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**CORROSION STUDIES OF Al 7075 ALLOY REINFORCED WITH
ZIRCON METAL MATRIX COMPOSITES.**

**THESIS SUBMITTED TO DRAVIDIAN UNIVERSITY IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHYLLOSOPHY IN CHEMISTRY.**

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2012



DECLARATION

I, **G. BANU PRAKASH** hereby state that the thesis entitled “*Corrosion studies of Al 7075 alloy reinforced with zircon, metal matrix composites*” submitted to Dravidian University, is a partial fulfillment of the requirements for the award of the Doctor of Philosophy in Chemistry is my original work under the supervision and guidance of **Dr. H.G. BHEEMANNA**, Head, Department of Chemistry, Vivekananda Institute of Technology, Bangalore. It has not previously formed the basis for the award of any degree, diploma, associateship, fellowship or other similar title.

G. BANU PRAKASH

CERTIFICATE

This is to certify that the thesis entitled “*Corrosion studies of Al 7075 alloy reinforced with zircon, metal matrix composites*” submitted by **G. BANU PRAKASH** for the award of Doctor of Philosophy is a record of research work done under my guidance and supervision and the thesis has not formed the basis for the award to the scholar for any Degree, Diploma, Associateship, Fellowship or any other similar title and I also certify that the thesis represents an independent work on the part of the candidate.

Dr. H. G. BHEEMANNA

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Chapter – 1

Introduction:-

1.1 General introduction:

In the early stage of human civilization, man functioned like a biochemical machine deriving energy from the solar power through electrochemical reactions. Later, machines were fabricated to suit the needs of man and became a part of everyday life. A major obstacle, however, was noticed very soon – the machines started rusting. The study of rusting began with the realization that it affected the performance of machines and destroyed the metal fabrications. Measures were introduced to prevent the rusting process which initially involved coating of the metal surface with coal tar paints followed by galvanizing, tinning and electroplating.

Materials play vital role in the advancement of science and technology. When materials are fabricated into equipment's, it is not enough if we concentrate on the properties of the materials only. The study of its environment is also necessary for, the environment may be hostile to the materials in use. This attack of the environment can take place in different forms.

The process of degradation of materials is denoted as corrosion. During corrosion, metal will be converted into its compound i.e., the metal is oxidized. The process of oxidation of a metal is corrosion. Main nature of corrosions product depends only on nature of the environment¹.

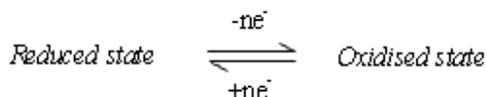
Word corrosion has its origin in the Latin word “corrodere” meaning “to eat away”. Corrosion is defined as deterioration or destruction of a metal as an outcome of chemical or electrochemical process amongst the metal outward and the environment.

Selection of material depends on many factors, including its corrosion behavior. Although we are primarily concerned with the corrosion resistance of materials, the final choice frequently depends on the factors other than corrosion resistance. Fabricability, which contains the affluence of making, welding and additional mechanical processes, must also be considered. In engineering applications, metals require high chemical resistance. The mechanical strength is also important even though the materials is being selected for its corrosion resistance. Finally, for highly resistant materials such as gold, platinum and some of the super-alloys, the availability of these materials frequently plays a deciding factor in whether or not they will be used. In many instances the delivery time for some of the exotic metals and alloys is prohibitive².

Corrosion once was thought of as a problem concerned with metallurgists and chemists. It is now a field of interdisciplinary study as metals is universal in their use. There cannot be any field of material use which does not use metals. May it be a small metal object like pin or a huge metallic structure like bridge or offshore structure, corrosion impairs their proper function and use. Therefore, corrosion has been correctly referred to as “Cancer” to metals.

1.2 Electrochemistry of corrosion:

Electrochemical reactions involve always the transfer of one or more electrons from one of the reaction partners to the other one. They involve two partial reactions-oxidation and reduction. Oxidation is the process through which an atom or a molecule loses electrons; reduction is the process of gaining electrons. A neutral atom or molecule is often attributed an oxidation number of zero. Gaining of one electron diminishes the oxidation number by one, while losing one electron enlarges it by one.



Thus in an electrochemical process the net chemical reaction takes place by the transfer of electrons³.

1.3 Thermodynamic aspects of corrosion:

The transformation in free energy associated with the change of a structure from one state to alternative state is negative and reaction is spontaneous. The free energy transformation associated an electro-chemical response can be calculated by the following equation.

$$\Delta G = -n F E$$

where n = Electrons number, F = Constant of Faraday, E = Potential of the Cell and ΔG = free energy change. Majority of metals occur in the nature in combined states. Pure metals are obtained from ores at the expense of large amount of energy. Therefore thermodynamically, return of the metal to the combined state by corrosion can be a spontaneous process. The possibility of corrosion is indicated by the negative free energy change, ΔG , of the process.

1.4 Kinetics of corrosion:

Rusting structures are not at equilibrium and therefore thermodynamic calculations cannot be functional. When metal deterioration occurs current flows between anode and cathode of the short-circuited corrosion cell. The extent of corrosion depends on the quantity of current that flows in the cell. Two important parameters, the potential of corrosion (V_{mp}) and current of corrosion (I_{corr}), are used to understanding essential features of the electrochemical corrosion of metals. An equation relating these two parameters are of good help to study the corrosion process.

Electrode reactions can be reversible as well as irreversible. Considering the electrode reactions under reversible and irreversible conditions of a reaction, Butler and Volmer derived an equation relating potential and current, for electrochemical charge transfer reactions at an electrified interface. During corrosion, the current that flows between anode and cathode results in the change of corrosion potential and corrosion current, i.e., causes "polarization". Based on these facts Horiuti and Polanyi developed a model for corrosion process.

1.5 Mechanism of corrosion:

In 1958 the potential energy of various states of metal in solution, on the surface at the edge and at the kink site, are discussed by Bockris and Conway⁴. According to them for some metal at low current density, there is a stage in which diffusion occurs across the surface from the kink site to a dissolution site and it is the rate determining step in the metal dissolution i.e., metal corrosion. At high overpotential the electron transfer from the adion on the planar site to the metal is the rate determining step in dissolution.

These concepts which have received multiple supports in the literature have felt the contribution of Harrison Thrisk who suggested that the rate determining step in metal dissolution arise from the hemispherical diffusion to the edges rather than across the surface of the metal⁵.

The mechanism postulated for the hydrogen evolution and oxygen reduction reactions on some of the metals are given below.

Hydrogen evolution reaction:

In the acid solution, the cathodic reaction is,



and in the alkaline solution it is,



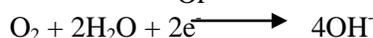
These reactions take place through discharging of H^+ ion or water to give M-H, where H is adsorbed on M.

Oxygen reduction reaction:

The cathodic reaction in neutral and alkaline solutions, without evolving H_2 is often the reduction of oxygen.



Or



1.6 Classification of corrosion:

A distinction is made between chemical, biochemical and electrochemical corrosion of metals. The destruction of metals by the aggressive medium and subsequent dissolution of metals in contact with non-conducting organic media belongs to chemical corrosion. Earths of particular composition, stationary water and biological products significantly favor's the progress of biochemical corrosion.

The Electrochemical corrosion is encountered more frequently than the other forms of corrosion and it is the most dangerous form of corrosion. It may also occur in solid, liquid and gaseous atmosphere when moisture condenses on the metal surface⁶.

Depending upon the environment corrosion may be classified as;

Dry corrosion:

The metal is directly attacked by a gas or even oxygen in the air at ambient room temperature. The entire metal surface is uniformly covered with the corrosion product. This is a simple chemical process.

Wet corrosion:

Presence of acidic oxide gases in moist atmosphere, continuous contact with water or sea water, constant tensile stress coupled with corroding environment, all these impose on the natural tendency of the metal to undergo oxidation or corrosion. This is an electrochemical process⁷.

Most common types of corrosion are

1.6.1 Galvanic corrosion:

As soon as a two dissimilar metals are in close interaction with each other and are also in contact with water/moisture, a galvanic cell will operate at the junction, due to the difference in the E° values of the two metals. The metal with a lower reduction potential acts as the anode and undergoes oxidation or corrosion. The other metal with higher reduction potential acts as the cathode.

1.6.2 Crevice corrosion:

When a metal is in contact with the same or dissimilar metal or non-metallic material like rubber, crevices or cracks would develop. In presence of an aqueous solution, crevice acts as an anodic region as the supply of oxygen to this area is rather low. Hence, severe localized corrosion takes place at this site.

1.6.3 Pitting corrosion:

This is the utmost similar and dangerous method of corrosion attack and is extremely localized in nature, in which appreciable penetration into the metal occurs, either due to chemical or galvanic action in the arrangement of holes and pits on the external part. The pitting may occur in any metal system, but is mostly observed in aluminium and magnesium alloys.

1.6.4 Intergranular corrosion:

It is an attack along the grain boundaries of a metal or alloy, due to the preferential dissolution of the grain boundaries, phases or zones immediately adjacent to them with a slight or negligible effect on the main body of the grain.

1.6.5 Stress corrosion:

It is a premature failure due to cracking of metals resulting from the simultaneous action of applied tensile or residual stress and chemical action by a corrosive environment. The fractured surface of a wrought aluminium-zinc alloy extrusion exhibits this form of corrosion.

1.6.6 Fretting corrosion:

It is a form of wear or destruction happening at the boundary of two communicating outer parts, when subjected to oscillatory motion involving relative displacements or slip of small magnitude. This happens when particles of corrosion by products constantly scratch away the passivating film as two metal outer parts are wiped each other.

1.6.7 Microbial corrosion:

It is defined as the corrosion affected by the metabolic accomplishment of several microorganisms like bacteria or fungi. The microorganisms can develop and propagate in an environment in the attendance of oxygen, sometimes in the absence of oxygen also⁸.

1.7 Factors affecting corrosion:

There are several parameters which affect corrosion rate and are classified as main features (associated to the metal) and subordinate feature (associated to the atmosphere)⁹. These features are commonly symbiotic and therefore a firm organization is impossible.

Primary factors:

1.7.1 Nature of the metal:

The affinity of a metal to corrode in aqueous solution can be predicted from its effective electrode potential, which is mutable, subject to further circumstances such as concentration, temperature and pressure. Each metal has its own characteristic potential at a given metal ion concentration. Based on the values “electrochemical series” was developed which provides information about the thermodynamic stability of the metal. The metal with more positive potentials is unstable. Thus the study of the relative electrode potentials in the given environment serves as an alternative method of describing the tendencies of metals to corrode.

In the cases where hydrogen evolution is the cathodic reaction, hydrogen overpotential is also an important factor of corrosion. In a given environmental conditions of temperature, pressure and flow rate of the medium, each metal exhibits its own characteristic resistance (hydrogen overpotential) to the hydrogen evolution reaction, the magnitude of which be contingent on the nature and conditions of the metal surface. A low overpotential facilitates corrosion rate and hence any factor, which increases the hydrogen overpotential, will considerably retard the corrosion rate. Thus in the case of alloys, other components added in micro quantities will alter the hydrogen overpotential which finally affect the corrosion process.

1.7.2 Surface state of the metal:

The term 'surface state' defines all the characteristics of the surface, important among them being physical and chemical characteristics. No solid surface is smooth and uniform on an atomic scale and a real solid surface is liable to contain various types of imperfections such as cleavage steps, dislocations, point defects etc., which will render it heterogeneous. The frequency of corrosion is mainly reliant on the degree of heterogeneity. It is witnessed that an extremely polished surface displays early corrosion opposition which is considerable rough surface of the same metal. Thus the surface heterogeneity of a metal or an alloy is a factor that influences corrosion.

1.7.3 Characteristic propensity of metals to form shielding films:

The oxide or other film made by the response with the ingredients existing in the atmosphere inclines to passivate the metal and alloys. Passivity is the things essential the convenient natural corrosion resistance of numerous operational metals, including aluminium, nickel and steel. The protective ability is due to the formation of impervious visible or invisible film on the surface. The defensive film designed on the outer part progresses a physical obstruction, which essentially isolates the metal outer part from the corrosive atmosphere.

Secondary factors:

1.7.4 The pH of corrosive medium:

During electrochemical corrosion, the cathodic reaction is commonly both hydrogen development or oxygen reduction: one being predominant over the other depending on the pH of the environment and the nature of the metal. For reactive metals like zinc, iron, magnesium etc., the hydrogen evolution is thermodynamically favoured cathodic reaction. Therefore, corrosion of such metals in acidic solutions is highly pH dependent. Obviously lowering of pH facilitates the rate of hydrogen evolution and hence increases the corrosion rate. In some cases the corrosion rate is organized by the formation of protective film and affect the corrosion process. Thus the corrosion individualities of metals are so delicate to the pH of the atmosphere, thus exhibits activity, immunity and passivity.

1.7.4 Influence of oxygen:

Dissolved oxygen in the medium plays an important role when corrosion involves its reduction as the cathodic reaction. In many cases, irrespective of the pH of the solution, the hydrogen evolution is not feasible, but corrosion occurs at relatively slow rate involving oxygen depolarization. Differential aeration or oxygen concentration cell is formed on the metal surface which is exposed partially to the environment. Oxygen rich area becomes cathodic whereas oxygen deficient area becomes anodic. The metal gets dissolved and the electrons generated on the anode is neutralized by the oxygen and converting into oxide ion. This process will continue as long as corrosion rate depends on oxygen concentration. In more or less cases metal oxide performances as a passive layer concerning metal and atmosphere.

1.7.5 Effect of ions present in the solution:

The presence of other ions usually Fe^{3+} , Cl^- , NO_3^- , SO_4^{2-} etc., in certain concentrations, affect the rate of corrosion process. For instance chloride ions interfere with the formation of protective film on the metals such as iron, aluminium and copper and can cause extensive damage. Because of the specific activity of chloride ions, it is difficult and sometimes becomes impossible to passivate iron if the medium contains chloride ions. The same properties with less rigorousness were also detected in the existence of sulphate ions. Some times in the case of corrosion of metals in nitric acid, the intermediate corrosion products become major in governing the rate of the development where chemical outcome will be appreciable.

1.7.6 Flow rate of the corrosive medium:

Flow rate of the corrosive medium affects the rate of the corrosion process by regulating the mass transfer of the corrosion products and oxygen in the medium. The increase in the rate of agitation

promotes corrosion of metals in aqueous medium. If the flow rate of the solution exceeds the critical value, i.e., turbulent flow is established, the specimen suffers impingement attack. Therefore the flow rate of the solution influences physical as well as chemical forces which are acting on the corroding surface.

1.7.7 Temperature of the system:

Increase in the temperature of the medium usually enhances the rate of corrosion process, particularly in the medium in which corrosion is escorted by the hydrogen development. But in circumstances where oxygen takes part in corrosion reactions the result of temperature becomes additional complex due to its effect on the solubility of oxygen. Existence of thermal gradient in electrolytic solution near laboratory temperature leads to the metallic corrosion by local cell formation, i.e., the part of the material at high temperature acts as anode and other at relatively low temperature acts as cathode.

Thus the main effects of increase in temperature are:

- Increase in the chemical reactions,
- Decrease in the solubility of gases in the solution,
- Change in the nature of the corrosion products and
- Decrease in the viscosity and increase in the circulation of solution

1.8 Expression of Corrosion rate:

Kinetics of corrosion gives the rate of corrosion in terms of current which is flowing during the corrosion process. The magnitude of I_{corr} is expressed in a variety of ways. The following are the commonly used units for corrosion rate.

- i) ipy = inches per year
- ii) mpy = miles per year
- iii) ipmo = inches per month
- iv) mdd = milligrams per square decimeter per day

The unit mpy is the popularly used unit for the corrosion speed despite the increased usage of metric units in the current decade. The corrosion speed in mils ($1 \text{ mil} = 0.001^{\text{in}}$) diffusion per year (mpy) could be calculated by using the below relation

$$\text{mpy} = 534W/\text{DAT}$$

Where, W is mass loss in mg, D is density in g/cc, A is area in square inch, and T is time in hour. Units of diffusion per unit time are greatest necessary from an technical stand point, whereas mass loss at particular area at particular time is in corrosion research area.

Metric units of penetration rates will probably see further use as future generations of engineers become more familiar with metric units and use them more frequently in design specifications. The most promising unit appears to be mm/yr and $\mu\text{m}/\text{yr}$ for great and small corrosion changes, respectively. The proportionality constant, 534, in above equation differs conditional on the units mandatory for corrosion rate and used for the limitations in the equation.

$$\mu\text{m}/\text{yr} = 87600W/\text{DAT}$$

$$\text{mm}/\text{yr} = 87.6W/\text{DAT}$$

where area A, is measured in square cms.

1.9 The significance and economic overtones of corrosion:

Metallic corrosion is a global calamity of major importance and costs several million dollars every year. Studies claim that the cost of corrosion is 6 % of a country's gross domestic product (GDP). It

has been assessed that the money spent in controlling corrosion is of the order of Rs. 50 crores in India, Rs. 250 crores in UK, Rs. 200 crores in Australia and Rs. 400 crores in USA each year. But our country due to its tropical environment the corrosion difficulty is extra problem than in the colder countries¹⁰.

The corrosion is a slow development enchanting place mainly on the metal surfaces, but the losses incurred due to corrosion are of high order. The losses cannot be estimated by considering only the metal loss. The indirect losses are much higher. The fabrication cost and the cost incurred in preventing the corrosion are also have to be taken into consideration. The corrosion in metal substances such as structural instruments and chemical plants etc., may brand them unproductive, useless, hopeless and their unnoticed deficiencies owing to corrosion might affect their failure. In such cases, the indirect loss may be much higher than the direct loss. When a structure like building or bridge collapses due to corrosion problems the loss also includes the loss of human life and properties, and the cost of subsequent repair and alternate arrangement. In some forms of corrosion, the corrosion is quite invisible and seen only when an accident takes place¹¹. Atmospheric pollution, relative humidity, state of exposure and composition of material has been found to have great influence on corrosion rate.

The acute corrosion problem is being faced by India's growing navy and her sea going vessels, installations in sea, etc. Some economic consequences of corrosion are the following:

- Plant shutdown due to failure
- Replacement of corroded equipment
- Preventive maintenance such as painting
- Loss of efficiency
- Contamination or loss of the product e.g., from a corroded container
- Incompetence to use necessary materials
- Destruction of apparatus in which corrosion disaster happens

Quiet other significances are social; these can include the bellow concerns:

- The fire hazard or explosion or release of a toxic product or a collapse of construction because of a sudden failure
- Health, for example, corrosion byproducts of more or less metals for example copper and lead may pollute food and source of food poisoning, from pollution due to a corrosion product or due to an escaping chemical from corroded equipment
- Diminution of metals and the fuels used to produce
- Presence when corroded material is harm to the eye

In every such case, the causes of corrosion need to be found out and necessary preventive measures taken to arrest the process.

1.10 Corrosion control:

Corrosion of a metal is a natural spontaneous process, by which a metal is converted into a more stable compound. Therefore, corrosion control is more realistic than corrosion prevention. The corrosion types are so numerous, the mechanisms of corrosion are so different and conditions under which corrosion takes place are so varied that no single method can be used to control all possible corrosion cases. The choice of a rheostat method be contingent on factors such as the kind of the structure, the nature of prevailing corrosion, the residual stress in the fabricated articles, the nature of the environment and similar other factors. Some of the important methods commonly used in curtailing corrosion of metals are:

1.10.1 Selection and design of materials:

Corrosion can be controlled by selecting proper materials which resist the corrosive environment and designing them suitably during fabrication. Some practical considerations are given below:

- By avoiding the use of two dissimilar metals. If their use is unavoidable the position of the metals chosen shall be as close as possible in the galvanic series.
- To reduce the rate of corrosion, the anode material must have a high potential while the cathode should be small.
- An insulator should preferably be used at the contact point of two dissimilar metals. However, porous insulators such as asbestos, magnesia and wood should not be used since they absorb and hold liquids which act as electrolytic conductors.
- While joining metals care should be taken not to leave gaps between them. The gaps can be avoided by proper designing.
- Alloys and composites have better mechanical properties and fabricability. Therefore they can be used as best alternatives for metals.
- Stress corrosion may be avoided by annealing the equipment wherever possible.
- Proper designing of the equipment reduces the corrosion possibilities. Wherever possible, the equipment should be supported on legs instead of on large blocks to facilitate free circulation of air and prevent the formation of stagnant pool or damp areas. Similarly, sharp corners and recesses should be avoided.

1.10.2 Protective coatings:

Protective coating involves a change in the surface composition of the metallic component. It forms an outer layer on the material which provides obstruction amongst the base metal and the corrosive atmosphere. There are two categories of coatings: (A) Metallic coating and (B) non-metallic coating or organic coating or ceramic coatings.

(A) Metallic coating:

Metallic coatings are basically applied on metal surfaces to control corrosion, prevent structural damages and preserve their appearance. The selection of coating material depends upon the requirements. The effectiveness of metal coatings is governed to a great amount by the nature of coating given.

(B) Organic coating:

These coatings include organic films such as paints, varnish, lacquers, tar, bitumen, oils, grease and polymers. The protective film of the organic coating depends on

- the chemical inertness of the corrosive environment.
- Adhesion to the surface.
- The impermeability to the corrosive atmosphere and
- Mode of application.

1.10.3 Corrosion Inhibitors:

Inhibitors are the materials which slow down the rate and range of corrosion when it is additional to environment in traces. In the earlier times, products like flour, bran, yeast, etc., were added to the corrosive medium to retard the corrosion of metals during the pickling process. In 1920 onwards, a steady progress in the use of vegetable products, plant extracts and animal proteins as corrosion inhibitors were noticed. Hundreds of inorganic and organic chemicals have been studied and recommended as inhibitors of corrosion for various metals in different environments like aqueous, molten salt and dry atmospheres¹²⁻¹⁸.

The rehearsal of corrosion embarrassment is importantly predisposed by the new guidelines that have been established because of poisonousness and ecological effects subsequent from industrial effects. The inclination to substitute some extensively used inhibitors, which causes toxicity, environmental damage and pollution.

However, there is no unified theory to account for corrosion inhibition mechanism and the relation of inhibitor for a particular metal. Some attempts have been made to relate structure of the corrosion inhibitor with its inhibiting effects on the corrosion of metal. Based on the mode of collaboration amongst the inhibitors and metal outer parts, they are classified as:

A. Passivating inhibitors:

There are many long chain organic compounds and polymers which isolates the metal surface from the corroding solution by forming a film on the surface. Many inorganic salts such as chromates, nitrates, etc., inhibit corrosion by producing passive material on the metal surface which shows active - passive transition¹⁹.

B. Adsorption inhibitors:

Adsorption is the primary step in all inhibition processes. The adsorption of an inhibitor is a specific process and depends on many characteristic features of the metal surface and the adsorbent. The mechanism of embarrasment is attributed to the interaction of the inhibitor molecule with the metal outer part by adsorption process. The adsorption type inhibitors can be of anodic, cathodic and mixed type. These inhibitors do not significantly react with the metal surface but are adsorbed at the reaction sites and bring down the rate of appropriate electrochemical reactions. A study of Evans diagrams shows that the adsorption leads to shift of the corrosion potential or alter the Tafel slope of the electrochemical process.

C. Pickling inhibitors:

Furthermost pickling inhibitors purpose by creating an adsorbed layer on the metal outer part, which fundamentally blocks the liberation of H^+ ion and suspension of metal ions. Compounds helping as pickling inhibitors necessitate, by and large, a promising polar group or groups by which the molecule can attribute itself to the metal outer part.

D. Vapour-phase inhibitors:

These are the adsorption inhibitors type and possess a very high vapour pressure and the vapours of these compounds have corrosion inhibiting properties. Film creation on the metal outer part by these inhibitors delivers defense in contradiction of water or oxygen or both. Volatile nitrates, may source of definite quantity of NO_2^- , which passivates the outer part.

1.11 Composites – Materials of future:

The composite as its name recommends is finished by merging two or more different materials in such a way that the subsequent material is capable with possessions greater to any of its machineries. Endless appraisal of the developing tendencies and motivations to present novel materials to meet the necessities of numerous calculated applications has led to the improvement of functionally incline materials and composites. A composite material can also be designated as a combination of constituent materials deliberate to meet a exact engineering role by manipulating the anticipated properties of the components, while minimizing the damaging properties of the less anticipated properties²⁰.

But unlike an alloy or a chemically synthesized compound, the components of a composite neither takings part in a chemical reaction nor do they dissolve or totally combine with one another. However, they endure powerfully attached together while continuing the boundary amongst one another and act in performance to give abundant enhanced presentation. The main objective in developing composites is to provide performance characteristics and properties beyond the established properties of currently available materials²¹.

Composites are not new. Ever since it was recognized that combinations of different materials often resulted in superior products, materials have been combined to produce composites. Mud bricks reinforced with straw were known to have been made since hundreds of years, as were laminated woods.

The primary composite was probably born in scriptural times when man supplementary hacked straw to clay to create durable elements.

The trend continued unabated. As man's understanding of nature increased, and he dug deeper into the treasure that nature offered, a host of new materials became available to him. But with the inexorable march of civilization, man felt that more novel materials were required. The ever increasing and expanding requirements, man started constructing novel materials from a sensible mixture or management of the old. These alternatives to traditional materials have taken the industry by storm.

As the industrial revolution progressed in the 19th century, and encompassed every aspect of human life, an ever-increasing need was felt for materials which are robust in nature, and capable of resisting fatigue, environmental corrosion, pressure and exposure to chemicals. These materials had to be adaptable for use under extreme temperature variations. Newer and more versatile composite materials evolved as an answer to this need.

Their emergence has had a tremendous impact on several fields like transportation, marine engineering, chemical equipment, machinery, construction, electrical and electronic equipment, sports goods and medical engineering. The aerospace and defense industries have also been benefited greatly from the lightweight and hard composites.

1.12 Definition of composites:

In the world of material science, composites may be designated as comprising of at smallest two distinctly distinguishable components. In the widest intellect this may be taken to comprise even chemically or mechanically engineered products such as duplex segment alloys. Conversely, composites have been recognized as that domestic of materials subsequent from the strengthening of one constituent with another.

Composites are tailor made materials to suit particular requirements like reduction in density or improvement in ultimate tensile strength (UTS), yield strength, stiffness and wear resistance which can be interpreted to condensed mechanical weight²².

A composite can be defined as a macroscopic combination of two or more distinct materials, which are essentially insoluble in each other and having a recognizable interface between them²³.

The composite materials represent a giant step in the ever-constant endeavor of optimization in materials. Composites are materials based on the meticulous dissemination of one or additional materials, termed reinforcement, in a uninterrupted phase of a second material named as matrix.

In universal, a composite material is one in which a extraordinary strength or high modulus material called the corroboration is collective with a additional material called the matrix which authorizations of making into anticipated engineering configuration and handovers the loads on to the booming reinforcement.

1.13 Behavior of composites:

The composites comprise of matrix and reinforcement. The chief purpose of the matrix is to relocation and dispense the load to the reinforcements. The removal of load be contingent on the bonding interface between matrix and reinforcement. The properties of composites are powerfully subjective by the type and behaviour of the boundary that exists between the matrix and the reinforcement.

The load is shifted commencing by the matrix to the reinforcement by resources of shear forces substitute on their outer parts, their outer part area essentially be superior in next of kin to their cross sectional area.

The composite materials can be complete by scattering of particles, whiskers and fibers as dispersions in a metal matrix and demonstration of mixture of properties that never be attained in uniform materials. Such a combination of dispersion and matrix is selected depending on property requirements for specific applications.

Composite materials exhibit properties like high specific strength, high specific stiffness, damping properties, wear and seizure resistance²⁴, improved high temperature performance²⁵, improved corrosion resistance etc. The strength and stiffness of a composite material remain very much a function of the reinforcing material, with the synergy existing between the reinforcement and the geometry of the reinforcement.

The outstanding physical properties of these materials composed with mass equivalent which creates them actual striking for a diversity of engineering uses in the sports goods, automobile and aircraft manufacturing and also in the structural unit²⁶.

In choosing a matrix four factors are measured

- Matrix essentially consists of physical property proportionate to the reinforcement will not communicate stresses professionally to the reinforcement.
- Matrix commitment i.e., humidity, temperature, acquaintance to other types of radiations, disclosure to chemical environment.
- Matrix necessity is easily used in the fabrication.
- The cost of the resultant composite must be justifiable.

1.14 Types of composites:

Depending on the microstructure of the composite material, they can be classified into three major types.

1.14.1 Fiber reinforced composites:

These are the most important and widely used lightweight composites as they have high UTS and great modulus. The matrix transmits the load to the fibers. Load transfer occurs from the filament by shear stresses at the fiber matrix interface.

The important factors that contribute to the performance of the fiber matrix composites are the orientation, length, shape and composition of the fiber, the mechanical property of the matrix and the integrity of the bond between the fiber and matrix²⁷. Both organic and inorganic fibers are used.

1.14.2 Dispersion strengthened composites:

In this case, fine second phase particles which are used could be metallic, inter-metallic or non-metallic but matrix is the load bearing constituent. Work hardening of the matrix is most important establishment appliance. Dispersion of particles contribute strength by impeding the dislocation movement. They also possess improved high temperature strength and creep resistance.

1.15 Metal matrix composites (MMC's):

MMC's have a matrix alloy containing reinforcements including particle (solid and hollow particles), whisker and short or continuous fibers as reinforcements²⁸. Judicious selection of alloy and reinforcement facilitates tailoring the properties of MMC's with unique combination of properties not possible with individual components chosen for MMC's, including high temperature strength, toughness,

fatigue strength²⁹, thermal conductivity, thermal expansion, wear resistance³⁰, resistance to service environment and damping properties.

MMCs have a ductile matrix but brittle fibers. Continuous fibers bonded to matrix strongly are desired for maximum strength in a particular direction. The possible problems are due to thermal stresses consequently of enlargement discrepancy amongst fiber and matrix and the reactions at fiber/matrix interface during fabrication. Some of the properties recommended in a MMC to exhibit toughness are maximum inter-fiber spacing for a particular fiber volume fraction and fibers with a high in situ strength and low density of critical flaws. Variations in the alignments of fibers can make a considerable variation of the stress-strain behavior. It is due to this aspect that the thermal stresses reach critical levels in MMCs. Even a small variation in temperature can cause thermal stresses in the composite system that grows sufficiently to plastically deform the matrix.

Suppose the maximum cycling temperature exceeds the recrystallization temperature of the metallic matrix, the thermal cycling damage in MMCs generally gets reduced. In such a situation, the plastic deformation due to thermal stresses cause work hardening in the matrix. Research studies have attributed the increase in aging response of few metal matrices to high dislocation density which is the result of thermal discrepancy with reinforcement and matrix because of presence of interface of high diffusivity. The inclusion of fibers can cause variations in the properties of the matrix which has to be analysed to attain optimum properties in the composite.

The liquid flow becomes a problem due to high fiber volume fractions and the diffusion of semi solid metal may not be possible. In a fiber composite, the possibility of difference in the microstructure between the metallic matrix and that of the unreinforced metal has been accepted³¹.

Other advantages of MMCs include fatigue resistance and toughness. Studies have indicated that the reduction of cluster of reinforcement whiskers and the number and size of the inter metallic's resulted in enhanced fatigue life. Uniform distributions of dislocations in the metal matrix are caused due to cyclic loading. Fatigue failure is considerably influenced by the interfacial bond strength and variations in matrix and fiber lengths³¹.

1.16 Fabrication of MMCs:

A multiplicity of fabrication technique has progressed in recent years in an struggle to improve the structure and properties of MMC's³²⁻³⁴. Due to the choice of matrix and reinforcement material and of the categories of reinforcement, the fabrication techniques will be fluctuate substantially.

Aluminum alloys containing nonmetallic refractory particles such as alumina³⁵, talc, silica, silicon carbide³⁵, mica³⁶ and zircon³⁷ can be fabricated either by foundry technique or by powder metallurgy route. The conventional powder metallurgy route is not very attractive and viable, because of high investment costs involved in the development of infrastructure, such as high pressure equipment's for the compaction of powder mixtures into desirable forms and controlled atmosphere conditions required for subsequent sintering. In contrast, the liquid or fusion metallurgy technique, which is gaining importance because it is amenable to simple conventional foundry methods, is relatively simple, straight forward and inexpensive.

It is a more convenient and efficient method of introducing particles into the melt, prior to solidification. Because of several advantages over powder metallurgy method, it is preferred to the later technique. Several techniques of fabricating the composite by conventional foundry practices are available. A general outline of all these processes is as follows.

Aluminium alloy is melted and superheated up to 750⁰- 780⁰C. The metal is then degassed with nitrogen or hexachloro-ethane. The ceramic particles are then introduced into the melt at a melt temperature between 720⁰-730⁰C by any one of the methods described below. After uniform dispersion, the composite melt is cast into the required shape.

1.16.1 Injection method:

The main advantage in this process³⁸ is the dispersoid addition along with degassing of the melt. But due to longer injection time, it may result in nonhomogeneous distribution of the particles and also at times, the clogging of particles in the injection gun may also occur.

1.16.2 Pellet method:

This process³⁹ is well suited to disperse particles finer than 5 mm which otherwise is not possible by vortex method. A few drawbacks encountered in this process are

1. Non-uniform dispersion
2. Rejection of the particles to the melt surface

1.16.3 Pressure casting/Forging:

This improved method of producing particulate composites yields castings free of porosity and shrinkage. Here the melt is squeezed and cast into the final product in a suitable mould. Due to the application of pressure, the defects due to the entrapped gasses such as porosities and shrinkages are eliminated. Higher rates of cooling, facilitates in the uniform dispersion of particles.

1.16.4 Compo casting:

In this technique the fine ceramic particles are injected externally into a nondentrific and semi-solid slurry and the melt is stirred prior to casting. Addition of particles in a semi-solid slurry of high viscosity, eliminates most of agglomeration and rejection problems. Good bonding of the melt with the particles can be achieved by increased time of mixing. With this technique, it is possible to produce composites with 10-30 wt% of alumina, silicon carbide particles.

