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Study of Corrosion of Al-Cu Hypoeutectic Alloys and Al-Cu Composite Fabricated Using Stir Casting Technique

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Abstract

The aim of the present investigation is to know the corrosion resistance of Al–5-wt% Cu alloy, Al–10-wt% Cu alloy and Al–5-wt%Cu alloy as matrix and 5-wt% Cu powder(105 microns particle size) as reinforcement. The castings with above percentage of compositions are obtained by stir casting. The corrosion test was conducted by keeping the samples in 5% NaCl solution for different time intervals (1hr, 2hrs, upto 8hrs). Then the test was also conducted by keeping the samples in 2.5% HCl solution for 2hrs, 4hrs, 6hrs and 8hrs and by varying the percentage of concentration of HCl solution by keeping the time constant i.e. 4hrs. The obtained results proved that the alloys and composite studied have more resistance to corrosion in neutral aqueous NaCl solution than aqueous HCl acidic solution and such materials are more suitable in the transportation industry applications.

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1. Introduction

The natural process of corrosion is when nature reacts against a man made forms of material by attempting to reduce them to their natural forms, as in the case of Aluminium to its natural oxide. Aluminium alloys are widely used in structures where a high strength to weight ratio is important, such as in the transportation industry.

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Aluminium is thermodynamically reactive metal, but it owes its excellent corrosion resistance to the natural formation of a thin but very stable oxide film.

From a thermodynamically reactive metal point of view aluminium is active. However, in oxygen containing environment air, water aluminium is rapidly covered with a dense oxide layer (1). The oxide layer is chemically inert and prevents corrosion. According to Pilling–Bedworth rule volume of the oxide \geq volume of the parent metal, then the oxide layer has non-porous and consequently, the rate of oxidation and thus oxidation corrosion decreases to zero. The thickness of the layer may vary as a function of temperature, environment and alloying elements. Oxide films formed in air at room temperature are 2-3 nm thick on pure aluminium. Heating to 425°C may give film upto 20 nm.(2) If the oxide film is damaged, e.g. by a scratch, new oxide will form immediately on the base metal(3). In this way aluminium is given excellent corrosion protection.

Aluminium and its alloys have assessed as a possible replacement for steel, due to a high corrosion resistance and a potential of considerable weight reducing, as its density is almost three times lower than the density of steel, (2.739 gms/cm³ for aluminium and for the steel is 7.85 gms/cm³).

For public transportation systems such as high speed trains, trams, underground and regional trains, aluminium is the market leader in the construction of body shells of the above. As in the automotive industry energy reducing light weight materials and design flexibility are the paramount criteria for the operators railway system now a days(4,6,8,9). The bus body building manufacturers are also looking for new, economic light weight designs with enable them to build bus bodies with less tooling costs and reducing assembly time than require for traditional design(5).

Aluminium and its alloys are generally passive and corrosion resistant in aqueous solutions except for pitting corrosion due to some reactive species, such as chloride(7).

Keller and Edward(10) have shown that such intermetallic particles are dissolved faster than the aluminium rich matrix during the anodizing process and induce heterogeneous coatings with a low corrosion resistance. Liu.et. al. (11) stated that due to the cathodic nature of the CuAl₂ particles relative to the aluminium rich α -phase, the rise of corrosion potential of the α -phase reduce the galvanic coupling between the CuAl₂ and α -matrix, and reducing the driving force for pitting corrosion in the α - solid solution. According to Rao.et. al.(12) electron beam welds of aluminium alloy 2219 exhibit superior corrosion properties due to the dissolution of CuAl₂ particles and an even distribution of copper in the matrix. Wang. et. al(13) stated that when Cu is in solid solution, it has lesser effect on the alloys corrosion resistance than, when it is present as CuAl₂, provided that the alloy is not aged to the point when it becomes susceptible to intergranular corrosion or to stress corrosion.

