

Corrosion behaviour of sintered 6061 aluminium alloy–graphite particle composites

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The corrosion behaviour of sintered 6061 aluminium alloy and its composite dispersed with 7.0 vol % graphite particles is described. Techniques, namely immersion, tafel and impedance, were employed to study the corrosion behaviour. Immersion tests were performed in different media, namely HCl, NaCl and lubricating oil (used and fresh) while tafel and impedance tests were performed in 0.1N HCl and 3 % NaCl solution. Corrosion behaviour was monitored by measuring the weight change in immersion studies and corrosion current, i_{corr} , in tafel and impedance tests. The values of corrosion potential, E_{corr} , and i_{corr} were calculated from the tafel plots obtained at a scanning rate of 1 mV s^{-1} . In impedance study, i_{corr} was calculated from the value of polarization resistance, R_p , obtained from the Nyquist plot; the latter was obtained by merging the lock-in and FFT plots. Aluminium alloy and its composite suffered from corrosion in HCl and NaCl. However, the extent of severity was greater in the case of HCl. The i_{corr} values obtained by the impedance method also revealed a similar trend. The higher corrosion rate of the alloy and composites in HCl was due to the dissolution of the thin oxide (protective) film in the solution. The decreased corrosion rate of the composite and the base alloy in NaCl was attributed to the formation of stable corrosion product, $\text{Al}(\text{OH})_3$, on the surface, which prevented further attack on the surface of the specimen. There was practically no evidence of corrosion attack on the alloy and the composite surface in used and fresh lubricating oil.

1. Introduction

Aluminium alloy-based composites are being studied extensively by researchers and technologists due to their versatile properties, and enormous potential for use in engineering applications. Hard, as well as soft, particles are incorporated into aluminium alloys to impart a range of properties to the resultant composites [1–4]. Although extensive work on preparation and physical and mechanical properties of cast aluminium–graphite composites has been reported [1, 3], literature on sintered composites is very limited. Available reports [4, 5] on sintered aluminium graphite composites pertain to their preparation and mechanical properties, and information related to corrosion properties of the material is virtually unavailable in the literature. The present study, therefore, was carried out to investigate the corrosion behaviour of sintered 6061 aluminium alloy–7.0 vol% graphite composite in different environments, namely HCl, NaCl and lubricating (SAE-30) oil. Immersion, tafel and impedance techniques were employed for corrosion studies.

2. Experimental procedure

2.1. Composite preparation

Compacts of 6061 aluminium alloy (Al 98.05, Mg 1.00,

Si 0.60, Cu 0.25, Cr 0.10, wt %) and the composite dispersed with 7.0 vol % graphite particles, were prepared by the conventional route of powder metallurgy involving mixing, compaction and sintering. Details of the preparation technique are reported elsewhere [6].

2.2. Corrosion studies

Corrosion studies using the immersion technique were carried out in solutions of HCl (0.1N) and NaCl (3%) and in used and fresh SAE 30 lubricating oil. Degreased cylindrical compacts (12.74 mm diameter and 6.0 mm height) were suspended in the environments for different periods. Corrosion products were removed from the specimen by the procedure reported by Cocks [7]. Corrosion rates were computed from the weight change of the compacts after removal of corrosion products.

Electrochemical tests (tafel and impedance) were conducted using EG and G PAR model 378–1 electrochemical system consisting of potentiostat/galvanostat (M–273) and lock-in amplifier (M–5208). Softwares M378 and M342 were used for tafel and impedance measurements, respectively. Corrosion current was calculated from the value of the polarization resistance, R_p , obtained from the Nyquist plot using the Stern–Geary equation [8].

2.3. Roughness studies

The roughness parameter, R_a , of the specimens was measured using a profilometer model Talysurf-6 of Rank Taylor and Hobson, UK.

2.4. Metallography

Scanning electron microscopic (SEM) examinations of the uncorroded and corroded specimens were carried out after sputtering them with a thin layer of gold.