1.16.5 Vortex method or Liquid metallurgy technique:

In this method⁴⁰ the metal bath is stirred mechanically by an impeller blade rotating at an optimum speed of 1000 rpm. The desired amount of powder is added at the center of the deep vortex formed due to violent agitation of the melt. Stirring is continued for about 2 to 3 min to ensure proper alloying and dispersion. After dispersion, the impeller is pulled out and the melt is poured into various moulds. This method is more versatile and efficient than the previous techniques for the following reasons:

1. It can be easily adapted to any foundry.
2. It is more efficient in comparison with other methods in the aspects of retention and distribution of particles in the melt.
3. The particles in the size range of 50-250 μm can easily be distributed in the melt.
4. It is inexpensive

In spite of all the advantages mentioned above it suffers from certain drawbacks such as gas entrapment in the melt during stirring.

Chapter-2

Literature survey

2.1 State of the art in MMCs

Intensive research in metal matrix composites was started twenty five years ago in order to obtain materials for aerospace application having high strengths at elevated temperatures. These usually were carbon or ceramic reinforced ferrous and a few non-ferrous metals. Fiber reinforced metals too were used but long fibers such as boron fibers, though possessing requisite properties, made costs prohibitive for general applications.

Now, due to the feasibility of inexpensive particulate reinforced composites, the costs have come down within reach. This has also been made possible by the feasibility of using conventional casting processes to produce these composites.

In the area of applications, the first was by Toyota of Japan which introduced ceramic fiber reinforced squeeze cast aluminium piston for high speed diesel engines. There is considerable research activity for producing composite materials for automotive purpose likes pistons, connecting rods and other engine parts due to their durability, high temperature strength, low weight and low cost.

Thus low cost mass manufacturable metal matrix composites represent the biggest metal matrix composites activity in developing countries. The ingredients required for them are available and can also be easily imported into the developing countries and once usage is started composites such as aluminium-silicon carbide composite can save considerable amounts of energy and fuel which are in short supply in these countries. The search for antifriction materials in India, United States of America, Europe and Japan has thrown up aluminium-graphite composites from which pistons, cylinder linings and bearings can be made. These result in considerable reduction of wear and consumption of fuel. They can also replace the heavier and more expensive conventional bearings which rely on the presence of toxic lead in the matrix of copper and tin alloys. These can be replaced by graphite in place of lead, thus also reducing toxicity, weight and cost. The technology for preparation consists of stirring pretreated graphite particles in the melts of aluminium alloy and using conventional foundry equipment, followed by casting either in permanent moulds, die-casting or centrifugal casting most of which are available in the developing countries and thus can be productionized without much difficulty.

The need for housing, energy generation and transportation in the developing countries is driving the development of metal matrix composites into the developed world. There is also a great increase in the metal matrix composite research in the developing countries like China, India, Egypt and Argentina. These efforts recognize the fact that the ease of production, economical costs and the strength and durability of metal matrix composites make them the ideal raw material for low cost long lasting products.

Another problem promoting research in developing countries is the lack of reinforcements. Continuous fiber reinforcements are very expensive and hence are not viable. Thus there is an increase in the concentration on in-situ composites made by unidirectional solidification or powder extrusion where the reinforcements are produced in-situ during processing itself, thus eliminating the need for expensive, external reinforcements. Particle reinforced, on short fiber reinforced composites are inexpensive and have large scale application properties. For example, graphite being available in both mineral and manufactured form in most of the developing countries, graphite particle reinforced metal matrix composites should be given emphasis. Aluminium also being cheaply and readily available, the production can be set up easily. Also, attempts should be made to use the readily available mineral based fibers or naturally occurring aluminosilicate fibers or fibers readily made by melt spinning of oxides.

This learning experience will ready the developing world for entry into hi-performance continuous fiber composite research in the next few years.

The attractive physical and mechanical properties that can be obtained from MMCs such as high specific modulus, strength and thermal stability have been documented extensively⁴¹⁻⁴⁵.

The tendency is now in the direction of the harmless practice of the MMCs as components in the automobiles parts like piston, engine walls etc., for the most part at in height thermal environment and pressure atmosphere. Typical examples are piston, cylinder liner, brake caliper etc⁴⁶. Over the last two decades, MMCs are of particular interest and famous.

2.1.1 Aluminium and its properties

Aluminium is a versatile weight saving engineering metal having successfully demonstrated its potential for most high volume applications. The main advantage of aluminium alloys over ferrous alloys is their low specific weight. There is an increasing demand for lightweight materials in almost all the applications. Lightweight materials prove worth in increasing the fuel efficiency and also better maneuverability and comfort.

For aircraft and rocket parts, the gain in weight saving is enormous. Many developed countries like Germany, UK, USA and Japan have replaced many cast iron automobile components by aluminium alloys and composites.

2.1.2 Competitiveness of aluminium matrix composites (AMCs)

To select the best possible material for a given purpose among the large amount of existing engineering materials, a systematic procedure should be used⁴⁷. It is natural to divide material selection into several stages.

1. The general function of the component.
2. The suggested geometrical form: AMCs many times have low ductility. This indicates that they are notch sensitive, or sensitive to crack initiation.
3. Service temperature interval for the component: AMCs can in general be used at higher temperature than conventional aluminium alloys, because of their improved high temperature properties.
4. The environment the material will be exposed to: Such as chemical, radio active or biological: These environments to which AMCs can be exposed to are similar to those to which aluminium alloys can be exposed to.
5. AMCs have lower electrical and heat conductivities than aluminium and copper, but better conductivities than any other engineering materials.
6. AMCs can be high performance materials with high elastic modulus and strength compared to the aluminium alloys.
7. Design life of the component.
8. Objective function: i.e. the quantity which is to be optimized. This can be the performance at a given component cost.

AMCs can be created by varieties of process. The solidification processes (vortex method or stir casting) are stated to be the cheapest for manufacturing great size complicated shape casting⁴⁸⁻⁵⁰.

Studies have been carried out on characterization of composites in terms of abrasive and sliding wear, slurry wear, mechanical properties and corrosion resistance⁵¹⁻⁵⁶.

2.2 Corrosion of AMCs

It was recognized as early as 1912 that aluminium gets corroded by salt solutions and furthermore, that this corrosion was enhanced by impurities. Subsequent investigators^{57,58} have elaborated on this behaviour, and the general impression was developed that the chloride ion was unique in promoting the corrosion of aluminium⁵⁹⁻⁶¹.

Acceleration of corrosion by halide ions depends strongly on metallurgical, electrochemical and other parameters. Presence of chloride ion in solution can generate widespread confined outbreak by absorbing into the fragile outer surface of the oxide film formed on the outer part, in this manner establishing soluble complexes. This will be supplementary enhanced by numerous micro structural properties of the alloy^{62,63}.

It was observed that aluminum was corroded by organic acids. This was not a pitting type of attack, but the information gathered by such studies was useful in formulating a mechanism for localized attack.

Subsequent investigations of the corrosion of aluminum alloys by organic compounds⁶⁴⁻⁷¹ were numerous and can be related to localized corrosion through the relative tendencies of anions to form soluble complexes⁷².

The notable case that illustrated complex formation was the enhanced corrosion of aluminum in fluoride ion solution⁷³ in which the existence of aluminum fluoride complexes was well recognized.

It was evident that the most serious cases of aluminium corrosion, involved anions, such as the halides, but it was apparent that aluminium would not corrode in pure water or water relatively free of electrolytes⁷⁴⁻⁷⁵.

Basically, aluminium alloys owe their corrosion resistance by stability of oxide film designed on the outer part in normal environments. Essential role of the oxide film on aluminium was mentioned in 1920 and subsequent reports⁷⁶⁻⁷⁸ emphasized this feature of aluminium behavior. It was recognized that the oxide film could be produced by anodizing⁷⁹ as well as by exposure to air. This encouraged studies of the structure of the film as well as the corroding metal^{80,81} and attempts were made to correlate the structure with corrosion rates.

It is reported that⁸² the outer part of oxide film contains of Al_2O_3 , $\text{Al}(\text{OH})_3$ and $\text{AlO}(\text{OH})$, everywhere the corresponding aluminium cation is guaranteed to oxygen or oxygen-comprising class in varieties of energies.

The colloidal nature of the aluminium hydroxide reaction product and the relationship between this colloidal character and aluminium corrosion was recognized very early by Latvian workers⁸³. The approach of these researchers suggests that an application of the principles of colloid chemistry provides an alternative, useful contribution to reaching a more complete understanding of corrosion mechanisms.

The chemical reactions of aluminium are infrequent in intellect the aluminium is amphoteric, i.e., soluble in acid solutions and alkali^{84, 85}. This fact bears heavily in the formulation of localized corrosion mechanism.

The following steps are involved in localized corrosion.

1. The adsorption of the reactive anion on the oxide covered aluminium.
2. The chemical reaction of the adsorbed anion with aluminium ion in the aluminium oxide lattice or the precipitated aluminium hydroxide.

3. Penetration of the oxide film.
4. Shortest occurrence of the unprotected metal by the anion, possibly supported to the anodic potential (pitting propagation).

2.2.1 Pitting of aluminium

The effect of electric potential on the corrosion of aluminium was investigated in many laboratories. The potential enters the mechanism in two ways, 1) in connection with pit initiation and 2) with pit propagation. It has been postulated that the potential enters the initiation step by providing the potential for anion adsorption on the surface. Once the pitting process has been initiated, metal dissolution can occur at lower potentials.

Broll and Holtan⁸⁶ examined three methods for determination of the pitting potential and protection potential of aluminium in deaerated solutions of 3% NaCl.

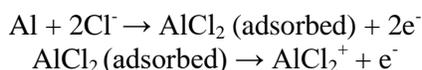
1. Potentiodynamic method
2. Quasi stationery method
3. Stationery method

The results of these investigations were summarized by Nisanoglu and Holtan⁸⁷. Both current controlled methods and potential controlled methods have been used in measurement of critical pitting potential. Out of the three methods, the most reliable is the potentiostatic method, which is a stationary method. Attempts have been made to use the pitting potential as criteria for the pitting susceptibility of different aluminium alloys⁸⁸.

2.2.2 Chemical reaction step

A number of investigators have concluded from work on pitting in chloride solutions that intermediate soluble complexes are formed. Feroules and Thubrikar⁸⁹ using Engeli stolica method of measurement of pit initiation on pure Al in neutral solutions proposed the establishment of $\text{Al}(\text{OH})_2\text{Cl}$. Stirrup et al.,⁹⁰ in a study of pit formation in chloride solutions, found a logarithmic requirement of serious pitting potential on chloride. It was concluded that the chloride ion reacted directly with the surface to promote pitting and furthermore that chloride was aggressive as a result of the solubility of the aluminium-chlorine compound⁹¹.

Further, $\text{Al}(\text{OH})_2\text{Cl}$ and $\text{Al}(\text{OH})\text{Cl}_2$ were categorized by Turner and Ross⁹² in the learning of hydrolysis of aluminum chloride. The work of Sussek et al.,⁹³ in a study on pit formation on oxide free pure aluminium in chloride and sulphate solutions, supports the concept that a primary step is the formation of transitory complexes such as the following⁹⁴.



2.2.3 Thinning of oxide film

The studies on the oxide film of aluminium offer independent evidence that even in the absence of other effects (mechanical etc) the oxide film on aluminium would be expected to be thinned upon exposure to aqueous solution.

The old-fashioned interpretation of the oxide film on aluminium contributing in a corrosion reaction in moisture medium is an essentially anhydrous and inert barrier. A more realistic view of the nature of the film contributing in a reaction occurring over an extended period of time must involve recognition of colloidal state of oxide. This view of the corrosion reaction has been well presented by Liepina et al.,⁸³.

2.2.4 The Direct attack of exposed metal

Once film is sufficiently thinned, the high degree of reactivity of metallic aluminum ensures rapid attack and pit propagation. The initiation reaction is concerned with the interaction, chemically or physically of the oxide film with the solution environment. The growth of the pit involves the interaction of aluminium metal directly with an environment that is changing as the reaction proceeds.

The direct attack on any metal surface is not a smooth continuous reaction rather it is an erratic process and becomes apparent in potential cycling. In the analysis and review of localized corrosion, it has been found to be more logical to recognize corrosion and then attempt to mold all the experimental findings into this framework.

2.3 Corrosion in MMCs

Studies on pit structure suggested that there were two states in pit development⁹⁵⁻⁹⁶. The first involved initial dissolution of metal atoms and opening of the pit and the second involved pit enlargement or growth. During the preparation and processing of the composite, a greater number of intermetallic phases were designed in the composite compared to alloy, hence the composite had more pit initiation sites. It was found that for alloy-600 density of the pits detected on the outer parts of the specimens was fewer are found at greater temperatures, pit development was superior at 100°C and at greater temperatures.

The products of corrosion were collected on pits which improved in Chromium, Titanium, Sulphur and disadvantaged in Iron and Nickel⁹⁷. It was found that the pit nucleation had the same potential dependency and possibly the same frequency in Al-Zn alloys and pure Al and that the effect of zinc was to enhance the dissolution kinetics in the local environment facilitating the translation to stable pitting⁹⁸⁻⁹⁹.

It was observed that the pitting behaviour of aluminium alloys was often influenced by nature of precipitates and their concentration because precipitate could serve as pit nucleation sites¹⁰⁰. Nunes et al.,¹⁰¹ during the study on corrosion of Al/SiC and Al/Al₂O₃ MMCs found that pits at the SiC particles acted as efficient cathodic sites. Pit initiation and propagation occurred at weak spots in the air formed film corresponding to phase discontinuities and second phase particles and to oxygen reduction at the particles or precipitates. Anodization and ceria coatings improved corrosion resistance of the composites.

Results obtained during the studies on in-situ monitoring of corrosion of Al alloys confirmed the importance of intermetallic constituents in promoting initiation and growth of pits in aluminium alloys. Heterogeneous distribution of these particles served to define the location and extent of pitting¹⁰². While Al 6061/SiC MMCs underwent corrosion, it was found to exhibit some different corrosions.

Pitting and crevice corrosion everywhere the fibers where gathering of Mg at the fiber/matrix boundary during manufacture^{27, 103}.

It was found that faster the cooling rate of Al Mg alloys, the lesser the grain size. The size of Al₈Mg₅ occurred in a serious cooling rate at maximum size¹⁰⁴.

Owing to nobler electro potential of intermetallic phase, these were expected to act as cathodes in Al/SiC MMCs. This was confirmed by the finding of magnesium hydroxide on the outer part of the intermetallics after exposure in MgCl₂ solution. Principal cause of corrosion was found in the interaction between aluminium alloy and the intermetallics¹⁰⁵.

The choosy corrosion and passivation repeatedly supplemented to great outer surface stresses which causes plastic fracture¹⁰⁶. Due to micro structural changes of the matrix and conceivable residual

stresses, heat handling of the composite and alloy was originate to demonstration inferior rate of corrosion¹⁰⁷.

The corrosion behavior of MMC's are predisposed by the matrix with the strengthening using dispersion of Cu, Mg, Si in Al-MMCs¹⁰⁸.

2.4 Stress corrosion in MMCs

Pure aluminium is corrosion resistant but unfortunately, it is soft and has low strength. Alloying Al with Cu, Mg, Zn and Si can substantially increase its strength. However alloying increase the likelihood of cracking when the metal is exposed under stress to salt water or industrial environment. Three conditions are necessary for SSC (stress corrosion cracking) to occur.

1. The alloy must be susceptible
2. There must be a specific environment (water or salt water for aluminium alloys).
3. There must be a tensile stress.

All aluminium alloys are not susceptible to SCC. Additionally, SCC depends on the orientation of the grains within the specimen. For SCC to occur, the stress (or a component of the stress) must be applied perpendicular to the grain boundaries so as to open them up. SCC is also a time dependent process.

During SCC, aluminium alloy's surface often appears almost corrosion free, making SCC quite dangerous; although outwardly a structure might appear uncorroded, and fine cracks could cause it to be a near failure. There are three main theories for SCC to occur¹⁰⁹.

The first philosophy accepts that the exceedingly is due to a superior corrosion along the grain boundaries (anodic dissolution) the second philosophy assumes that atomic hydrogen is absorbed and deteriorates the grain boundaries, which allows the cracking (hydrogen induced cracking) the third theory attributes cracking to the rupturing of the passive film along the grain boundary (passive film).

The Stress corrosion resistance of an Al 6061/albite MMCs in high temperature acidic media has been evaluated using autoclave by Vijayalakshmi et al.,¹¹⁰. Pruthviraj et al.,¹¹¹ conducted similar type of experiments in ZA 27/SiC MMCs.

Monticelli et al., found that the tensile stress created a rise within the corrosion rate of Al 6061 primarily based MMCs that were clearly detected by noise analysis. However, the concomitant presence of erosion (in some cases of inhome granular corrosion) and stress corrosion created it troublesome to tell apart between specimens affected by the assorted localized corrosion forms¹¹².

Comparison of experimental information with the expected crack growth rates of SCC for Al alloys indicated that; Al alloy 7022 suffers from chemical element embrittlement up to a temperature of 50° C. thanks to comparatively high yield strength of this alloy, the chemical element concentration at triaxial stresses behind the crack tip becomes high, increasing the influence of chemical element effects. each the interior chemical element model and also the surface quality model together with chemical element interactions square measure able to predict the influence of temperature on SCC growth correctly¹¹³.

When reversed U bend tests were performed on alloy 600 and alloy 690 specimens in a very 380° C, hydrogen/steam setting, cracking occurred for each material samples that had been subjected to an occasional mil toughen temperature. The orientation of the cracks within the U bend specimens was found to diverge for the 600 and 690 alloys as a result of variations in strain distribution for specimens factory-made from the various alloys¹¹⁴.

It was found that the prolonged ageing of the 7010Al-Zn-Mg-Cu French alloy resulted in decrease in susceptibleness to SCC. The ascertained fall in fracture energy was owing to electro chemical corrosion and stress corrosion for beneath aged and peek aged alloys and nearly wholly to electro chemical corrosion for over aged alloy.

The result of prolonged ageing is susceptibleness to SCC and it's going to be attributed to the amendment in volume and distribution of MgZn₂ part precipitates, smallest for T 351 beneath aged alloy and greatest for T 7451 over aged alloy.

The lowest susceptibleness to SCC of over aged alloy has been explained by the presence of enormous part precipitates that inflated the alloy resistance to corroding and intergranular corrosion, modified the conditions of crack initiation and unfree the absorbed hydrogen¹¹⁵.

Conde et al.,¹¹⁶ observed that the Al-Li alloys possess high resistance to SCC compared to more conventional alloys. The slow strain rate technique makes it doable to observe the susceptibleness to SCC in systems that it can not be observed with different testing techniques or takes for much longer to detect.

Higher and lower strain rates LED to failure as a results of different mechanisms, accelerated fracture attributable to a corrosion method and mechanical overloading severally. the sort of SCC that the variations in corrosion potential were freelance of the strain and strain rate. One the addition of 0.4 -0.7% zinc to aluminium-lithium alloys, SCC resistance of the same was found to improve while the addition of indium proved ineffective. Such a bearing of minor part addition on SCC resistance is closely related to status to a neighborhood anodic dissolution on the grain boundaries¹¹⁷.

Once the synergic impact of element and stress on corrosion rate was analysed thermodynamically, the result showed that associate interaction of stress and element may increase the corrosion rate remarkably¹¹⁸. the number of localized strain developed at the specimen close to surface region before nucleation of stress corrosion cracks was found to be love the strain needed for ductile fracture of the fabric in air, suggesting the existence of a basic fracture criterion¹¹⁹.

It was suggested that the formation of the steady pH region at the tips of stress corrosion cracks in aluminium 7075 alloys was also associated with the onset of precipitation of Al (OH)₃ and that the pH in this region can be calculated by the solubility product of freshly precipitated Al (OH)₃.

There is a considerable disagreement in the literature on the mechanism of SCC in aluminium alloys. It appears that the proposed mechanism of SCC depends on the alloy system in question; anodic dissolution is favored by most researchers in the 2XXX alloys (Al - Cu and Al - Cu - Li) while hydrogen induced cracking is favored by most researchers in the 7XXX and 5XXX alloys (5XXX are also dependent on the β phase). But these are not the only proposed mechanisms. Rupture of a brittle passive film and other mechanisms are also viable alternatives.

Thus, while SCC phenomenon of Al alloys is well documented, the actual mechanisms are still disputed and this is an important area of continued research.

2.4.1 Hydrogen induced cracking

Bond, Robertson, Birnbaum¹²⁰ examined the effect of hydrogen on the motion of dislocations in high purity aluminium. They admitted hydrogen gas saturated with water into the strained TEM specimens. Hydrogen caused crack growth and increased dislocation density. Bond et al., concluded that during SCC, dissolved hydrogen softened the metal matrix and allowed plastic deformation.

2.4.2 Anodic dissolution

Hintz¹²¹ proposed that SCC results from a combination of both dissolution and chemisorptions in the crack tip. It was hypothesized that the SCC mechanism would be analogous to liquid metal embrittlement of an alloy by its corrosion products. Byrne compared the potentiodynamic polarization diagrams of 7075-T651 and 7075-T351 in IM NaCl. Byrne showed that the polarization curve of 7075-T6 had an extra elbow which he attributed to the anodic dissolution of the grain boundary region.

2.4.3 Passive film rupture

Pugh¹²² distinguished between the trans granular stress corrosion cracking (TGSCC) and inter granular stress corrosion cracking (IGSCC) by saying that TGSCC occurs by discontinuous brittle fracture (cleavage) through the grains while the IGSCC occurs by anodic dissolution at the crack tip. Pugh used a film induced cleavage model to explain the cracking of Al-Zn-Mg alloys. Kanematsu, Okido and Oki¹²³ used a potentiostatic slow strain rate technique to compare three Al-Zn-Mg alloys in 0.6 N NaCl solution. They concluded that inter granular SCC was due to rupture of the brittle oxide film along the grain boundaries, while trans granular cracking was initiated by pitting corrosion. The effect of aging was explained from the viewpoint of the oxide film growth. The passive current decreased as aging time increased. The rapidly growing film (higher current density) corresponded to the film, which also cracked over the grain boundary allowing SCC.

2.5 Oxidation

2.5.1 Oxidation of aluminium composites

The oxide formed first on alloys at ambient temperature is usually contaminated by impurities from the atmosphere or substrate such as chlorine or sulphur, when a freshly prepared surface is exposed to nominally dry oxygen or air at room temperature¹²⁴⁻¹²⁵. These contaminated oxides are not the corrosion products formed by action involving thin electrolyte layers when a metal or alloy is attacked by a moist environment, as in the rusting of iron.

Oxide development on a clean or contaminated, freshly prepared metal surface involves adsorption of gas, formation of two and three dimensional nuclei, nuclei coalescence to give a complete reasonably uniform oxide film, comprising grains and subsequent film thickening by metal or oxygen transport through the film, usually by diffusion or ion migration. The affinities of metals for oxygen are usually presented in an Ellingham Diagram (per mole of oxygen) is plotted against temperature. For most metals, oxidation is spontaneous because this free energy change is large and negative. Following conclusion may be drawn:

1. Chromium and particularly aluminium have a greater affinity for oxygen than nickel, cobalt or iron.
2. A further important quantity is π_{MO} , the equilibrium dissociation pressure of MO, given by, $\pi_{MO} = \exp(\Delta G^0/RT)$

Where ΔG^0 is that the commonplace Josiah Willard Gibbs energy of formation of the compound (per mole of oxygen) R is that the universal gas const, and T is that the temperature, the dissociation pressure for many oxides is low, therefore oxidisation tends to occur in several sensible oxidizing media. Multi part diffusion theory could also be wont to analyze the relation between transport rates and free energy for alloy oxidizer systems, wherever transport controlled growth of single or multilayer scales happens. Superposition of the diffusion knowledge on equal sections of the part diagram offers the doubtless corrosion product morphology, as well as the part sequence within the scale, internal compound development, and irregular alloy/oxide interface formation¹²⁶.

2.6 Galvanic corrosion

Galvanic corrosion may be a primary concern relating to the corrosion behavior of MMCs. this can be significantly true once a vigorous metal like aluminium or metal is galvanically coupled to a noble conductor like black lead fiber. comparatively inert materials like black lead, assault and TiB₂ area unit typically noble as a result of they function inert electrodes for nucleon and O reduction. Thus, a metal can typically corrode at AN accelerated rate once galvanically coupled to a comparatively inert material. Utilizing polarization diagrams and therefore the mixed potential theory¹²⁷ MMC corrosion behavior may be expected.

Sometimes, the corrosion behaviour of AN actual MMC may be totally different from that expected victimization mixed potential theory. this can be a lot of probably to occur once the most important constituents (e.g. fiber and matrix) area unit the sole element thought-about within the mixed potential theory. Segregation of alloying parts, the formation of AN interphase between the reinforcement and matrix, and impurities introduced into the MMC small structure throughout process can also have an effect on corrosion behavior. Discrepancies in corrosion behavior may be known by comparison the particular polarization diagram of MMC thereto of a mixed conductor model generated from the diagrams of the famed constituents of the MMC victimization mixed potential theory.

2.6.1. Corrosion of aluminium

Al typically pits in salt containing solutions. E_{pit} is linearly smitten by the power of the salt particle concentration. but so as for Al to pit within the electric circuit condition, it should be polarized to potentials noble to E_{pit} by a electrode reaction. nucleon and element reduction area unit 2 attainable electrode reactions, however in neutral and chloride containing solutions element reduction is important to initiate roughness. it had been found that pits don't nucleate on metallic element within the electric circuit condition if solutions area unit deaerated. In aerated solutions, immoderate pure Al (99.99%) that could be a poor catalyst for element reduction mechanics on immoderate pure Al area unit believe to be caused by the high resistance of corundum that restricts negatron migration through the passive film.

Galvanic corrosion between the reinforcement and also the metal matrix governs the corrosion behaviour of the many MMCs, different factors like residual contaminants of MMCs process and also the formation of interphases between the reinforcement and matrix also can have pronounced effects on MMCs corrosion behavior¹²⁸. It appears that galvanic attack^{129,130} on aluminium is greater than other metals as a result of its activity.

A number of electro chemical studies^{131,132} that have recognized the important role of changes in the electrode potential during the corrosion reaction. These studies include polarization curves and the measurement of pitting potentials¹³³⁻¹³⁷.

2.6.2 Corrosion of MMCs

During the corrosion studies on Al 6061/Al₂O₃ in aerated and deaerated NaCl no significant influence of Al₂O₃ particles on corrosion behavior of MMCs was revealed. Corrosion attacks occurred preferentially in the vicinity of the reinforcing particles. It is also found that extrusion or forging did not affect corrosion behaviour of MMC. The estimated value of activation energy supported the view that the galvanic corrosion of the aluminum alloys was under control of the cathodic process on the composite material¹³⁸.

Measurements on the corrosion of aluminum alloy in weakly alkaline solutions showed that the rate of cathodic reaction was a function of electrode potential but not of pH¹³⁹ and was independent of film thickness. Hihara and et al.,¹⁴⁰ found that the galvanic corrosion current density of aluminum matrix coupled to graphite fiber in aerated 3.15 Wt% NaCl was found to be highest. Results also indicated that galvanic corrosion rate of aluminum should be thirty times less than when coupled to SiC or TiB₂.

According to the studies carried out by Giriffiths¹⁴¹ the effects of SiC reinforcement on the electro chemistry of Al 6061 cannot be generalized and are specific functions of the environmental conditions and the procession route. For a large ratio of surface area of cathode to anode and small free corrosion potential difference between the alloys, it was shown that the galvanic current density through the anode was independent of the surface area ratio. It was also shown to be less than the product of the area ratio and the current density due to oxygen reduction at the cathode¹⁴².

Analysis of photo current spectra suggested that the composition of the surface oxide does not change in a large thickness interval. From the values of the threshold energy derived from both anodic and cathodic spectra recorded in different conditions, it was postulated that this passive film consisted of a mixed oxide of the main components of the alloy¹⁴³.

Complimentary micro structural studies were carried out on corroded surfaces and sections through corroded material of Al alloy containing a range of reinforcements in 3.5% NaCl solution. This study has identified a number of potential corrosion sites including fiber/matrix interface¹⁴⁴.

It was found that Al/SiC MMCs showed increased susceptibility to pitting attack compared with unreinforced alloys and the major contribution to this enhanced attack arised from voids at the reinforcement/matrix interface¹⁴⁵.

When Al alloy 2014 reinforced with 20-40 vol% of alumina or SiC samples were tested by potentiodynamic polarization technique in 0.1 M Lithium per chlorate solution, results showed no impairment of the corrosion performance of the matrix alloy as a result of reinforcement phase¹⁴⁶.

2.7 Mechanical Properties

Dispersion of second phase particles in the molten metals and alloys was initiated way back in late fifties. Williams, Roberts and Jaffe in 1960, for the first time, successfully produced copper- nickel oxide dispersion hardened composite material by a melting and casting technique. Fine nickel oxide dispersion in copper matrix was produced by rotating a nickel rod at moderate speeds in an oxygen saturated copper melt and then casting it.

Regan et al.,¹⁴⁷ produced composites by mechanically introducing the particles into the melt prior to casting. In 1963, Badia and Rohatgi¹⁴⁸ produced an aluminium graphite particulate composite by injecting nickel coated graphite powder into aluminium alloy melts by gas streams techniques prior to casting these alloys in permanent moulds.

Cast aluminium-alloy mica particulate composites of varying mica content tested in tension, compression and impact by Deonath et al.,¹⁴⁹ with 2.2% mica content size ranging from 40 μm to 120 μm . The tensile and compressive strength of aluminium alloy decreased by 56% and 22% respectively.

A method for fabrication of cast aluminium alloy feldspar particulate composites by fine dispersion of feldspar particulates of average size (90-150 μm) in molten alloy above their liquidus temperature followed by casting in permanent moulds is described by Sharma et al.,¹⁵⁰.

Al-Zn-Mg-Cu alloys which are heat treatable and possessing high strength were prepared by Sharma et al.,¹⁵¹. Before casting, upto 4% by wt. of flyash was dispersed in the melt. Then the castings were subjected to stress relieving heat treatment and subsequent hot forging at 500°C.

Metallic glass strips were interspersed between the discs of aluminium stacked into a 2.54 m diameter cavity of hot press and put under a small sustained pressure. The composite was found to contain no fragmentation of metallic glass. Addition of glass particles in varying volume fraction to the matrix

alloy determines the various properties exhibited by the composite material. Testing of such composites shows improvement in hardness, tensile strength, compressive strength and the impact strength was found to reduce. It should be possible to fabricate a wide range of metallic glass-metal alloy composites if these properties are exploited for large scale applications¹⁵².

2.7.1 Aluminium alloy-zircon composites

The addition of brittle ceramics to metals having high ductility was intended to conglomerate the high temperature stability along with other positive mechanical properties. Metal-ceramic composites were recently developed to facilitate the fabrication components of large size and complex shapes with ease. The common hurdle that had to be overcome in these preparations was the incompatibility between the liquid metal and the second phase resulting in non-uniform distribution. This incapacitated production of large castings and larger amounts of second phase too exist in the composite.

Utilizing particulate ceramic oxides to develop aluminium based composite e.g., zircon can open new vistas, exhibiting high hardness and modulus of elasticity and excellent thermal expansion gives it a thrust over other such particles. Thus high thermal stresses can be effectively avoided by using zircon particulates.

Wetting agents do not merely change the physical nature of the bounding surface. In liquid metals, the presence of alkali and alkali earth metals, often change the chemical compositions by reducing reactions. Wettability can be increased with the addition of magnesium. Uniform distribution can be enforced by creating vortex using ceramic coated steel impellers¹⁵³. Zirconia can also be dispersed by mixing 25 gm of it with 500 cc of acetone in stainless steel beakers and ultrasonically agitated at 25 KHz for fifteen minutes and excess acetone can be decanted¹⁵⁴.

It was possible to disperse 3% by wt of zircon particles (40 – 200 μm size) in commercially pure aluminium and upto 5% by wt of zircon particles in aluminium-80% silicon alloy melts. Possibility of increased dispersion was increased by adding greater amounts of magnesium but beyond a certain limit, it reduced fluidity in gravity castings thus resulting in poor castings.

Round tensile specimens of diameter 7.1 mm and gage length 28.3 mm were machined from the forged as well as the cast composites with longitudinal axis of castings parallel to the gage length of the specimen. The composite showed limited plastic deformation preceding tensile fracture. As the wt% of zircon increased beyond 30, the plastic deformation becomes practically non-existent.

Forged composites of zircon exhibit greater tensile strength and percentage elongation than the cast composites. This was attributed to the improved matrix structure and the breakdown of coarse dendritic structure of casting. With increase in wt% of particulate phase, the strength properties and ductility have a tendency to decrease. Thus, zircon being a hard phase, the aluminium-zircon composites can provide wear resistance and abrasion resistance properties¹⁵⁵. These alloys can replace copper, lead and tin base bearing alloys with projected cost saving and superior performance.

2.8 Scope of the present investigation

The unique combination of characteristics of aluminium and increasing exploration in the techniques of processing and application forms the basis for increasing use of Al in newer fields and has brought it into competition with other engineering materials. Important among its advantages are its lightness combined with high strength to weight ratio, resistance to corrosion, weathering and other chemical attacks, high electrical and thermal conductivity, good reflectivity to light and good surface capability of being finished in variety of colours and textures.

There are many reasons for Al to be used in aircraft industries, automobile industries, domestic industries, etc., although the properties of these alloys still fall far short of the standard necessary to enable them to perform the difficult task for which they were intended. The Al alloys possess a wide variety of favorable properties such as a good resistance to corrosion, low density, relatively high strength, lightness combined with high strength to weight ratio, high electrical and thermal conductivity. Al alloys have been in use in industries for quite some time, they can provide an effective base matrix for MMCs with particulate dispersions. A new area of fruitful research exists wherein a thorough investigation can be made regarding the possibility of using ceramic as dispersoid with Al alloy as base metal to get an effective composite material.

A few materials like SiC, graphite, alumina, mica etc have already been successfully used as dispersoids in aluminium alloys for corrosion studies. Ceramic particle reinforced AMCs find extensive applications in engineering and automobile applications.

Chapter-3

Materials and methods

3.1 Materials used

3.1.1 Matrix used

The matrix selected is Al 7075 of commercial grade, which displays outstanding casting properties and reasonable strength. This alloy is finest suited for mass production of lightweight metal castings. The chemical composition of the Al 7075 alloy is agreed in table 1.

