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Study on Corrosion behaviour of Heat Treated Hybrid Metal Matrix Composites Reinforced with B_4C and Graphite Particles

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Abstract—*Aluminium metal matrix composites have gained much importance due to their properties like high strength to weight ratio and non-corrosive behavior. In the present work an alloy of Aluminium 2219 is used as the matrix material with B_4C_p as the reinforcement material in mono composite. Another hybrid composite of Al2219 and B_4C_p and graphite is also prepared by stir casting technique. The distribution of the particles in the matrix material is confirmed by the optical images. One set of all the three samples are tested for corrosion behavior in 3.5 wt% NaCl solution maintained at 6.5 pH according to a standard procedure by potentiodynamic anodic polarization technique at room temperature. Another set of samples were heat treated according to T6 condition and were put to the same corrosion testing as that of non heat treated composites for the same conditions. The results revealed that the corrosion rate of the hybrid composite is highest and that of alloy is least. The heat treated specimen showed lower corrosion rates and the heat treated base alloy showed the least corrosion rate among all the samples.*

Keywords*: Hybrid MMC, Stir casting technique, Pit corrosion, Cyclic polarization technique, Heat treatment.*

1. INTRODUCTION

Composite materials are the mixture of two or more insoluble constituents casted in an alloy to gain better properties than the base alloy. In the recent days, composites materials have gained very large interest in researchers all over the world because of their excellent properties. The continuous phase of the alloy is called as matrix and the dis-continuous added to the matrix material are known as reinforcements. They are further classified as mono-composite and hybrid-composite based on one and two reinforcements added respectively. Bhargavi Rebba et. al. says that the advantage of using particulates as reinforcements rather than fibres or whiskers is low formability costs of the composites. According to Himanshu Kala et. al. stir casting technique is the most widely and economically used route for the fabrication of the particulate reinforced metal matrix composites. He has also said that during casting, upto 30% volume fraction of the reinforcements can be distributed evenly by mechanical stirring.

Among various alloys of aluminium, 2xxx, 6xxx, 7xxx are the heat treatable wrought alloys used extensively in space application for the cryogenic fuel tanks. According to Venkatasubramanian G et. al. the main disadvantage of Al2xxx series is its poor corrosion resistance against the chloride environment. This is because of the distribution of copper, which causes localized corrosion. Nicoleta Radutoiu et. al. have stated that by heat treatment and aging the mechanical properties can be increased leading to the improved corrosion resistance which largely depends on the microstructure of the alloy. N Nafsin et. al. have studied that the copper presence leads to lower corrosion resistance. This is because of the copper precipitation at the grain boundaries making the alloy prone to intergranullar, stress and pitting corrosion. In this region even galvanic corrosion takes place in which copper acts as cathodic material compared to the aluminium matrix material which acts as anode material. In the present research work, corrosion behaviour of the aluminium and its composites with B4C and graphite has been studied. Corrosive medium used is 3.5 wt % NaCl solution, since we have come to know that chlorine is the most dangerous pitting corrosion agent. Heat treated composites are also tested with the same solution and the results are found out.

2. EXPERIMENTAL MATERIALS

2.1 Matrix material

In our present research work we have used 2xxx series of aluminium alloy. Specifically Al2219 alloy is used which contains copper as the largest alloying element. Al2219 has high strength hence used in space application, because of the presence of copper, this alloy can also be applied in high temperature application. The presence of copper itself leads to lower corrosion resistance, hence this has to be come over. The composition details of the Al2219 is as given below in table 1.

Table 1: Composition of Al2219 in wt %.

Element	Mg	Si	Cu	Zr	Fe
wt %	0.02 max	0.20 max	5.8 – 6.8	0.10-0.25	0.30 max
Element	Zn	Ti	V	Mn	Al
wt %	0.10 max	0.02-0.1	0.05-0.15	0.1 max	remaining

2.2 Reinforcement material

The discontinuous phase present in the composite are known as reinforcement. In our present work we have used particulate form of reinforcement. Boron carbide which is a ceramic material is used as a primary reinforcement. Boron carbide has such an excellent hardness property that it ranks third next to diamond and cubic boron nitride. Particle size of B4C are in the range of 60-90 µm. To impart self-lubricating properties fir applications such as piston rings, journal bearings, shafts etc we have added graphite with the particle size of 10-15 µm. Graphite is the best known for its industrial application for wet and dry self-lubrication properties.