It has been reported in the literature that the microstructural and the macrostructural morphologies have a strong influence on the corrosion resistance(14-17). Recently, pure metals macrostructural(18,19) and binary alloy castings microstructural(20,21) effect upon the tendency of corrosion resistance have been reported. It has found that the tendency of corrosion resistance improvement depends on the cooling rate imposed during solidification which affects the solute redistribution, dendrite atom size, and on the electrochemical behaviour of solute and solvent

As reported in the literature, the role of CuAl₂ intermetallic particles is important in both conversion coatings or anodizing films(22,23). There have been extensive investigation on the role of chloride ions in the breakdown of the passive film, repassivation and initiation of localised corrosion of aluminium and high strength aluminium based alloys. Furthermore the effect of alloying content(24-27), electrolytic composition(28), heat treatment(29) and mechanical stress(30) on pitting and repassivation of aluminium based alloys in halide media have been reported. There is some evidence from literature(31-33) proving the occurrence of the pitting corrosion on the surface of some metals as a result of passivity breakdown by perchlorate ions.

2. Experimental Procedure

Aluminium with 99.17% purity was used as the base metal in the experiments for the fabrication of the alloys and composite. In this study, an Al–5-wt% Cu alloy, an Al–10-wt% Cu alloy (hypoeutectic alloy), and an innovative composite combination of the Al–5-wt% Cu alloy as the matrix and 5-wt% Cu powder (average particle size of 105 μ m) as the reinforcement are considered. The chemical compositions for these materials are listed in Table 1. The aim of the present work was the evaluation of corrosion rate of Al–5-wt% Cu and Al–10-wt% Cu alloys, Al–5-wt% Cu alloy and Al–5-wt% Cu composite, in selected corrosion environment.

The MMC was prepared and fabricated by using the stir-casting method by dispersing the Cu powder in the molten base Al–5-wt% Cu alloy. The Al–5-wt% Cu and Al–10-wt% Cu alloy castings were prepared by adding Cu in the form of chunks to the molten aluminium. Cu powders were produced by fixing a Cu rod in a lathe and manually filing the rod by rotating it at high speeds. Next, the powder was placed in a ball mill for 2 h. Then, the powder was placed in the top sieve of a sieve shaker for 5 to 10 min. For reinforcement, Cu powder particles with an average size 105 µm were used.

TABLE 1: Chemical composition of investigated materials

Element Concentration (wt%)	Material		
	Al–5.0-wt% Cu alloy	Al–10.0-wt% Cu alloy	Al–5.0-wt% Cu alloy and 5-wt% Cu composite
Al	94.753	89.663	89.159
Cu	4.955	10.094	10.265
Mn	0.120	0.101	0.002
Mg	0.097	0.092	0.097
Fe	0.012	0.023	0.224
Si	0.021	0.011	0.129
Zn	0.008	-----	0.075
Pb	0.017	-----	0.031
Cr	0.003	0.003	0.002
Ti	0.004	0.003	0.006
V	0.010	0.010	0.010

For producing castings of the Al–5-wt% Cu and Al–10-wt% Cu alloys, a weighed quantity of pure Al is initially placed in the Inconel alloy crucible (bottom poured) of an electric resistance furnace, as shown in Figure 1 shows line diagram of the furnace. The furnace temperature was increased to approximately 750°C and maintained at this temperature for 2 h. Then, Cu is added to the molten aluminium at 750°C for producing the Al–5-wt% Cu alloy castings. The melting process is continued for another 30 minutes for complete solubility of the solute metal in the molten base Al. After complete solubility, the crucible bottom was opened by operating the control switch on the control panel to pour the molten metal into the die, which was located exactly below the crucible opening. During the melting process, Argon gas was circulated in the crucible chamber and the die chamber to reduce the oxidation and to obtain defect-free castings. The same procedure was followed for producing the Al–10-wt% Cu alloy castings.

