Asian Journal of Chemistry

Corrosion Behaviour of Al 6061/Zircon Metal Matrix Composites in Alkali Medium by Open Circuit Potential Studies

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An aluminium 6061 alloy reinforced with zircon particle composite, synthesized by liquid melt metallurgy technique using Vortex method has been characterized for corrosion properties by open circuit potential method. Specimens were designed according to ASTM standards. The corrodents used for the tests were 1.00, 0.50 and 0.25 M sodium hydroxide solution. In each case the potential decreases with increase in exposure time and becomes constant due to passivation induced by aluminium for matrix and metal matrix composites.

Key Words: Composite, Vortex, Potential, Passivation.

INTRODUCTION

Metal matrix composites (MMCs) are engineered combinations of two or more materials in which tailored properties can be achieved. These composite materials can be made by dispersion of fibers, whiskers or particles as dispersoids in a metal matrix and exhibit combinations of properties which can not be achieved in monolithic materials. Such a combination of dispersoid and metal matrix is selected depending on property requirements for specific applications. Metal matrix composites exhibit properties like high specific strength, high specific stiffness, damping properties, improved wear and seizure resistance, etc. Due to such versatile properties, MMCs are finding applications in automobile parts (break rotors, drive shafts, connecting rods, piston rings and cylinder liners), sporting goods, aerospace components and other industrial applications¹. Among various MMCs, Al-alloy composites are getting much attention due to their low density, high strength to weight ratio, heat treatment capability and processing flexibility. A variety of dispersoids viz. silicion carbide^{2,3}, alumina⁴, etc. have been reinforced in the form of fibers, whisker or particulates in aluminium alloy matrices to develop composites for various applications. However, as far as MMCs containing particulates are concerned, no information is available in literature on the corrosion behaviour of Al 6061/zircon MMCs. In view of the above, the objective of the present investigation is to understand the role

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Vol. 22, No. 5 (2010) Corrosion Behaviour of Al 6061/Zircon Metal Matrix Composites 3911

of the matrix microstructure and reinforcement in corrosion behaviour of Al 6061/ zircon MMCs in varied concentrations of NaOH solution by open circuit potential studies.

EXPERIMENTAL

The matrix selected is Al 6061, which exhibits excellent casting properties and reasonable strength. This alloy is best suited for mass production of light weight metal castings. The chemical composition of the Al 6061 alloy is given in Table-1.

TABLE-1						
COMPOSITION OF AI 6061						

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

Zircon (ZrSiO₄) is used for reinforcement in the form of particulates. Zircon is a very hard material, its hardness is 7.5 on Mohr's scale and specific gravity is 4.1. The principal structural unit of zircon is a chain of alternating edge-sharing SiO₄ tetrahedron and ZrO₈ triangular decahedra. The composition of zircon is given in Table-2.

TABLE-2 COMPOSITION OF ZIRCON

Silica	32.8
Zirconica	67.2

Composite preparation: The liquid-metallurgy Vortex method was employed to prepare the composites. The reinforcement material (Zircon) used is of size 40-50 µm. The SEM micrograph of the zircon is given in Fig. 1. The composites containing 3, 5 and 7 weight percentage of zircon were prepared. The matrix alloy was also cast under identical processing condition for comparison. Zircon is added in to the molten Al 6061 alloy melt by creating a vortex using a stirrer. The composite melt was thoroughly stirred and subsequently degassed and poured into preheated split-type permanent moulds⁵. Samples for microscopic examinations were prepared by standard metallographic procedures, etched with Keller's agent and examined under optical microscope.

Specimen preparation: Rectangular specimen of 2 cm length and 1 cm breath and 1 mm thickness was prepared by adopting standard metallographic procedure using an abrasive cutting wheel⁶. They were polished and degreased in acetone and dried.

Open circuit potential test: The open circuit potential (also referred to as the equilibrium potential, the rest potential or the corrosion potential) is the potential at which there is no current. These experiments are based on the measurement of the open circuit potential (OCP) or these are potentiometric experiments. Although

3912 Abdul Jameel et al.

Asian J. Chem.



Fig. 1. SEM of zircon

such measurements are very simple, they have many important applications. The equipment contains a multimeter where resistance, alternate current and direct current can be measured with two outlet wires given and it runs with a cell of 9 volt capacity. An aluminium wire is used to hold the specimen. One sq cm area of the specimen is exposed to corrosive medium. Specimen is connected to the wire suitably covered by Teflon tape so that aluminium is not exposed to electrolyte medium. The specimen is made anode and the cathode will be the reference electrode that is standard calomel electrode. Before testing each specimen was cleaned in acetone for 5 min and air dried. Both electrodes are connected to multimeter and the same is switched on to measure the DC voltage developed after dipping them in different concentrations of sodium hydroxide, which is used as electrolyte solution. The voltage developed and displayed by the multimeter is noted for every hour for a period of 30 h. The procedure is repeated for all the four specimens. Then the graphs are plotted by taking exposure time *versus* the potential developed.

RESULTS AND DISCUSSION

Microscopy: It is observed from the microstructures of unreinforced matrix alloy and composites that, there is invariably a uniform particulate distribution and that the average particulate size was 40-50 μ m no matter what the weight percentage of reinforcement was. This is the same size as that of the original zircon particulates, indicating that the zircon particulates were not noticeably damaged or affected during preparation of the composite.