3. EXPERIMENTAL PROCEDURE

3.1 Fabrication microstructure study of composite

As concluded from the literature survey, stir casting technique is used to fabricate our composites. Al2219 is the base alloy and we have received it in the billet form, these billets are cut into small pieces to achieve required weight for casting and put in crucible. The crucible is then placed in composite furnace and heated till temperature of 750^{o}C. Reinforcements and cast iron mould are preheated for a temperature of around 300^{o}C. Once the melt is ready, it is degasified to avoid pores in castingsand cover flux is added to remove the impurities in the alloy and form slag. After removal of slag the melt is poured in the preheated mould to get the castings. For mono-composite 8 wt. % of B_4C and for hybrid composite 8wt. % B_4C and 3 wt. % graphite are added to the melt after removal of the slag by putting cover flux. During addition of reinforcement mechanical stirring is carried out and was extended for 5 min after addition of reinforcement till pouring and care is taken such that the melt temperature never falls below its melting point. After solidification of the casting they are taken out of the mould and machined to cylinders of diameter 12mm and length 10mm for microstructure study. All three samples were polished against the emery papers of silicon carbide for specific duration from the increasing order of paper number from 220, 400, 600, 800, 1000 and 1200 respectively. Then the samples surfaces are buffed against the velvet cloth and observed in the optical microscope to know about distribution of reinforcement particles in the base alloy.

3.2 Heat treatment

Heat treatment is the combination of operations in which the metals or alloys are passed through the process of heating and cooling in their solid state to obtain desirable properties. T6 condition of heat treatment is carried over a set of samples of all three composites. Accordingly the samples were first solution heat treated at the temperature of 535±2^{o}Cfor duration of 2 hours as done by N R Prabhu Swamy (2010). While holding the samples at this temperature, its constituents enter into a solid solution form and then the samples were quenched in normal water to hold the constituents in the solid solution. Then the samples were artificially aged, according to which the controlled heating of solution heat treated samples were carried out by maintaining these at the temperature of 165±2^{o}C for 18 hours to increase its properties.

3.3 Solution preparation

According to venkatasubramanian et. al.(2013) chlorine present in the water is the active pitting agent. Corrosion medium is prepared by dissolving 3.5 wt % NaCl in distilled water to obtain a 0.6M solution. The pH of the solution was adjusted to 6.5pH by adding diluted NaOH to decrease and diluted HCl to increase the pH of the solution. The pH was set to 6.5 so that the solution should be slightly acidic than being neutral solution.

3.4 Corrosion procedure

The casted samples were cut into cylinders of 12mm, length of 5mm and installed in the flat cell of the corrosion testing setup as shown in fig. 1.

Fig. 1: Corrosion setup

Before testing the specimen were polished and micro graphed. Corrosion test was carried according to ASTM G5 by potentiodynamic anodic polarization technique. The test was conducted from Metallurgical corrosion analyser system Gill AC and Electrochemical corrosion cell, supplied by ACM instruments, England, United Kingdom through tech science services Pvt. Ltd. Chennai. The corrosion setup consists of aFlat cell, Potentiostat and an computer system which interprets the data from potentiostat through a corrosion analysis software Princeton Applied Research 352 softcorr™ III and plots the graph of potential v/s current. Cyclic polarization scanning with start potential of -800 mv and reverse potential of+500 mv with a sweep rate of 3mv/min is applied over the specimen. Flat cell consists of auxiliary electrode which is platinum electrodeand reference electrode which is calomel electrode and a working electrode, the specimen itself as shown below in schematic diagram fig. 2.