Table 1: Composition of Al 7075

Element	Mg	Si	Fe	Cu	Zn	Cr	Mn	Ti	Pb	Sn	Ni	Al
Weight (%)	2.1	0.4	0.5	1.2	5.1	0.18	0.3	0.2	0.05	0.05	0.05	Balance

3.1.2 Dispersoid used

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 main structural unit of zircon is a chain of interchanging edge-sharing SiO_4 tetrahedron and ZrO_8 triangular decahedra¹⁵⁵. The composition of zircon is given in table 2.

Table 2:-Composition of zircon

Silica	32.8
Zirconia	67.2

3.1.3 X-Ray diffraction analysis of zircon

Zircon powder of average particle size 50 microns was used and diffraction pattern was taken. The chart speed, scanning speed, intensity ratio (count/sec) were controlled through a controller. Equipment was operated at 30 kV and 10 ma scanning speed of 0.04 deg s^{-1} and chart speed of 1 cm/deg . Scanning was carried out between 20 and 80 degrees. The XRD spectrum of zircon is agreed in figure 1.

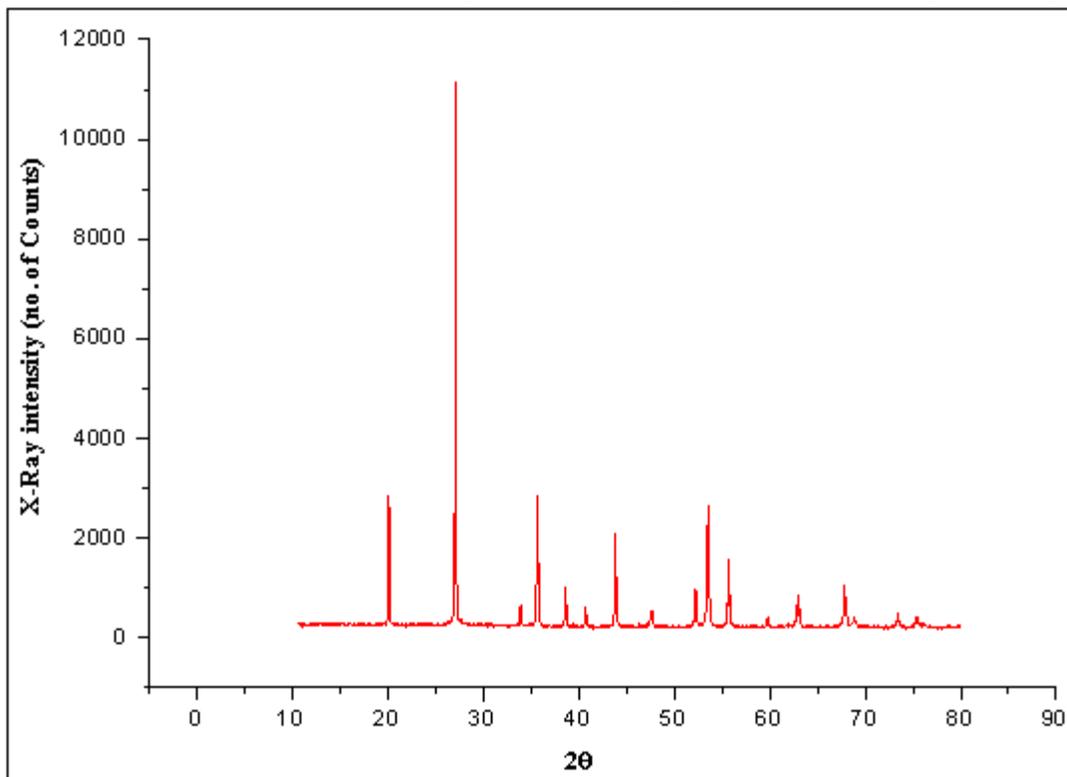


Figure 1:-XRD Spectra of zircon

3.1.4 Grain size and shape of zircon

Zircon powder of average size 50 microns was washed with water to eliminate soluble inorganic impurities and then by means of acetone to remove any adhered organic matter. About 2-3 g of zircon powder, free from both organic and inorganic impurities, was treated with isophthalic polyester resin along with 2% each of methyl ethyl ketone peroxide (hardener) and cobalt naphthanate (accelerator) and poured into a glass tube, open at both ends and placed on a flat rectangular glass plate. It is allowed to solidify. After about half an hour, solidified resin containing zircon particles was ground using emery paper of grain size 220, 400 and 600 successively. The direction of grinding changed by 90 degree on change of each emery paper. The specimen was then polished manually using cloth and abrasive solution. The polished specimen, free from scratches, was observed under a metallurgical microscope to know grain size and shape of zircon particles embedded in resin matrix. The scanning electron micrograph (SEM) of the zircon is given in figure 2.

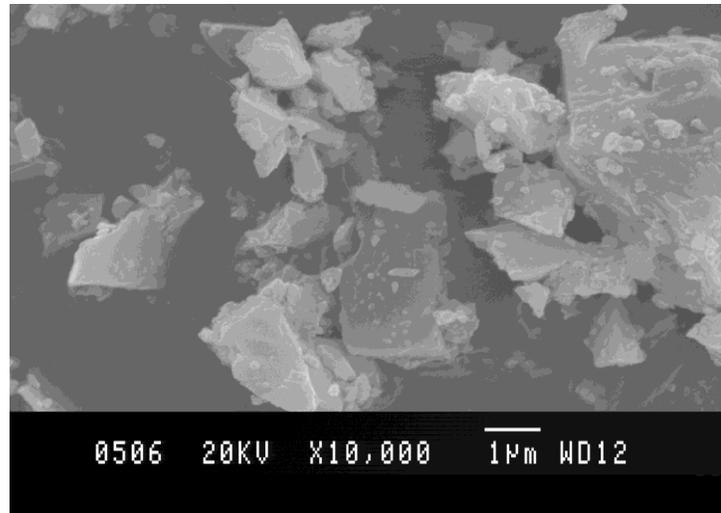


Figure 2:-SEM of zircon

3.2 Composite preparation

The microstructure of any material depends on the advanced perform of the casting method and later cooling rates. Thus fabrication of composites is taken into account mutually of the foremost difficult and troublesome task. Within the gift study, liquid-metallurgy vortex method¹⁵⁶ was utilized to organize the composites.

3.2.1 Furnace details

The chamber used for the preparation of the composites is essentially an electrically heated three-part resistance chamber of 12kW capacity fitted with 3 pairs of 14 gauge Kanthal, A1 grade heating coils. The temperature vary of the chamber is 1200°C with a temperature management accuracy of +/- 1°C. it is fitted with a digital temperature controller. The heating capability of the chamber is 500°C per hour. The chamber is fitted with analumina crucible at its center and also the chamber is tilted by 90 degrees on its horizontal axis that allows the gushing of the soften.

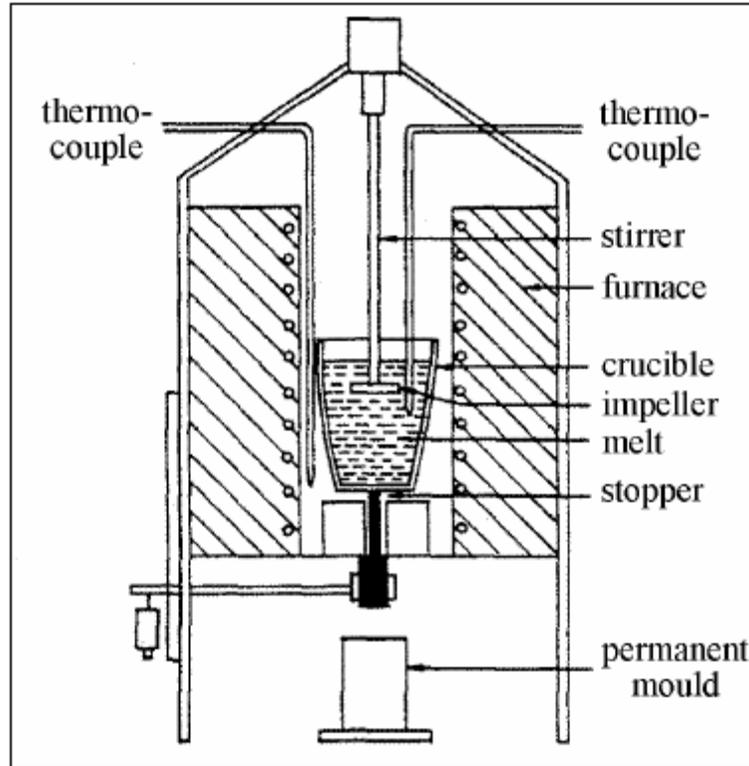


Figure 3:-Scheme of vortex method

3.2.2 Stirrer assembly

Stirrer assembly consists of a stirrer, motor, flexible shaft and arrangements for both vertical and horizontal movements of stirrer. The stirrer is connected to the motor (5 H.P.) by means of a flexible shaft. Speed of the motor can be varied by movement of stirrer and by means of clamping and horizontal movement can be achieved by means of the trolley.

3.2.3 Standardization of stirring conditions

In casting MMCs, particulate addition requires utmost care. For the better properties it should be evenly distributed in the melt. Stirring of liquid melt improves the properties of the composite, as grain refinement is likely to occur. Various stirring conditions like depth of stirring, speed etc. are to be optimized to get a good quality casting. To optimize the speed and depth of stirring, a water model is selected as a working fluid as it is a

- transparent fluid
- a good solvent
- abundantly available

The main objective of water model studies is to simulate similar conditions as in liquid metal with a well-defined vortex in which homogeneous mixing of entire particles take place. Entrapping of air, which may cause secondary cavitations, may lead to defective casting and hence should be prevented. Presence of air bubbles can be visualized clearly through transparent media. A dye is added to note the particle movement.

The formation of vortex depends on the depth and speed of stirring in the fluid mass. Optimized conditions lead to a well-defined vortex resulting in a homogeneous mixing of water. The same conditions are applied for liquid melt, kept in a crucible having the same dimensions as that of the fluid container¹⁵⁷. The fluid motion is defined by (a) Lagrangian (b) Eulerian methods.

In the Lagrangian methodology a fluid particle is followed throughout its motion and its velocity, acceleration and density described, whereas in Eulerian methodology the above properties are defined at a point in a flow field .

A vortex flow is a type of rotational flow in which flow of fluid is along a curved path. The vortex flow is classified as

- a) free vortex flow
- b) forced vortex flow

In free vortex flow, no external torque is needed to rotate the fluid. In forced vortex flow, application of external torque is needed to rotate the fluid mass. Stirring rotates the fluid at a constant angular velocity to generate a vortex of the shape V in the fluid mass. Depending on the depth of stirring, different cone angles as well as different base diameters are obtained.

3.2.4 Standardization of depth and speed of stirring

At certain depth and speed of stirring, well-defined vortex is formed at which the particles in the system get mixed forming a uniform homogeneous solution. The process of determining depth and speed which produces well defined vortex is known as standardization technique. The stirrer blade plays a major role in vortex formation. Hence a thorough study is made with available references to choose an optimum blade shape for this purpose¹⁵⁸.

3.2.5 Standardization of degassing of melt slurry

3.2.5.1 Flow meter

Flow meter consists of a N₂ cylinder, connected to an empty wash bottle with a rubber tube. The empty wash bottle stabilize the pressure. However, the passage of pressurized gas directly into the concentrated sulphuric acid (Conc. H₂SO₄) may cause accidents. The empty wash bottle is then linked to the second wash bottle comprising conc. H₂SO₄. The conc. H₂SO₄ is used for removing the impurities as well as moisture.

The third wash bottle, that is connected to the second wash bottle, contains calcium chloride. The N₂ gas escaping from the conc. H₂SO₄ bottle may carry some sulphuric acid and sulphur dioxide and these are absorbed by the calcium chloride, it also absorbs the moisture content present in the N₂ gas.

3.2.5.2 The degassing lance

From the third wash bottle the gas is introduced into the molten metal with the help of a degassing lance. The degassing lance is made up of mild steel pipes. The degassing lance is connected to the wash bottle containing calcium carbonate with a rubber tube and a nipple. The surface of the degassing lance is completely coated with a paste made up of finely powdered fire clay, sodium silicate and water in the desired proportion so that the lance could withstand high temperatures. The coating acts as a refractory. The perforated part of the lance is dipped into the molten metal while degassing.

3.2.5.3 Test conditions

The conditions particularly rate of atomic number 7, pressure of N₂ gas within the cylinder and degassing time were maintained constant throughout the course of the investigation at the subsequent optimized values to attain economical degassing of Al composites

1. Flow rate of N₂ gas - 4.5 dm³ min⁻¹
2. Pressure of N₂ gas from the nitrogen cylinder - 2.4 kg cm⁻²
3. Degassing time – 3 min.

The potency of degassing method depends on the depth of the soften. At the lower values of the on top of parameters were inadequate to cause penetration throughout the depth of the soften and thus a reduction in the efficiency of degassing was discovered.

On the opposite hand, higher values of pressure, rate of flow and time of passage of gas caused excessive effervescent of the melted metal, that resulted in jetting of the melted alloy from the melting pot.

3.2.6 Preheating of reinforcement

Muffle chamber was used to preheat the reinforcement particles to a temperature of 400°C and to take care of at that temperature until it absolutely was introduced into the aluminium alloy soften. The preheating of the reinforcement is important in order to reduce the temperature gradient between the liquefied metal and also the zirconium reinforcement, to boost the wettability and to reduce the distinction in surface energies of each matrix and reinforcement.

3.2.7 Melting of the matrix alloy

Known quantities of the aluminium alloy ingots were preserved in 100% NaOH solution at 25°C for ten minutes to get rid of the surface impurities. The scales fashioned was removed by immersing the ingots for 1 minute during a mixture of 1 part nitric acid and 1 part water followed by washing in methanol. These cleaned ingots when drying in air were immediately charged into the alumina crucible in the chamber for melting.

The melting point of Al 7075 alloy is 900 °C. The soften was superheated to a temperature of 950 °C and maintained at that temperature. The temperature was recorded using chromel-alumel thermocouple. The liquefied metal was then degassed using refined N₂ gas. Nitrogen was passed at the rate of 4.5 L/min under a pressure of 2.4 kg cm⁻² for about 8 minutes. A stainless steel impeller or stirrer coated with aluminite was used to stir the molten metal and to create a vortex. The aluminite coating is critical also to stop the migration of metal ions from the stirrer material to the soften, leading to the contamination of the soften. The impeller used for stirring was of centrifugal type, having 3 blades welded at 45 degrees and 120 degrees apart. The stirrer was turned at a speed of 500 rpm and a vortex was created within the soften. The depth to which the impeller was immersed was 60% of the height of the molten metal from the surface of the melt. Then the reinforcement (zircon) particulates which were preheated in the furnace were introduced into the vortex at the rate of 120 g/min. Stirring was continued till interface interactions between the reinforcement particulate and therefore the matrix promotes wetting. Then the soften was degassed exploitation pure nitrogen for about 3-4 minutes and at superheated temperature, it was poured into the preheated lower half die of the hydraulic press. The top die is brought down to solidify the composite by applying a pressure of 100 kg cm⁻² both the lower die and the top dies are pre-heated to 280 °C before the melt was poured. The pressure applied enables the reinforcement particulate to be distributed randomly in the developed composite.

3.3 Parameters for preparation of Al particulate composites

3.3.1 Shape of the reinforcement

Shape and morphology of the reinforcement play a crucial role in getting uniform dispersion of the dispersoids within the casting. Earlier reports indicate that it would be troublesome to disperse large volume percentage of flake type mica particles in aluminum melts, whereas dispersoids like zircon, alumina, which are close to spherical morphology would be spread in aluminum melts in large quantities with a lot of ease¹⁵⁹. Within the present study spherical reinforcement particles of 40-50 μm were used. Since the dispersoids utilized in the current studies were particulate, it absolutely was potential to disperse solely up to 7% of the reinforcement particles in aluminium melts.

3.3.2 Temperature and duration of pre-heat treatment of reinforcement particles

Reinforcement particles were pre-heated to a temperature of 400 °C, for two hours. It was observed that after pre-heat treatment, the dispersion was more uniform and also the casting was found to be sound with less porosity. This is expected since preheating of the reinforcement particles to a temperature of 400 °C would remove absorbed layer of gases from the surfaces of the particles partially. However, absorbed layer of gases on the surface can also be removed by vacuum treatment. Also pre-heat treatment reduces chilling of the melt which would otherwise occur due to the addition of large quantities of particles. Optimum preheating temperature of reinforcement particulate was found to be 400 °C and the preheating reduces surface energy difference of the reinforcing phase.

3.3.3 Degassing of the melt

Degassing of the softening was done to reduce blowholes and minimize porosity in the casting. Composite melts may well be degassed using degassing tablets containing hexachloroethane and additionally by passing the N_2 gas to remove the hydrogen absorbed. The flow and pressure of flow was optimized when analyzing variety of castings for corrosion properties.

3.3.4 Speed and design of the impeller used

Vortex on the surface of the softening was necessary to disperse the reinforcement particles in liquified atomic number 13, stirring the liquified metal at the upper speeds would produce additional intense vortex, however at terribly high speeds there's a danger of air defence. thus Associate in Nursing optimum speed of 500 rpm was acquired by standardizing the speed of stirring within the water model study victimisation color pigment as dispersoid.

3.3.5 Residence time

Residence time is that the actual period that the reinforcement particulates square measure control within the softening. In different words, it's the period simply when introduction of the reinforcement particulate into the softening and simply before completion of natural action of the composite softening within the die. Here, the optimum continuance was found to be between 5-7 minutes. once the continuance was augmented on the far side seven minutes, the reinforcement particles were found to segregate. once the continuance was low (less than five minutes) distribution of the particles within the casting wasn't uniform, and a couple of blowholes were seen within the composites.

3.3.6 Pouring temperature

Throughout the investigation, the composites were ready by keeping the liquified metal at 950°C to facilitate straightforward flow of liquified metal. The temperature of Al 7075 alloy is 900°C and thence the softening was super-heated to a temperature of 950°C and also the call temperature was calculable to be 20°C by the time it absolutely was poured into the permanent mould. However, a rise of holding temperature resulted in flotation of the reinforcement particulate since the consistency of the softening was low at hot temperature and also the yield was found to be less.

3.3.7 Rate of addition of dispersoid

Rate of addition of reinforcement particles via crucial role in getting uniform dispersion and distribution of the particulate within the composite casting. Once the speed of addition was redoubled on top of 120g/min, reinforcement particles were found to segregate on the surface of the soften. However, once the speed of addition of the particulate was lower, the duration was large and it resulted within the redoubled time of casting and reduced flowability. The optimum rate of addition was found to be 120 g/min.

3.3.8 Effect of application of pressure on the molten metal containing the dispersoid

The permanent dies of the mechanical press, during which the casting of the composites was administered, were pre-heated to a temperature of 280 °C. The liquefied metal containing the reinforcement particle is transferred into the lower 0.5 die of the mechanical press. The highest die is then brought right down to solidify the composite by applying an optimum pressure of a 100 kg cm⁻². This can be necessary to keep up the gradient of the hardening composite. The applied pressure permits to cut back the residual consistence between the particulate and defense of gases, which might cause casting defects. So the method permits to get castings with minimum defects.

3.3.9 Casting of the composite melt

The distribution of the reinforcement particulate in the soften was uniform and {without any|with none} noticeable agglomeration once the composite soften was forged in permanent dies once applying an optimum pressure in an mechanical press. It had been found that because the rate of warmth transfer between the composite soften and therefore the die multiplied, the reinforcement particulate distribution was a lot of uniform within the castings. The composites were forged in permanent moulds of 25 x 300 mm, with variable reinforcement proportion 3, 5 and 7 % by weight. The castings therefore obtained were machined and tested in accordance with yankee Society for Testing and Materials (ASTM) standards for varied corrosion tests.

3.4 Micro-structural studies

The microscopic study of the structural characteristics of a metal or associate alloy was meted out via victimization associate scanning microscope interfaced with a pc. It's attainable to see grain size and also the form and distribution of assorted phases and inclusion, that have an excellent impact on the corrosion properties of the metal. The microstructure can reveal the corrosion and thermal treatment of the metal and it's going to be attainable to predict its expected behavior below a given set of conditions. Expertise has indicated that success in microscopic study depends for the most part upon the care taken within the preparation of the specimens. The foremost price a magnifier won't reveal the structure of a specimen that has not been ready as per standards. The procedure to be followed within the preparation of a specimen is relatively straightforward and involves a way that is developed solely when constant observe. The last word objective is to provide a flat, scratch-free mirror surface.

3.4.1 Sampling

The choice of a sample for microscopic study could also be important. If a failure is to be investigated, the sample ought to be chosen as shut as potential to the realm of failure and may be compared with one taken from the traditional section. The specimen ought to be unbroken cool throughout the cutting operation¹⁶⁰. Within the gift study the specimens were obtained from the castings at completely different region mistreatment specimen- cutting machine and were machined to needed dimensions.

3.4.2 Rough grinding

Whenever attainable, the specimen ought to be of a size that's convenient to handle. A soft sample could also be created flat by slowly moving it across the surface of a flat sleek file. The soft or laborious specimen could also be rough-ground on a belt drum sander, with the specimen unbroken cool

by often dropping in water throughout the grinding operation. All told grinding and sharpening operations, the specimen ought to be affected perpendicular to the prevailing scratches. This can facilitate recognition of the stage once the deeper scratches are replaced by shallower ones characteristic of the finer abrasive. The rough grinding was continued till the surface was flat and freed from nicks, burrs, etc., and every one scratches thanks to the saw or discontinuous wheel were now not visible¹⁶⁰.

3.4.3 Mounting

Specimens that are little or on an irregular basis formed ought to be mounted to facilitate intermediate and final sprucing. Wires, sheet specimens, skinny sections, etc. should be fitly mounted during appropriate material or stiffly clamped during a mechanical mount. Artificial plastic materials applied during a special mounting press can yield mounts of a regular and convenient size (usually 1 in thirty metric linear unit or thirty six metric linear unit in diameter) for handling in consequent sprucing operations. These mounts, once properly created, are terribly proof against the etching reagents usually used. The foremost common plastic for mounting is Bakelite. Bakelite molding powders are obtainable during a sort of colors, that simplifies the identification of mounted specimens. The specimen and therefore the correct quantity of Bakelite powder was placed within the cylinder of the mounting press. The temperature is bit by bit raised to one hundred fifty °C and a molding pressure of concerning 3649 mpa is applied at the same time. Since Bakelite is about and cured once this temperature is reached, the specimen mount could also be ejected from the molding die whereas it's still hot. Polymethyl methacrylate is that the commonest plastic for mounting.

Specimens that are small or irregularly shaped should be mounted to facilitate intermediate and final polishing. Wires, sheet metal specimens, thin sections, etc. must be appropriately mounted in a suitable material or rigidly clamped in a mechanical mount. Synthetic plastic materials applied in a special mounting press will yield mounts of a uniform and convenient size (usually 1 in 30 mm or 36 mm in diameter) for handling in subsequent polishing operations. These mounts, when properly made, are very resistant to the etching reagents commonly used. The most common thermosetting resin for mounting is bakelite. Bakelite molding powders are available in a variety of colours, which simplifies the identification of mounted specimens. The specimen and the correct amount of bakelite powder was placed in the cylinder of the mounting press.

The temperature is step by step raised to 150°C and a molding pressure of concerning 3649 mpa is applied at the same time. Since Bakelite is ready and cured once this temperature is reached, the specimen mount is also ejected from the molding die whereas it's still hot. Lucite is that the most typical thermoplastic for mounting. Lucite is completely transparent when properly molded. This transparency is helpful on it's necessary to watch the precise section that's being polished or on it's fascinating for the other reason to examine the complete specimens within the mount. In contrast to the thermoplastics the thermoplastic resins don't endure cutting at the molding temperature; rather they attack cooling. The specimen and the proper amount of Lucite powder are placed in the mounting press and are subjected to the same temperature and pressure as for Bakelite (150 °C and 3649 mpa). After the temperature has been reached, the heating coil is removed and cooling fins area unit placed round the cylinder to cool down the mount below 75°C in 7 minutes whereas the moulding pressure is maintained. Then the mount is also ejected from the mould. Ejecting the mount whereas it's still hot or permitting it to cool down slowly within the molding cylinder to standard temperature before ejection can cause the mount to be opaque.

Thin sheet specimens may be conveniently mounted for metallographic study, in a laboratory-made clamping device. Small specimens, when mounted in such a clamping device, are usually alternated with metal "filler" sheets, which have approximately the same hardness as the specimens. The use of filler sheets will preserve surface irregularities of the specimen and will prevent, to some extent, the edges of the specimen from becoming rounded during polishing¹⁶⁰.

3.4.4 Intermediate polishing

After mounting, the specimen was polished on a series of emery papers containing in turn finer abrasives. The primary paper was sometimes No.1. Then 1/0, 2/0, 3/0 and eventually 4/0 grade was used. The surface once intermediate sharpening operations using emery paper was sometimes dried; but, in bound cases like the preparation of soft materials, silicon carbide abrasive could also be used. As compared to emery paper, silicon carbide includes a larger removal rate and because it is resin-bonded, can be used with a lubricant. Use of a lubricant prevents warming of the sample, minimizes smearing of soft metals and conjointly provides a removal action to flush away surface product that the paper won't become clogged. Within the present investigation, the intermediate sharpening was achieved using water mineral sheets (starting from no. 100 to 800 in steps of 100)

3.4.5 Fine polishing

The time consumed and therefore the success of fine polishing depends for the most part upon the care that was exercised throughout the previous polishing steps. The ultimate approximation to a flat scratch-free surface is obtained by the utilization of a rotating wheel covered with a special material that's charged with carefully sized abrasive particles. Wide ranges of abrasives are available for final polishing, whereas several can do a satisfactory job, there seems to be a preference for the gamma form of aluminum oxide for ferrous and copper based materials and cerium oxide for Al, Mg and their alloys. Alternative final polishing abrasives typically used are diamond paste, chromium oxide and magnesium oxide. The final finishing was achieved by using the polishing machine in two stages.

In first stage, the specimens were polished by rubbing with uniform force on the rotating wheel of the polishing machine, covered with canvas cloth and the paste prepared with abrasive powder of magnesium oxide and water, as per ASTM standards.

In final stage, the velvet cloth was used on the rotating wheel and the fine grade of diamond paste was used as abrasive. The mirror like fine polishing was achieved over specimen surface, by applying kerosene as lubricant.

The choice of a correct proper polishing cloth depends upon the actual material being polished and also the purpose of the metallographic study. Several cloths are accessible of varied nap or pile, from those having no pile, like silk, to those of intermediate pile, like velvet. artificial sprucing cloths are accessible for general polishing purposes, of that two, below the trade names of Gamal and Microcloth, are most generally used. A properly polished sample can show solely the non-metallic inclusions and can be scratch free¹⁶⁰.

After all the polishing procedures, the specimens were kept in desiccators to avoid further corrosion due to atmosphere before the study of microstructure. The specimens were observed under microscope of high resolution. Figure 4, 5, 6 and 7 shows micrographs of without dispersed matrix alloy, 3%, 5% and 7% zircon reinforced composite respectively.

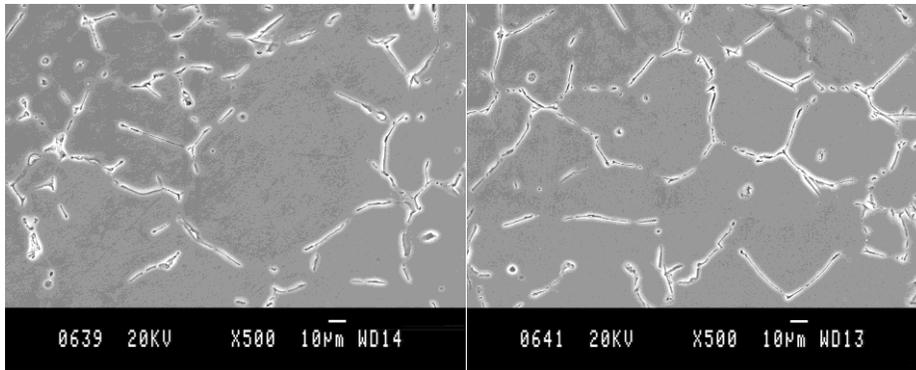


Figure 4: Micrographs of unreinforced Al 7075 alloy

Figure 5: Micrographs of Al 7075/3% zircon reinforced MMC

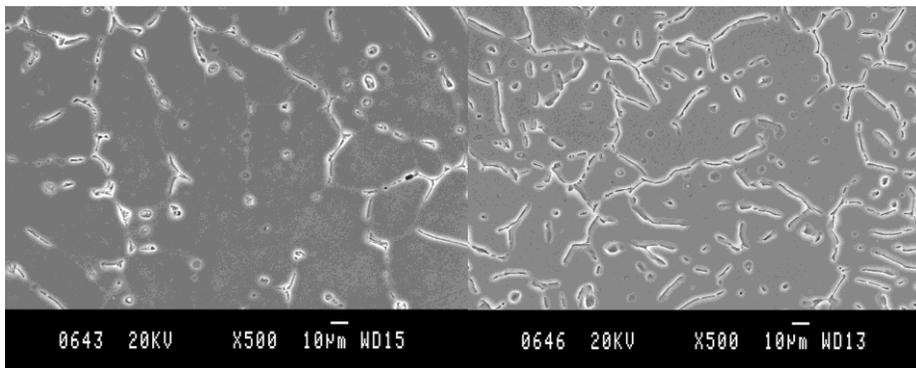


Figure 6: Micrographs of Al 7075/5% zircon reinforced MMC

Figure 7: Micrographs of Al 7075/7% zircon reinforced MMC

It is discovered from the microstructures of unreinforced matrix alloy and composites that, there's invariably a standardized particulate distribution which the typical particulate size was 40-50 μm despite what the burden proportion of reinforcement was. This is often constant size as that of the first zirconium silicate particulates, indicating that the zirconium silicate particulates weren't perceptibly broken or affected throughout preparation of the composite.

Specimens for studying corrosion and mechanical properties were prepared according to ASTM standards. After casting, only those rods, having no observable voids or defects were selected for preparing the specimens.

3.5 Corrosion test procedures

3.5.1 Static corrosion

The corrosion take a look at was dispersed mistreatment static immersion weight loss technique as per ASTM G69-80 take a look at standards. The specimens were machined into commonplace discs of 20mm diameter and 20mm height. Before testing, the specimens' surfaces were ground with carbide paper of a 100 grit size and polished in steps of 1.5 to 3 μm diamond paste to get a mirror surface end. Once sequentrinse with water and dissolvent and once drying totally the specimens were weighed accurately to fourth decimal place before beginning the take a look at by weight loss technique.

The procedure adopted for measuring the corrosion rate is as described below. The polishing procedures as per ASTM standards were carried out for unreinforced and 3%, 5% and 7% zircon reinforced composites and the uniform dispersion of particles was studied. The corrodants used were different concentrations of HCl, NaCl, NaOH, eqimolar solution of NaOH and NaCl and natural sea water.

The corrosion tests were conducted exploitation standard weight loss methodology on all kinds of specimens and therefore the exposure time was varied from 24 to 96 hours, in steps of 24 hours. The cradles containing the weighed specimens were unbroken within the flask containing the corrodent. A quantitative relation of 50ml of HCl to 1 mm² of area was maintained consistent with ASTM standards. to attenuate the contamination of the solution and loss owing to evaporation, the flasks were lined with paraffin throughout the complete period. when the corrosion check, the specimens were immersed in solvent answer for 10 minutes and gently clean with a soft brush to get rid of adhered scales. when drying totally, the specimens were reweighed to work out the share weight loss, weight loss per unit space of exposure and corrosion rate in mpy. Corrosion rate was calculated exploitation the formula,

$$\text{The rate of Corrosion} = 534 \frac{W}{DAT} \text{ mpy,}$$

where W is that the weight loss in grams, D is density of the specimen (gm/cc), A is that the space of the specimen (inch) and T is that the exposure time in hours. Once the check, the unsound surfaces of the specimens were studied underneath scanning microscope.

3.5.2 Potential of Open circuit studies

The electric circuit potential (also observed because the equilibrium potential, the remainder potential, or the corrosion potential) is that the potential at that there's no current. though electric circuit potential (OCP) measurements area unit terribly straightforward, they need several vital applications. Rectangular specimen 20mm length Associate in Nursing 10mm breath and 1mm thickness was ready by adopting commonplace metallographic procedure exploitation an abrasive cutting wheel¹⁶¹. They were polished and degreased in ketone and dried.

Associate in Nursing Al wire is employed to carry the specimen. One cm² space of the specimen is exposed to corrosive medium. The specimen is connected to the wire befittingly coated by Teflon tape so just one cm² space of the specimen exposed to solution medium. The specimen is created anode and therefore the cathode are going to be the reference conductor that's commonplace mercurous chloride conductor. Before testing every specimen was cleansed in ketone for 5 minutes and air dried. each electrodes area unit connected to multimeter and therefore the same is switched on to live the DC voltage developed when dipping them in corrodent, that is employed as solution resolution.

The corrodants used were different concentrations of HCl, NaCl, NaOH, eqimolar solution of NaOH and NaCl and natural sea water.

The voltage developed and displayed by the multimeter is noted for each hour over a amount of 30 hours. The procedure is perennial for all the four specimens. Then the graphs square measure aforesaid by taking exposure time versus the potential developed.

3.5.3 Galvanic corrosion

The chemical science behaviour was examined mistreatment potentiodynamic polarization technique in numerous corrodents at temperature. The corrodent resolution was deaerated with atomic number 7 for 1 hour before activity, to get rid of atomic number 8 from resolution and therefore assist in decisive the polarization behavior. The polarization effects area unit cloaked in aerated solutions, wherever the corrosion potential approaches closely the erosion potential.