3. Results

Fig. 1 shows the weight change of the 6061 alloy and composite in HCl and NaCl solution with the duration of exposure. The weight loss values for both types of specimen were noted to be identical after immersion in HCl for 1 day. However, immersion for 3 days in HCl resulted in an increase in weight loss of 6061 alloy, followed by a decrease with duration up to 36 days. Finally, a sharp increase in weight loss in this case was observed after 36 days exposure. In the case of the composites, on the other hand, weight loss increased in a narrow range up to 36 days immersion, beyond which there was a sharp reduction in weight loss. Immersion in NaCl resulted in marginal weight change of the composites as compared to those immersed in HCl. Insignificant weight gain by the alloy and composites was noted after the immersion test in used and fresh oil (Fig. 2).

Typical tafel and merged Nyquist impedance plots for the base alloy and its composite after exposure to

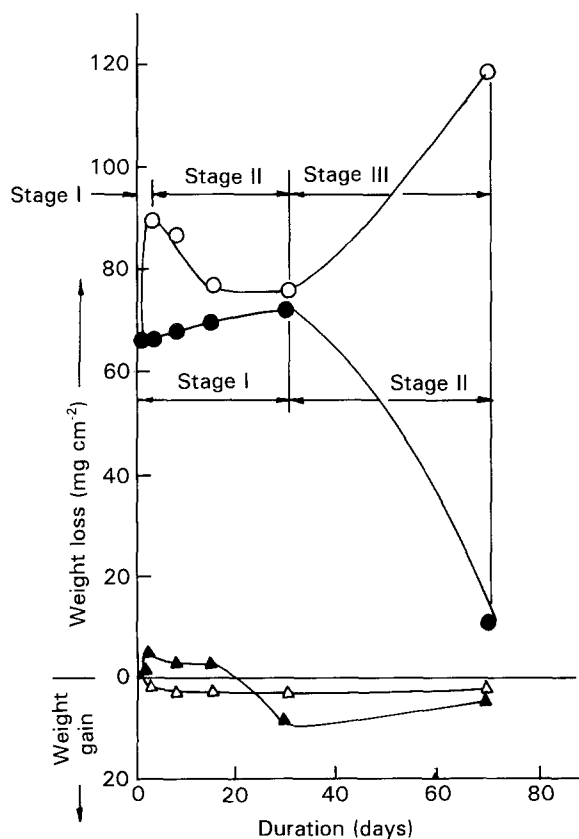


Figure 1 Weight change of the (○, △) 6061 alloy and (●, ▲) composites in (○, ●) HCl and (△, ▲) NaCl solution as a function of time.

HCl are shown in Figs 3 and 4, respectively. Corresponding values of i_{corr} and corrosion rate (m^{-1}) are listed in Table I. It is clear from the table that i_{corr} of the 6061 alloy is approximately three times higher than that of the composites in HCl medium. In NaCl solution, the reverse trend was observed; the value of i_{corr} was more for the composite than the base alloy. The value of i_{corr} of the base alloy decreased by approximately 300 times when immersed in NaCl as compared to tests in the HCl solution.

Table II shows the roughness parameter, R_a , of corroded and uncorroded surfaces of the base alloy and composites. Although the R_a value of the base alloy and composites were comparable before the test,

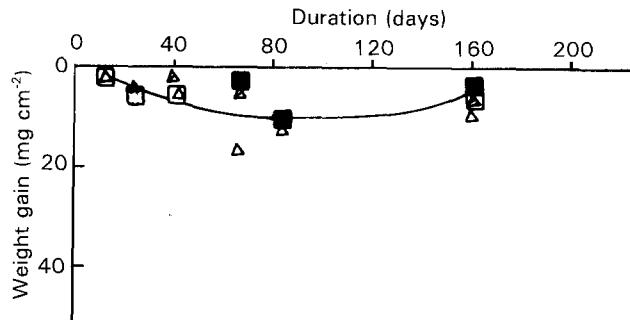


Figure 2 Weight changes of the (△, □) 6061 alloy and (▲, ■) composite in SAE30 lubricating oil ((□, ■) used and (△, ▲) fresh) as a function of time.