The innovative composite metal castings consisting of an Al–5-wt% Cu alloy and a 5-wt% Cu powder were prepared by the stir-casting technique using a mechanical stirrer. To obtain the composite castings, the melting process is same as that for the Al–5-wt% Cu alloy. The temperature was reduced from 750°C to approximately 675°C, meanwhile, the Cu powder was separately preheated to approximately 200°C for 30 min. The preheated Cu powder was slowly added to the molten Al and Cu alloy through a pipe located above the crucible. The molten metal was then stirred with a motor-operated stirrer for a few seconds at 200 rpm to mix and obtain an equal distribution of reinforced Cu particles in the Al–Cu alloy and immediately poured into the die cavity. During the melting period, argon gas was circulated in the crucible and die chamber. Both the alloys and composite were cast into fingers with dimensions of 150 mm × 18 mm dia. After removing the castings from the die, they were homogenized for 24 h at 100°C and quenched in water. Further, the castings were solutionized at 500°C for 2 h, followed by water quenching. Finally, cast samples of the alloys and composite were age-hardened at 190°C for several hours followed by cooling to determine the (T6) peak time and hardness.

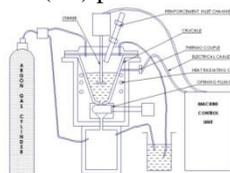


Fig. 1 Line diagram of Electric resistance furnace

The present investigation aims to contribute to the understanding of the effects of solute redistribution along with the matrix (varying concentration of α-phase) of dendritic spacing and of CuAl₂ particle distribution in the

interdendritic region upon the general corrosion of an Al–5-wt% Cu and Al–10-wt% Cu alloys and Al–5-wt% Cu alloy as the matrix and 5-wt% Cu powder as the reinforcement.

Furthermore, an Al–5-wt% Cu and Al–10-wt% Cu alloys, Al–5-wt% Cu alloy and 5-wt% Cu composite samples (10mm diameter X 10mm thickness) were cut or by machining process from age hardened cast fingers in order to clarify and give support to the discussions. The samples are thoroughly polished, cleaned with acetone, washed with distilled water and kept in a furnace for 1hr. at 105⁰C.

The corrosion rate of samples was found out by weight loss method ^[34]. Corrosion rates can be expressed in terms of “mpy”(millimetre per year) . These values of a given alloy/composite can be obtained by simple gravimeter method. The following formula can be used to obtain mpy of any type of alloy/composite.

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

Where W represents weight loss in milligrams, D is density of the metal in gms./cm³, A is area of the specimen in cm², and T is immersion time in hours.

The corrosion rate and impedance parameters were determined of such samples i.e. as a function of local content, in order to clarify the roll of Al-rich matrix and the intermetallic CuAl₂ in an Al–5-wt% Cu and Al–10-wt% Cu alloys, Al–5-wt% Cu alloy and 5-wt% Cu composite. Further more in terms of general corrosion behaviour and to investigate the effect of chloride ion on the pitting corrosion behaviour of pure aluminium in aerated neutral sodium chloride solution. It was also the purpose of the present work to study the effect of Cu as an alloying element, on the pitting corrosion resistance of pure Al. in chloride solution. For this purpose Al–5-wt% Cu and Al–10-wt% Cu alloys, Al–5-wt% Cu alloy and 5-wt% Cu composite samples were used.

The corrosion rate of samples was carried out by weight loss method ⁽³⁴⁾.The corrosion measurements were carried out in 5% NaCl solution and 2.5% HCl. Solution at room temperature separately. The individual samples were taken into a separate Erlenmeyer flasks and it was kept in above solutions for varying time intervals. The Erlenmeyer flasks must be kept on the heavy rotary stirrer and operate for the above time periods for stirring the solution and is as shown in the figure 2. The corrosion measurements were also carried by varying the concentration of HCl solution. Kinetics of corrosion effect on samples of Al–5-wt% Cu and Al–10-wt% Cu alloys, Al–5-wt% Cu alloy and 5-wt% Cu composite are studied.