Before polarization testing, samples were ground flat and polished to a 1µm end. The

chemical science measurements were performed like a shotwhensharpening. a minimum of 3 separate samples were tested to confirm dependability of results. For SEM analysis the corrosion product were off from the specimen by immersion during a mixture of 1% and 0.75% ortho-phosphoric acid in water at 90°C for 300 seconds¹⁶²

This experiment was performed to see the corrosion mechanism of Al alloy including mineral particulate reinforcements. These experiments were performed at temperature in several concentrations of HCl, NaCl, NaOH, equimolar answer of NaOH and NaCl and natural ocean water that are derated. These environments were designated so as to see the impact of H₂ reduction and aluminum passivity on galvanic corrosion behavior of Al MMCs. The galvanic corrosion rate was calculable from the polarization diagrams exploitation tangential method¹⁶³. The microstructure of the surfaces was studied exploitation SEM technique.

The Potentiostat- Galvanostat (model CL 95) that is employed for this study consists of a perform generator and a graphic plotter. These devices are unit interfaced with a private laptop. The instrument consists of a noble metal counter conductor, a saturated chloride conductor as reference conductor and also the polished specimens because the operating conductor and a five-mouthed flat bottom flask. The polished specimens were connected to copper holders. One cm² space of the surface of the specimen was exposed to the solution and also the remainder of the surface was coated by Teflon tape. Before testing, every specimen was cleansed in fuel for 5 minutes and air dried.

In generating potentiodynamic polarization diagrams, electrodes were allowed to stabilize at their E_{corr} before afterwards polarizing at a scan rate of 0.167 mV/s. 3 or additional polarization curves were generated for every experiment. The exponent of current was averaged and premeditated as a operate of potential to come up with polarization diagrams. The plot was obtained directly from the small laptop.

3.5.4 Stress corrosion studies

Three point- loaded specimens square measure usually flat strip of 8mm thickness, 40mm wide and 150mm long dimensions and were ready from the composite and therefore the matrix alloy for stress corrosion testing. Before testing, the specimen surfaces were ground with carbide paper of 100 grit then polished in steps of 15 to 3 μm diamond paste to get a mirror surface end. when result antrise with water and ketone, the specimens were weighed exactly to four decimal places by associate degree automatic balance before testing. The specimens were stressed by supporting at finish|the top|the tip}s and bent by forcing a screw equipped with a ball against it at some extent halfway between the end supports.

Autoclaves square measure usually used for testing at warmth and pressure. The Teflon coating protects the autoclave from severe aggressive environments. Figure 8 shows a bracket accustomed load corrosion specimen placed within the autoclave. The specimen was supported at each ends and bending stress was applied employing a screw equipped with a ball up-to-date against specimen at a degree middle approach between the top supports. A model specimen mounted with strain gauges was used for standardization. The model specimens of identical dimensions were used as take a look at specimens and were stressed to the middle length of the specimen, decreases linearly to zero at the ends. The specimens were subjected to 1 third of matrix alloy's ultimate tensile strength.

For each check, 2 liters of various corrosive solution was used. Autoclave check was conducted by filling check liquids (various normality of HCl, NaCl and seawater), loading the check specimens. Once loading the specimen autoclave was closed and heated to check temperature with increase in within pressure. Tests were conducted for various share of composite specimens, unsound for numerous period of 10, 20, 30, 40, 50 and 60 min severally at completely different temperatures with solutions of various normality.

After every corrosion check, the specimen was immersed in Clark's solution for 10 minutes and gently cleansed with a soft brush to get rid of adhered scales. Once drying totally, the specimens were weighed once more. Weight loss was calculated and regenerate into corrosion rate expressed in mils annually (mpy)¹⁶⁴. The unsound surface small structure was studied with SEM and EDAX getting used to ascertain the chemical composition of salient micro structural options.

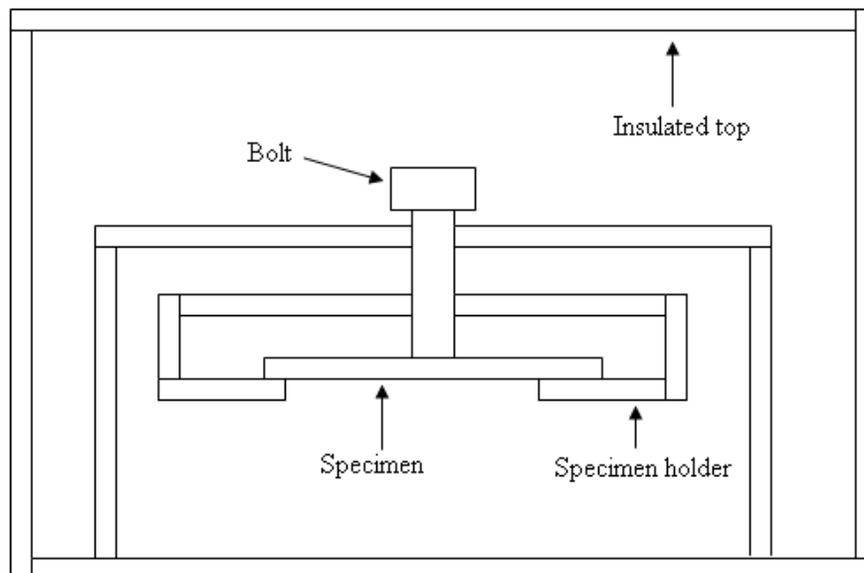


Figure 8: Autoclave

3.5.5 Mechanical properties

To understand effect of reinforcement on mechanical properties of composites, mechanical tests like hardness, compression, ultimate tensile strength, impact and wear tests were done on the prepared composites after machining them to standard sizes. Only those test bar castings having no voids or defects were selected for the tests.

A Brinell hardness (B.H.) was used with an indenter of the 5 mm dia and 500 Kg load for evaluating the hardness of the proposed composites. The load was applied for 30 seconds. Dimensions of the test specimens were 20 mm diameter and 20 mm height. This testing method was chosen to obtain an depression which would be illustrative of the macrograph of the material. Numerous readings were taken to confirm the elimination of possible segregation effects.

Compression properties were measured using an 1175 model Instron Universal Testing Machine (U.T.M.) speed of 0.2 mm/min. Dimensions of the test specimens were 20 mm dia and 20 mm height.

Tensile properties were evaluated using 1175 model Instron U.T.M. at a speed of 0.5 mm/min. Measurements of the tensile samples used 20 mm diameter, 120 mm overall length, gauge length 40 mm and gauge diameter of 12 mm. Ultimate tensile strength (UTS) was recorded automatically for matrix alloy, 3, 5 and 7 weight percentages of zircon particles impregnated in Al 7075.

Impact toughness is one of the important properties of materials of any engineering component for structural application. Impact strength was determined by Charpy test using an Avery impact testing machine. Dimensions of the specimen were 55 mm length and 10 mm height.

A pin-on-disc wear **take a look at** was conducted **exploitation** the pin specimen of dimensions **eightmillimetre** diameter and **20MM** height, **during which** surface of the specimen was rubbed against a rotating, hardened steel disc with **a far better** surface **end**. The **take a look at** was conducted at **slippy** speed of 1.35 ms^{-1} with applied load of **30 N**. **the particular** gravity measurements were conducted **in line with** ASTM **customary** C127-88. **the amount** losses from the surface of specimens were calculated from the **distinction** in weight of the specimen measured before and **once** the tests to **the closest** 0.1 mg **exploitationassociate** **degreebalanceand** also the density of that specimen. **of these** tests were conducted at **close** temperature (300 K) and a **ratio** of **48%**.

3.5.5 Salt spray test

Salt spray check may be a standardized check methodology accustomed check corrosion resistance of metals and alloys. Reinforcements give corrosion resistance to MMCs product of Al. Since reinforcements will give a high corrosion resistance through the supposed lifetime of the half in use, it's necessary to examine corrosion resistance by different suggests that. Salt spray check is Associate in Nursing accelerated corrosion check that produces a corrosive attack to the samples so as to predict its suitability in use for various applications. the looks of corrosion merchandise (oxides) is evaluated once a amount of your time. check period depends on the corrosion resistance of the MMC; the a lot of corrosion resistant the MMC is, the longer the amount in testing while not showing signs of corrosion. there's solely a weak correlation between the period in salt spray check and therefore the expected lifetime of a composite, since corrosion may be a terribly sophisticated method and might be influenced by several external factors. all the same, salt spray check is widely utilized in the economic sector for the analysis of corrosion resistance of finished surfaces or components.

The equipment for testing consists of a closed testing chamber, wherever a salt-cured answer (mainly, an answer of Na chloride) is sprayed by suggests that of a nozzle. This produces a corrosion atmosphere within the chamber and therefore, components in it square measure attacked beneath this severe corrosion atmosphere. the amount of the chamber is of 15 cubic feet (420 L). The tests were performed in keeping with ASTM-B-117¹⁶⁵. Tests performed with an answer of NaCl square measure referred to as NSS (neutral salt spray). The concentration of the NaCl answer used was 5% and therefore the pH of take a look at answer used was 7.08. The specimens were clean with iso propanol, before the take a look at. Hot, wet air is formed by effervescent compressed gas through a bubble (humidifying) tower containing hot deionised water. take a look at temperature was maintained around $35^\circ \pm 2^\circ\text{C}$. Salt answer is often rapt from a reservoir through a filter to the nozzle by a gravity-feed system.

Volume of the take a look at answer collected per hour per 80 Cm² space of the cupboard was 1.41 ml. Once the new, wet air and therefore the salt answer combine at the nozzle, it's atomized into a corrosive fog. This creates a 100 % ratio condition within the exposure zone. The specimens were exposed to the corrosive fog for 72 hours. When the take a look at the specimens were clean with running water and dried totally. Results were delineate as testing hours in NSS while not look of corrosion product.

Chapter 4

Results and Discussion

4.1 Static corrosion

4.1.1 Variation of corrosion rate with test duration

The results (Tables 3 - 15) and graphs (Fig. 9 - 21) show that for every composite similarly as for unreinforced Al 7075 alloys, the corrosion rate is found to decrease with the test period of the corrosion tests. The observation of gradual decrease in corrosion rate indicates a attainable passivation of the matrix alloy. Visual scrutiny of the specimens, once the corrosion tests, disclosed the presence of a black film covering the surface. The passive layer in all probability consisting of Al(OH)₃ protects the surface from any corrosion.

The exact chemical nature of such a protecting film continues to be not absolutely understood. Corrosion rate depends on the stability, nature and thickness of the passive layer. After a specific duration, the film may be stable but it contains pores and micro cracks through which solution may come in contact with the specimen surface and hence oxygen drifting might take place through these defects in the passive layer. However, such passive layer reduces the contact between the specimen surface and corrosion media and leads to reduction in corrosion rate drastically after a specific duration.

The decrease in corrosion rate with time may additionally result to the very fact that, a increased the dissolution of Al in the increase in H₂ and pH of solution. Due to the saturation of the solution with the anodic ions Al³⁺, the anodic reaction is slowed down. The H₂ evolved also remains entrapped in the crevices or cavities protecting these regions from further corrosion.

According to McCafferty¹⁶⁶, the solution becomes depleted in hydrogen ions as the reaction proceeds and stops when all the H⁺ ions are removed. Gireesha¹⁶⁷ et al., who obtained similar results in Al 6061/red mud MMCs, supports the view of McCafferty and our results.

4.1.2 Effect of reinforcement on corrosion rate

It is apparent that for all the specimens tested (Tables 3 – 15 and Fig.9 - 21), there's a trend of decreasing corrosion rate with increase in reinforcement content. The corrosion rate of the unreinforced matrix alloy is beyond those of the zircon reinforced composites. The alloy doesn't exhibit abundant corrosion resistance to the corrosion medium. Zircon being ceramic, remains inert and it's unaffected throughout the tests. The inert reinforcement particulates also are not expected to have an effect on electrochemically the corrosion mechanism of the composite. However, the results showed improvement in corrosion resistance, because the reinforcement content is inflated within the composite.

Sharma et al.,¹⁶⁸ studied similar results in short glass fiber reinforced ZA27 aluminium composites, and observed increased in corrosion resistance rate with increase in reinforcement content.

Better corrosion resistance of the MMCs is probably due to the reinforcement network interfering with the reaction between the acid and the metallic matrix¹⁶⁹. Furthermore, the electrochemically inert reinforcement particulates, which are present on the exposed surfaces of these MMCs, reduce the effective area of the electrochemically active matrix alloy, which is exposed to the corrodent, thereby reducing corrosion rates.

Table 3:- Influence of reinforcement on the corrosion rate of Al 7075 in 1M HCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	Corrosion Rate (mpy)			
24	0.0239	0.023	0.022	0.0163
48	0.0135	0.0122	0.0121	0.0115
72	0.0091	0.0086	0.0085	0.0083
96	0.0073	0.0072	0.0066	0.0064

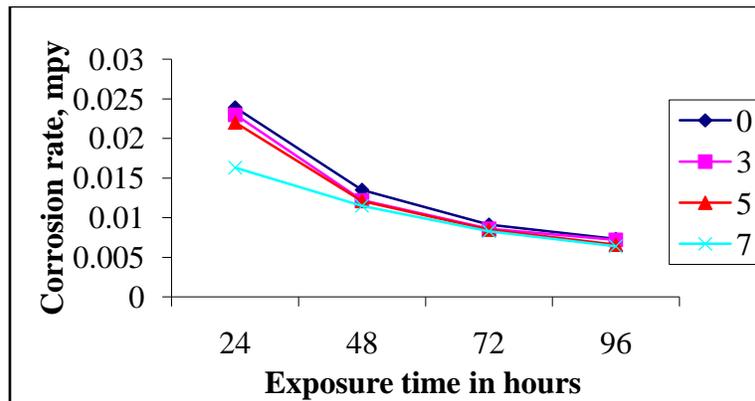


Figure 9:- Influence of reinforcement on the corrosion rate of Al 7075 in 1M HCl

Table 4:- Influence of reinforcement on the corrosion rate of Al 7075 in 0.5M HCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	Corrosion Rate (mpy)			
24	0.01	0.0092	0.0066	0.006
48	0.0067	0.0062	0.006	0.0058
72	0.0054	0.0053	0.005	0.0046
96	0.0046	0.0042	0.0041	0.0038

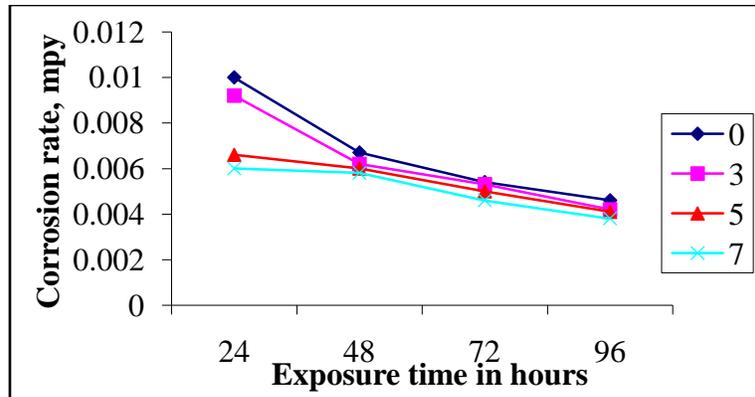


Figure 10:- Influence of reinforcement on the corrosion rate of Al 7075 in 0.5M HCl

Table 5:- Influence of reinforcement on the corrosion rate of Al 7075 in 0.25M HCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	Corrosion Rate (mpy)			
24	0.0026	0.0024	0.0021	0.0015
48	0.0025	0.0023	0.002	0.0015
72	0.0023	0.0021	0.0019	0.0014
96	0.002	0.0018	0.0016	0.0013

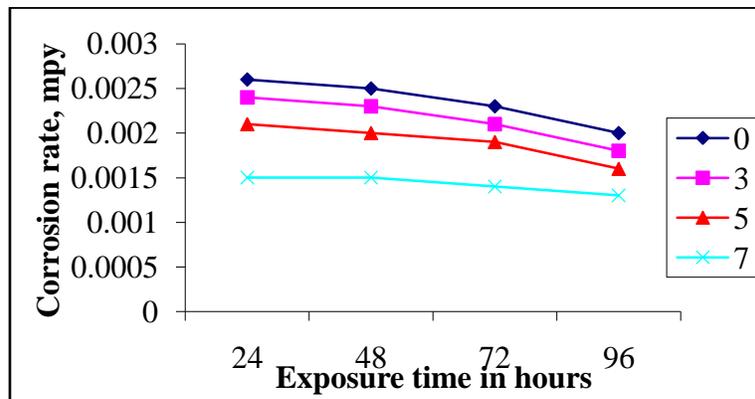


Figure 11:- Influence of reinforcement on the corrosion rate of Al 7075 in 0.25M HCl

Table 6:- Influence of reinforcement on the corrosion rate of Al 7075 in 3.5% NaCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	Corrosion Rate (mpy)			
24	0.0424	0.0346	0.0301	0.0281
48	0.0378	0.0311	0.0268	0.0249
72	0.0339	0.0271	0.0243	0.0232
96	0.0303	0.0243	0.0209	0.0197

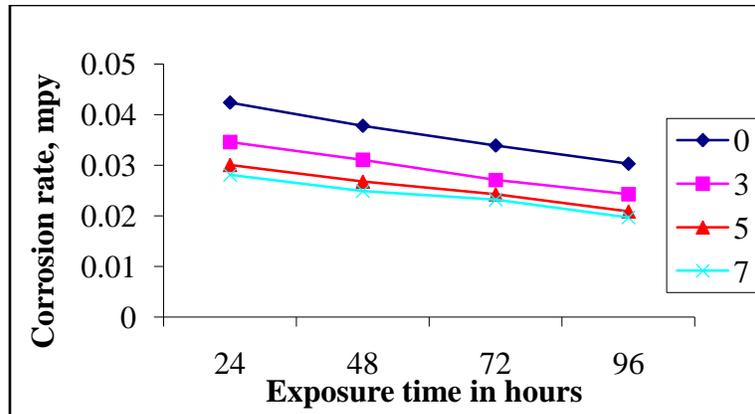


Figure 12:- Influence of reinforcement on the corrosion rate of Al 7075 in 3.5% NaCl

Table 7:- Influence of reinforcement on the corrosion rate of Al 7075 in 0.35% NaCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	Corrosion Rate (mpy)			
24	0.0134	0.0095	0.0038	0.0032
48	0.0064	0.0039	0.003	0.0029
72	0.0051	0.0031	0.0024	0.0021
96	0.0037	0.0028	0.002	0.0018

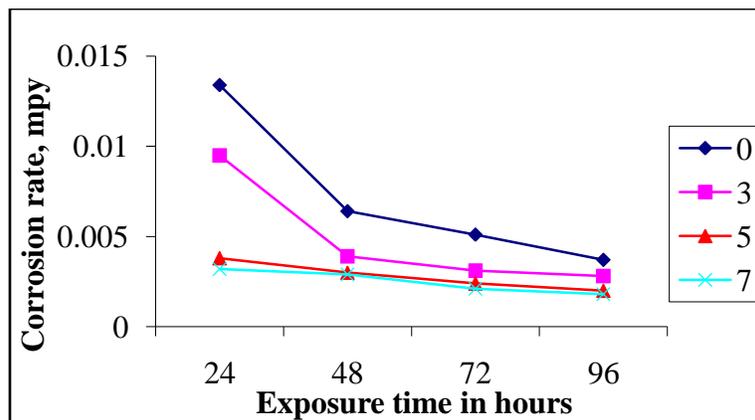


Figure 13:- Influence of reinforcement on the corrosion rate of Al 7075 in 0.35% NaCl

Table 8:- Influence of reinforcement on the corrosion rate of Al 7075 in 0.035% NaCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	Corrosion Rate (mpy)			
24	0.0086	0.0061	0.0049	0.0043
48	0.0079	0.0055	0.0041	0.0037
72	0.0062	0.0047	0.0033	0.0028
96	0.004	0.0032	0.0023	0.0014

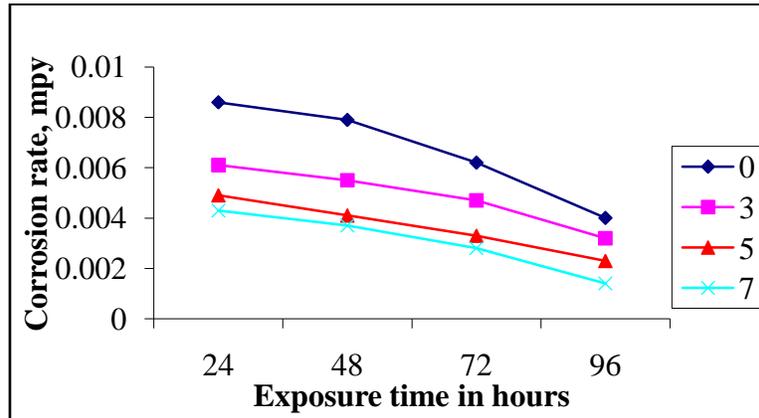


Figure 14:- Influence of reinforcement on the corrosion rate of Al 7075 in 0.035% NaCl

Table 9:- Influence of reinforcement on the corrosion rate of Al 7075 in 1M NaOH

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	Corrosion Rate (mpy)			
24	0.0302	0.0298	0.0226	0.0204
48	0.0151	0.0143	0.013	0.0116
72	0.0117	0.0092	0.0087	0.007
96	0.0096	0.0072	0.0065	0.0051

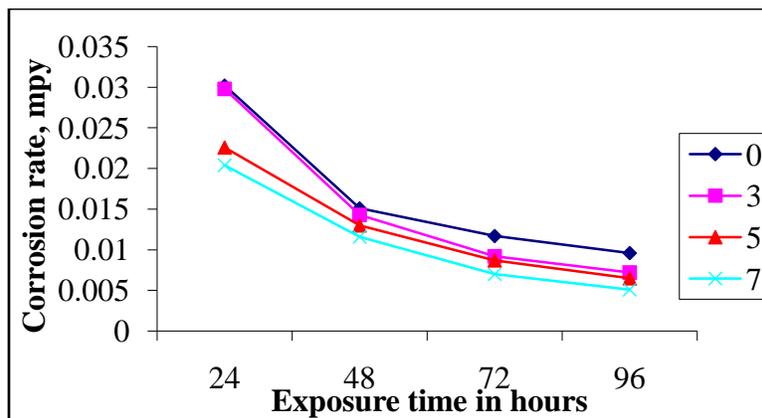


Figure 15:- Influence of reinforcement on the corrosion rate of Al 7075 in 1M NaOH

Table 10:- Influence of reinforcement on the corrosion rate of Al 7075 in 0.5M NaOH

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	Corrosion Rate (mpy)			
24	0.0166	0.0155	0.0136	0.0117
48	0.011	0.0078	0.0074	0.007
72	0.0054	0.005	0.0047	0.0046
96	0.0046	0.0042	0.0035	0.0034

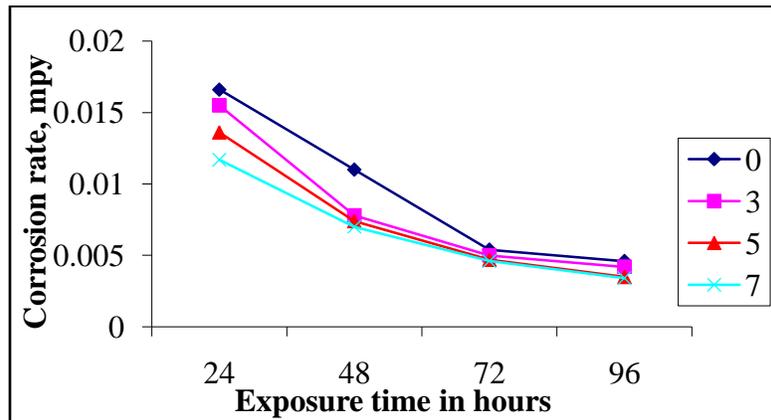


Figure 16:- Influence of reinforcement on the corrosion rate of Al 7075 in 0.5M NaOH

Table 11:- Influence of reinforcement on the corrosion rate of Al 7075 in 0.25M NaOH

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	Corrosion Rate (mpy)			
24	0.0102	0.0097	0.0091	0.0084
48	0.0054	0.0052	0.005	0.0049
72	0.0036	0.003	0.0029	0.0024
96	0.0022	0.0021	0.002	0.0018

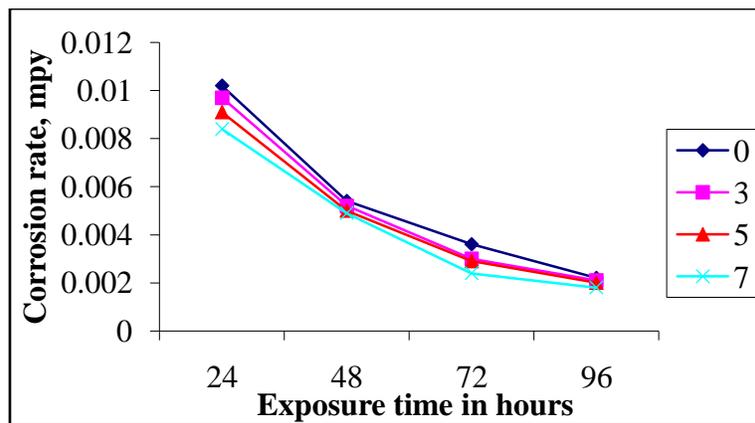


Figure 17:- Influence of reinforcement on the corrosion rate of Al 7075 in 0.25M NaOH

Table 12:- Influence of reinforcement on the corrosion rate of Al 7075 in equimolar solution of 1M NaOH + 1M NaCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	Corrosion Rate (mpy)			
24	0.0148	0.0136	0.0113	0.0093
48	0.0088	0.0086	0.0058	0.0052
72	0.0046	0.0044	0.0041	0.0038

96	0.0045	0.0042	0.0034	0.0029
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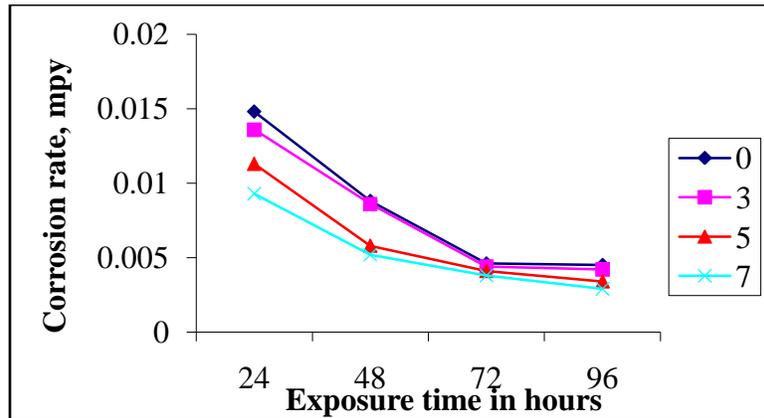


Figure 18:- Influence of reinforcement on the corrosion rate of Al 7075 in equimolar solution of 1M NaOH + 1M NaCl

Table 13:- Influence of reinforcement on the corrosion rate of Al 7075 in equimolar solution of 0.5M NaOH + 0.5M NaCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	Corrosion Rate (mpy)			
24	0.0092	0.0088	0.0081	0.0066
48	0.0054	0.0046	0.0044	0.0039
72	0.0038	0.003	0.0028	0.0024
96	0.0025	0.0022	0.0021	0.002

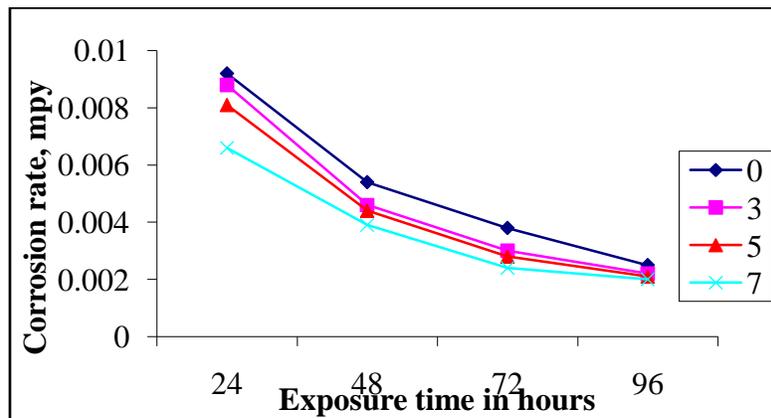


Figure 19:- Influence of reinforcement on the corrosion rate of Al 7075 in equimolar solution of 0.5M NaOH + 0.5M NaCl

Table 14:- Influence of reinforcement on the corrosion rate of Al 7075 in equimolar solution of 0.25M NaOH + 0.25M NaCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	Corrosion Rate (mpy)			
24	0.0135	0.0099	0.0092	0.0051

48	0.0055	0.0044	0.0032	0.0025
72	0.0034	0.0028	0.0026	0.0023
96	0.0029	0.0025	0.002	0.0012

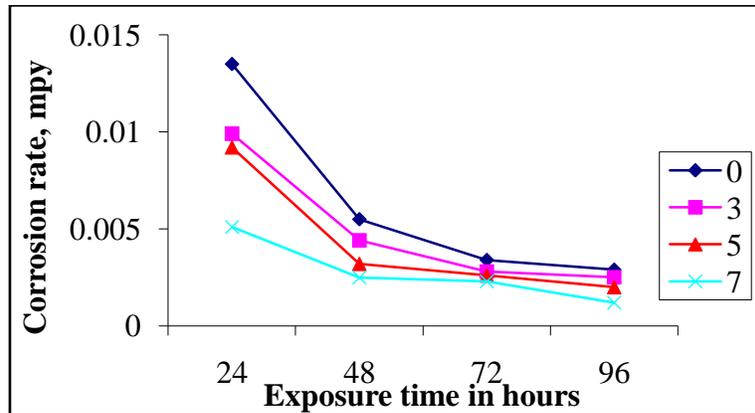


Figure 20:- Influence of reinforcement on the corrosion rate of Al 7075 in equimolar solution of 0.25M NaOH + 0.25M NaCl

Table 15:- Influence of reinforcement on the corrosion rate of Al 7075 in sea water

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	Corrosion Rate (mpy)			
24	0.000396	0.00032	0.000266	0.000264
48	0.000209	0.000198	0.000159	0.000126
72	0.000187	0.000184	0.000158	0.000067
96	0.000066	0.000058	0.000041	0.000015

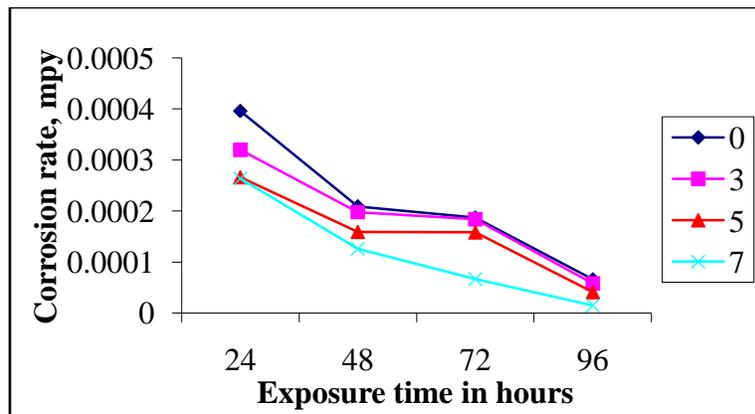


Figure 21:- Influence of reinforcement on the corrosion rate of Al 7075 in sea water

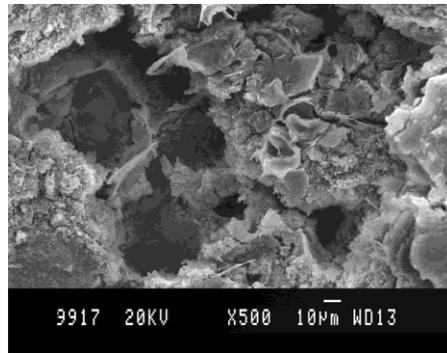


Figure 22:- Microstructure of unreinforced Al 7075 alloy after static corrosion studies in 1M HCl

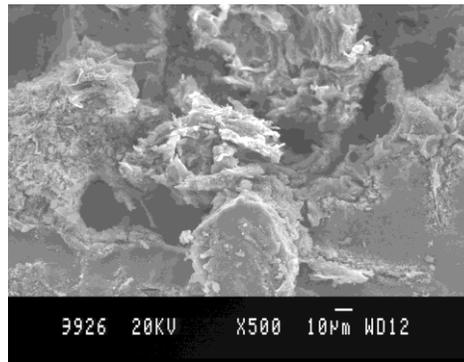


Figure 23:- Microstructure of Al 7075/3% zircon reinforced composite after static corrosion studies in 1M HCl

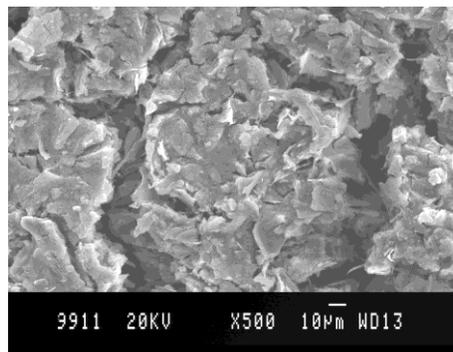


Figure 24:- Microstructure of Al 7075/5% zircon reinforced composite after static corrosion studies in 1M HCl

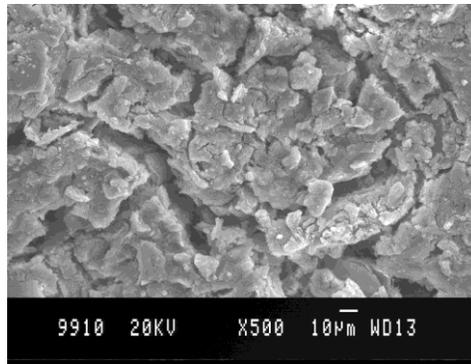


Figure 25:- Microstructure of Al 7075/7% zircon reinforced composite in after static corrosion studies 1M HCl

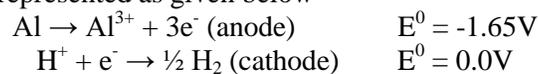
4.1.3 Morphology of corroded alloy

The presence of cracks and pits on the base of the alloy was clearly ascertained (Fig. 22). Since there's no reinforcement provided in any type, the base of the alloy fails to supply any type of resistance to the corrosion medium.