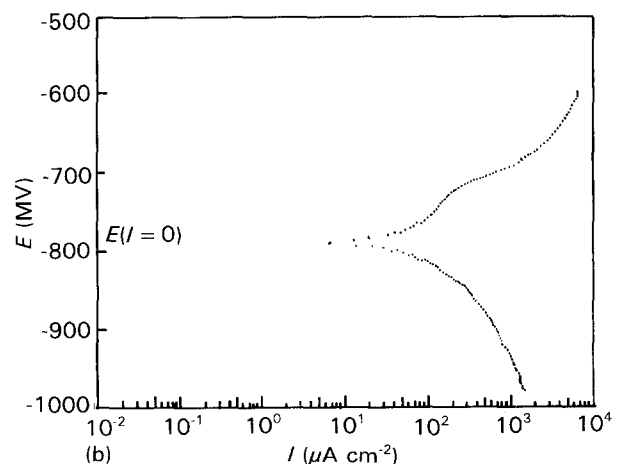
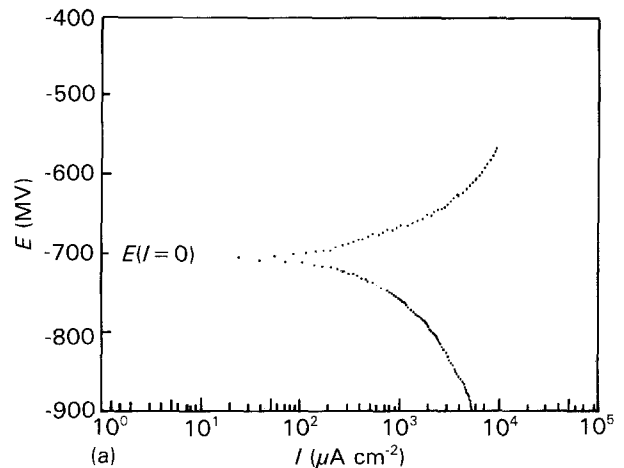


Figure 3 Tafel plots for (a) 6061 alloy and (b) 6061-7% graphite composite in HCl solution.

TABLE I Corrosion values in different environments

Environments	Technique used	6061		6061-7	
		i_{corr} ($\mu\text{A cm}^{-2}$)	Corrosion rate (m y^{-1})	i_{corr} ($\mu\text{A cm}^{-2}$)	Corrosion rate (m y^{-1})
0.1 N HCl	Tafel	984.56	426.64	299.74	129.88
	Impedance	988.23	428.22	292.79	126.88
3% NaCl	Tafel	2.45	1.06	5.86	2.5
	Impedance	4.09	1.77	5.15	2.23

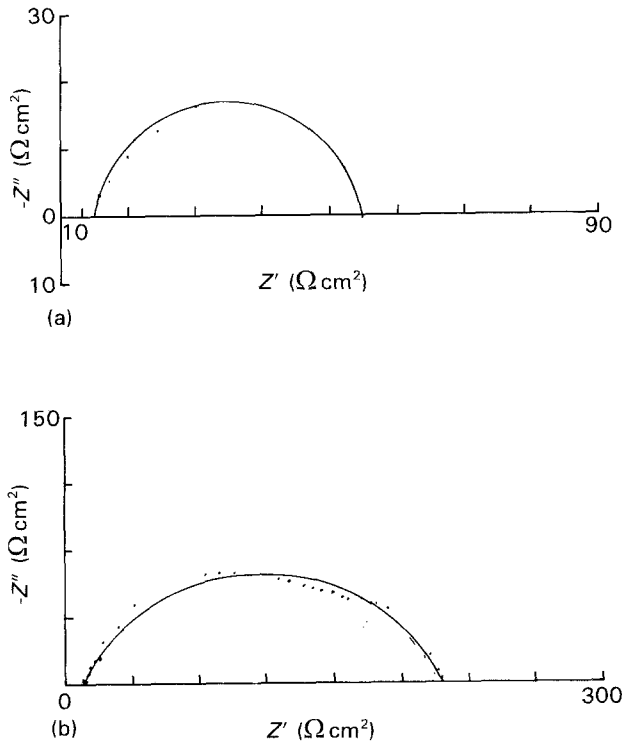


Figure 4 Merged Nyquist impedance plots for (a) 6061 alloy and (b) 6061-7% graphite composites in HCl solution.

TABLE II Roughness parameter

Specimen	R_a (μm)	
	6061	6061-7
Uncorroded	0.74	0.70
Corroded		
0.1-N HCl	0.882	1.84
3% NaCl	0.38	1.9

the values increased substantially for the composites after the tests in either solution.

