

Influence of coating on short steel fiber reinforcements on corrosion behavior of aluminium base short steel fiber reinforced composites

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Abstract Steel fiber reinforced aluminium composites are attractive materials of high specific strength but exhibit poor resistance against electrochemical corrosion. The study discusses the electrochemical corrosion behavior of uncoated, copper and nickel coated short steel fiber reinforced aluminium and Al–2Mg matrix composites in 1 (N) NaCl solution. Galvanic corrosion between the steel fiber and aluminium governs the corrosion behavior of these composites. It has been observed that open circuit potential (OCP) is shifted to more negative side with copper coating on the fibers and to the more positive side on coating the fibers with nickel. Compared to the uncoated fiber higher corrosion current density indicates corrosion rate was observed for the copper coated fiber reinforced composites where as a lower current density was noted for the nickel coated fiber reinforced composites was observed. Addition of 2 wt% magnesium to aluminium alloy matrix increased the corrosion current density. The corrosion mechanism in these composites is dominated by galvanic cell formation that is evident from the dissolution of Al matrix near the peripheral region of steel fibers.

Introduction

Metal matrix composites (MMCs) are capable of providing unique combination of properties, which expand the range of potential application of the unreinforced metals. MMCs have been used for structural application where high specific strength and modulus as well as low density are desirable. They also offer improved wear resistance, optimized thermal expansion, and are capable of retaining their excellent mechanical properties to a high temperature [1–4]. However, MMCs are very susceptible to electrochemical corrosion [5–7]. In particular the use of MMCs in marine environment demands adequate corrosion resistance.

As per the available literature MMCs are prone to severe corrosive attack even at low temperatures during storage and transport [8, 9]. The corrosion behavior of MMCs is controlled by the galvanic behavior of dissimilar elements, the role of interface between matrix and reinforcing elements, microstructural features and residual stress as resulting from the processing. Galvanic corrosion occurs between the two dissimilar metals like aluminium and plain steel fiber. This is particularly true when an active metal such as aluminium is galvanically coupled to a relatively noble metal such as steel fiber. Relatively inert material such as steel fiber is usually noble because they serve as inert electrode for proton and oxygen reduction. The difference between the reversible potentials is E_{rev} (at 25 °C, unit activity, pH set to 7) of $O_2 + 4H^+ = 2H_2O$ ($E_{rev} = 0.82 V_{she}$) and $Al^{+3} + 3e = Al$ ($E_{rev} = -1.66 V_{she}$) is 2.48 V. The difference between $2H^+ + 2e = H_2$ ($E_{rev} = -0.41 V_{she}$) and $Al^{+3} + 3e = Al$ is 1.25V [10]. Therefore, there is a tendency for a

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galvanic couple to form between aluminium and reinforcing constituents, which act as inert electrodes and upon which O_2 and H^+ reduction may occur. Thus, a metal will usually corrode at an accelerated rate when galvanically coupled to relatively inert materials. MMC corrosion behavior can be predicted utilising polarization diagram and the mixed potential theory. The cathodic polarization diagram of the noble constituent (steel) was plotted with anodic polarization diagram of aluminium. The point of intersection between cathodic and anodic curves gives I_{corr} and E_{corr} for composites corresponding to galvanic couples.

The coatings have been used with some success to protect Gr–Al composites. Al composites with graphite fibers (without Ni coating) exhibit higher rates of electrochemical corrosion in 3.5 wt% NaCl solutions [11]. Nickel coating decreases the corrosion rate [12]. Another effect of the nickel coating is caused by the change in the galvanic couple between the aluminium matrix and the circumferential fiber surface to one between aluminium and nickel on surface. An Al–Ni couple is less deleterious than an Al–Gr couple.

In the present investigation plain carbon short steel fiber are used as a reinforcement. The steel fibers were coated with copper and nickel. The plain carbon steel has been chosen due low cost and easy available. The objective was to study the corrosion behavior of such composites at NaCl solution and study the effect of copper and nickel coating on corrosion properties.

Experimental procedure

In the present study plain carbon steel, copper and nickel-coated short steel fiber reinforced aluminium and Al–2Mg base composites were prepared by stir cast technique shown in Table 1, and examined for their electrochemical behavior.