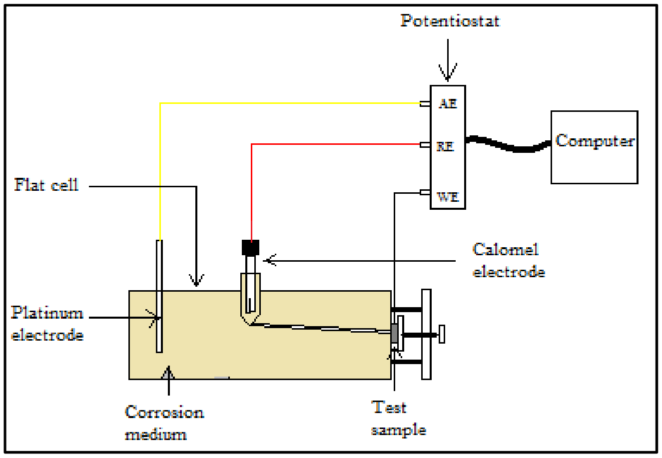

Fig. 2: Schematic representation of flat cell

4. RESULTS AND DISCUSSION

4.1 Microstructure study

Optical microscopic images of the samples before corrosion are shown below in fig. 3. Fig. 3a shows the microstructure of as-cast aluminium base alloy.

Fig. 3b shows the microstructure of the as-cast mono composite. Particles with sharp edges as encircled in the image confirm that it is a boron carbide particle. Fig. 3c shows microstructure of as-cast hybrid composite. In this image the spheroidal black particles are graphite as shown by square boxes. According to Canakci et. al. (2007) the wetting of the B4C particles in the aluminium alloy is very poor at temperatures below 1000°C. In order to achieve good wettability we have added K_2TiF_6 as the wetting agent during casting.

Below fig. 4a shows the corroded surface of the base alloy Al2219. Corrosion of the base alloy is least compared to composites. As studied by B Dikici et. al. in case of aluminium alloy $CuAl_2$ acts as cathode in Cu containing Al alloy and this initiates potential difference between Al and its composites. In case of mono composites aluminium carbide formed during casting settle at the grain boundaries of the alloy causing intergranular corrosion. According to C Muthagzhagan et. al.(2014) inclusion of B4C in aluminium increases corrosion rate in chloride atmosphere. In case of hybrid composite as shown in fig. 4c graphite is an electrical conductor and it acts as efficient cathodic element along with oxygen in aerated environment and hence galvanic corrosion takes place according to M A Afifi. Pits formed are indicated by rhombus.+