Figs 5 and 6 show scanning electron micrographs of the 6061 alloy and composite before and after exposure to the corrosion medium. The micrographs reveal the presence of closed porosity (marked X) on the surface of the uncorroded specimen (Fig. 5a). Dispersoid/matrix interfacial porosity (marked p) was also present in the composites (Fig. 6a). Corrosion attack at closed as well as interfacial porosity (arrowed) is evident from Fig. 6 b and c. The severity of attack in the HCl environment was greater compared to NaCl for both the alloy and composites (Figs 5 and 6).

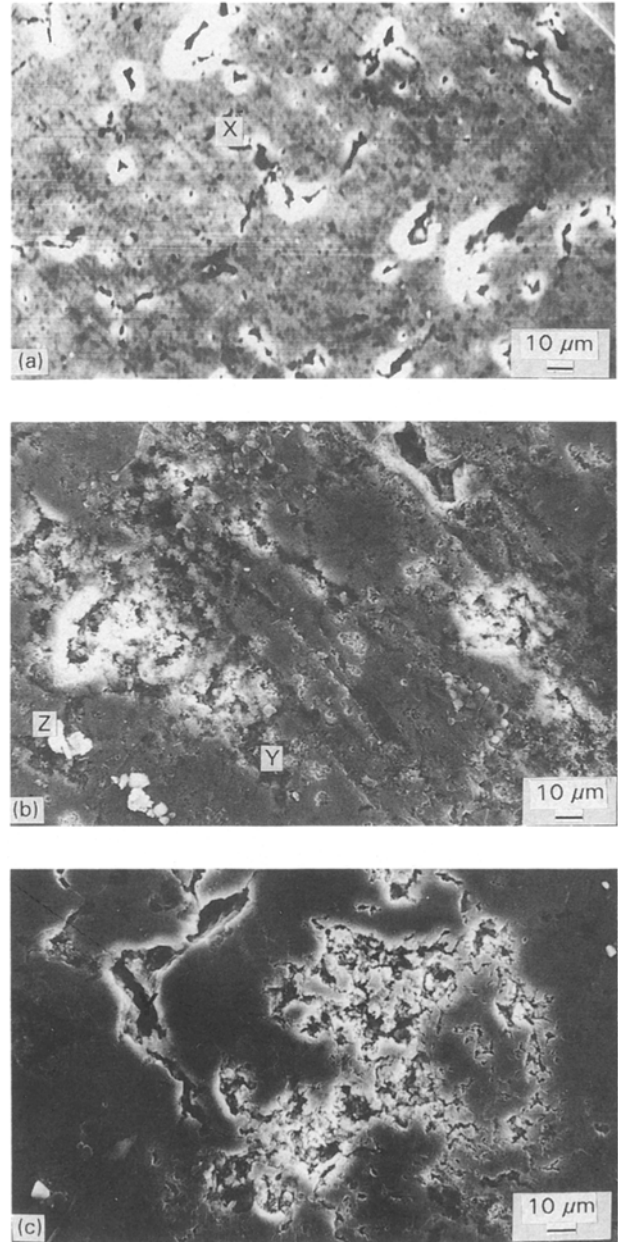


Figure 5 Scanning electron micrographs of 6061 alloy: (a) uncorroded, and corroded (for 72 days) in (b) HCl and (c) NaCl solutions.

4. Discussion

In view of the presence of an increased amount of porosity (50% more than the base alloy) and interfaces between the graphite particles and the matrix, the composite becomes more prone to corrosion attack.