Commercially pure aluminium was melted in clay and 2 wt% pure Mg was added into the molten aluminium to prepared Al–2Mg alloy. Short plain steel fibers were used as reinforcement. Plain steel fibers were coated

with copper and nickel by electroless deposition technique to obtain the fiber length 850 μm to 550 μm and diameter 80 μm to 120 μm , respectively. The thickness of copper and nickel coating on the fiber was 2 μm and 1.64 μm . It has been reported in an earlier publication [13]. Commercially pure Al and Al–2Mg alloy was melted in a resistance furnace at 700 $^\circ\text{C}$, the melt was stirred with a graphite impeller revolving at 700–750 rpm. About 5-wt% short plain steel fibers, copper coated and nickel coated steel fibers preheated at 200 $^\circ\text{C}$ was added to the center of the vortex in a continuous stream and stirred for 2 min to prepare the composites. The composite melt was then bottom poured into cast iron dies. Plates of 8 mm thickness 65 mm width and 180 mm height were obtained. Copper and nickel diffuse into the molten aluminium during processing and form an interface containing higher copper and nickel. The dissolution of the coating is not complete. In case of nickel coating intermetallic compounds containing Fe and Ni forms as detected by XRD [13].

The electrochemical response of cast aluminium, Al–2Mg alloy and the composites were studied in 1(N) NaCl solution. Samples of 10[mm] \times 10[mm] \times 6[mm] size were used for the corrosion study. The samples were polished using standard set of emery papers (1.0, 2.0, 3.0, and 4.0) and then polished on cloth wheel with diamond pest following the conventional metallographic procedure. Potentio-dynamic corrosion tests were conducted using three-electrode principle with a PS6 Mainsberger potentiostat/galvanostat, where platinum is used as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The schematic experimental set up used for corrosion testing is shown in Fig 1. Only top surface of the samples was exposed for corrosion attack and the rest of the surfaces coated with enamel. Current flowed through a conducting wire spot welded to the sample near one of the edges of the sample. This was connected to the positive terminal of the power supply, so that the sample acted as an anode. Before the potentio-dynamic test, the samples were allowed to stabilize at their corrosion potential for at least

Table 1 Sample assemblies

Sample name	Matrix	Fiber	Fraction of fibre (wt%)	Coating
Al	Al	–	–	–
Al–5Fe	Al	Plain carbon steel	5	–
Al–5FeCu	Al	Plain carbon steel	5	Copper
Al–5FeNi	Al	Plain carbon steel	5	Nickel
Al–2Mg	Al–2Mg alloy	–	–	–
Al–2Mg–5Fe	Al–2Mg alloy	Plain carbon steel	5	–
Al–2Mg–5FeCu	Al–2Mg alloy	Plain carbon steel	5	Copper
Al–2Mg–5FeNi	Al–2Mg alloy	Plain carbon steel	5	Nickel

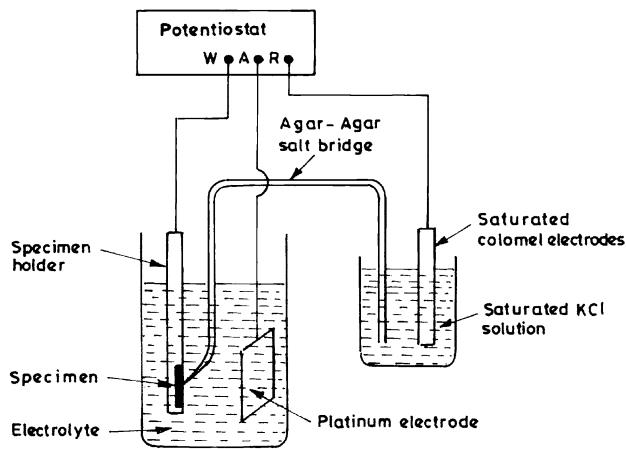


Fig. 1 Schematic diagram of corrosion testing set up

10 min. The tests were carried out at a scanning rate of 0.5 mV/s, starting from a negative (cathodic) over-potential and ending at a suitable positive (anodic) over-potential. The surfaces were exposed to solution, potential ranging from -350 mV to $+350$ mV (depending upon the nature of samples). The results presented are average of at least three corrosion tests. After the test, the samples were washed with water and followed by alcohol and preserved for microscopic studies.

