave. The specimen was supported at both ends and bending stress was applied using a screw equipped with a ball to bear against specimen at a point mid way between the end supports. A prototype specimen mounted with strain gauges was used for calibration. The prototype specimens of the same dimensions were used as test specimens and were stressed to the mid length of the specimen, decreases linearly to zero at the ends. The specimens were subjected to one third of matrix alloy's ultimate tensile strength.

For each test, two liters of natural sea water was used as corredent. An autoclave test was conducted by filling test liquids (Corrodent), loading the test specimens. After loading the specimen autoclave was canceled and heated to test temperature with increase in inside pressure. Tests were conducted for different percentage of composite specimens, with different temperatures different normality and corroded for various duration of 10, 20, 30, 40, 50 and 60 min respectively.

After each corrosion test, the specimen was immersed in Clark's solution for 10 minutes and gently cleaned with a soft brush to remove adhered scales. After drying thoroughly, the specimens were weighed again. Weight loss was calculated and converted into corrosion rate expressed in mils per year (mpy)[12]. The corroded surface microstructure was studied with SEM and EDAX being used to establish the chemical composition of salient micro structural features.

Results and Discussion

The stress corrosion rates of Al 7075 and its MMCs in sea water for 30 minutes exposure time at different temperatures increased with increasing temperature as shown in the figure 2. This effect was attributed to the increased diffusion rate of hydrogen with increase in temperature. Hydrogen has been found to evolve even when aluminium exposed to boiling water[13]. The hydrogen generation and entry is probably a localized action other than a general surface phenomenon. Hydrogen permeation is related to the kinetics and mechanism of hydrogen generation on the external surface of the sample. Aluminium dissolves in corrodent solution with generation of H_2.

The effect of temperature on the value of corrosion rate depends on two factors: the energy of activation of hydrogen ions and the temperature variation of the hydrogen gradient. Activation energy of acid solution depends on the temperature[14,15]. Corrosion rate increases with activation energy because of the increase in both permeation rate and hydrogen evaluation. The inhibition efficiency increased with rising temperatures. According to the experimental results, rate increases more rapidly than reactions occurred at lower temperature of both matrix alloy and composites.

Figure 3 shows stress corrosion rate V/S exposure time of Al 7075 and Al 7075/Zircon MMCs at 100 °C in sea water. The corrosion rates of both matrix alloy and composites increases with increase in the exposure time. From literature survey[11,16,17] on static corrosion, the composites as well as for the unreinforced

matrix alloy, the corrosion rate seems to decrease with duration of the test. The phenomenon of gradually decreasing corrosion rate is probably due to their respective hydroxide layer. But in this study the aluminium hydroxide layer did not take any major role on corrosion rate with respect to time. Whereas the corrosion rate increased with increase in exposure time, which may be due to the cracking of hydroxide film formed between the metal and acidic medium upon application of stress. With increase in time the thickness of the $Al(OH)_3$ layer increased which is prone to cracking. Hence the corrosion rate increases with exposure time.

Corrosion Morphology :

Visual examination of specimens after the stress corrosion experiments showed a few deep pits, flakes and cracks formed on the unreinforced matrix alloy and the cracks were perpendicular to axis of the specimen. Whereas more widespread superficial pitting was observed and few or no cracks were seen on the surface of the reinforced composites. However few cracks were observed in 2% zircon reinforced Al 7075 MMCs and no Cracks were observed in 4% and 6% zircon reinforced MMC specimens.

The corroded surface morphology of Al 7075 alloy and Al 7075/zircon MMCs were exposed at 100 °C temperature and exposure time of 30 min is shown in figures 4, 5 and 6. In Al 7075/zircon MMCs, pitting is dependent on the local zircon distribution as well as the integrity of the surface film. Larger weight % of zircon could result in more opportunities for film disruption and more sites for pit initiation. Although they found that the pits in the reinforced system were smaller and more numerous than

in the unreinforced matrix, pitting was initiated at random sites on the surface of the Al 7075 alloy where imperfections in the protective oxide occur whereas pitting in the Al 7075/ zircon composite is associated with particle matrix interface because of the higher magnesium concentration[18].

The SEM micrographs of the typical corroded surfaces of the 0% and 6% zircon reinforced composite specimens are presented in figures, which show the corroded surface morphology of the tested specimens. It was observed that in zircon reinforced aluminium composites, pitting depends on the film distribution of zircon. The larger weight percentages of zircon could result in more opportunities for film disruption and more sites for pit initiation. The composites show the formation of pits on the surfaces, which is more with an increase in the % of zircon composites. The SEM micrograph of the matrix alloy and 6% zircon reinforced composites shows the evidence of more pit formation on the surface than that of the matrix alloy although they found that the pits in the reinforced system were smaller and more numerous than in the unreinforced matrix[19].