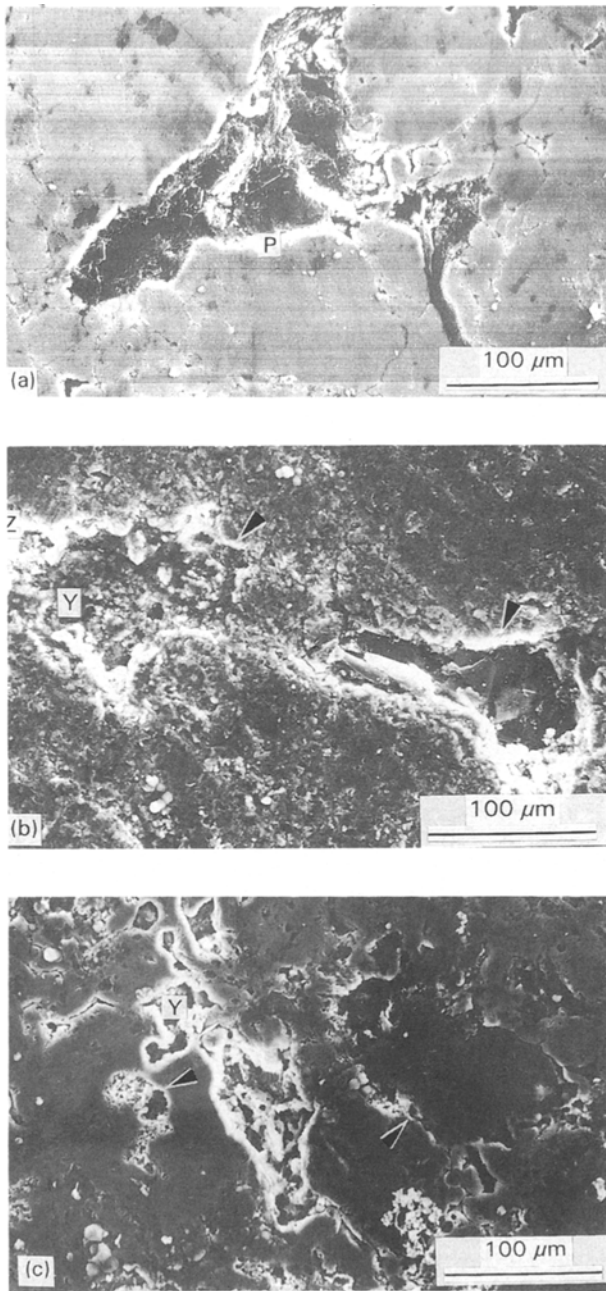
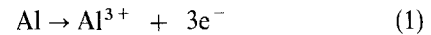


Figure 6 Scanning electron micrographs of composites (a) uncorroded, and corroded (for 72 days) in (b) HCl and (c) NaCl solution.

Further, the composite would also suffer from galvanic corrosion due to the presence of cathodic graphite particles. The results of the immersion study in HCl showed an unusual corrosion trend of the base alloy and composite. The corrosion rate of the composite was found to be less than that of the base alloy (Fig. 1). Also the values of i_{corr} and corrosion rate (m y^{-1}) obtained from tafel and impedance techniques in HCl (Table I) supported the findings of the immersion test, i.e. the value of i_{corr} for the base alloy was two to three times higher than that of the composites.

It is well known that a very thin oxide layer is quickly formed on a fresh aluminium surface after exposure to air. The thickness of this layer usually does not exceed 5 nm even after extended exposure [9]. During mechanical polishing and subsequent washing with water, such a film with a minor hydrated phase is formed on the surface. During exposure of the

surface to the acid solution the corrosion proceeds according to the reaction



and the thin film present on the electrode surface is ineffective in passivating the specimen. A rapid formation of a soluble complex $\text{Al}(\text{OH})_2\text{Cl}$ takes place and the brittle corrosion products are separated easily from the specimen, resulting in weight loss. The mechanism of corrosion of aluminium alloys in HCl has been reported earlier by Summerson and Sprowls [10]. The authors have described the presence of duplex film, comprising a permeable outer bulk film facing the surroundings and a non-porous barrier film in between the bulk film and the specimen.

In the present circumstances following factors would affect the weight change of the base alloy and composite after immersion in HCl.

1. Instantaneous dissolution of permeable bulk oxide film on the specimen.
2. Further attack on the non-porous barrier film immediately adjacent to the specimen.
3. Penetration of the acid through porosities in to the bulk specimen.
4. Corrosion attack and non-removal of the corrosion product from within the specimen [11].
5. Massive removal of the entrapped corrosion product after attaining a critical thickness from the surface.

The final weight loss or gain values of the specimens would depend on the extent of corrosion, as well as removal of the corrosion product by the cleaning process adopted [7] in the present study. There was a common trend in the corrosion behaviour of the base alloy and composite in HCl up to a certain duration. For example, in both cases, there was an increase in weight loss with the duration of exposure for a specific period, followed by a decrease with further increase in exposure period. However, the duration of the inflexion varied from 3 days for the base alloy to 36 days for the composite.