Composites shows the formation of pits on the surfaces, which decreases with increase in the zircon content. Corroded surface of the 3% zircon reinforced composites shows crack as well as pit formation on the surface (Fig. 23). It appears that the lower content of zircon can hardly restrict the severity of the corrodent attack. It behaves almost similar to that of the base alloy with insignificant improve the resistance of the corrosion. But for the 7% zircon reinforced composite, there is an indication of the presence of pits only (Fig. 25). This clearly proves the influence of zircon reinforcement on the corrosion resistance of the composites. This is clearly due to the matrix/reinforcement interface, which offer favorable site for formation of pits on the surface. Corrosion resistance gives 5% zircon reinforced composite lies in between 3% and 7% reinforced composites. Only very few cracks are observed (Fig. 24). Microscopic examination of composites after exposure to 1M HCl showed development of pits on the surface and also preferential attack of the matrix at the interface (Fig.23 - 25). The microstructure of the cast alloy tested under similar conditions is shown (Fig. 22), for comparison. As the number of pits increases, it leads to the formation of cracks. The crack propagation culminates in uplifting and flaking of the surface¹⁶⁷. These flakes were random in size and shape.

4.1.4 Effect of corrodant on corrosion rate

Aluminium and its alloys are covered with a dense oxide layer. Its not stable in acidic (pH < 4) and alkaline (pH > 9) environments and it is uniformly dissolved in these environments¹⁷⁰. In HCl media, after oxide film is dissolved, the underlying aluminium substrate dissolves due to hydrogen evolution type reactions¹⁷¹. The commercial aluminium alloys contain several types of intermetallic phases. The phases with Fe content act as microcathodes and the surrounding aluminium matrix act as microanodes¹⁷². The reaction taking place may be represented as given below



The dissolution of the metal in HCl occurs uniformly over the surface. The corrosion rate is expressed in mpy (milli inch per year), which is a penetration rate and not a mass loss rate such as $\text{g m}^{-2} \text{day}^{-1}$ and therefore the corrosion rate is found to be lower in HCl media than in neutral NaCl media (Tables 3, 4, 5, 6, 7 and 8).

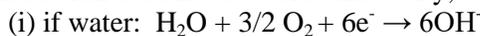
Aluminium and its oxide layer dissolves vigorously with intense evolution of H_2 in alkaline media, because in these media the potential of Al/Al^{3+} is decreased far below that of H^+/H_2 ¹⁷³.

Pitting is originated at the weak sites of the oxide film by Cl^- attack^{172, 174}. The Cl^- ions are adsorbed in the oxide film followed by rupture of film in the weak points, with the formation of microcracks which few nanometer wide. Many pits are originated within a very short time. But, most pits will stop after one or two days and these pits will be repaired¹⁷⁵. A minute fraction of initiated pits to spread.

Oxidation at the anode formed by the pit's bottom.

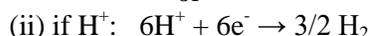


Reduction at cathode outside the cavity,

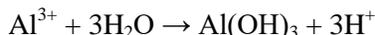


(Dissolved oxygen)

or



The dissolution of Al at the base of the pit creates an electric field that shifts the Cl^- ion to the bottom of pit forming $AlCl_4^-$. The hydrolysis of Al^{3+} leads to acidification of the bottom of the pit as shown in the following equation,



It leads to the acidification of the pits base up to a $pH < 3$. Medium becomes aggressive, leads to auto propagation of the pit.

The Al^{3+} ions being highly concentrated at the base it will diffuse towards pits opening, where they meet OH^- because the cathodic reaction taking place here leads to alkanisation. The hydrogen microbubbles, from the reduction of H^+ , push the formed $Al(OH)_3$ precipitate to open the pit, where it forms a deposit of white pustules. This block the entry point of the pit and slow down pitting.

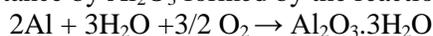
As salinity increases, the amount of O_2 dissolved decreases because more water molecules are immobilized by salt ions¹⁷⁶. The salting out effect of salts on dissolved oxygen is given by¹⁷⁷.

$$\log (C_o/C) = K C_e$$

C_o – Concentration of oxygen in water

C – Concentration of oxygen in salt solution of salt concentration, C_e

Therefore the corrosion resistance by Al_2O_3 formed by the reaction with O_2 ,



is less probable in NaCl solution¹⁷³.

However the above corrosion resistance process is possible in sea water because of its high DO content ($4 - 8 \text{ mg L}^{-1}$) in surface sea water due to atmospheric O_2 dissolved and photosynthesis by sea weeds, though it contains approximately 0.35 N NaCl. Therefore seawater corrosion rate is less than those values in NaCl media (Tables 6, 7, 8 and 15).

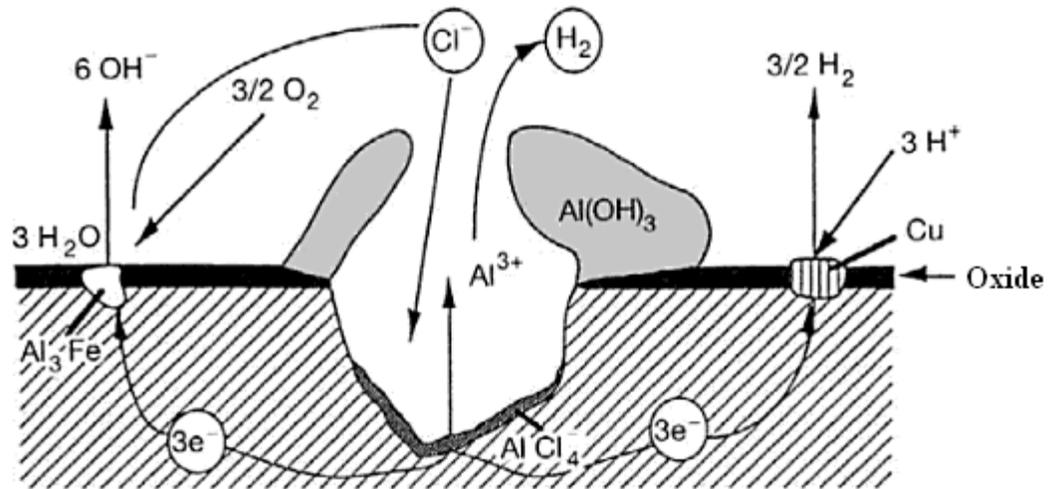


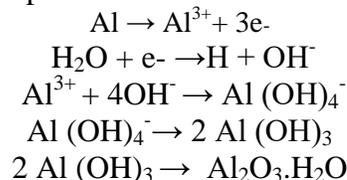
Figure 26:- Mechanism of pitting corrosion of aluminium.

In the medium containing NaCl and NaOH, the corrosion rate is less than those in neutral NaCl media (Tables 6, 7, 8, 12, 13 and 14). As the acidity at the pit bottom is not possible in alkaline medium, the downward propagation of the pit may not occur.

4.2 Open circuit potential studies

4.2.1 Influence of test duration

The function of exposure time of OCP measurements are shown in Fig. 27 to 39. In all the cases its observed that the potential decreases in the beginning with test duration and remains constant at the end possibly due to passivation. Its clear from the graph that the resistance of the composite to corrosion increases as the zircon percentage increases. Observed gradual decrease in potential indicates the probable gradual increase in passivation of the matrix alloy. Visual inspection of the specimens after the tests revealed the presence of a black film covering the surface and that could have retarded the process of corrosion.



In neutral and alkaline corrosion medium, base alloy and composite corrode due to the formation of AlO_2^- ions, which in turn reacts with water to form oxides and hydroxides. AlO_2^- is highly soluble in alkaline solution. Thus as soon as the film is formed it is washed off by the alkaline solution so that surface remains always in contact with the solution. However, as time passes, more and more OH^- ions are consumed from the solution and more AlO_2^- ions released are dissolved into the solution so that the pH of the solution increases. When the pH of the solution reaches a constant value the solution attains saturation. It is notable that during this period, there is a possibility of formation of $\text{Al}(\text{OH})_3$ on Al-alloy and composite surfaces. This layer is highly porous and unstable in nature¹⁶¹. Jayaprakash¹⁷⁸ et al., reported the corrosion of ZA27/quartz MMCs, reported similar type of results from the OCP studies.

4.2.2 Effect of reinforcement

It can be clearly observed (Fig. 27 to 39) that, both alloy and composites are potential decreases with increase in zircon content. In bottom of alloy the strength of the media is used to induces the crack formation of the surface, which eventually leads to the formation of pits, there by causing the loss of material. Presence of cracks and pits on the bottom of the alloy surface was ascertained clearly on visual examination of the specimens once the take a look at. Since there's no reinforcement other in any type, the bottom alloy fails to supply any variety of resistance to the corrosion medium. Less decrease in potential in case of unreinforced alloy is possibly due to the observed pits and cracks on the surface compared to that of composites¹⁷⁹.

Zircon being the ceramic material remains inert and is hardly plagued by corrosion medium throughout the test and it's not expected to have an effect on the corrosion mechanism of the composites. Results indicate that there's associate improvement in corrosion resistance because the proportion of zircon particulates enhanced within the composites. Zircon particulates in all probability act as a physical barrier to the initiation and development of corrosion pits and additionally modifies the micro structure of the matrix material and thus reduces the potential.

Table 16:- Open circuit potential studies in 1M HCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	-E (V)			
0	0.79	0.77	0.75	0.72
1	0.78	0.77	0.75	0.72
2	0.77	0.76	0.74	0.71
3	0.76	0.75	0.73	0.71
4	0.75	0.74	0.72	0.7
5	0.74	0.73	0.71	0.7
6	0.73	0.72	0.71	0.68
7	0.73	0.72	0.71	0.67
8	0.72	0.71	0.69	0.66
9	0.72	0.7	0.68	0.65
10	0.72	0.7	0.67	0.64
11	0.71	0.69	0.66	0.64
12	0.71	0.68	0.65	0.63
13	0.71	0.68	0.64	0.63
14	0.71	0.68	0.64	0.62
15	0.7	0.67	0.64	0.61
16	0.7	0.67	0.64	0.6
17	0.7	0.67	0.63	0.6
18	0.7	0.67	0.63	0.6
19	0.7	0.66	0.63	0.6
20	0.7	0.66	0.63	0.6
21	0.7	0.66	0.63	0.6
22	0.7	0.66	0.63	0.6
23	0.7	0.66	0.63	0.6
24	0.7	0.66	0.63	0.6
25	0.7	0.66	0.63	0.6

Table 17:- Open circuit potential studies in 0.5M HCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	-E (V)			
0	0.74	0.73	0.72	0.71
1	0.73	0.72	0.71	0.69
2	0.73	0.71	0.7	0.68
3	0.72	0.71	0.69	0.67
4	0.71	0.7	0.68	0.66
5	0.69	0.68	0.67	0.65
6	0.69	0.67	0.66	0.64
7	0.68	0.66	0.65	0.63
8	0.67	0.65	0.64	0.62
9	0.67	0.64	0.63	0.61
10	0.66	0.63	0.62	0.6
11	0.65	0.62	0.61	0.59
12	0.64	0.61	0.6	0.58
13	0.64	0.61	0.59	0.57
14	0.63	0.6	0.59	0.56
15	0.63	0.6	0.58	0.54
16	0.62	0.59	0.57	0.53
17	0.61	0.58	0.56	0.52
18	0.61	0.57	0.55	0.51
19	0.6	0.57	0.54	0.51
20	0.6	0.57	0.54	0.51
21	0.6	0.57	0.54	0.51
22	0.6	0.57	0.54	0.51
23	0.6	0.57	0.54	0.51
24	0.6	0.57	0.54	0.51
25	0.6	0.57	0.54	0.51

Table 18:- Open circuit potential studies in 0.25M HCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	-E (V)			
0	0.7	0.68	0.67	0.66
1	0.69	0.67	0.66	0.65
2	0.68	0.65	0.64	0.63
3	0.67	0.64	0.63	0.62
4	0.66	0.63	0.62	0.6
5	0.65	0.62	0.6	0.58
6	0.64	0.61	0.58	0.57
7	0.63	0.6	0.57	0.56
8	0.62	0.59	0.56	0.55
9	0.61	0.58	0.55	0.53
10	0.6	0.57	0.54	0.52
11	0.59	0.56	0.53	0.5

12	0.58	0.55	0.52	0.49
13	0.57	0.54	0.51	0.48
14	0.56	0.53	0.5	0.47
15	0.55	0.52	0.49	0.46
16	0.54	0.51	0.48	0.45
17	0.53	0.5	0.47	0.44
18	0.52	0.49	0.46	0.43
19	0.51	0.48	0.45	0.42
20	0.5	0.47	0.44	0.41
21	0.49	0.47	0.44	0.4
22	0.49	0.47	0.44	0.4
23	0.49	0.47	0.44	0.4
24	0.49	0.47	0.44	0.4
25	0.49	0.47	0.44	0.4

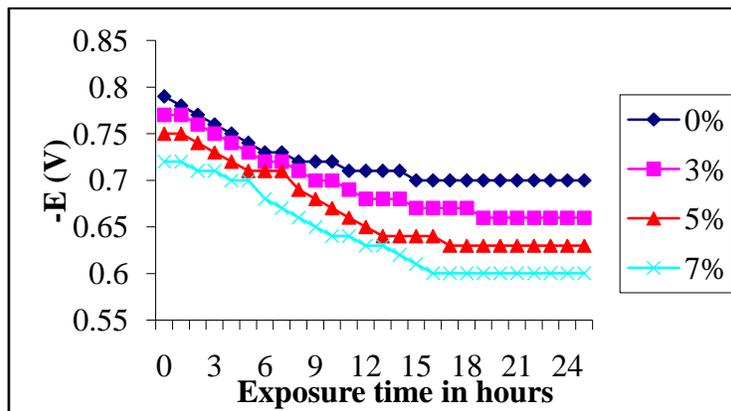


Figure 27:- Open circuit potential studies in 1M HCl .

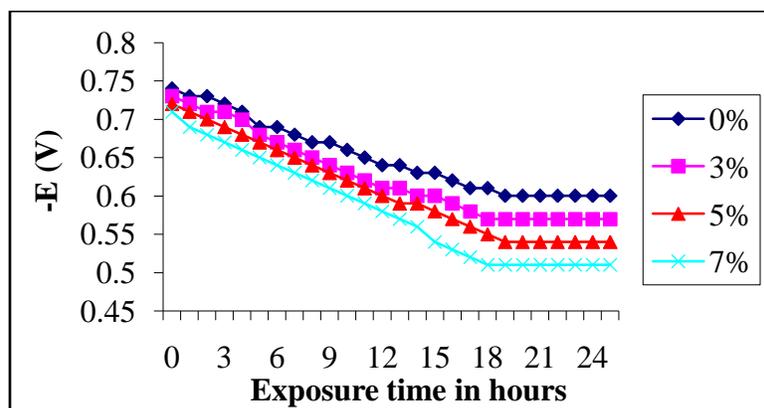


Figure 28:- Open circuit potential studies in 0.5M HCl

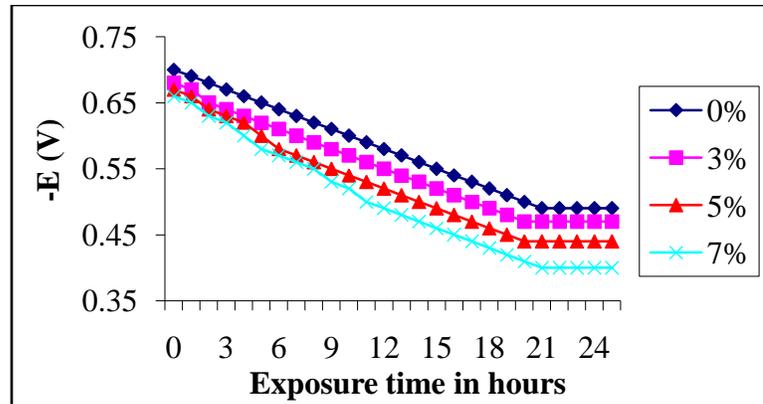


Figure 29:- Open circuit potential studies in 0.25M HCl

Table 19:- Open circuit potential studies in 3.5% NaCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	-E (V)			
0	0.74	0.73	0.72	0.71
1	0.73	0.72	0.71	0.7
2	0.72	0.71	0.7	0.69
3	0.71	0.7	0.69	0.68
4	0.7	0.69	0.68	0.67
5	0.69	0.68	0.67	0.66
6	0.68	0.67	0.66	0.65
7	0.67	0.66	0.65	0.64
8	0.66	0.65	0.64	0.63
9	0.65	0.64	0.63	0.62
10	0.64	0.63	0.62	0.61
11	0.63	0.62	0.61	0.6
12	0.62	0.61	0.6	0.59
13	0.61	0.6	0.59	0.58
14	0.6	0.59	0.58	0.57
15	0.6	0.59	0.58	0.57
16	0.59	0.58	0.57	0.56
17	0.59	0.58	0.57	0.56
18	0.58	0.57	0.56	0.55
19	0.58	0.57	0.56	0.54
20	0.58	0.57	0.56	0.54
21	0.57	0.56	0.55	0.53
22	0.57	0.56	0.55	0.53
23	0.57	0.56	0.55	0.53
24	0.57	0.56	0.55	0.53
25	0.57	0.56	0.55	0.53
26	0.57	0.56	0.55	0.53

Table 20:- Open circuit potential studies in 0.35% NaCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	-E (V)			
0	0.65	0.64	0.63	0.62
1	0.63	0.62	0.61	0.6
2	0.6	0.59	0.57	0.56
3	0.57	0.56	0.54	0.53
4	0.55	0.54	0.52	0.51
5	0.53	0.52	0.5	0.48
6	0.51	0.5	0.48	0.46
7	0.49	0.48	0.47	0.45
8	0.47	0.45	0.44	0.42
9	0.45	0.43	0.41	0.4
10	0.43	0.41	0.39	0.37
11	0.41	0.39	0.37	0.35
12	0.39	0.37	0.35	0.33
13	0.38	0.36	0.34	0.32
14	0.37	0.35	0.33	0.31
15	0.35	0.34	0.32	0.3
16	0.33	0.32	0.31	0.29
17	0.32	0.31	0.3	0.29
18	0.31	0.3	0.29	0.28
19	0.3	0.29	0.28	0.27
20	0.29	0.28	0.27	0.26
21	0.28	0.27	0.26	0.25
22	0.28	0.27	0.26	0.25
23	0.28	0.27	0.26	0.25
24	0.28	0.27	0.26	0.25
25	0.28	0.27	0.26	0.25
26	0.28	0.27	0.26	0.25

Table 21:- Open circuit potential studies in 0.035% NaCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	-E (V)			
0	0.52	0.5	0.47	0.44
1	0.5	0.48	0.46	0.43
2	0.48	0.47	0.45	0.42
3	0.47	0.46	0.44	0.41
4	0.46	0.45	0.43	0.4
5	0.45	0.44	0.42	0.4
6	0.44	0.43	0.42	0.39
7	0.43	0.42	0.41	0.38
8	0.41	0.4	0.38	0.37
9	0.4	0.39	0.37	0.36
10	0.38	0.37	0.36	0.35

11	0.37	0.36	0.35	0.34
12	0.37	0.36	0.35	0.34
13	0.36	0.35	0.34	0.33
14	0.35	0.34	0.33	0.32
15	0.35	0.34	0.33	0.32
16	0.34	0.33	0.32	0.31
17	0.33	0.32	0.31	0.3
18	0.33	0.32	0.31	0.3
19	0.33	0.32	0.31	0.3
20	0.32	0.31	0.3	0.29
21	0.32	0.31	0.3	0.29
22	0.32	0.31	0.3	0.29
23	0.32	0.31	0.3	0.29
24	0.32	0.31	0.3	0.29
25	0.32	0.31	0.3	0.29
26	0.32	0.31	0.3	0.29

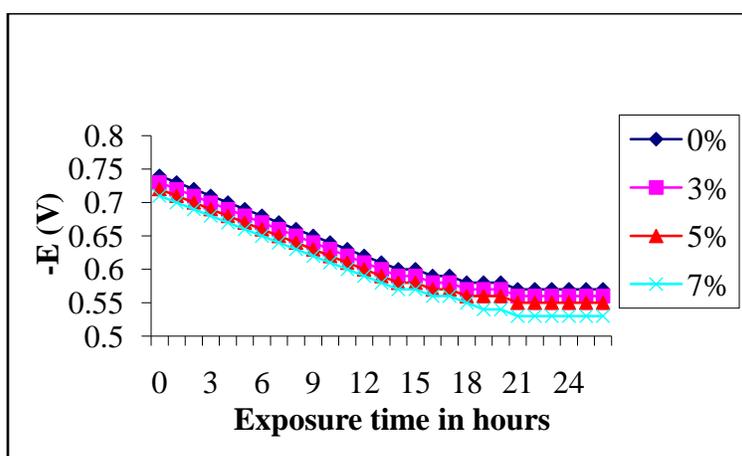


Figure 30:- Open circuit potential studies in 3.5% NaCl.

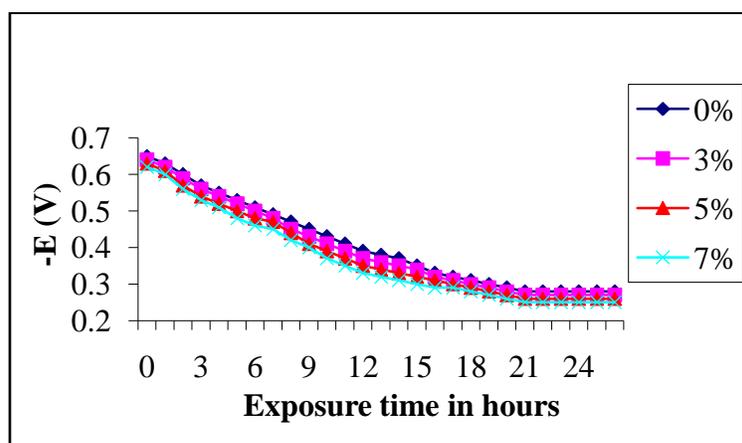


Figure 31:- Open circuit potential studies in 0.35% NaCl

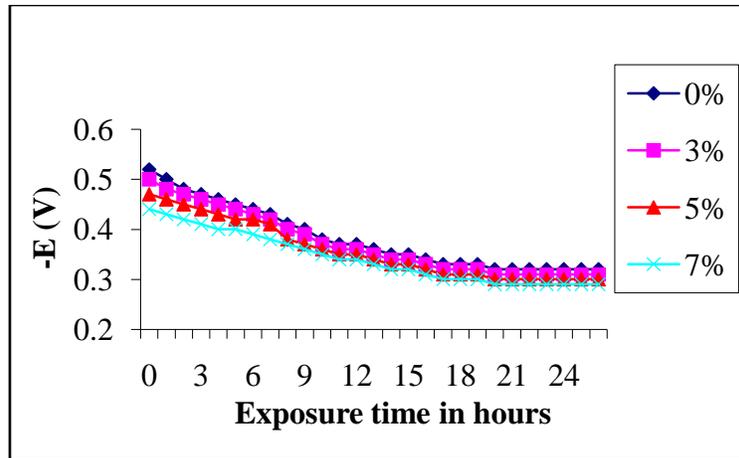


Figure 32: Open circuit potential studies in 0.035% NaCl

Table 22:- Open circuit potential studies in 1M NaOH

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	-E (V)			
0	1.69	1.66	1.64	1.62
1	1.67	1.65	1.62	1.6
2	1.64	1.63	1.6	1.59
3	1.62	1.6	1.58	1.57
4	1.59	1.58	1.56	1.54
5	1.57	1.55	1.54	1.52
6	1.56	1.54	1.53	1.51
7	1.53	1.52	1.51	1.49
8	1.51	1.49	1.48	1.46
9	1.48	1.46	1.45	1.43
10	1.46	1.44	1.42	1.4
11	1.44	1.42	1.4	1.38
12	1.41	1.4	1.38	1.36
13	1.39	1.37	1.36	1.34
14	1.36	1.35	1.33	1.31
15	1.33	1.32	1.3	1.29
16	1.3	1.29	1.27	1.26
17	1.26	1.25	1.24	1.23
18	1.24	1.23	1.21	1.2
19	1.21	1.2	1.18	1.16
20	1.18	1.16	1.15	1.13
21	1.15	1.13	1.12	1.1
22	1.12	1.11	1.09	1.08
23	1.09	1.08	1.06	1.05
24	1.06	1.05	1.04	1.03
25	1.04	1.03	1.02	1.01
26	1.01	0.99	0.98	0.97
27	0.99	0.96	0.95	0.94

28	0.99	0.96	0.95	0.94
29	0.99	0.96	0.95	0.94
30	0.99	0.96	0.95	0.94
31	0.99	0.96	0.95	0.94

Table 23:- Open circuit potential studies in 0.5M NaOH

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	-E (V)			
0	1.61	1.59	1.56	1.54
1	1.54	1.5	1.48	1.46
2	1.5	1.48	1.46	1.44
3	1.48	1.46	1.44	1.43
4	1.47	1.45	1.43	1.42
5	1.46	1.44	1.42	1.41
6	1.44	1.43	1.4	1.39
7	1.41	1.4	1.38	1.37
8	1.39	1.38	1.36	1.35
9	1.37	1.36	1.35	1.33
10	1.35	1.34	1.33	1.32
11	1.33	1.32	1.31	1.3
12	1.3	1.29	1.28	1.27
13	1.28	1.27	1.26	1.25
14	1.26	1.25	1.24	1.23
15	1.24	1.23	1.22	1.21
16	1.22	1.21	1.2	1.19
17	1.2	1.19	1.18	1.17
18	1.18	1.17	1.16	1.15
19	1.15	1.14	1.13	1.12
20	1.14	1.12	1.11	1.1
21	1.12	1.11	1.1	1.09
22	1.1	1.09	1.08	1.07
23	1.09	1.08	1.07	1.06
24	1.08	1.07	1.06	1.05
25	1.07	1.06	1.05	1.04
26	1.07	1.06	1.05	1.04
27	1.07	1.06	1.05	1.04
28	1.07	1.06	1.05	1.04
29	1.07	1.06	1.05	1.04
30	1.07	1.06	1.05	1.04
31	1.07	1.06	1.05	1.04

Table 24:- Open circuit potential studies in 0.25M NaOH

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	-E (V)			
0	1.52	1.5	1.48	1.46

1	1.5	1.47	1.46	1.44
2	1.48	1.46	1.44	1.42
3	1.45	1.44	1.42	1.4
4	1.42	1.41	1.39	1.38
5	1.4	1.38	1.36	1.35
6	1.38	1.36	1.34	1.33
7	1.36	1.34	1.32	1.3
8	1.34	1.32	1.3	1.28
9	1.32	1.3	1.28	1.26
10	1.3	1.28	1.26	1.24
11	1.29	1.27	1.25	1.23
12	1.28	1.26	1.24	1.22
13	1.27	1.25	1.23	1.2
14	1.25	1.24	1.22	1.19
15	1.24	1.23	1.21	1.18
16	1.23	1.22	1.2	1.17
17	1.22	1.21	1.19	1.16
18	1.21	1.2	1.18	1.15
19	1.2	1.19	1.17	1.14
20	1.19	1.18	1.16	1.13
21	1.18	1.17	1.16	1.13
22	1.18	1.17	1.16	1.13
23	1.17	1.16	1.15	1.12
24	1.16	1.15	1.14	1.12
25	1.15	1.14	1.13	1.12
26	1.15	1.14	1.13	1.12
27	1.15	1.14	1.13	1.12
28	1.15	1.14	1.13	1.12
29	1.15	1.14	1.13	1.12
30	1.15	1.14	1.13	1.12
31	1.15	1.14	1.13	1.12

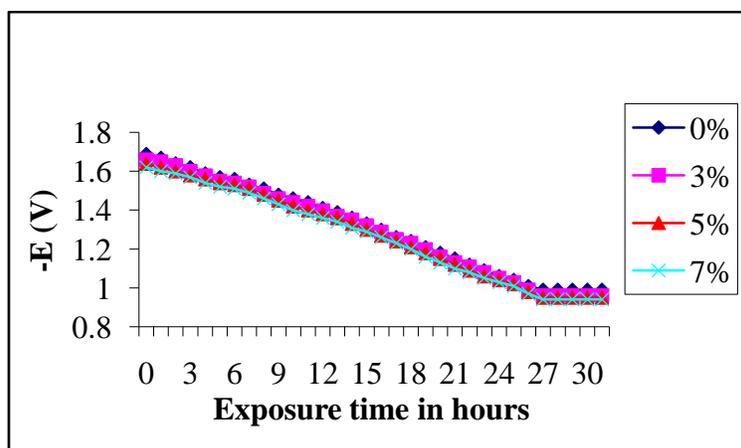


Figure 33:- Open circuit potential studies in 1M NaOH

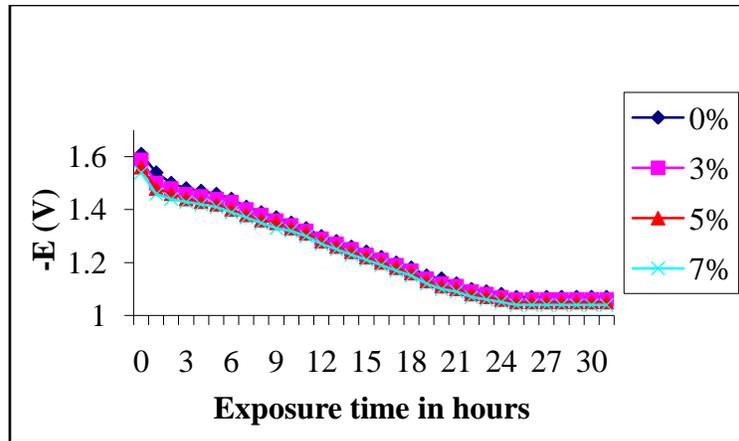


Figure 34:- Open circuit potential studies in 0.5M NaOH.