The corrosive attack was extensive with deep pits on the surface of the unreinforced matrix alloy extending and connecting in such a way so as to cause cracking. Cracks can be seen originating from the deep pits and traversing on to the surface. However no definite crack path can be clearly visualized. These connected cracks cause progressive removal of structure on the surface commonly called as flaking. SEMs of the flakes that were formed from the corroded sample and as well as the flakes still remaining on the sample were taken.

The chemical composition of micro-particles in thick corrosive product layer was determined by EDXA analysis as shown in figure 7. Spectra were obtained similar for all specimens with the exception that Al 7075/ Zircon spectra show strong aluminium and silica peaks, a consequence of the presence of zircon and the limitations in isolation of sampling volumes. It also shows some traces of magnesium.

The zircon particles are inert and are not expected to affect the corrosion mechanism of composite. The corrosion results indicate an improvement in corrosion resistance as the percentage of zircon particle increased in the composite. Which shows that the zircon particles directly or indirectly influence the corrosion property of the composites. Pruthviraj et al.[8] who obtained similar results in SiC reinforced ZA- 27 alloy composites reported that the corrosion resistance increases with increase in reinforcement. Sharma et al.[17] also reported similar results with glass short fiber reinforced ZA- 27 alloy.

Wu. Jianxin et al.[20] in their work on corrosion of aluminium based particle reinforced MMCs state that the corrosion is not affected to a significant extent by the presence of SiC particles in aluminium, whereas the particles definitely play a secondary role as a physical barrier as far as MMC corrosion characteristics are concerned. A particle acts as a relatively inert physical barrier to the initiation and development of a corrosion pits and also modifies the microstructure of the matrix material and hence reduces the rate of corrosion. Rodriguez[21] in his work quotes that the interface between the base matrix and the reinforcement is the

Table 1. Composition of Al 7075

Element	Mg	Si	Fe	Cu	Zn	Cr	Mn	Ti	Pb	Sn	Ni	Al
Weight (%)	1.0	0.6	0.5	0.25	0.2	0.15	0.15	0.1	0.05	0.05	0.05	Balance