A careful examination of the weight change versus duration of exposure curve (Fig. 1) indicates that the following stages of the process of weight change were encountered by the specimens: Stage I, initial increase in the weight loss; Stage II, decrease in weight loss; Stage III, final sharp increase in weight loss. The curve for the base alloy showed all three stages, compared with only the first two stages for the composites (Fig. 1). It is revealing that an instantaneous corrosion of the specimen in HCl took place within 1 day (in the shortest span of exposure time adopted). The weight loss was due to the dissolution of the porous bulk alumina film and the ease of release of the soluble corrosion products such as $\text{Al}(\text{OH})_2\text{Cl}$ [(10)] from the specimen. During the first stage of the weight loss for the base alloy, factor 1 was prevalent. After the complete dissolution of the outermost oxide layer (3 days in the present case) the barrier film immediately adjacent to the specimen surface resisted further attack by the environment. Simultaneously, acid solution is expected to penetrate and effect corrosion

within the alloy as described earlier (factors 3 and 4). The amount of corrosion product generated due to corrosion attack in the interior and which could not be removed from the specimen during cleaning, seems to be too small to alter the weight loss value in the first stage. Stage II corresponds to the resistance against corrosion offered by the barrier film. Additionally, the quantity of the irremovable corrosion products could be quite considerable to reduce the extent of corrosion loss. Both the above-mentioned factors would reduce the extent of material loss of the alloy with time as observed in Stage II. The resistance imposed by the barrier film would diminish slowly and finally it would be completely ineffective. A severe corrosion is likely to occur at this stage. Such may be the case in Stage III for the base alloy. The removal of a relatively large mass of the earlier accumulated corrosion product which is not in a position to stick any more to the interior surface such as pits and interfacial porosities, might also have taken place (factor 5), thereby increasing the weight loss to a great extent in Stage III (Fig. 1).

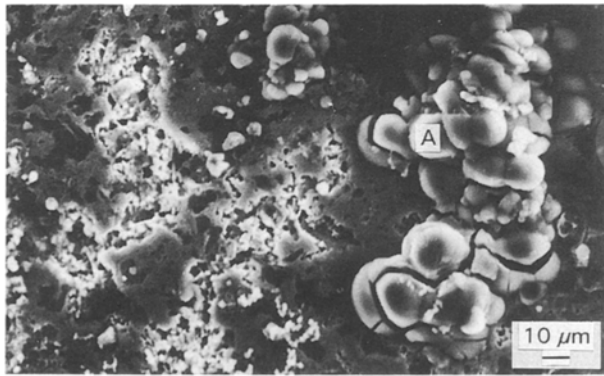


Figure 7 Scanning electron micrographs of composite corroded (for 72 days) in HCl solution showing adhered corrosion product on the surface.

In the case of the composite, the barrier film would be less effective as compared to the base alloy because the presence of graphite particles would weaken the film. As a result, factor 2 is expected to be predominant in Stage I for the composites. However, the amount of acid penetrated into the interior of the composite and thus the amount of irremovable corrosion product generated, would also be high, producing a counterbalancing effect. This would lead to the reduction in the extent of weight loss in stage I. Therefore, the rate of increase of weight loss is very slow upto 36 days, i.e. in the first stage. In stage II, the sharp drop in weight loss of the composite with time may be attributed to the entrapment of the irremovable corrosion product on the surface. It may be noted that the corrosion products are three times greater in weight and volume than the reactant metallic surface. This would certainly give rise to a weight gain by the composite. Adherence of corrosion products (marked A in Fig. 7) on the composite surfaces was confirmed by SEM examination of the corroded surface. No such corrosion products were found to have adhered to the base alloy surface even after exposure for 72 days. The value of roughness parameter, R_a (Table II) of the composite in the HCl environment also increased substantially, which confirmed the presence of irregularities (pits and products) on the exposed surface.