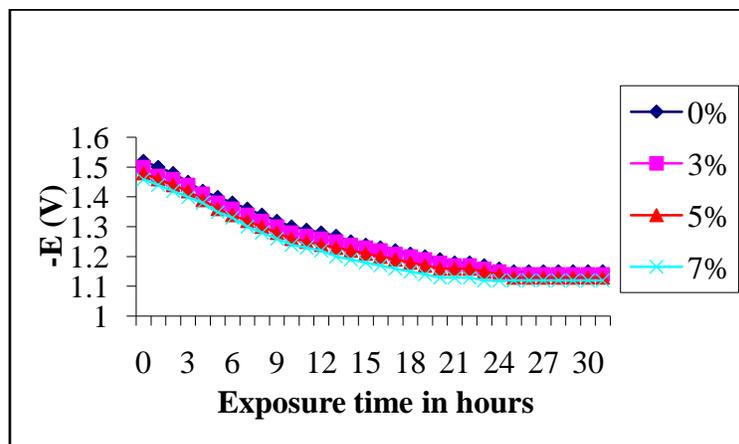


Figure 35:- Open circuit potential studies in 0.25M NaOH

Table 25:- Open circuit potential studies in equimolar solution of 1M NaOH + 1M NaCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	-E (V)			
0	1.62	1.6	1.58	1.56
1	1.57	1.56	1.54	1.52
2	1.54	1.51	1.5	1.48
3	1.52	1.49	1.48	1.46
4	1.49	1.46	1.45	1.43
5	1.46	1.43	1.42	1.4
6	1.44	1.42	1.4	1.38
7	1.42	1.4	1.38	1.36
8	1.4	1.38	1.36	1.34
9	1.38	1.36	1.34	1.32
10	1.37	1.35	1.33	1.31
11	1.35	1.33	1.31	1.3
12	1.34	1.32	1.3	1.29
13	1.33	1.32	1.29	1.28

14	1.32	1.3	1.28	1.26
15	1.31	1.29	1.27	1.25
16	1.3	1.28	1.26	1.25
17	1.29	1.27	1.25	1.24
18	1.28	1.27	1.25	1.23
19	1.27	1.26	1.24	1.23
20	1.27	1.25	1.24	1.23
21	1.26	1.25	1.24	1.23
22	1.26	1.25	1.24	1.23
23	1.26	1.25	1.24	1.23
24	1.26	1.25	1.24	1.23
25	1.26	1.25	1.24	1.23

Table 26:- Open circuit potential studies in equimolar solution of
0.5M NaOH + 0.5M NaCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	-E (V)			
0	1.55	1.54	1.5	1.49
1	1.5	1.49	1.48	1.47
2	1.48	1.46	1.45	1.44
3	1.46	1.45	1.44	1.43
4	1.43	1.41	1.4	1.39
5	1.42	1.4	1.38	1.37
6	1.4	1.38	1.37	1.36
7	1.39	1.37	1.36	1.35
8	1.38	1.36	1.35	1.34
9	1.36	1.35	1.34	1.33
10	1.35	1.34	1.33	1.32
11	1.34	1.33	1.32	1.31
12	1.33	1.32	1.31	1.3
13	1.32	1.31	1.3	1.29
14	1.31	1.3	1.29	1.28
15	1.3	1.29	1.28	1.27
16	1.29	1.28	1.27	1.26
17	1.28	1.27	1.26	1.25
18	1.27	1.26	1.25	1.24
19	1.26	1.25	1.24	1.23
20	1.25	1.24	1.23	1.22
21	1.25	1.24	1.23	1.22
22	1.25	1.24	1.23	1.22
23	1.25	1.24	1.23	1.22
24	1.25	1.24	1.23	1.22
25	1.25	1.24	1.23	1.22

Table 27:- Open circuit potential studies in equimolar solution of
0.25M NaOH + 0.25M NaCl

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	-E (V)			
0	1.46	1.45	1.43	1.41
1	1.4	1.38	1.36	1.34
2	1.36	1.35	1.33	1.32
3	1.33	1.32	1.31	1.3
4	1.32	1.31	1.3	1.29
5	1.3	1.29	1.28	1.27
6	1.29	1.28	1.27	1.26
7	1.28	1.27	1.26	1.25
8	1.27	1.26	1.25	1.24
9	1.26	1.25	1.24	1.23
10	1.25	1.24	1.23	1.22
11	1.24	1.23	1.22	1.21
12	1.23	1.22	1.21	1.2
13	1.22	1.21	1.2	1.19
14	1.21	1.2	1.19	1.18
15	1.2	1.19	1.18	1.17
16	1.19	1.18	1.17	1.16
17	1.18	1.17	1.16	1.15
18	1.18	1.17	1.16	1.15
19	1.17	1.16	1.15	1.14
20	1.16	1.15	1.14	1.13
21	1.16	1.15	1.14	1.13
22	1.16	1.15	1.14	1.13
23	1.16	1.15	1.14	1.13
24	1.16	1.15	1.14	1.13
25	1.16	1.15	1.14	1.13

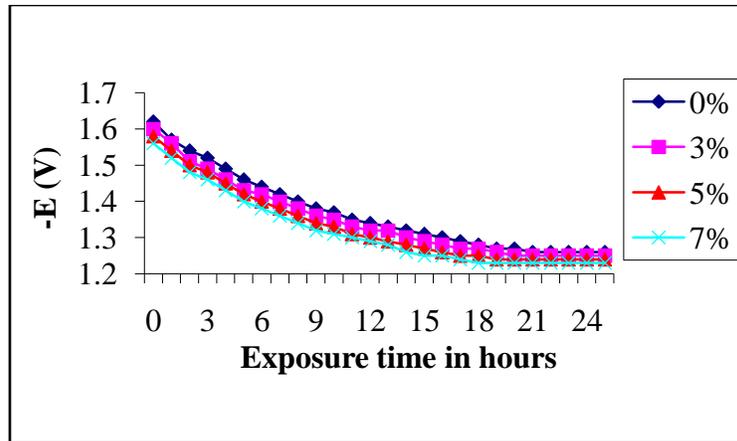


Figure 36:- Open circuit potential studies in equimolar solution of 1M NaOH + 1M NaCl

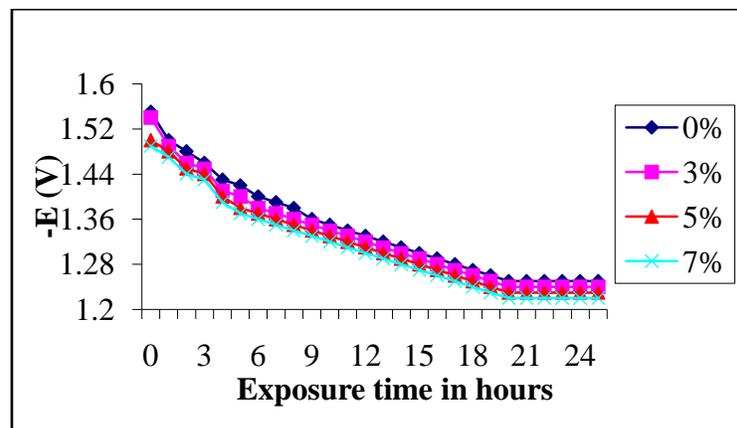


Figure 37:- Open circuit potential studies in equimolar solution of 0.5M NaOH + 0.5M NaCl

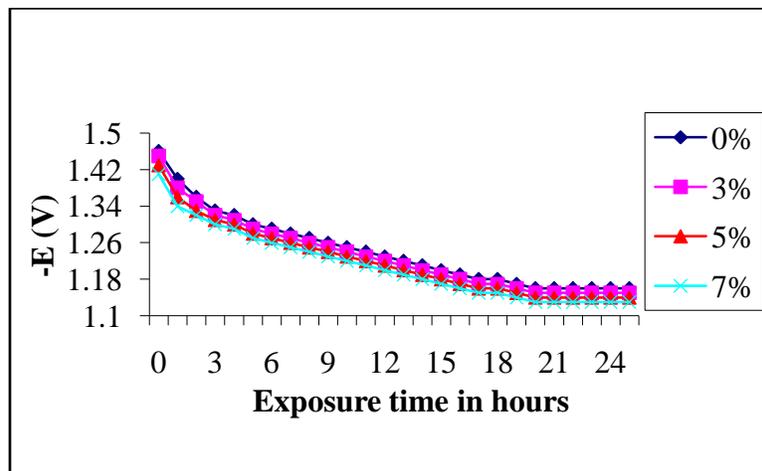


Figure 38:- Open circuit potential studies in equimolar solution of 0.25M NaOH + 0.25M NaCl

Table 28:- Open circuit potential studies in sea water

% zircon for reinforcement	0%	3%	5%	7%
Time in Hours	-E (V)			
0	0.73	0.72	0.71	0.69
1	0.72	0.71	0.69	0.68
2	0.72	0.70	0.68	0.66
3	0.71	0.69	0.66	0.65
4	0.70	0.68	0.65	0.64
5	0.69	0.67	0.64	0.63
6	0.68	0.66	0.63	0.61
7	0.68	0.65	0.62	0.60
8	0.67	0.64	0.61	0.58
9	0.66	0.63	0.61	0.57
10	0.65	0.63	0.60	0.57
11	0.64	0.63	0.60	0.56
12	0.63	0.62	0.60	0.55
13	0.63	0.62	0.60	0.54
14	0.63	0.60	0.59	0.53
15	0.62	0.60	0.58	0.52
16	0.62	0.60	0.57	0.51
17	0.62	0.59	0.56	0.51
18	0.62	0.58	0.55	0.51
19	0.62	0.58	0.55	0.51
20	0.61	0.58	0.55	0.51
21	0.61	0.58	0.55	0.51
22	0.61	0.58	0.55	0.51
23	0.61	0.58	0.55	0.51
24	0.61	0.58	0.55	0.51
25	0.61	0.58	0.55	0.51

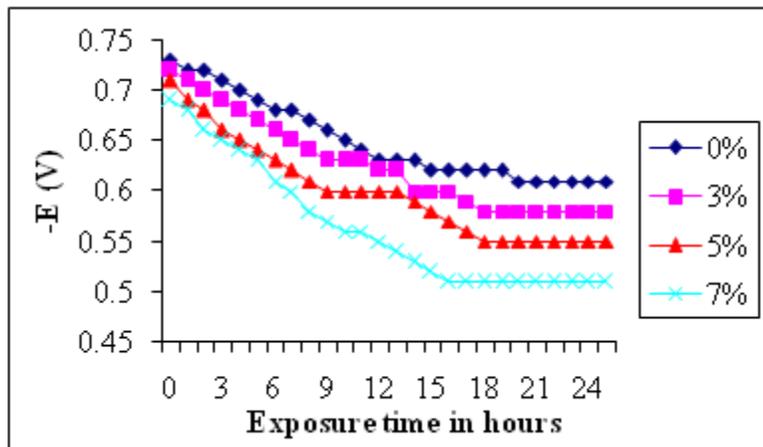


Figure 39:-Open circuit potential studies in sea water

4.2.3 Morphology of corroded alloy

The SEM images of typical corroded surfaces of the unreinforced, 3%, 5% and 7% zircon reinforced composite samples are presented in Fig. 40 – 43. The corroded surface morphology of the tested composite samples depends on the distribution of zircon.

The corrosive attack was intensive with deep pits on the surface of the unreinforced matrix alloy extending and connecting in such some way thus on cause cracking. Cracks may be seen originating from the deep pits and traversing on to the surface. but no definite crack path may be clearly visualised. These connected cracks cause progressive removal of structure on the surface normally referred to as as flaking. SEMs of the flakes that were fashioned from the corroded sample yet because the flakes still remaining on the sample were taken.

It can be clearly seen (Fig. 27 to 39) that the ceramic reinforcement particles act as insulators and stay inert within the corrosion medium throughout the test. Hence the potential decreases with increase in mineral content in MMCs, which can be decrease the area of exposure of the alloy with increase within the reinforcement. Exposure of less space of the MMCs to corrosive environments led to lesser corrosion additionally as corrosion than that of the matrix alloy.

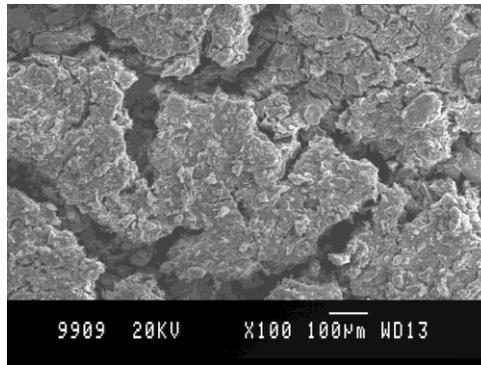


Figure 40:- Micrographs of unreinforced Al 7075 alloy after OCP studies in 3.5% NaCl

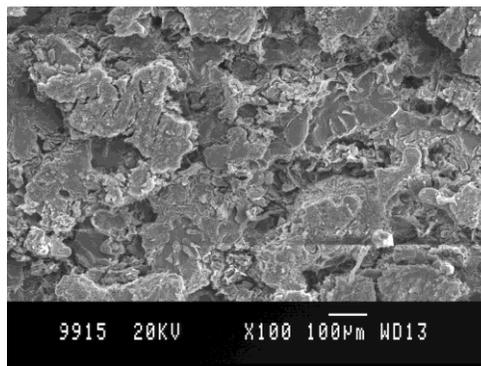


Figure 41:- Micrographs of Al 7075/3% zircon reinforced composite after OCP studies in 3.5% NaCl

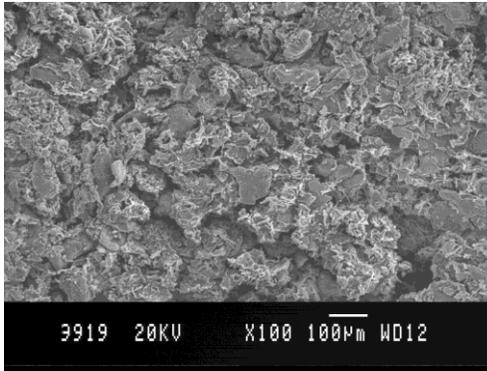


Figure 42:- Micrographs of Al 7075/5% zircon reinforced composite after OCP studies in 3.5% NaCl

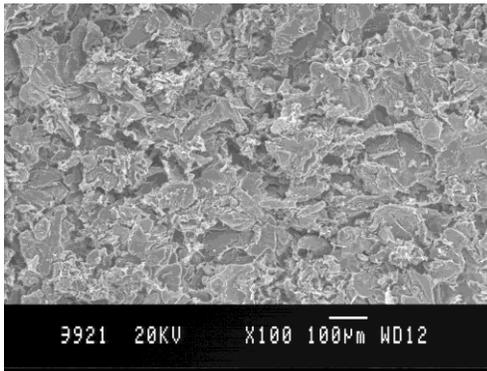


Figure 43:- Micrographs of Al 7075/7% zircon reinforced composite after OCP studies in 3.5% NaCl

4.3 Galvanic corrosion

4.3.1 Corrosion behavior

The polarization curves (Fig.44 – 56) for both the base matrix alloy and the Al 7075/zircon MMCs where potential is plotted versus galvanic current are presented. For tests conducted in different corrodents show that the decrease in the concentration of the corrodent, results in a marked increase in galvanic potential for both composites and the matrix alloy. This indicated the development of higher electrical resistance between corrosion media and electrodes. Corrosion resistance increases with increase in galvanic potential.

Tafel polarization curves (Fig.44 – 56) for both the unreinforced and reinforced aluminium alloys show that the cathodic and anodic curves are similar to each alloy and composites, however electrode curve of composites has slightly shifted to the less negative side, that is attributed to the decrease of H₂ gas evolution.

4.3.2 Effect of concentration of the solution

The concentration had a marked influence on the corrosion rate of all the samples. Increase in concentration of the corrodent solution, corrosion rate also increased (Fig. 44 – 56). The corrosion current was found to be proportional to the rate of hydrogen gas evolution. It is well known that the chemical reaction depends on the concentration of solution, area of the reaction surfaces, etc. The intensity of the corrosion attack increased with increase in concentration. Some researches^{180, 181} attributed this trend to the increase of chloride ion concentration of the solution, which increases corrosion rate.

The point of intersection between the cathodic and anodic curves provides current density of corrosion, I_{Cor} . The rate of corrosion was calculated by using conversion formula,

$$\text{corrosion rate in (mpy)} = CE_w I_{Cor} / d,$$

where C = conversion constant (1.287×10^5),
 E_w = the equivalent weight of the sample (g),
 d = density of sample (g/cc^3) and
 I_{Cor} = corrosion current A/cm^2 .

4.3.3 Effect of reinforcement

It is clearly observed (Tables 29 – 33) that the rate of corrosion Al 7075/zircon MMC, decreased with increase in zircon content and the corrosion rate of MMCs were less than that of the matrix alloy. This trend is attributed to the fact that zircon particulates are ceramic in nature and hence remains inert in aggressive corrosion media. Zircon particles also reduce the effective exposure area of MMC to react in the media. Ananda Murthy¹⁸² et al., reported the similar type of results in Al 6063/TiO₂ MMCs.

The presence of the zircon reinforcement phase decreases the corrosion current density, which is further retarded by additional reinforcement¹⁸³, probably because the reinforcement increase the bonding strength of the matrix.

Table 29: Potentiostatic studies in HCl

Normality of HCl	% zircon for reinforcement			
	0	3	5	7
	I_{corr} (mA/cm^2)			
0.100	1.8845	1.7781	1.6167	1.6020
0.050	1.8808	1.8036	1.7658	1.6989
0.025	1.7658	1.4649	1.4300	1.3188
	Corrosion rate, 10^5 mpy			
0.100	2.6948	2.5426	2.3118	2.2908
0.05	2.6895	2.5791	2.5250	2.4294
0.025	1.7658	1.4649	1.4300	1.3188

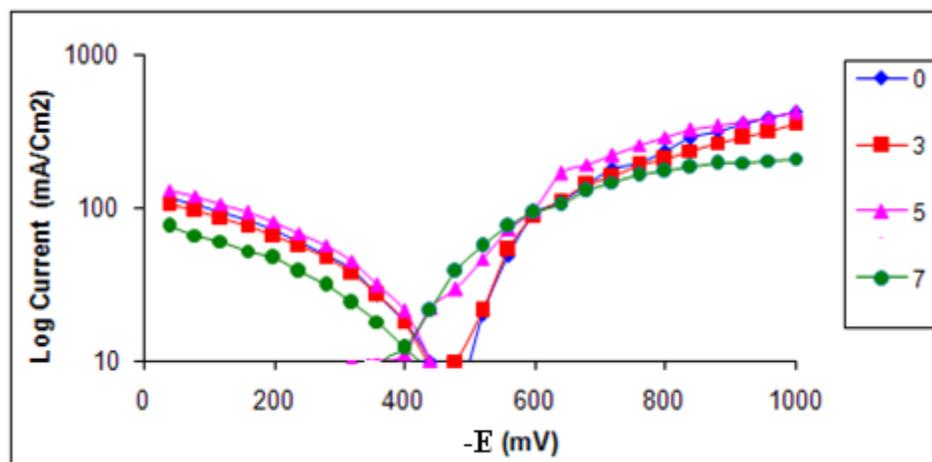


Figure 44:- Tafel curves for Al 7075/zircon composites in 0.1N HCl

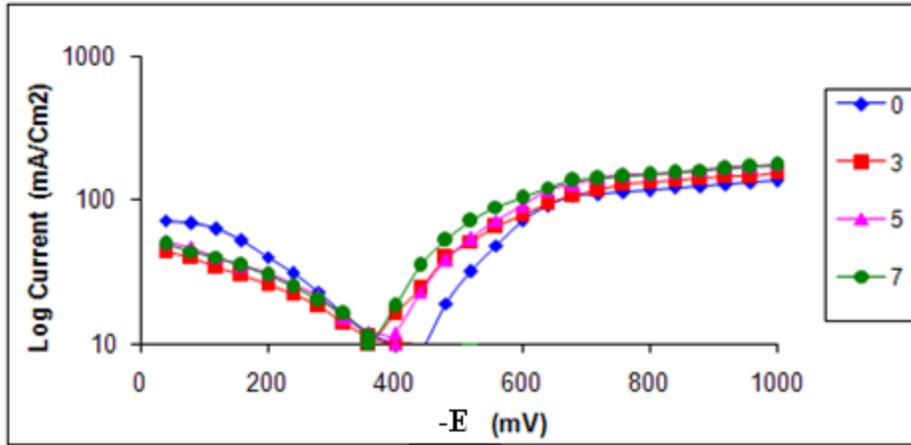


Figure 45:- Tafel curves for Al 7075/zircon composites in 0.05N HCl.

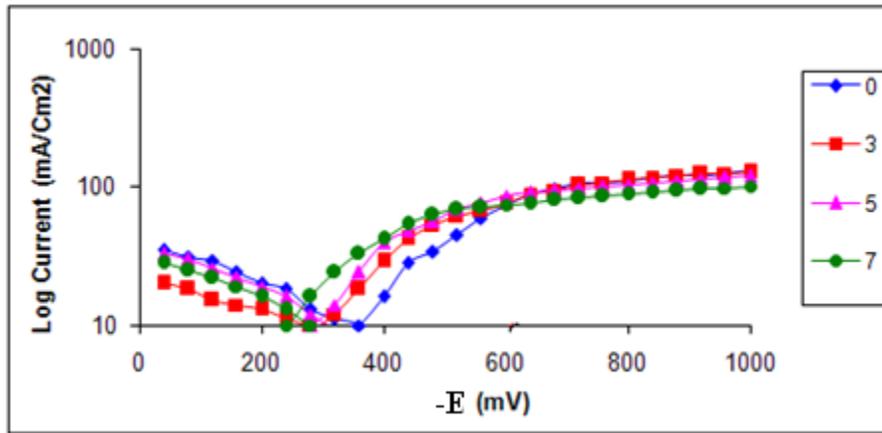


Figure 46:- Tafel curves for Al 7075/zircon composites in 0.025N HCl

Table 30:- Potentiostatic studies in NaCl

% of NaCl	% zircon for reinforcement			
	0	3	5	7
	I_{corr} (mA/cm ²)			
3.500	1.9836	1.9624	1.9009	1.8800
0.350	1.7891	1.6668	1.6263	1.5850
0.035	1.6319	1.5563	1.3979	1.2516
	Corrosion rate, 10 ⁵ mpy			
3.500	2.8365	2.8062	2.7182	2.6884
0.350	2.5584	2.3835	2.3286	2.2665
0.035	2.3336	2.2255	1.9989	1.7897

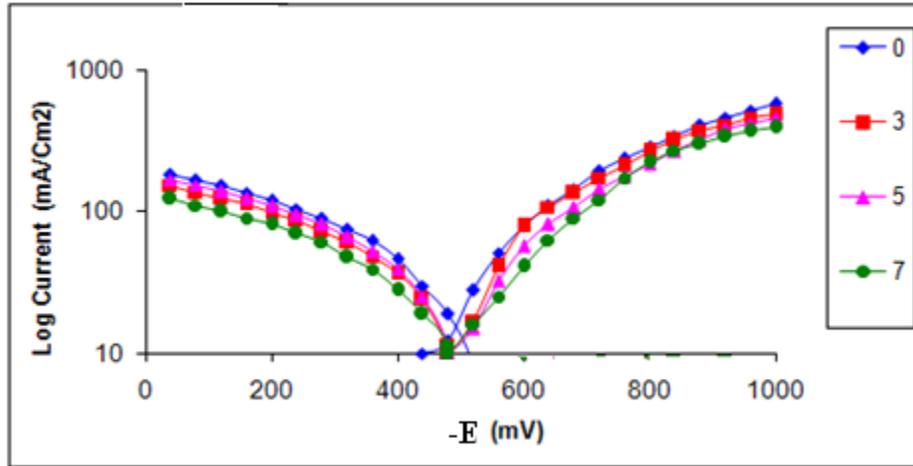


Figure 47:- Tafel curves for Al 7075/zircon composites in 3.5% NaCl.

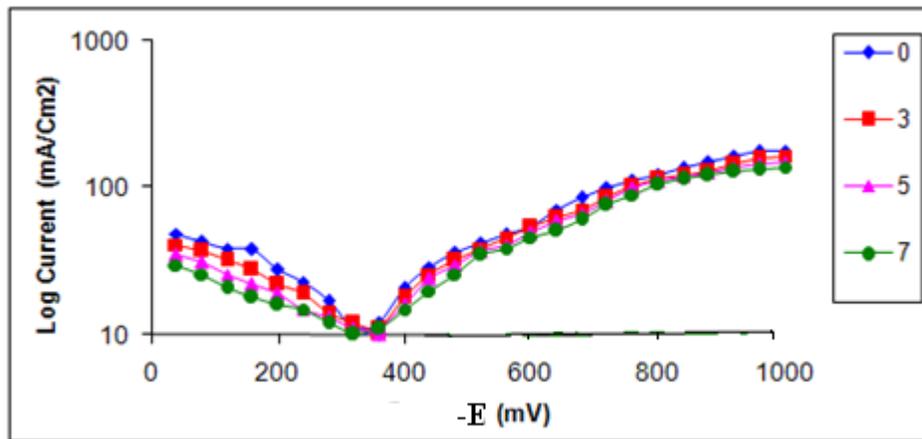


Figure 48:- Tafel curves for Al 7075/zircon composites in 0.35% NaCl.

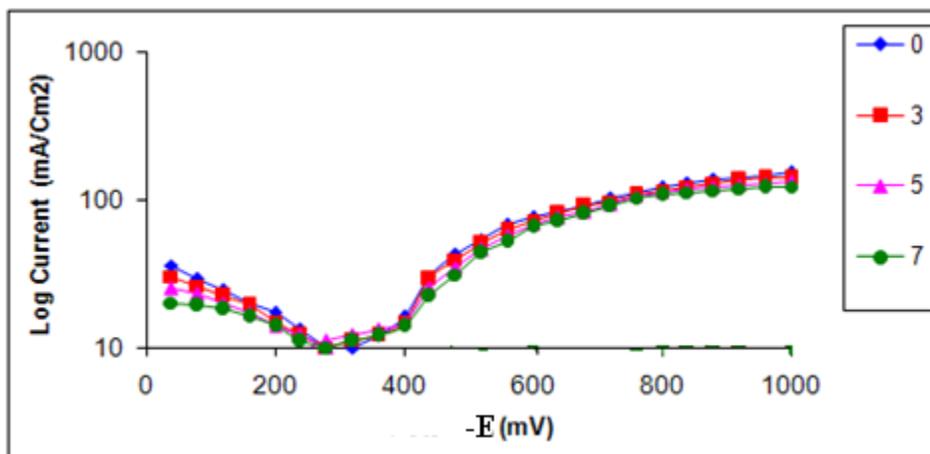


Figure 49:- Tafel curves for Al 7075/zircon composites in 0.035% NaCl.

Table 31:- Potentiostatic studies in NaOH

Normality of NaOH	% zircon for reinforcement			
	0	3	5	7
	I_{corr} (mA/cm ²)			
0.100	2.2218	2.2041	1.9030	1.7336
0.050	2.1461	1.9813	1.8325	1.7181
0.025	1.9242	1.8808	1.7160	1.6263
	Corrosion rate, 10 ⁵ mpy			
0.100	3.1772	3.1518	2.7212	2.4790
0.050	3.0689	2.8332	2.6204	2.4568
0.025	2.7516	2.6895	2.4538	2.356

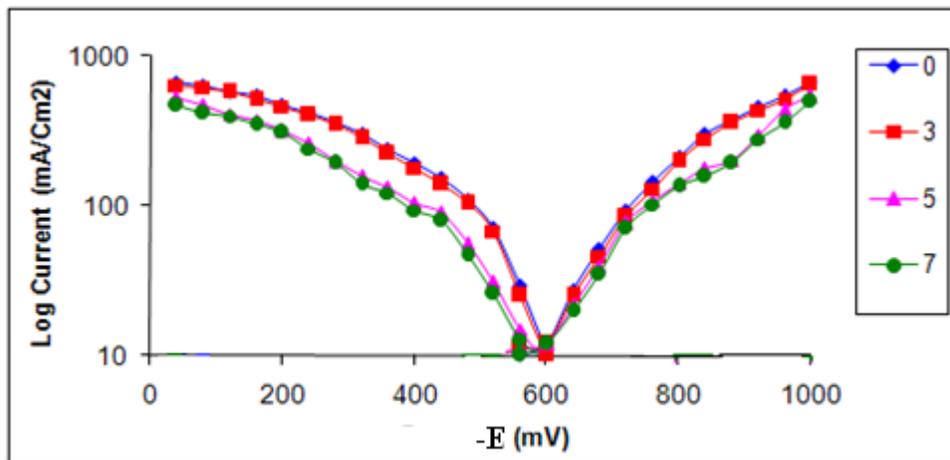


Figure 50:- Tafel curves for Al 7075/zircon composites in 0.1N NaOH.

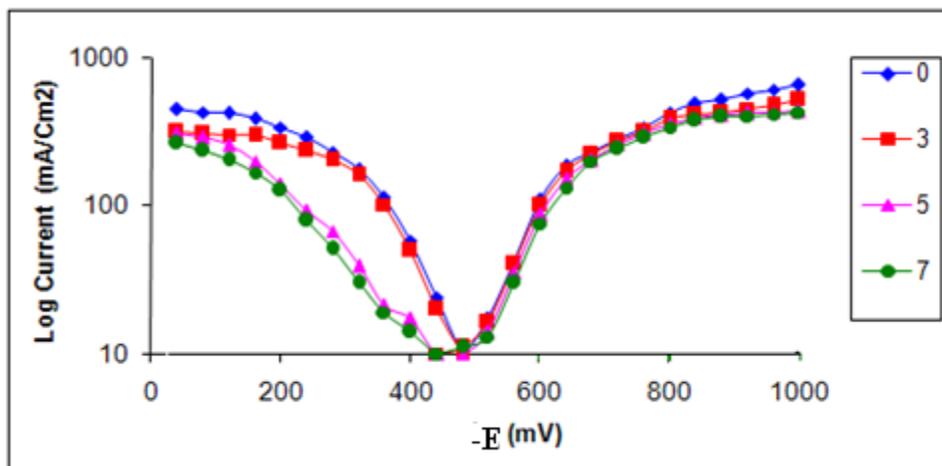


Figure 51:- Tafel curves for Al 7075/zircon composites in 0.05N NaOH.

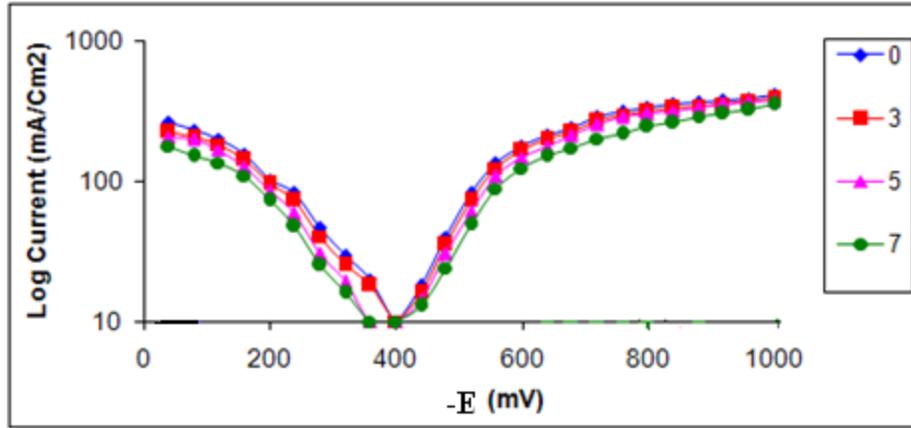


Figure 52:- Tafel curves for Al 7075/zircon composites in 0.025N NaOH

Table 32:- Potentiostatic studies in equimolar solution of NaOH + NaCl

Concentration of NaOH + NaCl	% zircon for reinforcement			
	0	3	5	7
	I_{corr} (mA/cm ²)			
0.100	2.2596	2.1690	1.9363	1.8880
0.050	1.9797	1.9565	1.9330	1.8818
0.025	1.6381	1.5606	1.5025	1.2576
	Corrosion rate, 10 ⁵ mpy			
0.100	3.2312	3.1016	2.7689	2.6998
0.050	2.8309	2.7977	2.7641	2.6909
0.025	2.3424	2.2316	2.1485	1.7983

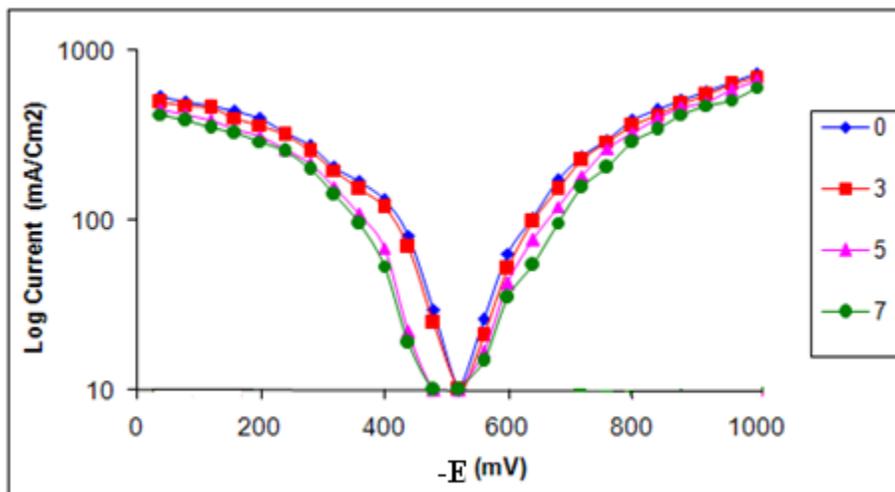


Figure 53:- Tafel curves for Al 7075/zircon composites in equimolar solution of 0.1M NaOH + 0.1M NaCl

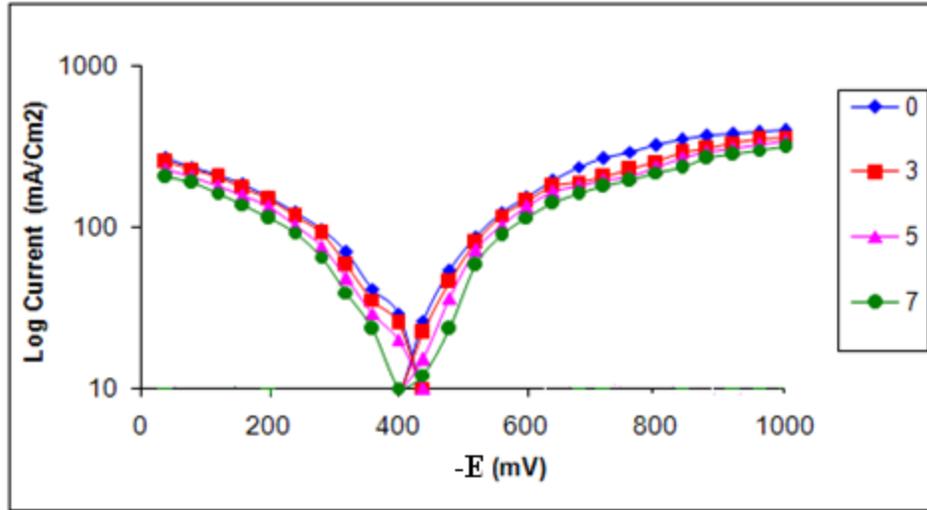


Figure 54:- Tafel curves for Al 7075/zircon composites in equimolar solution of 0.05M NaOH + 0.05M NaCl

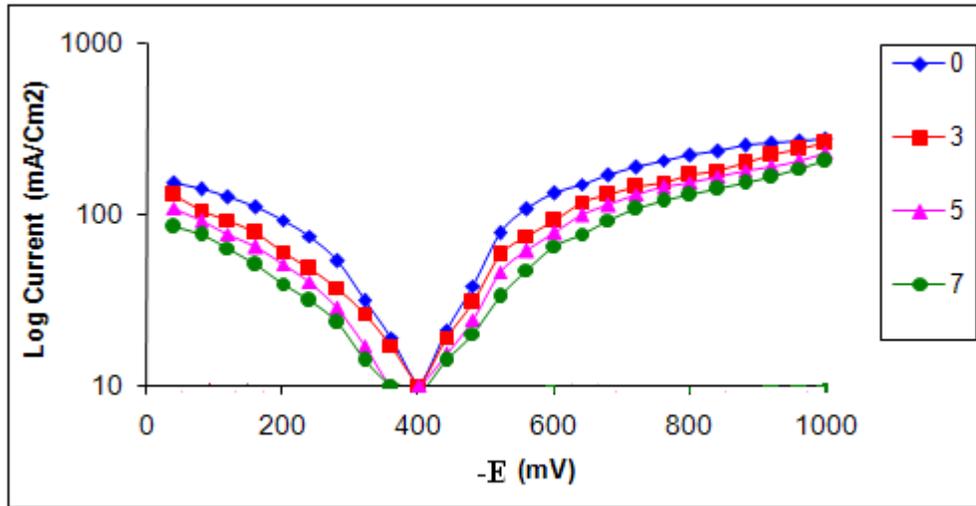


Figure 55:- Tafel curves for Al 7075/zircon composites in equimolar solution of 0.025M NaOH + 0.025M NaCl

Table 33:- Potentiostatic studies in Sea water

% zircon for reinforcement			
0	3	5	7
I_{corr} (mA/cm ²)			
2.0441	1.9847	1.9689	1.9525
Corrosion rate, 10 ⁵ mpy			
2.9230	2.8381	2.8155	2.7920

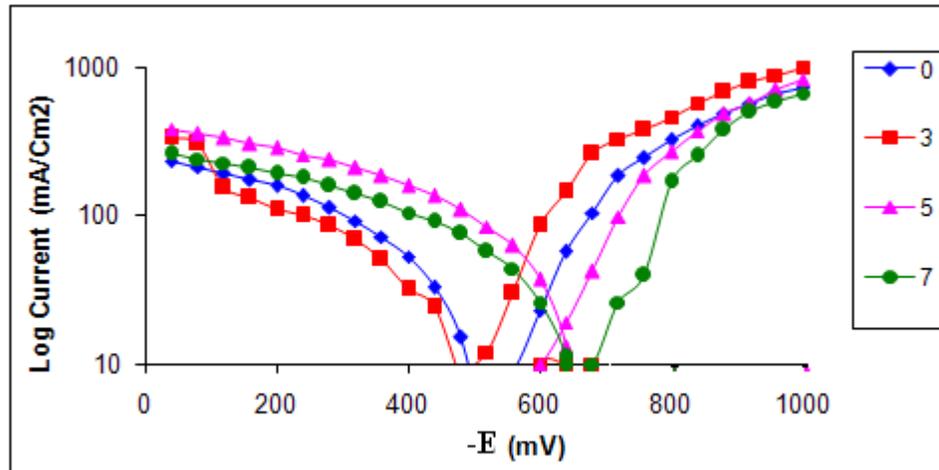


Figure 56:- Tafel curves for Al 7075/zircon composites in sea water

4.3.4 Morphology of corroded alloy

Microstructures of the unreinforced, 3%, 5% and 7% zircon reinforced composites after polarization studies in 0.1N NaOH were given (Fig. 57 – 60). The unreinforced matrix alloy shows more number of pits, cracks and flakes. The increased bonding strength avoids the crack getting developed in the zircon MMCs due to corrosion, this is also one of the main reason for the increase in the corrosion resistance. The interface of reinforcement and matrix is the site of corrosion. During the manufacture of magnesium intermetallic layer adjacent to the zircon particle improves the passivation behavior of the alloy, which turn to increases in the corrosion resistance of the MMC¹⁸².