Effect of test duration: The potential measurements as a function of exposure time in the open circuit potential (OCP) test are shown in the Figs. 2-4. In all the cases it is observed that the potential decreases in the beginning with increase in test duration and remains constant towards the end due to passivation. It is clear

from the graph that the resistance of the composite to corrosion increases as the exposure time increases. The phenomenon of gradually decreasing potential indicates the possible 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 might have retarded the corrosion.



Fig. 2. Open circuit potential (OCP) test in 1.00 M NaOH solution



Fig. 3. Open circuit potential (OCP) test in 0.50 M NaOH solution



Fig. 4. Open circuit potential (OCP) test in 0.25 M NaOH solution

3914 Abdul Jameel et al.

Asian J. Chem.

In alkaline medium, Al-alloy and composite corrodes due to the formation of AlO_2^- ions, which in turn reacts with water to form oxides and hydroxides, which are highly unstable and dissolved in the solution. Thus as soon as the film is formed it is washed off by the 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 alkalinity of the solution decreases and pH decreases (tending towards neutral). In fact the pH of the solution was very high initially, but it decreases with time to approach to a constant value when the solution attains saturation. It should be noted that during this period, there is a possibility of formation of $Al(OH)_3$ on Al-alloy and composite surfaces but this layer is highly porous and unstable in nature⁷.

According the previous reports on static corrosion^{8,9}, the composites as well as for the unreinforced matrix alloys, the corrosion rate seems to decrease with duration of the test. The phenomenon of gradually decreasing corrosion rate is probably due to their respective hydroxide layer. Castle *et al.*¹⁰ who studied SiC particulate-reinforced Al-based MMCs, believe that the black film formed on the surface consists of an aluminium hydroxide compound which protects the bulk material from further corrosion.

Effect of zircon content: From Figs. 2-4 it can be clearly observed that, for both alloy and composite potential decreases with increase in zircon content. In case of base alloy the strength of the media used induces crack formation on the surface, which eventually leads to the formation of pits, there by causing the loss of material. The presence of cracks and pits on the base alloy surface was observed clearly on visual inspection of the specimens after the test. Since there is no reinforcement added in any form, the base alloy fails to provide any sort of resistance to the corrosion medium. Hence, the decrease in potential in case of unreinforced alloy is higher when compared to composites¹¹.

The SEM micrographs of the typical corroded surfaces of the 0 and 7 % zircon reinforced composite specimens are presented in Figs. 5 and 6, which show the corroded surface morphology of the tested specimens. It was observed that in zircon reinforced aluminium composites pitting depends on the distribution of zircon.



Fig. 5. Microstructure of unreinforced Al 6061 alloy



Fig. 6. Microstructure of Al 6061/7 % zircon reinforced MMC

Vol. 22, No. 5 (2010) Corrosion Behaviour of Al 6061/Zircon Metal Matrix Composites 3915

Zircon being the ceramic material remains inert and is hardly affected by corrosion medium during the test and is not expected to affect the corrosion mechanism of the composites. The results indicate that there is an improvement in corrosion resistance as the percentage of zircon particulates increased in the composites which shows that zircon particulates directly or indirectly influence the corrosion property of the composites. Zircon particulates act as a physical barrier to the initiation and development of corrosion pits and also modifies the micro structure of the matrix material and hence reduces the potential.

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

From the graphs it can be clearly seen that the ceramic reinforcement particles act as insulator and remain inert in the alkali medium during the test. Hence the potential decreases with increase in zircon content in MMCs, which may decrease the area of exposure of the alloy with increase in the reinforcement. Less exposure of the MMCs area to alkali environments in corrosion testing led to lesser pitting as well as corrosion than that of the matrix alloy. The pits on the matrix alloy were more when compared with those of MMCs. This may be due to the exposure of less matrix alloy surface in MMCs than matrix alloy, by the addition of reinforcement¹². The chemical composition of micro-particles in thick corrosive product layer was determined by EDXA analysis as shown in Fig. 7. Spectra were obtained similar for all specimens with the exception that Al 6061/zircon spectra show strong aluminium and silica peaks, a consequence of the presence of zircon and the limitations in isolation of sampling volumes. It also shows some traces of magnesium.

Conclusion

Corrosion behaviours of Al 6061/zircon MMCs can be tested by open circuit potential (OCP) method. The zircon content in Al 6061 alloys plays a significant role in the corrosion resistance of the material. Increase in the percentage of zircon will be advantageous to reduce the density and increase the strength of the alloy. However, there is a significant reduction in the potential and corrosion rate. Al 6061 MMC reinforced with zircon of weight percentage from 0-7 % could be successfully produced by liquid melt metallurgy technique. The corrosion rate of both the alloy and composite decreased with increase in exposure time in alkali solution. The potential developed for the composites was lesser than that of the corresponding matrix alloy in alkali solution. The extent of corrosion damage was decreased with increase in reinforcement from 0-7 % in MMCs. The use of MMCs in bearing applications in basic environment is more suitable than matrix alloy.

3916 Abdul Jameel et al.





Fig. 7. EDAX spectra of Al 6061/7 % zircon reinforced metal matrix composites

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(Received: 22 August 2009; Accepted: 23 January 2010) AJC-8352