Fig. 2 Erlenmeyer flasks kept on heavy rotary stirrer

3. Results and Discussion:

3.1 Micro structural analysis



Fig. 3(a) Image of the microstructures of the Al–5-wt% Cu alloy

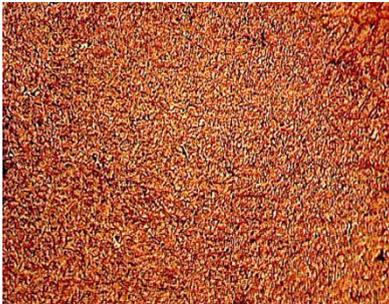


Fig. 3(b) Image of the microstructures of the Al–10-wt% Cu alloy

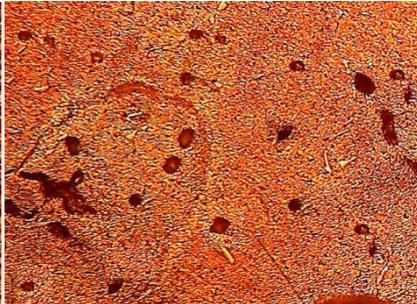


Fig. 3(c) Image of the microstructures of the Al–5-wt% Cu composite.

The figure 3(a) shows the etched Al–5-wt% Cu alloy matrix microstructure. It shows the interdendritic pattern of CuAl₂ phase in aluminium solid solution. The grain boundaries are clear with CuAl₂ phase. The microstructure is homogeneous without any segregation throughout the cross-section and is shown in the photo microstructure.

The figure 3(b) shows the etched Al–10-wt% Cu alloy matrix microstructure. It shows undissolved CuAl₂ phases as thick constituents at the grain boundaries and the matrix shows the aluminium. The overall microstructure is fine dendritic pattern due to rapid cooling of the casting.

The figure 3(c) shows the etched Al–5-wt% Cu alloy and 5-wt% Cu composite sample microstructure. It shows two distinct zones were observed in the age hardened cast Al–5-wt% Cu alloy with 5-wt% addition of Cu powder as composite material. The addition of Cu powder does not seemed to have dissolved in aluminium solid solution, as it already saturated with Cu. The solubility of Cu powder is not taken place and it is distributed randomly as particles throughout the structure of CuAl₂ phase.

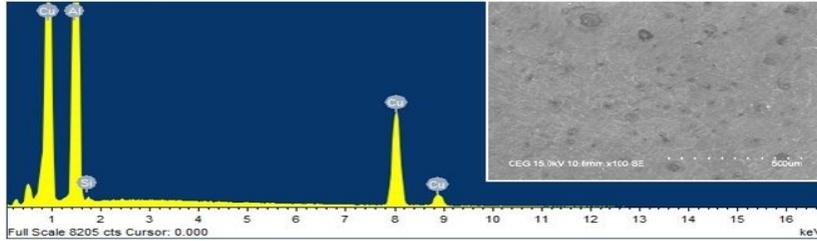


Fig. 4 SEM and EDX pattern for Al–Cu composite.

Figure 4 shows the Al and Cu peaks for the composite. The scanning electron microscopy (SEM) micrograph shows the Cu particle distribution in Al–Cu alloy matrix. It is also evident from the SEM micrograph that the Cu particles are not alloyed with the matrix material, instead they are distributed throughout the matrix and solidified as particles.

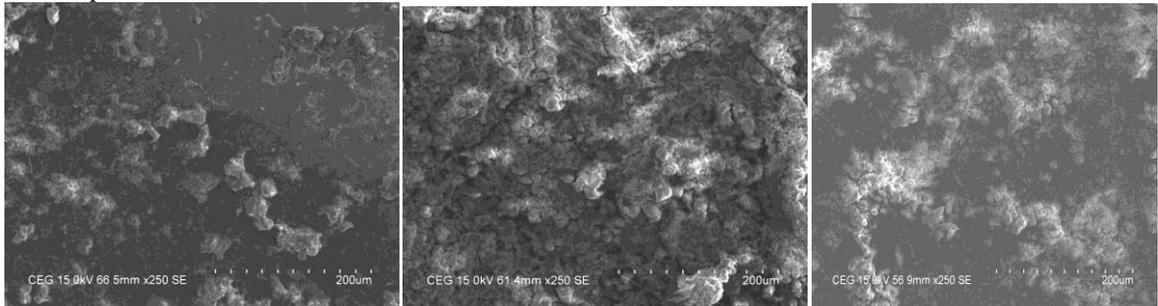


Fig. 5(a) shows the effect of pitting corrosion on 5-wt% Cu alloy

Fig. 5(b) shows the effect of pitting corrosion on 10-wt% Cu alloy

Fig. 5(c) shows the effect of pitting corrosion on 5-wt% CU Composite kept in 5% NaCl solution.