Chemical composition of micro-particles in thick corrosive product layer was examined by EDAX (Fig. 61). Spectra obtained by EDAX were similar to all specimens showed strong aluminium and silica peaks, due to the presence of zircon and the limitations in isolation of sampling volumes¹⁸⁴. It is also showed some traces of the magnesium.

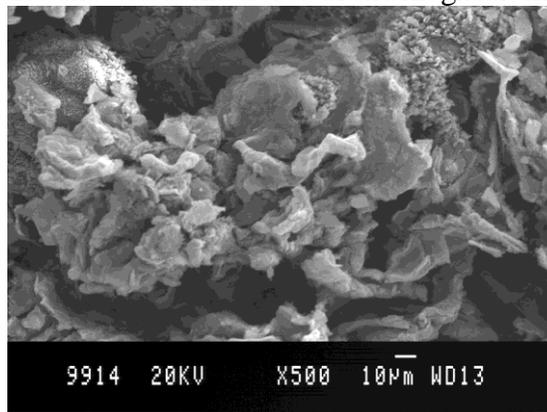


Figure 57:- Micrographs of unreinforced Al 7075 alloy after polarisation studies in 0.1N NaOH

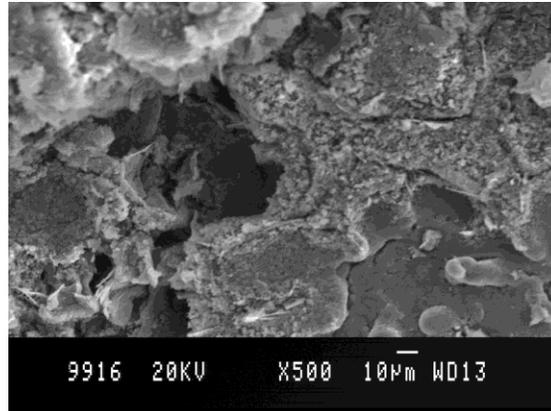


Figure 58:- Micrographs of Al 7075/3% zircon reinforced composite after polarisation studies in 0.1N NaOH

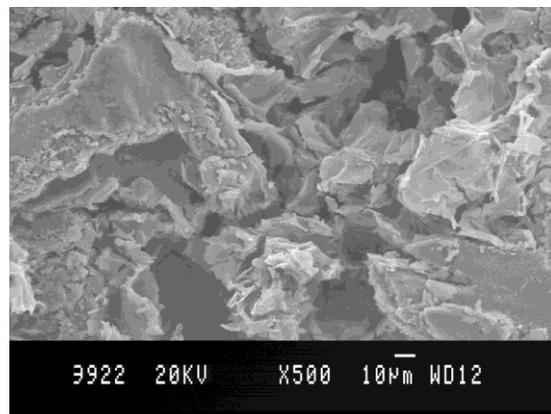


Figure 59:- Micrographs of Al 7075/5% zircon reinforced composite after polarisation studies in 0.1N NaOH

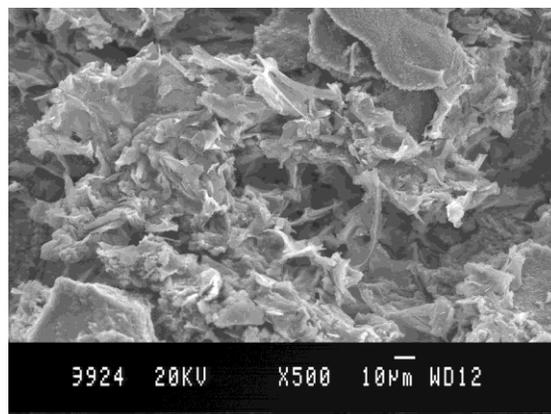


Figure 60:- Micrographs of Al 7075/7% zircon reinforced composite after polarisation studies in 0.1N NaOH

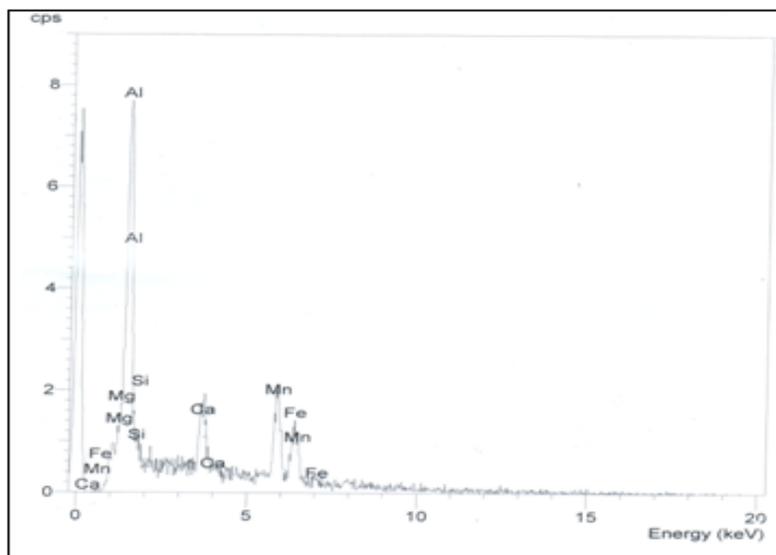


Figure 61:-EDAX spectra of Al 7075/7% zircon reinforced composite after polarization studies in 0.1N NaOH

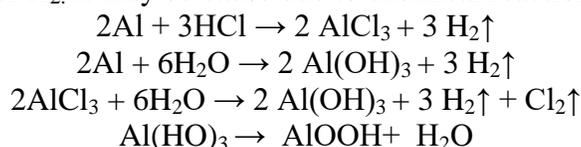
4.4 Stress Corrosion studies

4.4.1 Effect of test duration

On stress rate of corrosion versus exposure time of Al 7075 and Al 7075/zircon MMCs at 100 °C are shown (Fig. 64, 67 and 69). The rate of corrosion of both matrix alloy and composites increases with increase in exposure time. From previous works on Al composites^{167, 178, 182}, for the composites as well as for the unreinforced matrix alloy, in absence of stress, the rate of corrosion seems to decrease with time taken of the test. Decrease in rate of corrosion is probably due to the gradual deposition of hydroxide layer. But in stress corrosion study the rate of corrosion increased with increase in exposure time, and it may be due to the cracking of aluminium hydroxide film formed between the metal and corrosion medium upon application of stress. Increase in time the thickness of the Al(OH)₃ layer also increases which is disposed to cracking. Because of this the rate of corrosion increases with exposure time.

4.4.2 Effect of temperature

The stress rate of corrosion of Al 7075 and its MMCs in 1N HCl, 0.1N NaCl and immersed in sea water for 30 minutes at different temperatures increased with increase in temperature (Fig. 63, 66 and 68). This was attributed to the increased diffusion rate of hydrogen with increase in temperature. Hydrogen has been found to evolve even when aluminium is exposed to boiling water¹⁸⁵. Hydrogen generation and its entry into metal is probably a localized action other than a general surface phenomenon. Hydrogen permeation is related to kinetics and mechanism of hydrogen generation on external surface of the specimens. Aluminium dissolves in corrosive solution with generation of H₂. It may be caused due to chemical reaction as shown in below:



Influence of temperature on the rate of corrosion depends on the two factors: i) the energy of activation of hydrogen evolution reaction and ii) the temperature variation of the hydrogen concentration gradient. Activation energy depends on temperature¹⁶⁸. Rate of corrosion increased with temperature due

to increase in both hydrogen permeation rate and hydrogen evaluation. Inhibition efficiency increases with rise in temperatures. According to experimental results, the rate of corrosion increased with temperature for both matrix alloy and composites.

4.4.3 Effect of concentration

Plot of the stress rate of corrosion verses different concentrations of HCl and NaCl at 100 °C for 30 minutes of exposure time (Fig.62 and 65) show that the stress rate of corrosion of the samples increased with increase in concentrations of HCl and NaCl. The rate of corrosion of samples in 1N solution was greater than the corresponding corrosion rate in 0.25 N. The rate of corrosion are directly influenced by external variables, such as exposure to temperature of corrodent solution, exposure area of samples, concentration of hydrogen in solution, samples exposure time and samples area.

4.4.4 Effect of reinforcement

The reinforcement particles are inert and hence does not reacts with the matrix alloy. The rate of corrosion for both the matrix alloy and reinforced composite increases with exposure time, normality and temperature. Though, increase in rate of corrosion was lower for the zircon reinforced composite compared to that of base material Al-alloy under all conditions.

The interface between matrix alloy and reinforcement is the weakest part of the particulate reinforced composites. Therefore the nature of interfacial bond is critical in process of corrosion. Since the composites development showed improved mechanical properties it can be claimed that the interface between aluminium and reinforced particle is quite stronger⁵⁰. This could have effect on the improvement in resistance of corrosion of these composites. To backing this, it was observed that increase in reinforcement particle content there is a reduction in corrosion rate.

Decrease in rate of corrosion with increase in reinforcement content may be due to the formation of magnesium intermetallic compound at the interface during casting as reported by Trazaskoma¹⁰⁸. The magnesium intermetallic compound is more active than the matrix alloy, which is evident from the presence of pits at the interface. Active nature of crevices would cathodically protect the remainder of the matrix and restrict pit formation and propagation.

Magnesium reduction zones have an anodic behavior in relation to the adjacent zones that have higher Mg contents (cathodic zones). The rate of corrosion composites takes place preferentially near intermetallic phases such as Mg₂Si (noble precipitate) because of minor Mg content in adjacent matrix.

Table 34:- Normality V/S corrosion rate at 100 °C for 30 minutes

% reinforcement of zircon	0%	3%	5%	7%
Normality	Corrosion rate (mpy)			
0.25	1.9	1.51	1.22	1.01
0.5	4.99	4.01	3.47	2.26
0.75	9.45	8.31	7.71	6.28
1	16.72	15.1	14.56	10.06

Table 35:- Working temperature V/S corrosion rate in 1N HCl for 30 minutes exposure time

% reinforcement of zircon	0%	3%	5%	7%
Temperature in °C	Corrosion rate (mpy)			
100	16.72	15.1	14.56	10.06
110	23.09	20.01	18.55	15.01

120	29.99	26.12	23.29	20.49
130	38.06	32.58	28.93	25.16
140	47.6	39.89	35.06	33.21
150	57.19	48.96	41.92	40.1

Table 36:- Exposure time V/S corrosion rate at 100⁰ C in 1N HCl

% reinforcement of zircon	0%	3%	5%	7%
Exposure Time in minutes	Corrosion rate (mpy)			
10	5.98	4.95	3.81	3.09
20	11.01	9.72	8.88	6.13
30	16.72	15.1	14.56	10.06
40	19.2	16.85	15.12	13.28
50	21.58	19.02	18.02	15.01
60	22.36	20.91	19.96	17.27

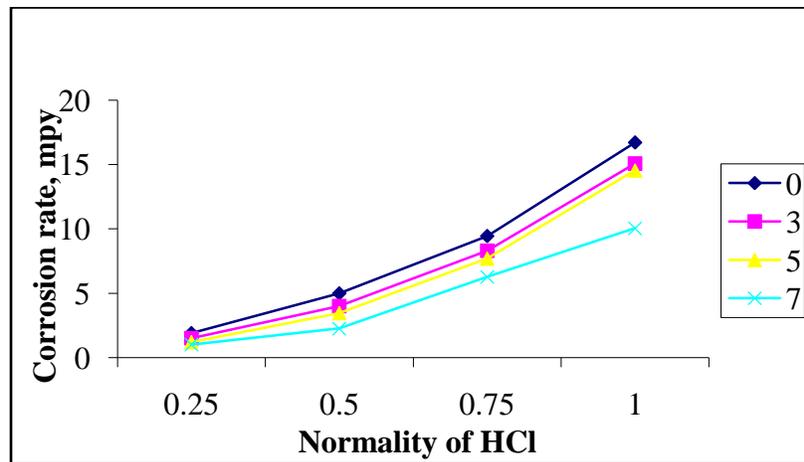


Figure 62:- Normality V/S corrosion rate at 100⁰ C for 30 minutes.

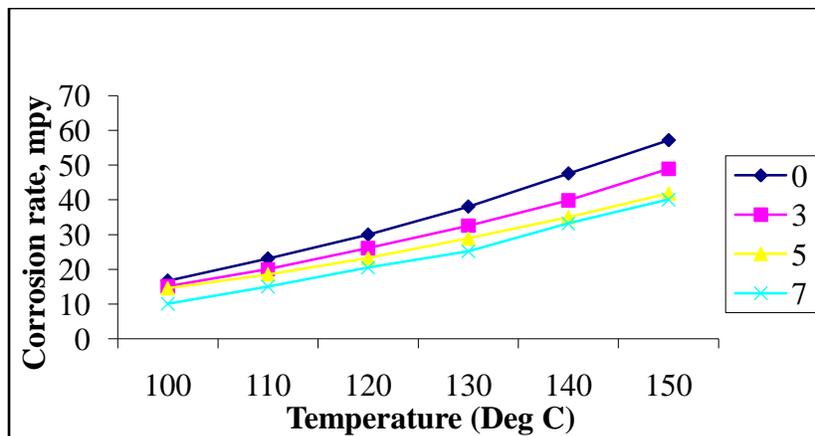


Figure 63:- Working temperature V/S corrosion rate in 1N HCl for 30 minutes exposure time

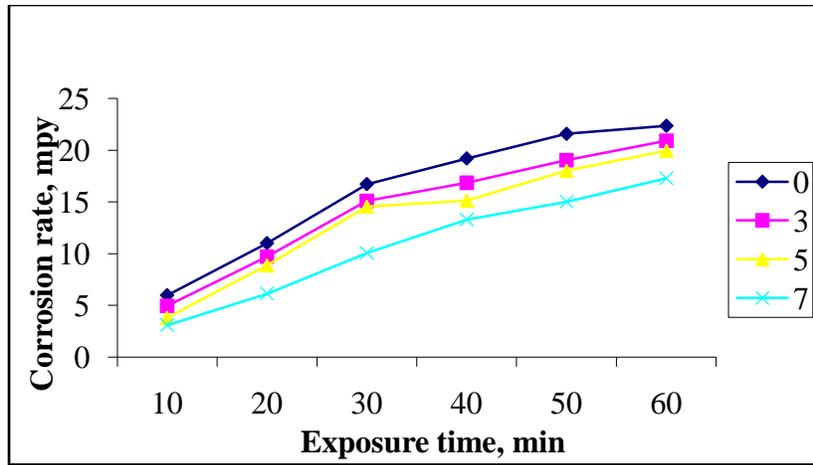


Figure 64:-Exposure time V/S corrosion rate at 100⁰ C in 1N HCl

Table 37:- Normality V/S corrosion rate at 100⁰ C for 30 minutes

% reinforcement of zircon	0%	3%	5%	7%
Normality	Corrosion rate (mpy)			
0.025	1.32	1.13	1.01	0.96
0.05	4.48	3.91	2.67	2.03
0.075	8.3	7.06	6.85	6.01
0.1	12.86	11.79	10.38	9.62

Table 38:- Working temperature V/S corrosion rate in 0.1N NaCl for 30 minutes exposure time

% reinforcement of zircon	0%	3%	5%	7%
Temperature in °C	Corrosion rate (mpy)			
100	12.86	11.79	10.38	9.62
110	18.99	17.48	16.86	14.06
120	24.67	20.11	19.71	17.67
130	29.29	26.71	23.64	21.09
140	37.7	33.37	29.93	27.01
150	45.67	40.6	37.13	31.08

Table 39:- Exposure time V/S corrosion rate at 100⁰ C in 0.1N NaCl

% reinforcement of zircon	0%	3%	5%	7%
Exposure Time in minutes	Corrosion rate (mpy)			
10	5.18	4.58	3.79	2.67
20	9.09	8.18	7.03	6.22
30	12.86	11.79	10.38	9.62
40	15.29	14.02	13.9	12.21
50	18.96	17.79	16.41	14.04
60	22.41	19.18	18.23	16.03

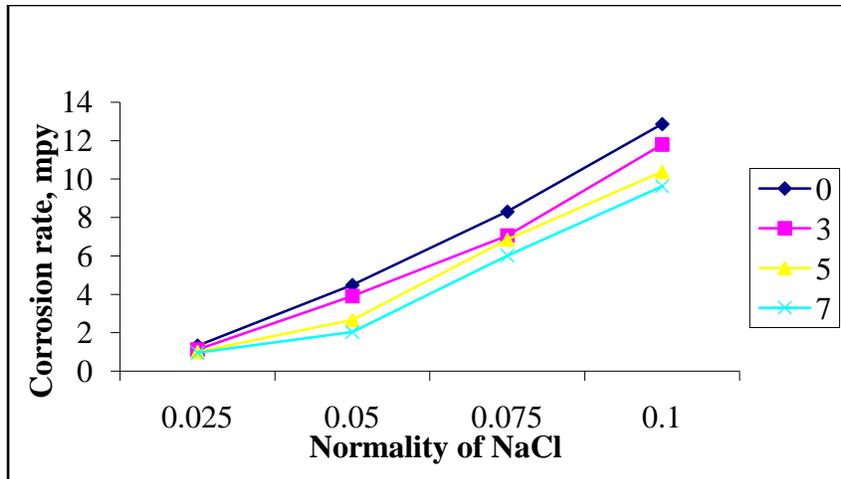


Figure 65:- Normality V/S corrosion rate at 100⁰ C for 30 minutes

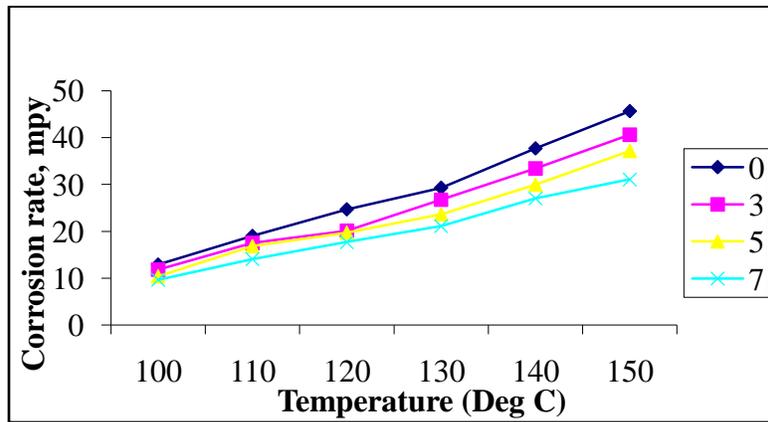


Figure 66:- Working temperature V/S corrosion rate in 0.1N NaCl for 30 minutes exposure time

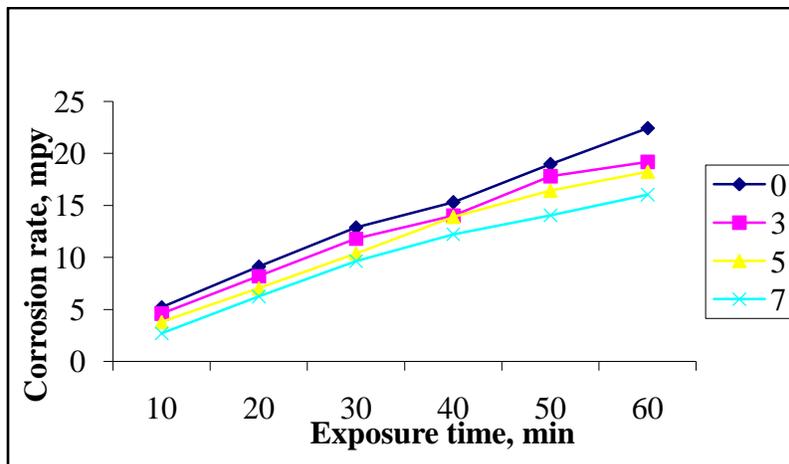


Figure 67:- Exposure time V/S corrosion rate at 100⁰ C in 0.1N NaCl

Table 40:-Working temperature V/S corrosion rate in sea water for 30 minutes exposure time

% reinforcement of zircon	0%	3%	5%	7%
Temperature in °C	Corrosion rate (mpy)			
100	15.74	15.42	14.19	12.61
110	22.26	21.81	19.84	17.9
120	29.18	28.71	25.76	23.85
130	37.73	36.89	33.11	29.12
140	46.72	45.33	41.19	38.92
150	56.69	54.16	49.58	46.06

Table 41:- Exposure time V/S corrosion rate at 100 °C in sea water

% reinforcement of zircon	0%	3%	5%	7%
Exposure Time in minutes	Corrosion rate (mpy)			
10	6.12	5.9	5.1	4.7
20	10.76	9.81	8.18	7.23
30	15.74	15.42	14.19	12.61
40	18.23	17.22	15.91	14.11
50	20.59	19.29	18.9	17.79
60	21.94	21.18	20.15	19.07

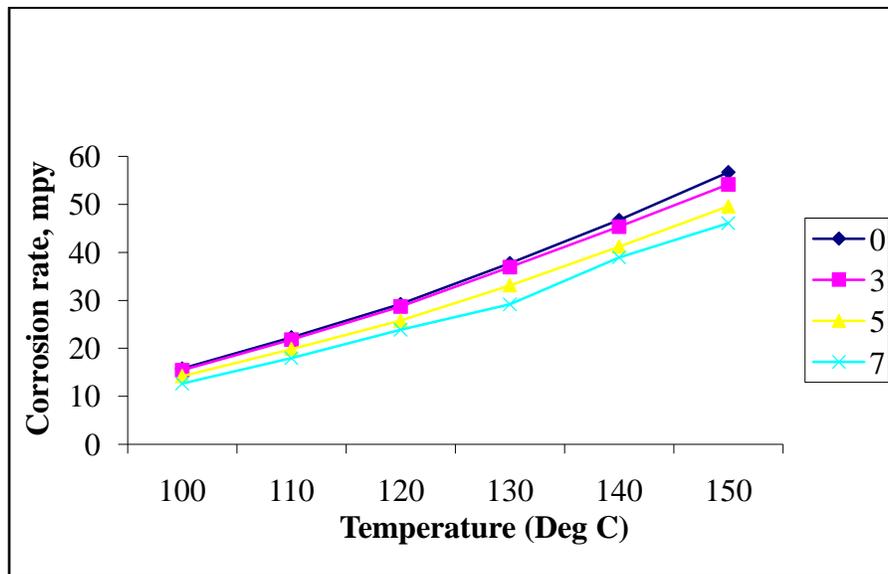


Figure 68:- Working temperature V/S corrosion rate in sea water for 30 minutes exposure time

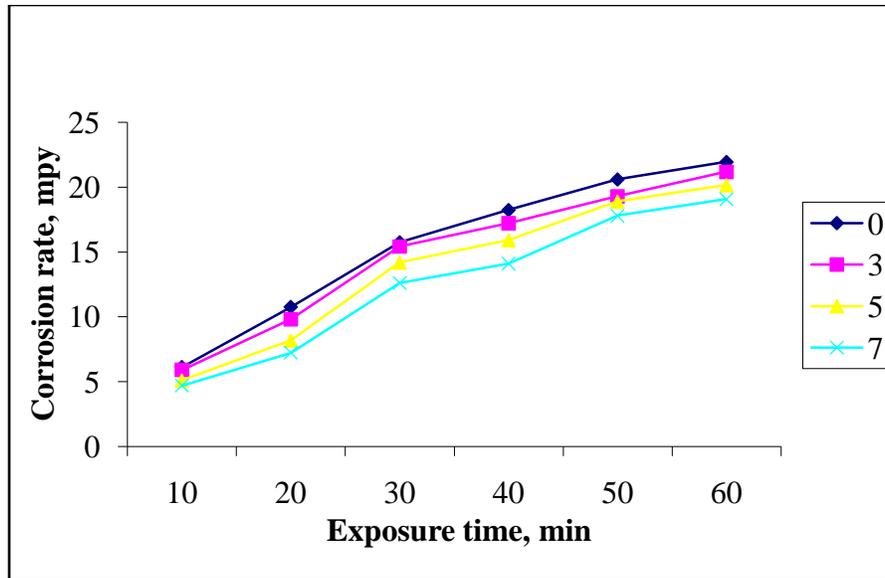


Figure 69:- Exposure time V/S corrosion rate at 100⁰ C in sea water

4.4.5 Corrosion morphology

By visually examined the samples 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 samples. Whereas widespread superficial pitting was observed more and few or absence of cracks were observed on the surface of reinforced composites. Though few cracks were observed in 3% zircon reinforced Al 7075 MMCs and absence of cracks were observed in 5% and 7% zircon reinforced MMC samples.

Corroded surface morphology of Al 7075 alloy and Al 7075/zircon MMCs were exposed at 100 °C temperature with 1N HCl and exposure time of 30 min (Fig. 70 – 73). In Al 7075/zircon MMCs, pitting is dependent on local zircon distribution as well as integrity of surface film. Larger weight % of zircon could result in more opportunities for film disruption and more sites for pit initiation. Although they found that pits in the reinforced system were smaller and more numerous than in unreinforced matrix, pitting was initiated at random sites on the surface of the Al 7075 alloy where imperfections in protective oxide occur whereas pitting in Al 7075/zircon composite is associated with particle matrix interface because of higher magnesium concentration.

The SEM images of the typical corroded surfaces of the 0% and 7% zircon reinforced composite specimens (Fig.70 and 73) showed in zircon reinforced aluminium composites, pitting depends on the distribution of zircon. Larger weight percentages of zircon could results in more opportunities for film disorder and initiation for more sites of pit. Composites showed the formation of pits on the surfaces, which is more with increase in the % of zircon composites. SEM images of matrix alloy and 7% zircon reinforced composites shows more pit formation on the surface than that of matrix alloy although they found that pits in reinforced system were smaller and more numerous than in unreinforced matrix¹⁰⁸.

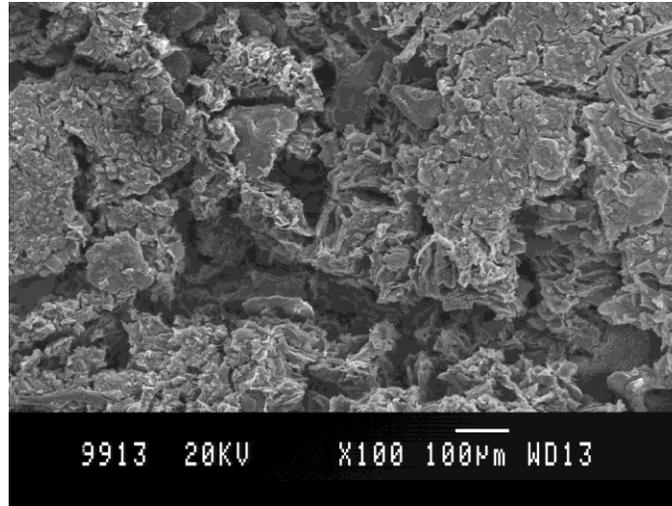


Figure 70:- Micrographs of unreinforced Al 7075 alloy after stress corrosion in 1N HCl at 100°C and 30 minutes exposure time

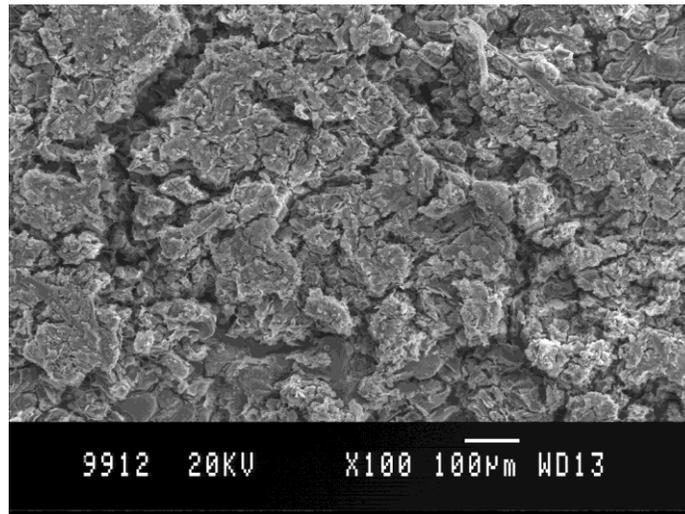


Figure 71:- Micrographs of Al 7075/3% zircon reinforced composite after stress corrosion in 1N HCl at 100°C and 30 minutes exposure time

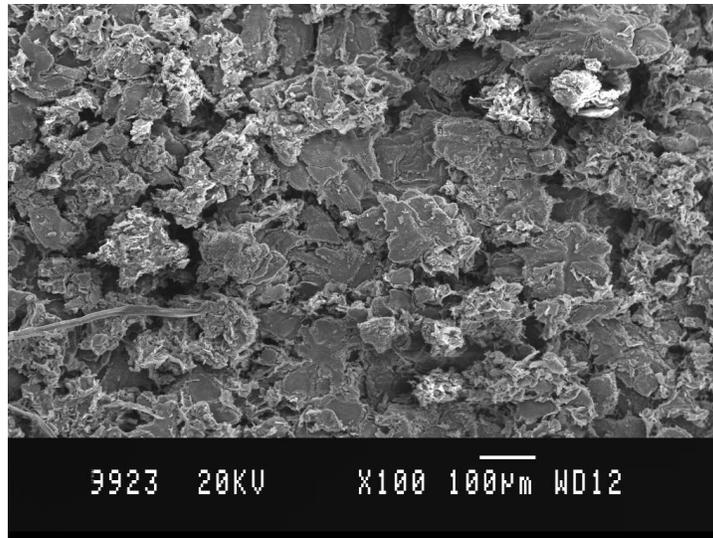


Figure 72:- Micrographs of Al 7075/5% zircon reinforced composite after stress corrosion in 1N HCl at 100°C and 30 minutes exposure time

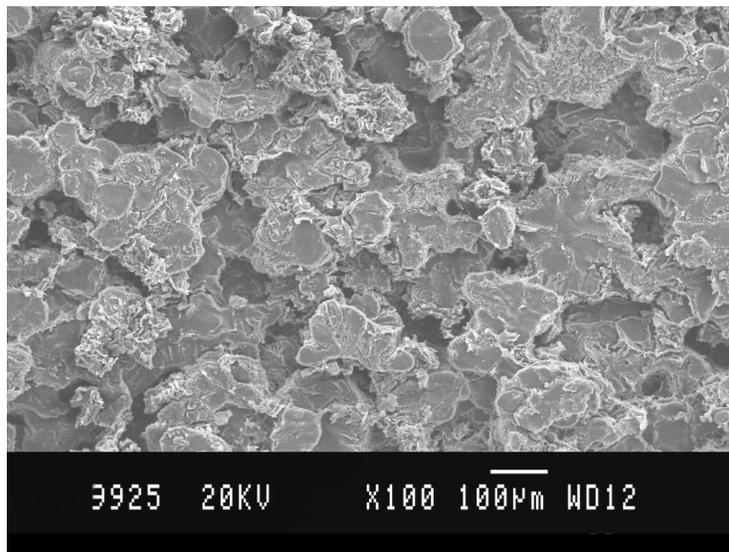


Figure 73:- Micrographs of Al 7075/7% zircon reinforced composite after stress corrosion in 1N HCl at 100°C and 30 minutes exposure time

EDAX spectra of Al 7075/7% zircon reinforced composite after stress corrosion studies in 1N HCl is shown (Fig. 74). Similar type of spectra is obtained for all specimens with a strong peak for aluminium and silica, traces of zirconium and magnesium are also found. The inert zircon particles are not involved in the process of corrosion of MMCs. Therefore the resistance of corrosion of the composites increases with the percentage of zircon particle in the composite. Sharma et al.,¹⁶⁹ observed similar results with glass short fiber reinforced ZA- 27 alloy.

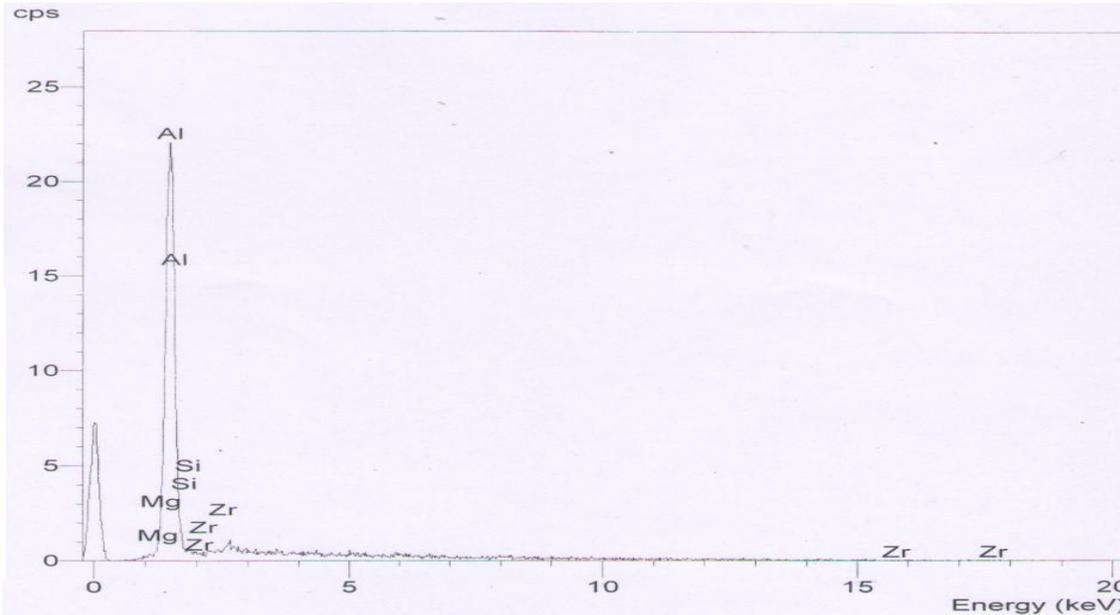


Figure 74:-EDAX spectra of Al 7075/7% zircon reinforced composite after stress corrosion studies in 1N HCl

Wu. Jianxin et al.,¹⁸⁶ studied that the corrosion of aluminium based particle reinforced MMCs and reported that corrosion is not affected to a significant extent by the presence of SiC particles in aluminium, whereas the particles definitely plays 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 initiate and development of a corrosion pits also modifies microstructure of matrix material and reduces the corrosion rate.