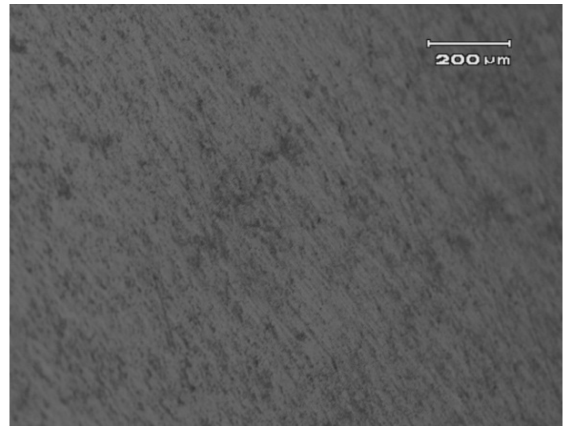

Fig. 3a: Base alloy microstructure

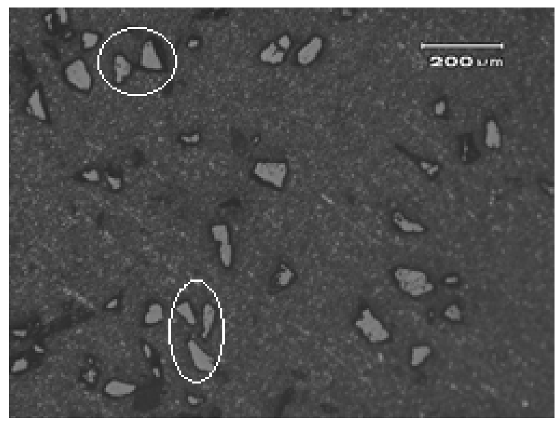

Fig. 3b: Al + B4C composite microstructure

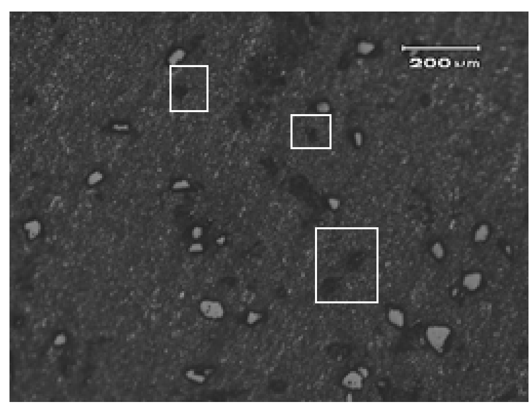

Fig. 3c: Al + B4C + Gr composite microstructure

4.2 Corrosion behaviour

Once the corrosion tests are carried over the specimen, the softcorr™ software plots the graph of potential v/s log current. The potentiodynamic curves also called as anodic cathodic curves of as-cast samples are as shown in fig. 5 below.

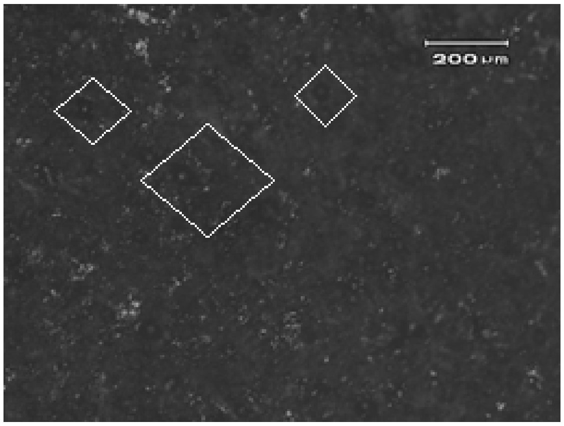

Fig. 4a: Corroded surface of base alloy

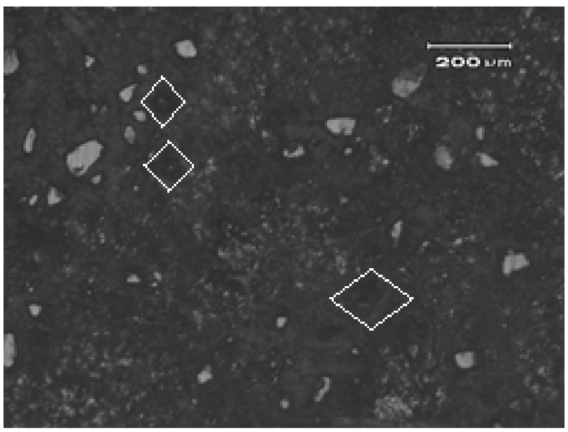

Fig. 4b: Al + B_4C corroded surface

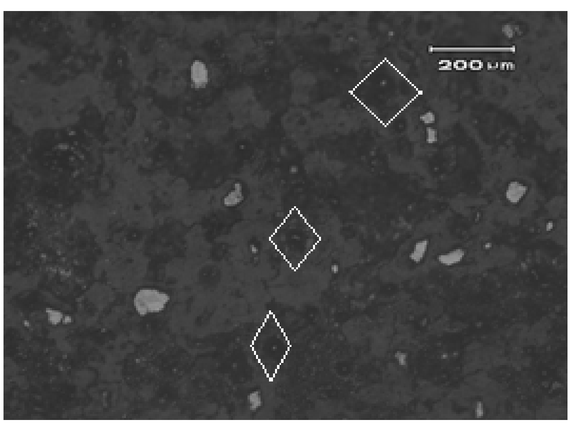

Fig. 4c: Al + B_4C + Gr corroded surface

Fig. 5a shows potentiodynamic curves (PDC) for as-cast base alloy. As said by N Nafsin et. al. (2013) copper present in alloy precipitates into grain boundaries and makes alloy vulnerable to stress, granular and pitting corrosion. PDC can be divide into five regions viz, active region, passive region, removal of film and trsanspassive region.