Table 2. Composition of Zircon

Silica	32.8
Zirconica	67.2
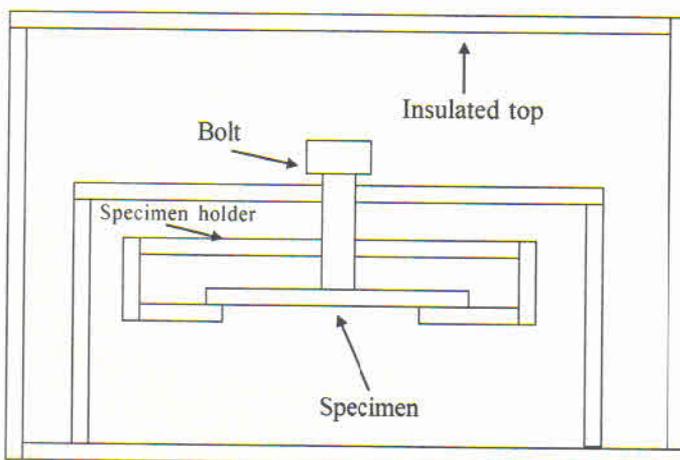
Figure 1. Autoclave
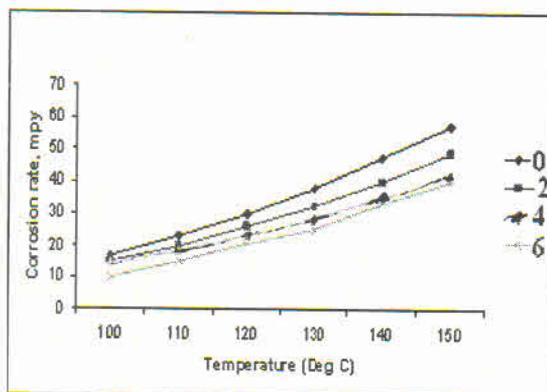
Figure 2. Stress corrosion rate V/S Temperature in sea water for 30 minutes exposure time
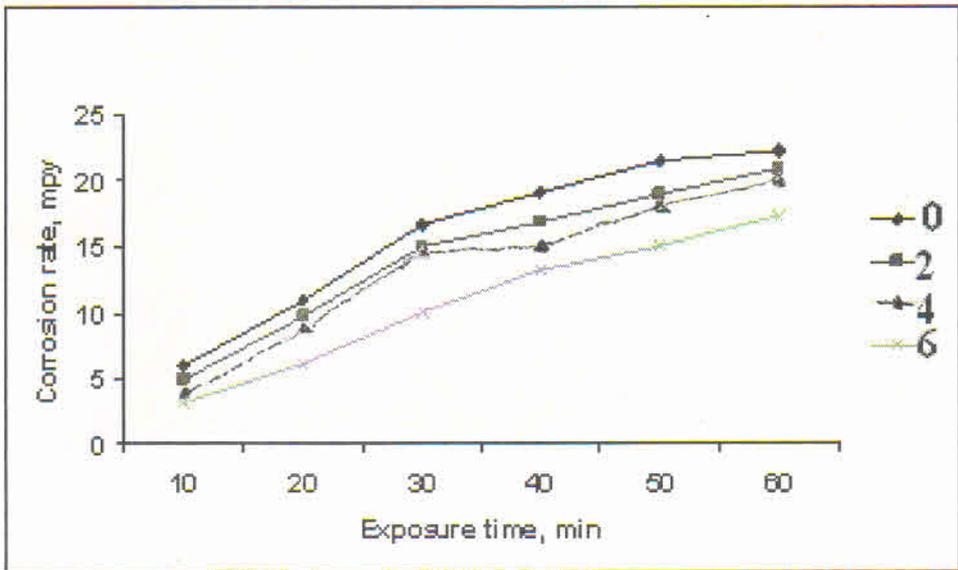
Figure 3. Stress corrosion rate V/S Exposure time in sea water at 100 ^{0}C
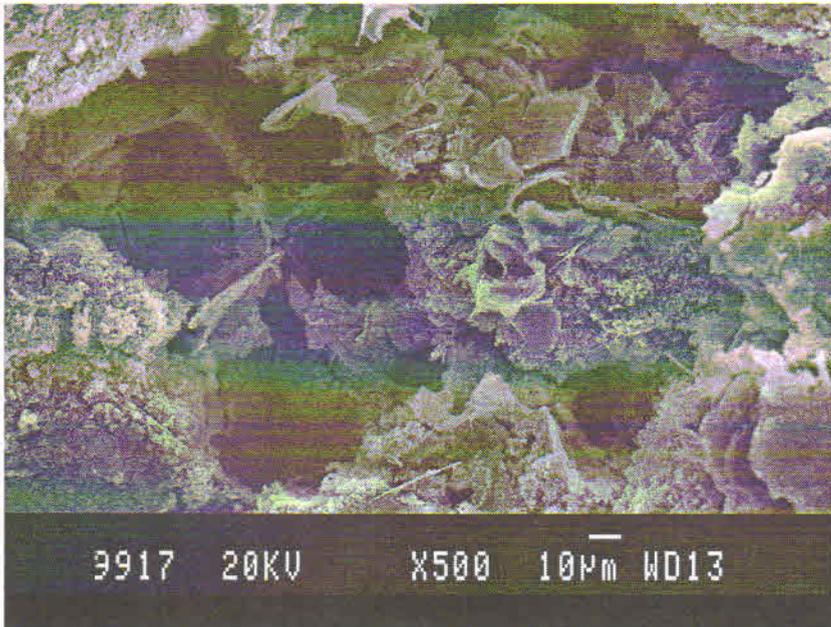

Figure 4. Microstructure of unreinforced Al 7075 alloy in sea water at 100°C and 30 minutes exposure time
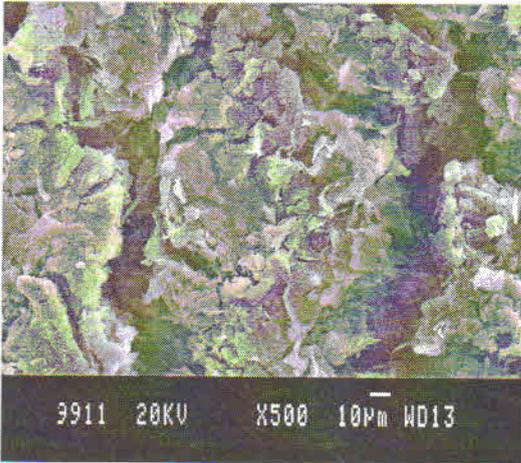
Figure 5. Microstructure of Al 7075/2% Zircon reinforced composite in sea water at 100°C and 30 minutes exposure time