Results and discussion

The electrochemical response of cast aluminium, Al-2Mg alloy and composites was studied in 1 (N) NaCl solution. Galvanic corrosion between the reinforcement constituents and the metal matrix governs the corrosion behavior of MMCs. Apart from this; other factors such as residual contaminants of MMC processing, residual stresses and the formation of interface also have pronounced effect on corrosion behavior. The results from the potentiodynamic corrosion tests of the aluminium matrix steel fiber reinforced composites are shown in Table 2. Representative polarization diagrams are shown in Fig 2. The electrochemical behavior of aluminium alloy and composites reflects highly [corrosion rate indicate by I_{corr} for Al is $5.69 \text{ mA/cm}^2 * 10^{-3}$ and for composite

Table 2 Electrochemical corrosion properties of aluminium base composites in 1 (N) NaCl solution

Sample	O.C.P	I_{corr} (mA/cm^2)* 10^{-3}	E_{corr} (mV)
Al	-763	5.69	-751
Al-5Fe	-735	12.75	-716
Al-5FeCu	-718	13.54	-787
Al-5FeNi	-758	11.842	-601

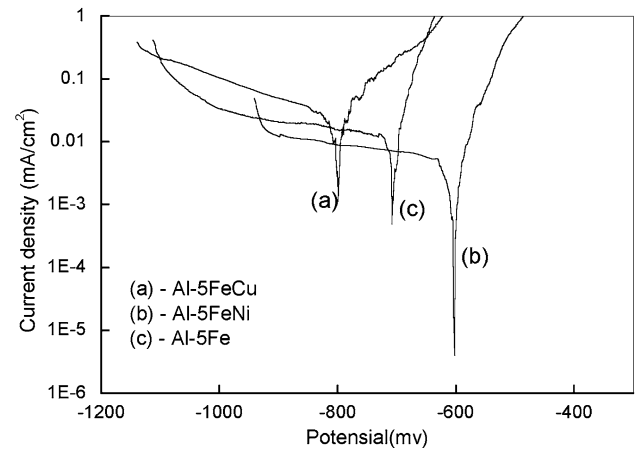


Fig. 2 Polarisation diagram of different aluminium base composites (a) Al-5Fe, (b) Al-5FeCu and (c) Al-5FeNi

$12.75 \text{ mA/cm}^2 * 10^{-3}$] active response in NaCl solution. Corrosion current density increased significantly after the incorporation of Fe fiber in aluminium matrix. Reinforcement with steel fiber has shown some effect on corrosion potential as well and the pit morphology has been affected by the presence of reinforcement. Galvanic corrosion is a major factor in the composites because aluminium an active metal coupled with Fe forms a local galvanic cell in MMC. The presence of steel fibers increases aluminium dissolution adjacent to the steel fiber of metal matrix composites and hence there is an increase in I_{corr} . I_{corr} is a commonly used indicator of corrosion rate.

Aluminium has good resistance to aqueous corrosion in near neutral solutions because of the formation of a passive oxide film. But in 1(N) NaCl solution aluminium and aluminium matrix composites (reinforced with steel fiber) showed no evidences of passive film formation, as evident from the absence of passive region in the polarization curves shown in Fig 2. The anodic and cathodic Tafel slopes determined after correcting the polarization curve for the effect of solution resistance are about -50 and $+50$ mV decade respectively by extrapolation indicate corrosion current density shown in Fig. 3. Above the corrosion potential the current density increases rapidly due to pitting of the Al alloy.

A change of the corrosion potential within 40 mV has been observed with the application of copper and nickel coating. The corrosion current density has also changed after the deposition of the coating. In case of copper coated fibers composites, the current density was higher than that of the un-coated fiber reinforced aluminium composites, at the same amount of fiber addition, nickel coating on the fiber reduces the I_{corr}

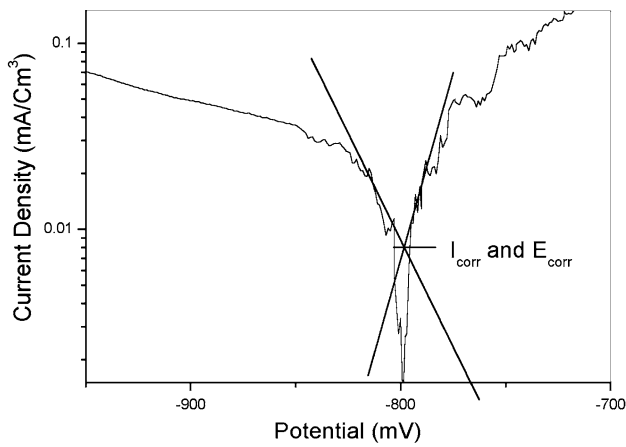


Fig. 3 I_{corr} and E_{corr} measurement from point of interaction

Table 3 Electrochemical corrosion properties of Al–2Mg base composites in 1 (N) NaCl solution

Sample	O.C.P	I_{corr} (mA/cm ²)*10 ⁻³	E_{corr} (mV)
Al–2Mg	–816	8.435	–796
Al–2Mg–5Fe	–759	13.271	–775
Al–2Mg–5FeCu	–654	16.257	–865
Al–2Mg–5FeNi	–778	12.324	–755

value slightly where as copper coating increases it. Nickel coated fiber composite; the corrosion rate was less than the uncoated ones. These data indicate that in case of nickel coated fiber composites corrosion resistance is maximum.