The extent of corrosion of the base alloy and the composite is insignificant in NaCl solution as compared to those immersed in HCl. In NaCl, the most stable oxide/hydroxide phase [12] on aluminium is $Al(OH)_3$. There are, however, some reports in the literature [12–14] which suggest that the prestep to the formation of $Al(OH)_3$ is the formation of $AlOOH$. Over extended periods of time, $AlOOH$ may sluggishly convert to hydroxide. The X-ray photoelectron spectroscopy (XPS) studies reported in the literature [15] later confirmed the formation of $AlOOH$. Formation of hydroxide/oxyhydroxide films, which

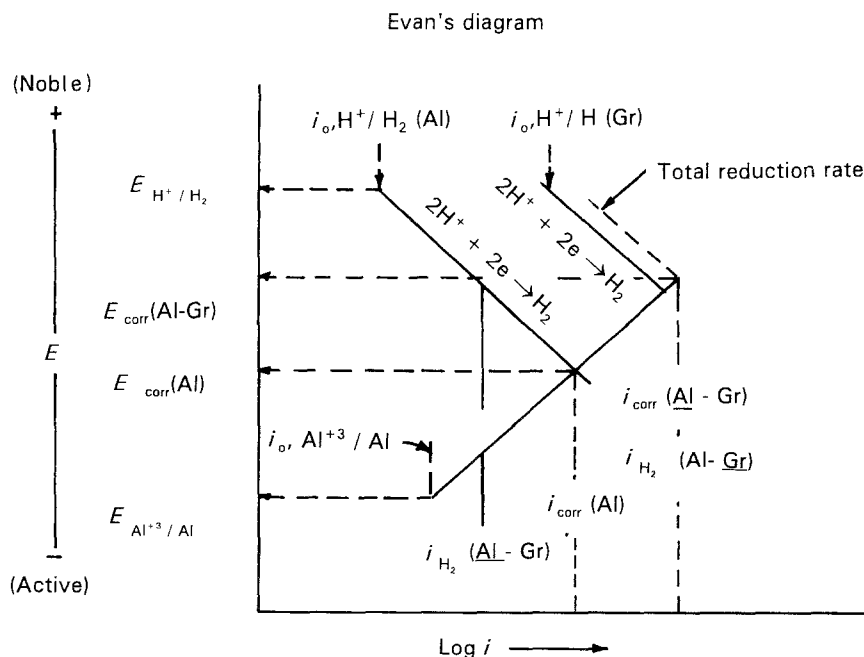


Figure 8 Evan's diagram for aluminium graphite composites.

may be significantly thick on the electrode surface due to corrosion reaction, leads, in turn, to the passivation of the surface. Mostly the weight gain by the alloy and composites in NaCl environment can be noticed from Fig. 1. Corrosion products, very small in quantity, are likely to adhere on the surface which may give rise to weight gain by the compacts. Scanning electron micrographs (Figs 5b and 6b) show the corrosion products adhered (marked Z) to the surface.

Results obtained from tafel and impedance studies in NaCl solution (Table I) show that the values of i_{corr} and the corrosion rate (m y^{-1}) for the composites are approximately twice the corresponding values for the base alloy. Evan's diagram for cast aluminium graphite composites [16] indicates (Fig. 8) that the graphite particles act as a cathode in aluminium-based composites and the incorporation of graphite particles shifts the anodic potential of the base alloy towards the cathodic side. Further increase in i_{corr} of the composites has been explained on the basis of the evolution of hydrogen from both (aluminium and graphite) surfaces [16].

Used oil has been reported to be more corrosive than fresh oil, due to the formation of sulphurous acid generated during the ignition process [17]. Corrosion attack could not be revealed in SEM observation of the specimens after the test in lubricating oil. Instead, weight gain by the alloy and composites were observed. A similar trend has been reported for the cast aluminium alloy composites [18]. However, the extent of weight gain in the present study is considerably higher than that of the cast composites. A higher porosity content in powder metallurgy composites prepared by the powder metallurgy route than the cast one, is responsible for the above. Identical to the reported observation [18], after a certain duration (80 days in the present case) the weight gain by the composites is reduced.

5. Conclusions

1. Aluminium alloy 6061-graphite particulate composites were not affected by immersion in used and fresh lubricating oil.

2. The extent of corrosion of the base alloy and composite was found to be severe in HCl solution in all three (immersion, tafel and impedance) studies, whereas it was marginal in NaCl. Weight loss of the

base alloy in HCl was greater compared to the composite.

3. The composites require no surface treatment for use in oil but demands surface modification for use in HCl and NaCl environments in order to avoid corrosion attack.

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