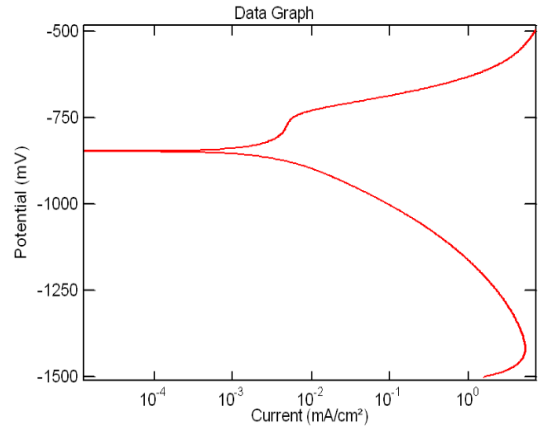

Fig. 5a: as-cast Al alloy

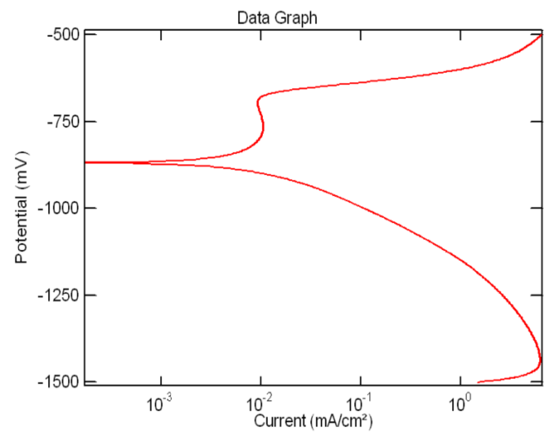

Fig. 5b: As-cast Al+B_4C mono composite

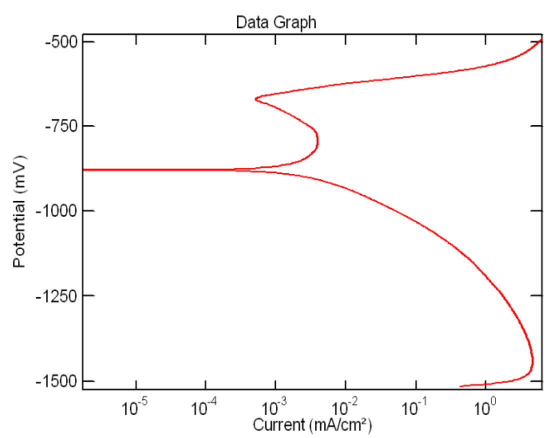

Fig. 5c: As-cast Al+B_4C+Gr Hybrid composite

These curves are also called as tafel plots. Fig. 5b shows PDC for monolithic composite from the nose of the curve we can clearly understand that pitting is increased and potential needed is lower than base alloy. Fig. 5c shows that the corrosion rate is more for the hybrid composite compared to the rest.