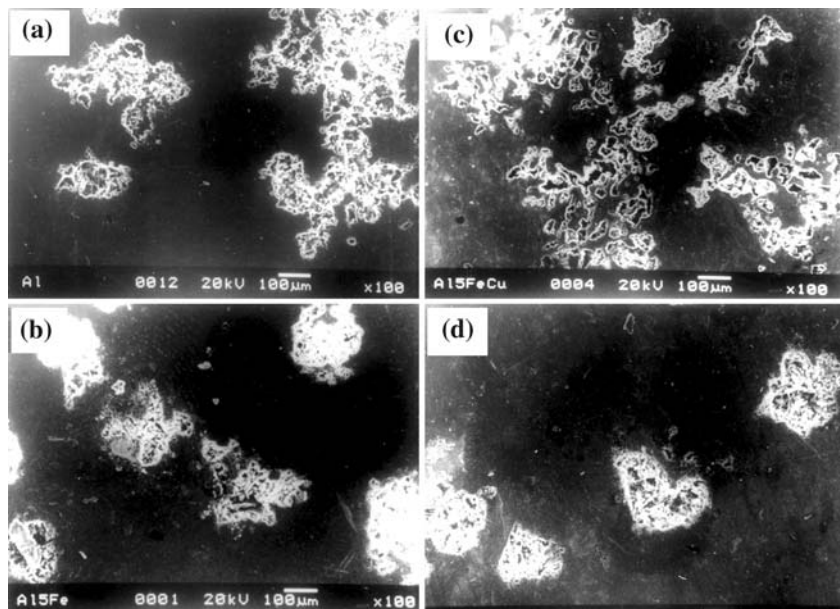
The corrosion rate of Al–2Mg matrix composites is shown in Table 3. The composites show higher corrosion rate than the matrix alloy. In case of Al–2Mg base

composites the corrosion current density indicates corrosion rate has been observed to be higher than aluminium matrix composites because Mg is more active metal than aluminium. The influence of coating applied on I_{corr} of Al–2Mg base alloy and composites follow a similar trend to Al matrix alloy and composites i.e., the corrosion rate of composites is higher than that of the matrix alloy. Nickel coated fiber in both Al and Al–2Mg base composites show minimum corrosion rate.

Copper and nickel could dissolve into the molten aluminium during processing and formed interface contains copper and nickel. The copper and nickel is segregated at the interface. It may be noted that the nickel-coated fibers contain Fe–Ni, Fe_{0.64}Ni_{0.36} intermetallic compounds are identified by X-ray diffraction. Nickel is not present in the elemental form [13]. These compounds further react with aluminium during stir casting and may form FeAlNi intermetallic compounds as reported earlier [14], at the interface affecting the fiber distribution. In case of copper-coated fibers, copper present on the fiber surface diffuses into the molten aluminium leading to better wetting, better fiber distribution and good interface bonding. The diffusivity and solubility of copper in aluminium being high there is little possibility of formation of CuAl₂.

The scanning electron micrographs (SEM) of the corroded surfaces of aluminium alloy and composites are shown in Fig. 4a–d. Corrosion pits are distributed all over the surface. Incorporation of steel fibers changed the corrosion behavior of aluminium alloy and formation of local galvanic cell in the composites increased the number of pits compared to base metal.

Fig. 4 SEM photographs of composites after electrochemical treated at 1(N) NaCl solution (a) Aluminium alloy (b) Al–5Fe composite (c) Al–5FeCu composite (d) Al–5FeNi



Corroded areas on Al–Fe composites are notably more numerous and much smaller in size but number of pits was higher compared to aluminium alloy.

Corrosion mechanism

In the present investigation local galvanic couples formed between aluminum matrix and steel fiber reinforcement could be predicted by using the mixed potential theory. The intersection of the tangent for cathodic curve from reinforcement constituent and anodic curve from aluminium matrix would measure the corrosion current density for the alloy and its composites are shown in Fig. 3. The point of intersection between cathodic and anodic curves gives I_{corr} and E_{corr} for composites corresponding to galvanic couples.