Another reason for decrease in rate of corrosion is inter metallic region, which is the site of corrosion around each particle, may be caused due the formation of magnesium inter metallic layer adjacent to the particle during manufacture as reported by Trzaskoma¹⁰⁸. This is evident from the EDAX results.

4.5 Mechanical properties

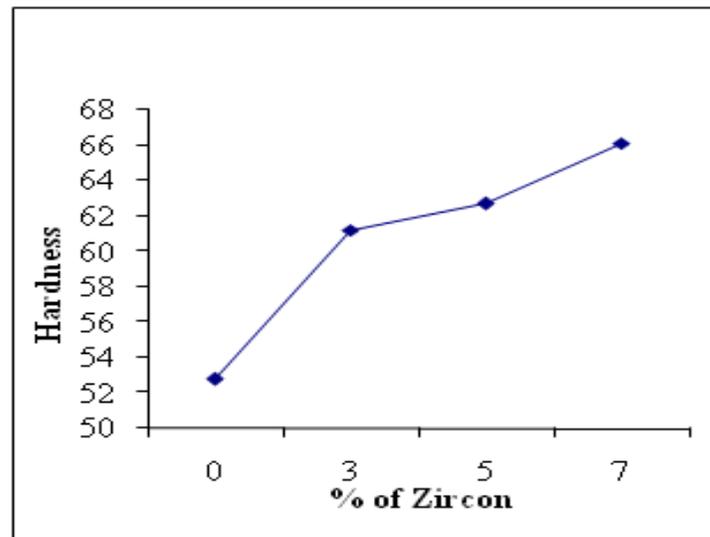
4.5.1 Hardness testing

B.H. values of unreinforced matrix and composites of aluminium are shown (Table 42). These values are an average of four measurements. In each case hardness increases with the content of zircon particles.

Increased resistance to indentation, carried out by means of B.H. test with an increase in zircon content shows a substantial material property improvement for a larger percentage of zircon addition. The resistance to indentation is a measure of the ability of material to bear static loads, abrasion, surface deformations etc. Its to be noted that its not essential to higher tensile strength and corresponding hardness value should be directly proportional. Similar increase in hardness when aluminium alloy is reinforced with TiO₂ has been reported by Reddappa et al.,⁴⁹. Zircon being hard, exhibited greater resistance to indentation of the hardness tests. The presence of hard zircon particles, which acts as a barriers to the movement of the dislocation within the matrix, might have increased the hardness.

Table 42:- Brinell hardness values of Al 7075/zircon composites

Composites	Brinell hardness number	Average Brinell hardness number
Base alloy	60.25	52.81
	47.66	
	46.00	
	57.33	
3% zircon	62.30	61.22
	59.60	
	60.00	
	63.00	
5% zircon	65.60	62.72
	63.60	
	60.60	
	60.60	
7% zircon	66.30	66.12
	66.33	
	65.60	
	66.30	

**Figure 75:-** Brinell hardness values of Al 7075/zircon composites

4.5.2 Compression testing

Outcomes of the compression test are shown in Table 43. It is evident with increasing proportions of the reinforcements, compression strength also increases.

Its evident that compressive strength increases with an increase in addition of zircon particles in the matrix. The intermolecular spaces give rise to lesser bonding strength; therefore the intermolecular spaces have to be filled up. This is achieved by compressing the material. The intermolecular spaces are thereby decreased by the application of the compressive load. Apart from this fact, it is possible that casting defects may also exist wherein the voids or any air bubbles or blowholes are created. In such cases the application of compressive load will tend to compact the material much closer, with the result that these voids will ultimately be filled up with material. This trend gives rise to the optimistic evaluation that

increasing the % of zircon will also increase the compressive strength of the material, a property that is characteristic of cast iron.

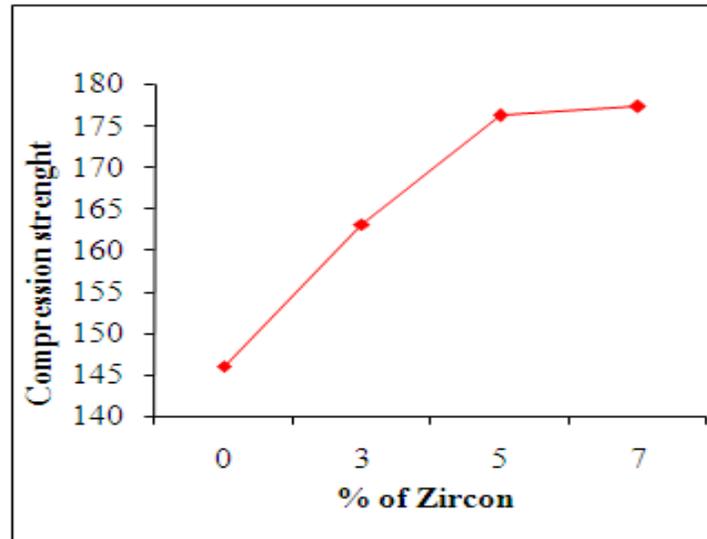


Figure 76:- Compressive strength values of Al 7075/zircon composites

Table 43:- Compressive strength values of Al 7075/zircon composites

Composites	Compressive strength (Mpa)	Average compressive strength (Mpa)
Base alloy	140.00	146.00
	112.00	
	104.00	
	228.00	
3% zircon	166.66	163.09
	125.70	
	160.00	
	200.00	
5% zircon	200.00	176.15
	184.61	
	160.00	
	150.00	
7% zircon	222.22	177.22
	120.00	
	166.66	
	200.00	

As the zircon particles content increased from 0 - 7%, the compressive strength of the composite also increases significantly. Presence of hard zircon particles improves the compressive strength, which impart strength to the matrix alloy thereby providing enhanced resistance to the compressive stresses. As the particle content is increased reduction in the interspacing distance between the hard zircon particles which causes an improvement in compression strength as explained by Pruthviraj et al.,¹⁸⁷.

4.5.3 Tensile testing

The results of tensile tests conducted on zircon particulate reinforced aluminium matrix composites are shown (Table 44). The results indicate that UTS of the composites increased with increasing reinforcement content.

The presence of hard zircon particles, which conveys the strength to the matrix alloy thereby providing improved resistance to tensile stresses, might have caused due to the increase in UTS. Due to the random distribution of the particles in the matrix there is a restriction to the plastic flow thereby providing enhanced tensile strength to the composites. The improvement in UTS may be due to the matrix strengthening following a reduction in composite grain size and the generation of a high dislocation density in the matrix as a result of the difference in the thermal expansion between the metal matrix and zircon particles reinforcement.

A similar explanation was reported by Praveen kumar et al.,¹⁸⁸. Also, there is a decrease in inter-particulate distance between the hard reinforced zircon particles which enables an increased dislocation pileup and hardening of the matrix, eventually requiring higher flow stress for the given strains as indicated by the increase in strength with the increasing percentage of particle dispersoid. The inclusion of zircon particles, which acts as barriers to dislocations in the microstructures, might have caused the increase in UTS.

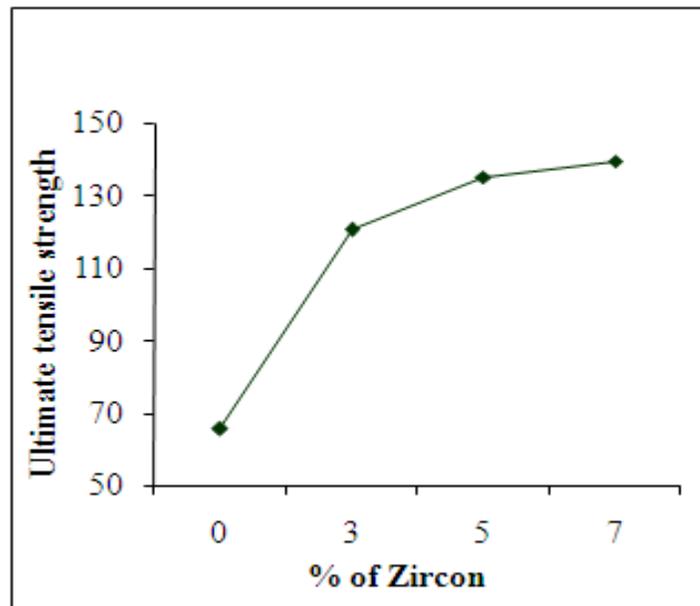


Figure 77:- UTS values of Al 7075/zircon composites

Table 44:- UTS values of Al 7075/zircon composites

Composites	Ultimate tensile strength (Mpa)	Average ultimate tensile strength (Mpa)
Base alloy	62.16	65.56
	72.62	
	69.14	
	58.32	
3% zircon	94.19	120.66
	129.92	
	120.18	
	138.37	
5% zircon	105.89	135.00
	120.83	
	162.41	
	152.66	
7% zircon	128.63	139.40
	138.00	
	148.63	
	142.36	

4.5.4 Impact testing

The results of impact test conducted on the proposed MMCs are shown (Table 45). This charpy test yielded lesser impact strength for higher weight percentage of dispersoids in the matrix. Decrease in impact strength with increase in zircon percentage as shown in Fig. 78. Zircon particles which cause an embitterment effect by acting as barriers to the movement of dislocations in the matrix thereby increasing the number of local stress concentration sites might have caused the reduction in impact strength. Since zircon particles are not reactive with the matrix phase, effect of zircon particles is expected to be mechanical in nature. Since it is generally true that the impact strength of material has been positive relationship with the ductility, all these results for impact strength of the material are to be expected. Hence the impact strength of the composite is strongly influenced by the toughness of the matrix¹⁸⁷.

The plot (Fig. 78) indicates that as the % of zircon increases the impact strength decreases. This is the representative fact that the absorption of energy per unit volume of material is apparently decreased. This is probably due to the fact that the increase in the zircon content reduces the material constitution susceptible to a decrease with dynamic capability of absorbing loads due to impact. Also a larger quantity of dispersion of the zircon particles in the material leads to a more brittle nature of fracture. One should be careful to interpret the graphs by judging that for the given percentage of zircon, the impact strength decreases at a proportional level. The percentage of zircon should be judiciously decided and the range in the increase of percentage must be limited. Probably, the best values would be within the range of three to five percentages, wherein the fall in the impact strength is not appreciable.

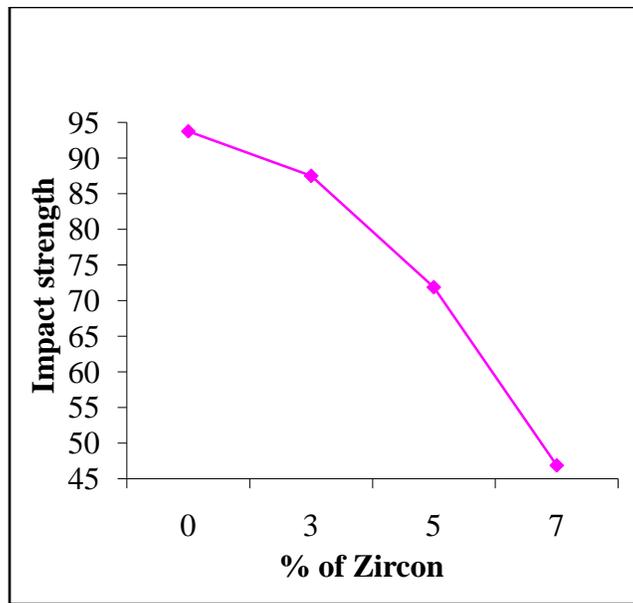


Figure 78:- Impact strength values of Al 7075/zircon composites

Table 45:- Impact strength values of Al 7075/zircon composites

Composites	Impact strength (J)	Average impact strength (J)
Base alloy	87.50	93.75
	100.00	
	62.50	
	125.00	
3% zircon	125.00	87.50
	75.00	
	87.50	
	62.50	
5% zircon	100.00	71.87
	75.00	
	50.00	
	62.50	
7% zircon	37.50	46.87
	50.00	
	50.00	
	50.00	

4.5.5 Wear test

The zircon particle reinforced Al composite shows greater wear resistance than that of Al alloys. Increasing the reinforcement increases the hardness of the composites, which in turn increases the wear resistance. Cracks developed in the unreinforced matrix at higher wear rate leads to delamination, which were absent in reinforced composites, where as fracture in the reinforced composite was eliminated by reinforced particle. The morphology of unreinforced alloy worn surface was covered by aluminium oxide, which was found to be extensively cracked.

Table 46: Wear rate values of Al 7075/zircon composites

Composites	Wear rate	Average wear rate
Base alloy	3.050×10^{-4}	1.115×10^{-4}
	7.116×10^{-5}	
	1.637×10^{-5}	
	5.360×10^{-5}	
3% zircon	3.615×10^{-5}	2.687×10^{-5}
	7.730×10^{-6}	
	2.110×10^{-5}	
	4.250×10^{-5}	
5% zircon	6.820×10^{-6}	2.611×10^{-5}
	1.130×10^{-6}	
	1.450×10^{-5}	
	4.200×10^{-5}	
7% zircon	2.273×10^{-5}	2.078×10^{-5}
	6.820×10^{-5}	
	2.273×10^{-5}	
	4.547×10^{-5}	

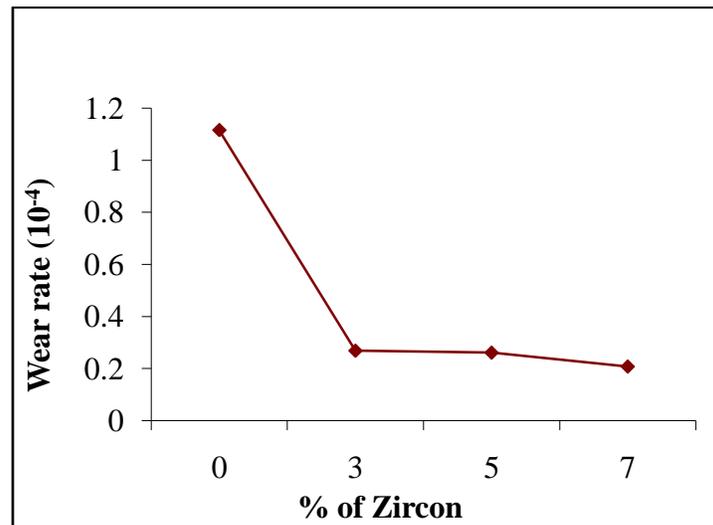


Figure 79:- Wear rate values of Al 7075/zircon composites.

Effects of reinforcement on the frictional coefficient and weight loss or wear resistance are given in (Fig. 79). Weight loss is decreased with increasing the reinforcement percentage. It may be noted that composite samples showed significantly lower weight loss than that of matrix alloy. The frictional coefficient of composite is lower than matrix alloy.

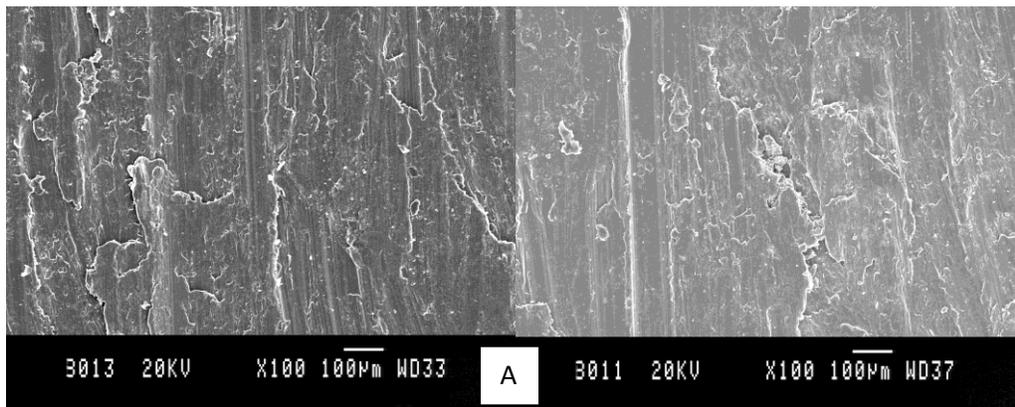
From results of Al MMCs have possessed better wear resistance than matrix alloy. According to the Friction theory, an anti-friction bearing alloy should be soft matrix distributed with hard particle, which can support load, while soft matrix can secure hard particle and transport load from matrix to hard touch area between composite and counter ring surface and decrease the friction coefficient, and can also prevent the scratch and cut form the hard little heave of counter face and improve wear resistance of composite essentially. Pruthviraj et al.,⁵⁰ studied that delaminating wear, the subsurface cracks which may either exist earlier or get nucleated due to the stresses, propagate during the course of wear. When such subsurface cracks join the wear surface, delaminating is the dominant wear mechanism.

Sreenivasan et al.,¹⁸⁹ reported that the delaminating wear of metal/material and observed that the large plastic strain in deformed layers give rise to void nucleation and subsurface crack initiation and

propagation of particle. The matrix has three functions. Firstly, it has to bond with the hard particle together so that the applied load is transmitted to the hard particles; secondly, it must protect the surface of hard particle from scratches, and thirdly, cracks do appear it should prevent them from spreading. In zircon reinforced Al MMCs, zircon support the load, so as to lessen the touch area between composite and counter ring surface and decrease the friction coefficient, and also prevent scratch and cut from the hard little heave of counter face and improved wear resistance of composite largely.

In order to further confirm wear mechanism of composite, SEM images of subsurface of composite are shown in Fig. 80. From the figures it can be seen that the resistance to wear became increased with increase in reinforcement. In the unreinforced matrix alloy, subsurface produce huge deformation and the material became broken up and huge void has formed, flake that will soon leave the surface can also be seen, which indicates that the wear has become very simple. The grooves formed are more distinct. Material loss during the process is in the form of small pieces resulting in the formation of flake-type debris. The shear strains induced in the process are transmitted to the matrix alloy and the wear mechanism proceeds by subsurface crack propagation caused by the delaminating wear. Surface materials are removed and the cracks get nearer to the surface layers and the shear strain is increased, thus causing the removal of the surface layers by delaminating.

In the zircon reinforced Al MMCs the subsurface has little deformation without evident hurt. In multiphase material like MMCs containing a dispersion of hard second phase particles (SPPs), latter carry the applied stress and protect the relatively softer matrix. This may be recognized to the fact that the particles remain on the specimen surface as protrusions. Under these circumstances effective contact between matrix and disc does not take place. Additionally, the hardness and the yield strength of the particles are high enough to carry the applied load. This leads to lesser wear rate of the composite as compared to that of matrix alloy. However, this is accurate only when the dispersoids are capable of withstanding the effective applied stress or the matrix is capable of holding them intact. Since dispersoid particles constitute only a minor volume fraction of the total area of the mating surface in the specimens, they are highly stressed.



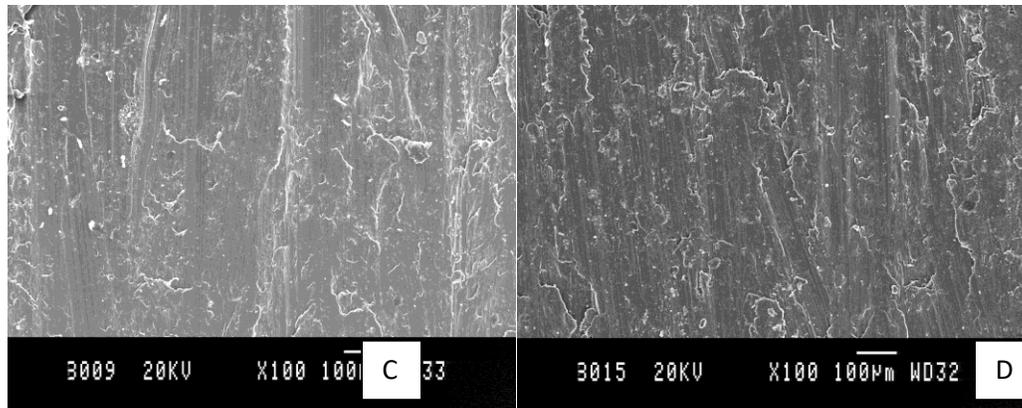


Figure 80:- Microstructures of “worn out” surface of A) unreinforced Al 7075 alloy, B) 3% zircon C) 5% zircon D) 7% zircon reinforced composites

4.6 Salt spray test

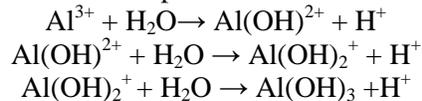
4.6.1 Corrosion mechanism

Chloride-containing solutions are the most harmful ones regarding localized corrosion of aluminum alloys. The electrochemical reactions involved in the corrosion of the Al 7075/zircon composites in a NaCl solution can be described as follows:

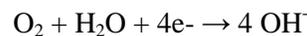
The anodic reaction:



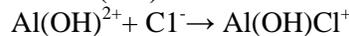
Hydrolysis of Al^{3+} ions occurs in several steps in the bulk solution:



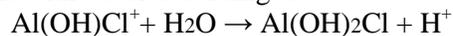
The cathodic reactions:



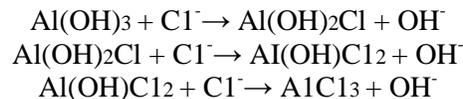
In the neutral solution, $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$ as intermediate species exist due to aluminum hydrolysis as shown in previous equations. $\text{Al}(\text{OH})^{2+}$ can also react with Cl^- ion, as following:



and then produce acidic conditions with water according to:



It has been proposed that aluminum chloride is formed by a stepwise chlorination of aluminum hydroxide, through following reactions:



The specimens exposed to the corrosive fog in the salt spray tests shows (Fig. 81) that the resistance to corrosion increased with increase in percentage of reinforcement from 3% to 7%. In the unreinforced matrix alloy nearly 20% of the specimen surface was corroded at the 40th hour. The time taken by the 3% zircon reinforced composite was more than the unreinforced alloy. The corrosion started at the 44th hour and 15% of the specimen surface was corroded. In the case of 5% zircon reinforced composite the time taken for the corrosion to start was further increased to 46th hour and the percentage of corrosion was reduced to 12%. But the 7% zircon reinforced composite show only 10% of the corrosion even at the 48th hour (Fig. 82). Zircon is a hard ceramic material, stays inert and its not affected during the tests. As the percentage of zircon increases the base alloy surface exposed to the corrosive media decreases and the resistance to corrosion increases.

The 75% of the base alloy was corroded after the 72 hours of exposure. This is because there is no reinforcement were added in any form to resist the corrosion. The matrix alloy was exposed to aggressive corrosion medium, results in higher percentage of corrosion. However the percentage of corrosion was decreased to 25% in the 7% zircon reinforced composite. Zircon particulates act as a physical barrier to the initiation and development of corrosion pits and also modifies micro structure of the matrix material.

Percentage of corrosion in 3% and 5% zircon reinforced composites lies between the unreinforced and 7% zircon reinforced composites. The 3% zircon reinforced composite shows 65% of the corrosion. Small amount of reinforcement was present, therefore the corrosion was reduced just by 10%. Large change in the corrosion occurs in the case of 5% zircon reinforced composite. The percentage of corrosion further reduced to 35%.



Figure 81:- Percentage of corrosion of Al 7075/zircon composites for 72 hours of exposure time

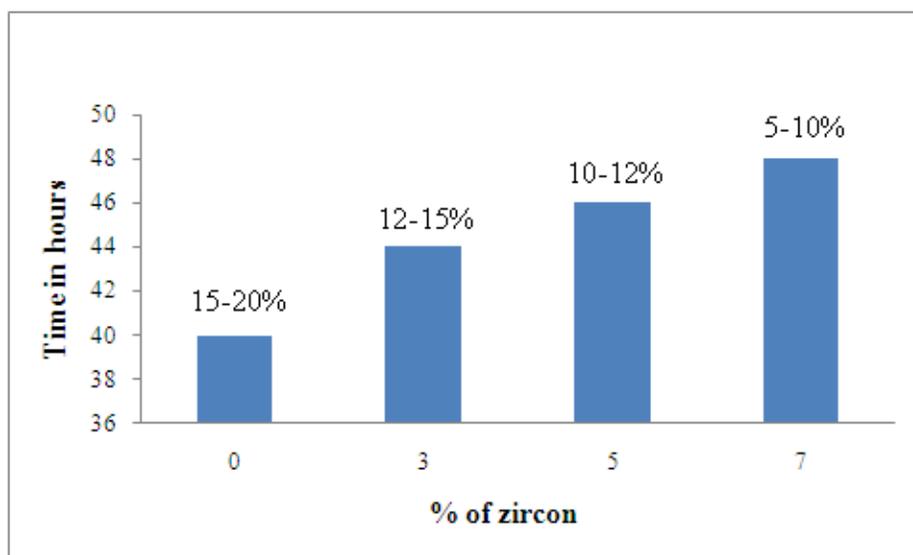
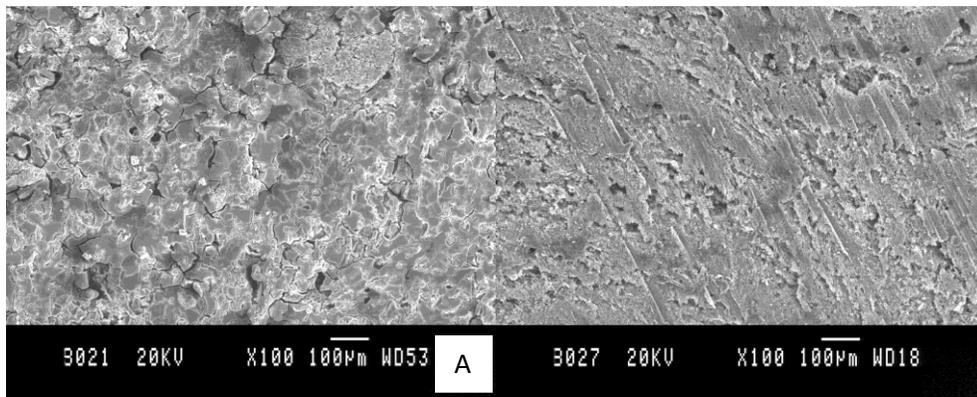


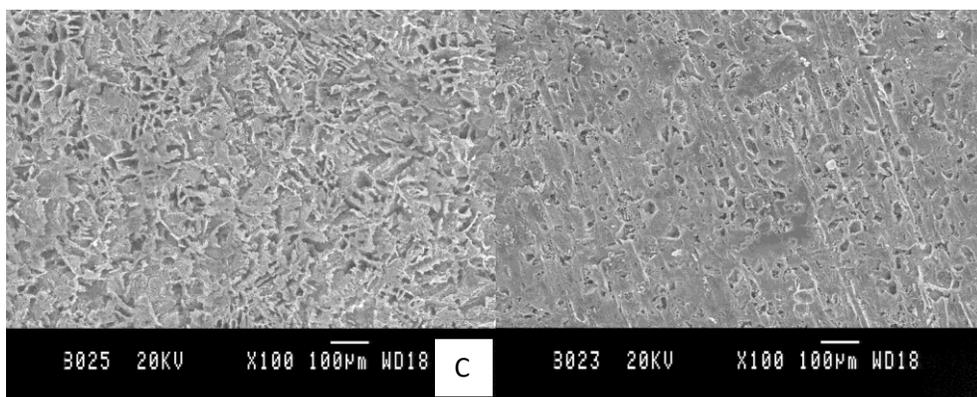
Figure 82:- Salt spray test values of Al 7075/zircon composites

Table 47:- Observations of salt spray test

% reinforcement of zircon	0%	3%	5%	7%
Exposure Time in minutes	Observation			
4	No corrosion	No corrosion	No corrosion	No corrosion
12	No corrosion	No corrosion	No corrosion	No corrosion
24	No corrosion	No corrosion	No corrosion	No corrosion
36	No corrosion	No corrosion	No corrosion	No corrosion
40	White corrosion (15 - 20%)	No corrosion	No corrosion	No corrosion
44	White corrosion	White corrosion (12 - 15%)	No corrosion	No corrosion
46	White corrosion	White corrosion	White corrosion (10 - 12%)	No corrosion
48	White corrosion	White corrosion	White corrosion	White corrosion (5 - 10%)
52	White corrosion	White corrosion	White corrosion	White corrosion
56	White corrosion	White corrosion	White corrosion	White corrosion
60	White corrosion	White corrosion	White corrosion	White corrosion
64	White corrosion	White corrosion	White corrosion	White corrosion
68	White corrosion	White corrosion	White corrosion	White corrosion
72	White corrosion (70 - 75%)	White corrosion (60 - 65%)	White corrosion (30 - 35%)	White corrosion (20 - 25%)



B



D

Figure 83:- Microstructures of corroded surface of A) unreinforced Al 7075 alloy, B) 3% zircon C) 5% zircon D)7% zircon reinforced composites

4.6.2 Morphology of corroded alloy

The microstructures of corroded surface of A) unreinforced Al 7075 alloy, B) 3% zircon C) 5% zircon D) 7% zircon reinforced composites after exposed to salt fog for 72 hours are shown (Fig. 83). Physical inspection of the specimens after salt spray test shows a few deep pits, flakes and cracks formed on unreinforced matrix alloy. The unreinforced matrix alloy was severely damaged after exposure to neutral chloride solutions. Note that the Al_2O_3 protective layer do not completely cover the material surface. Original protective layer presents both generalized and localized attack by chloride and also showed signs of nucleation and growth of a new layer of $\text{Al}(\text{OH})_3$. A few cracks were observed on the surface of 3% zircon reinforced composites and no cracks in other MMC specimens. But a more widespread superficial pitting was observed on 5% and 7% zircon reinforced composites.

In Al 7075/zircon MMCs, pitting is dependent upon the local ceramic distribution as well as the reliability of the surface film. The pits in reinforced system are lesser than in the unreinforced matrix, pitting is initiated at random sites on the surface of the Al 7075 alloy where imperfections in protective oxide occur whereas pitting in the composites is associated with the particle matrix interface. Several researchers have studied the similar type of observations¹⁹⁰.

The corrosive attack was extensive with deep pits on the surface of the unreinforced matrix alloy extending and connecting in such a way that so as to cracking as shown in Fig. 83. Cracks can be observed originating from the deep pits and traversing on the surface. However, absence of crack path can be clearly observed.

Chapter 5

Conclusions

Aluminium matrix composite reinforced with uniformly distributed zircon particles have been fabricated successfully using the vortex method followed by casting in permanent moulds. The adding of the particle in spray form has resulted in uniform distribution of the reinforcement. Al 7075 MMC reinforced with zircon of weight percentage from 3 - 7% were produced by liquid melt metallurgy technique.

Based on the static weight loss corrosion studies of the Al 7075/zircon MMCs the following conclusions were drawn:

- Corrosion rate of the MMCs were found to be less than that of the matrix alloy.
- Corrosion rate of the composites decreased with duration of exposure time and increasing weight percentage of reinforcement.
- Micro structural modifications of the matrix may probably be responsible for the lesser corrosion rate.

Corrosion behaviour of Al 7075/zircon MMCs were tested by OCP method. The observations made from the OCP tests are as follows:

- With the increase in the percentage of zircon, there is a significant reduction in the corrosion potential and corrosion rate.
- The corrosion rate of both the alloy and composites decrease with increase in exposure time. However, the corrosion potential developed for the composites is less than that of the corresponding matrix alloy.
- The extent of corrosion damage decreases with increase in reinforcement from 0 -7% in MMCs.

Galvanic corrosion studies of Al 7075/zircon MMCs revealed that:

- ◆ Corrosion rate decreased with decrease in concentration of corrosion media
- ◆ Corrosion rate decreases with increase in zircon content, and it is attributed to the fact that the ceramic zircon particulates remain inert in aggressive corrosion media.

Stress corrosion studies indicate that:

- ⦿ The rate of stress corrosion of both the matrix alloy and reinforced composites increased with exposure time, concentration and temperature.
- ⦿ However, the increase in corrosion rate was lower for the zircon reinforced composite compared to base Al-alloy under all conditions.

The results gathered from the mechanical tests suggest the following facts:

- Hardness improves satisfactorily and it is attributed to the dispersion of zircon in the matrix.
- Composites fabricated possess considerably higher compressive strength over that of the unreinforced matrix alloys. The compressive strength of these composites increased with increased content of zircon particles.
- The increase in percentage of the zircon particles, impart strength to the matrix alloy thereby providing improved resistance to tensile stresses.
- The ability to resist impact loads is not enhanced appreciably as a result of an increase in the dispersoid content.
- Al composites reinforced with the zircon particle show greater wear resistance than that of Al alloys. Increasing the reinforcement increases the hardness of the composites, which in turn increases the wear resistance.

Salt spray analysis also confirmed that the resistance to corrosion increases with increase in the percentage of the reinforcement from 3% to 7 %.

5.1 Suggestions for further work

- Hot worked and mechanically processed materials may be used.
- Fabrication of aluminium/zircon MMCs with finer reinforcements may provide much improved properties.
- Squeeze casting and compocasting methods followed by hiping and die forging may also be tried.
- Other alloys of aluminium like 2024, 7071, 8090 and 8091 can be used as the matrix materials with traces of zirconia, beryllium and silicon for crystal reinforcement.

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