Figure 6. Microstructure of Al 7075/6% Zircon reinforced composite in sea water at 100°C and 30 minutes exposure time
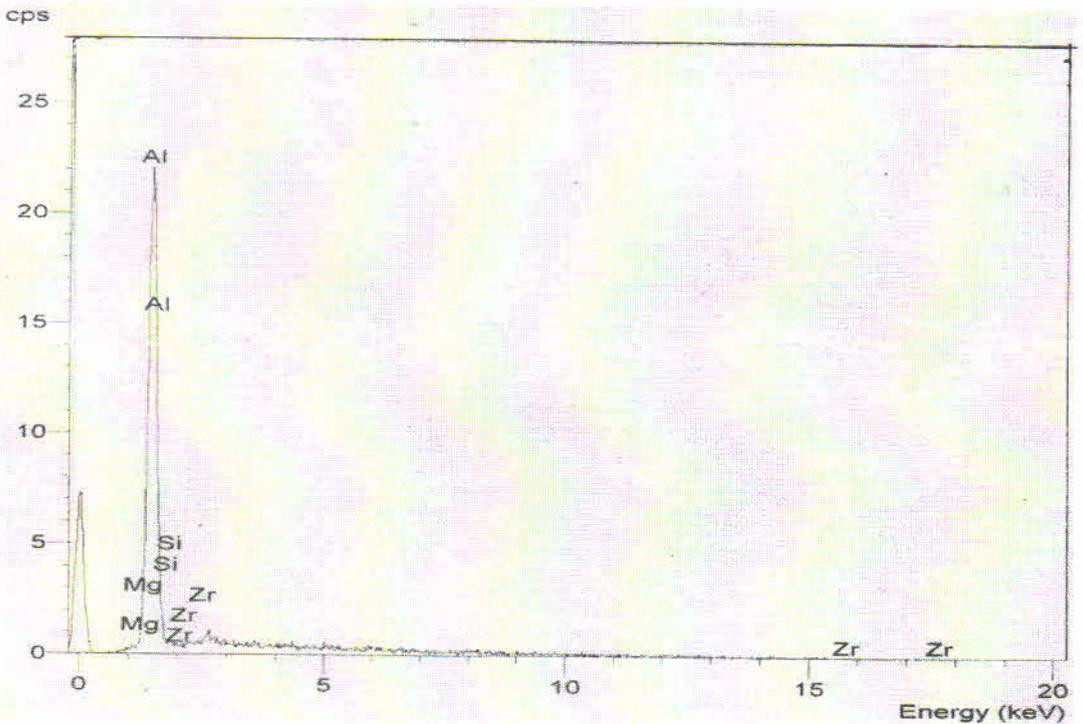

Figure 7. EDAX spectra of Al 7075/6% Zircon reinforced MMC

weakest part of particle or fiber reinforced composites. Hence the nature of the bond, whether weak or strong, is critical in the corrosion process. Since the composites developed show improved mechanical properties, it can be claimed that the interface between the aluminium and the reinforced zircon particle is quite strong[22]. this could have influenced the improvement in the corrosion resistance of these composites. To support this it was observed that when the zircon particle content is increased, there is a reduction in corrosion[23].

One more reason for decrease in the corrosion rate is the inter metallic region, which is the site of corrosion forming crevice around each particle. Which may be due formation of magnesium inter metallic layer adjacent to the particle during manufacture as discussed by Trzaskoma[19]. Which is evident from the EDXA results. McIntyre et al.[24] further showed that the magnesium inter metallic compounds are more active than the alloy matrix. Pitting in the composites is associated with the particle matrix interface, because of the higher magnesium concentration in this region. With increase in time pitting would continue to occur at random sites on the particle matrix interface. The active nature of the crevices would cathodically protect the remainder of the matrix and restrict pit formation and propagation.

Conclusion

The average corrosion rate increases as a function of solution temperature. Zircon is a ceramic material and hence is not involved in galvanic effect with matrix alloy. However, crevice corrosion can be observed at the zircon /

Al interface, probably because of magnesium arising at interface. Normality of solution plays a significant role in the corrosion of given MMCs. The increase in hydrogen reduction results in a higher corrosion rate. Time dependent and temperature dependent constant does not depend on the reinforcement. However the activation energy constant is decreased with increasing reinforcement of the composites. The extent of corrosion damage was reduced with increasing reinforcement which may be due to increase in the tensile strength as well as bonding strength of the MMCs. Material loss from corrosion was significantly higher in the case of matrix alloy than in the MMCs.

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