It has been observed that with the incorporation of steel fiber in aluminium matrix corrosion current density, which is a measure of corrosion rate, increases. In case of aluminium base steel fiber reinforced composites corrosion mechanism is dominated by local galvanic cell formation between Al matrix and steel fiber reinforcement. Aluminium and Al–2Mg matrix worked as a anode and steel fiber worked as a cathode which is evident from the dissolution of aluminium near the interface between Al matrix and steel fiber reinforcement as shown in Fig. 5. FeAl_5 and Fe_3Al_5 could be formed during processing of composites and influence the corrosion mechanism. Those phases are not identified. The electrolytic potential difference between FeAl_3 and the Al matrix reduces corrosion resistance. Nickel coating on the steel fiber has reduced corrosion current density while copper coating increases corrosion current density.

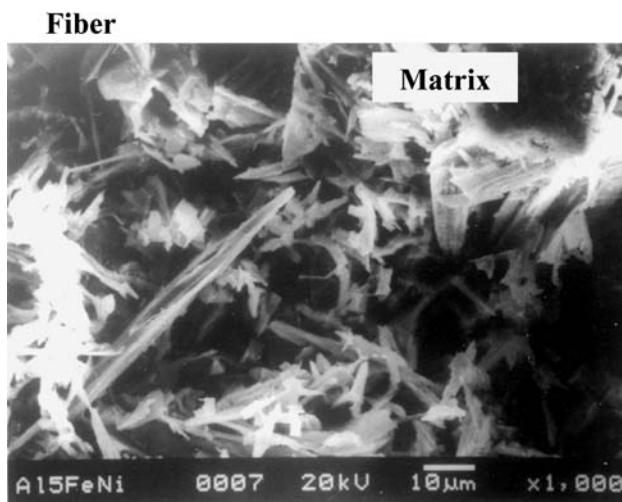


Fig. 5 SEM photographs of corrosion surface showing galvanic corrosion between Al Matrix and steel fiber

Steel fibers without any coating have steel in the core and Fe_3Al_5 and FeAl_3 at the interface. Galvanic cell is formed between FeAl_3 and aluminium instead of steel and aluminium, which results in increased corrosion rate. Also FeAl_3 and Fe_2Al_5 precipitates act as local oxygen reduction sites that cause pitting of aluminium alloys in chloride containing solutions [10]. Nickel coating should have changes the galvanic couple between aluminium and steel fibers to one between aluminium and nickel coated surface. Nickel coating on the steel fiber surfaces has to changed the galvanic couple from aluminium and steel fiber to between aluminium and nickel coated surface. FeAl intermetallic could be formed during processing which restrict the current flow from the matrix. As a result, nickel coated fiber reinforced composites show a lower corrosion current density. In case of copper coated fiber composite corrosion current density (I_{corr}) increased $0.79 \times 10^{-3} \text{ mA/cm}^2$ as compared to uncoated steel fiber reinforced composite. Copper dissolved into aluminium matrix and formed Al–Cu at interface that shifts the potential difference between steel fiber and Al–Cu at the interface leading to increased corrosion current density. Apart from this, the polarization curves show the open circuit potential (OCP) is shifted to more negative side with copper and to the more positive side with nickel coating. The intersection of the cathodic curve with the anodic curves would indicate a high corrosion current density for the copper-coated fiber and lower current density for the nickel coated fiber composite compared to the uncoated fiber composite.

The corrosion current density of Al–2Mg alloy matrix composites showed a higher corrosion rate than the aluminium. Mg is electrochemically more active than aluminium and so Al–Mg containing matrix develops higher potential difference with the reinforcement leading to higher galvanic corrosion.

Conclusions

1. Galvanic corrosion dominates the corrosion mechanism of the composites studied. Corrosion rate indicates by current density of composites in 1N NaCl solution increases with incorporation of fibers.
2. Copper and nickel coating deposited on the plain steel fiber by using electroless deposition techniques. The coating considerably influenced the electrochemical corrosion behavior of aluminium and steel fiber reinforced composites. Copper coating on the fibers increases the corrosion rate.

Nickel coated fiber composites shows minimum degradation.

3. The corrosion mechanism of the composites was dominated by pit formation throughout the matrix. The aluminium matrix near the fiber was dissolved indicates the galvanic cell formation between fiber and matrix.
4. Addition of magnesium further increases the corrosion rate because Mg is more active than aluminium, which increased potential difference between matrix and fiber.

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