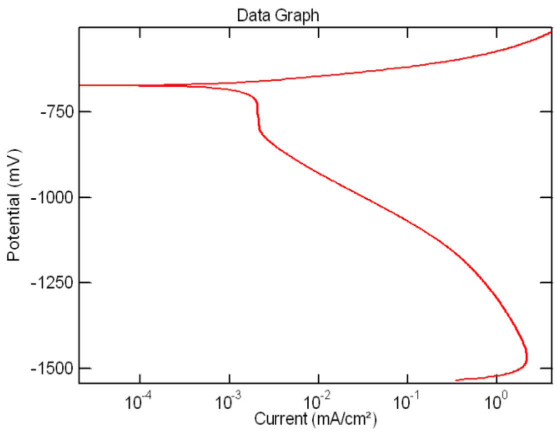

Fig. 6a: T6 Al alloy

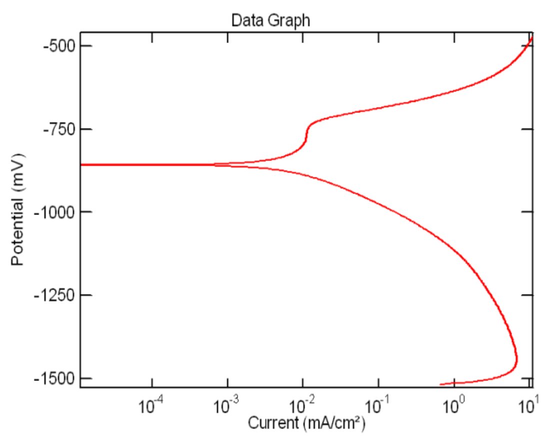

Fig. 6b: T6 Al+B_4C mono composite

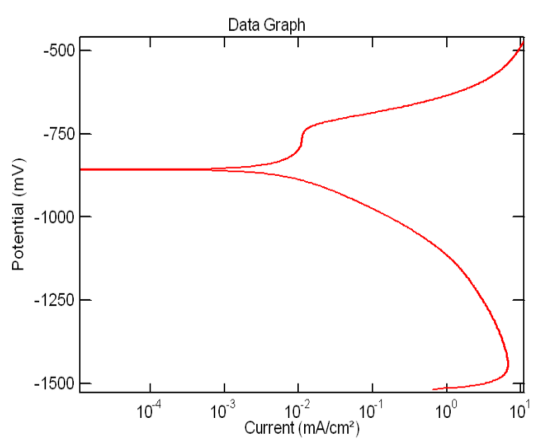

Fig. 6c: T6 Al+B_4C+Gr Hybrid composite

Fig. 6a shows the PDC for the T6 heat treated Al alloy. From the graph itself it is clear that there is no noticeable pit formation over the heat treated base alloy. This is because of the removal of internal stresses during heat treatment which would had led to stress corrosion cracking. According to joseph C et. al. corrosion property can be increased in the expense of other mechanical properties like strength. Fig. 6(b) and 6(c) also shows the PDC for the heat treated mono and hybrid composites respectively. With the help of above graphs corrosion potential (E_{corr}), pit potential (E_{pit}), corrosion current (I_{corr}) and corrosion rate (CR) are calculated and tabulated as shown in table 2 below.

Table 2: E_{corr}, E_{pit}, I_{corr} and CR values of composites in NaCl solution.

Composition	Ecorr (mV)	Epit (mV)	Icorr (mA/cm2)	CR(mmpy)
T0 Al	-848.29	-833.33	0.1749	1.8931
T0 Al+8wt%B4C	-869.43	-855.55	0.2206	2.6037
T0 Al+8wt%B4C+3wt%Gr	-877.75	-838.64	0.2468	3.0184
T6 Al	-672.55	-	0.0794	0.8358
T6 Al+8wt%B4C	-857.68	-835.53	0.2715	2.1153
T6 Al+8wt%B4C+3wt%Gr	-869.72	-849.96	0.3127	2.3821

5. CONCLUSION

In the present work, an uniformly distributed reinforced composite was fabricated by stir casting technique and were observed in optical microscope for proper distribution of reinforcement. Wettability was improved by adding K_2TiF_6 as an wetting agent with B_4C during casting. The same samples were made into two sets. One set of samples were corrosion tested in as-cast condition and another set was tested after T6 heat treatment. Corrosion testing was carried according to ASTM G5 by Potentiodynamic anodic polarization technique with 3.5 wt % NaCl solution maintained at pH of 6.5 the tests revealed the results that base alloy is most corrosion resistant than mono and hybrid composite. Corrosion resistance of hybrid composite was the least since there was formation of aluminium carbide which leads to galvanic and intergranular corrosion. Corrosion resistance of the heat treated base alloy has increased drastically and that of composites has also increased. This is because of the internal stress reliving and gaining solid solution form of the alloy during heat treatment.

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