The figure 5 microstructures show the pitting corrosion of investigating alloys and composite in 5% NaCl solution. The pitting corrosion is more in Al-10-wt% Cu alloy as compared to 5-wt% Cu alloy and composite.

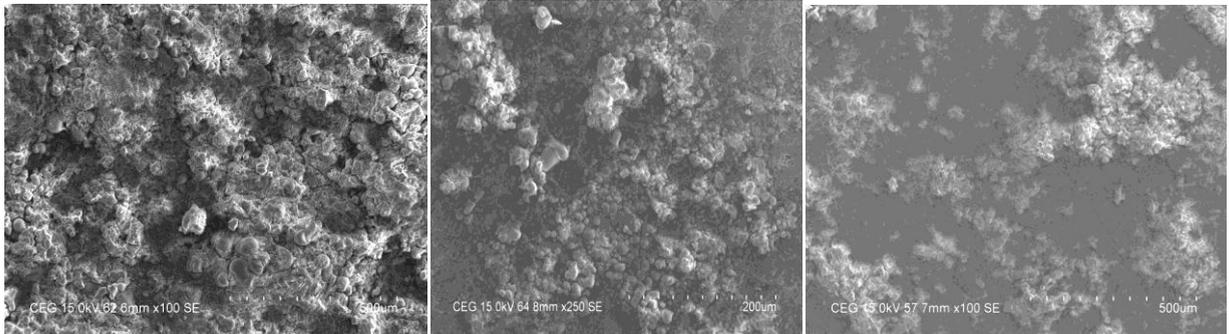


Fig. 6(a) shows the effect of pitting corrosion on 2.5% HCl for 6 Hrs. 5% Cu alloy

Fig. 6(b) shows the effect of pitting corrosion on 2.5% HCl for 6 Hrs. 10% Cu alloy

Fig. 6(c) shows the effect of pitting corrosion on 2.5 % HCl for 6 Hrs. 5% Cu Composite

The figure 6 microstructures shows the pitting corrosion of investigating alloys and composite in 2.5% HCl solution. The pitting corrosion is more in Al-5-wt% Cu alloy at 6 hours as compared to 10-wt% Cu alloy and composite.

The pitting corrosion susceptibility of Al-Cu alloys and composite namely Al-5-wt% Cu and Al-10-wt% Cu alloys, Al-5-wt% Cu alloy and 5-wt% Cu composite in 5.0% NaCl solution were examined. The pitting corrosion susceptibility were also examined for the above investigating alloys and composite in 2.5% of HCl solution and varying the concentration of HCl solution. Pitting corrosion occurs in aluminium, aluminium alloys and composite in both acidic and basic aqueous solution outside the P^H range of about 4 to 8.5. Within this range aluminium is passive, because it is protected by its oxide film.

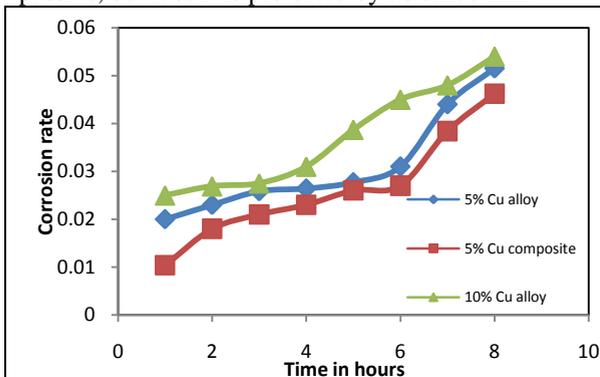


Fig. 7 Effect of immersion time of rate of corrosion on Al-Cu alloys and composite in presence of 5% NaCl solution.

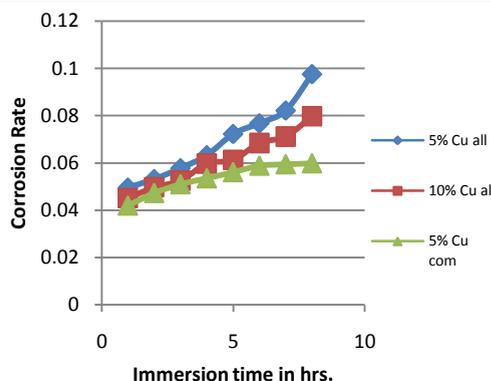


Fig. 8 shows effect of immersion time of rate of corrosion on Al-Cu alloys and composite in presence of 2.5% HCl solution.

The figure 7 depicts the effect of immersion time on corrosion rate of investigating Al-Cu alloys and composite in solution containing 5.0 % NaCl. Both alloys and composite show a similar trend of dissolution, i.e. gradual increase of corrosion with time. It is well known fact that as time increases the rate of corrosion also increases.

Al-10-wt% Cu alloy shows more corrosion rate than Al-5-wt% Cu alloy and Al-5-wt%Cu alloy and 5-wt%Cu composite as shown in the microstructure figure 3, this is due to the 10-Wt% Cu alloy matrix shows the un-dissolved $CuAl_2$ phase as thick constituents at the grain boundaries and presence of more Al_2O_3 layer. However 5-wt%Cu composite shows a better resistance towards dissolution than the Al-5-wt%Cu alloy. In case of alloy, presence of $CuAl_2$ makes it susceptible to corrosion action in the presence of chloride ions. Similar effect is also expected with the composite, but to a very little extent, and the alloy formation takes to a restricted region, i.e. where the Cu particles interacts with the matrix, resulting a dilute alloy in the vicinity of it. Presence of fine Al_2O_3 layer on the overall composite reduced this effect further resulting in decreased dissolution.

Figure 8 shows the rate of corrosion of investigating Al-Cu alloys and composite in 2.5% HCl solution. The corrosion rate increases with increase in immersion time for both the alloys and composite. The corrosion rate of Al-5-Wt% Cu alloy undergoes more corrosion rate than Al-10-Wt%Cu alloy and Al-5-Wt%Cu alloy and 5-Wt% of Cu composite, because of percentage of Cu content decreases the rate of corrosion increases. Cu shows more resistance to corrosion than aluminium. The grain boundaries are clear with $CuAl_2$ phases, the microstructure is homogeneous without any segregation throughout the cross section.

Corrosion rate of Al- 10- Wt% Cu alloy in 2.5% HCl solution is more as compared to AMMC and less corrosion rate compared to other alloy, because the matrix shows the un-dissolved $CuAl_2$ phases as thick constituents at the grain boundaries. More the immersion time chloride ions of acid attack more on Al_2O_3 protective layer, hence corrosion rate increases.

Figure 8 shows corrosion rate of Al-5-wt%Cu alloy and 5-wt% of Cu composite in 2.5% HCl solution, the rate of corrosion is less with increase in immersion time than both the alloys. The corrosion rate of composite increases up to 6 hrs and there is very less variation in corrosion rate as the immersion time increases. The investigating composite shows less corrosion rate than the alloys, because Al-5-wt%Cu alloy and 5-wt% of cu composite microstructure shows two distinct zones in the cast Al-Cu alloy with 5- wt% of Cu powder addition. The addition of Cu powder does not seemed to have dissolved in aluminium solid solution, as it is already saturated with Cu. The solubility of addition of Cu powder not taken place and is precipitated as particles and distributed randomly

throughout the structure of CuAl_2 phase.

Corrosion rate (weight loss) of alloys and composite in 5.0 % NaCl solution is less when compared to 2.5 % HCl solution, because P^{H} of NaCl solution is 7, in this PH range aluminium is passive, so it protected by its oxide film. Aluminium alloys and composite materials are more resistance to corrosion in neutral aqueous NaCl solution than comparative acidic HCl solution as shown in the figures 7 and 8.

Figure 9 depicts the dissolution behaviour of Al–5-wt% Cu alloy, Al–10-wt% Cu alloy and Al–5-wt% Cu alloy and 5- wt% Cu composite were studied with distilled water and varying % concentration of HCl. Solution kept the samples for 4hrs.in the solution. With distilled water the percentage of corrosion occurs is zero. The corrosion rate increases with increase in chloride ion concentration. Both the alloy and composite respond in a similar manner. However, Al–5-wt% Cu alloy has more corrosion resistance with varying the concentration of chloride ions. Upto 0.05% HCl solution the corrosion rate is zero for Al–5-wt% Cu alloy because more Al_2O_3 layer is passive, which protect the alloy and the strength of the solution is also less, than the concentration of HCl solution increases the corrosion rate also increases. At higher concentration the severity of the corrosion attack is more severe with the Al–10-wt% Cu alloy than the composite as shown in the figure 6. At 0.25% concentration of HCl solution for the alloys and composite the severity of the corrosion attack is maximum. However, Al-5-Wt% Cu alloy is more resistance to corrosion than Al-10 Wt% Cu alloy and composite, this may be due to volume protective layer of aluminium oxide of Al- 5-wt% Cu alloy is more, thus it is self protective, which shows more corrosion resistance.

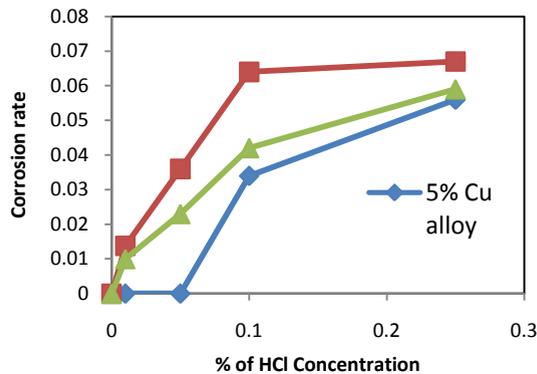


Fig. 9 The effect of the dissolution behaviour of 5-wt%Cu alloy, 10-wt%Cu alloy and 5-wt% Cu composite with distilled water and varying % concentration of HCl. solution kept the samples for 4hrs.

The dissolution behaviour of Al–Cu alloys and composite were studied with distilled water and varying % concentration of HCl. Solution kept the samples for 4hrs.in the solution. The dissolution behaviour of Al–5-wt% Cu alloy and Al–10-wt% Cu alloy was compared to know at what percentage of HCl concentration the corrosion starts. The corrosion of Al–10-wt% Cu alloy and composite was started at 0.01% concentration of HCl solution, where as for Al–5-wt% Cu alloy, the corrosion starts at 0.05 % concentration of HCl. The corrosion rate is low for Al–5-wt% Cu alloy as compared to Al–10-wt% Cu alloy and composite at any % concentration of HCl. Solution.

The corrosion rate is high in Al–10-wt% Cu alloy as compared to investigating composite, hence the pitting corrosion is more in above alloy and is as shown in the figure 9.

As per intergranular corrosion, segregation of Cu particles covering the entire grains of CuAl_2 are less anodic (more resistance to corrosion), thereby corrosion rate is less in composite compared to Al–Cu alloys. The immersion time with 2.5% HCl solution on Al-5-wt% Cu alloy and 5-wt% Cu composite increases, the corrosion rate decreases, because the grain boundaries which are covered by inactive $\text{Al}(\text{OH})_3$ layer.

4. Conclusions

1. Al–5-wt% Cu alloy, Al–10-wt% Cu alloy and Al–5-wt% Cu alloy and Al–5-wt% Cu composite have been prepared by stir casting technique
2. The immersion time of samples in electrolyte increases the corrosion rate increases on alloys and composite.

3. The concentration of HCl solution increases i.e. P^H decreases, the corrosion rate increases. Pitting corrosion occurs in Al–5-wt% Cu and Al–10-wt% Cu alloys and Cu composite in both acidic and basic solution outside the P^H range of about 4.0 to 8.5.
4. The investigated alloys and composite have more resistance to corrosion in neutral aqueous NaCl solution than aqueous acidic HCl solution.
5. The composite shows more resistance to corrosion as compare to alloys in 2.5% aqueous HCl acidic solution.
6. The above Al- Cu alloys and composite are more suitable to use in neutral environment.

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