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COMPARISON OF CORROSION BEHAVIOUR OF COMMERCIAL ALUMINIUM ENGINE BLOCK AND PISTON IN 3.5% NACL SOLUTION

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ABSTRACT

The corrosion behavior of commercial aluminium alloy engine block and piston was investigated in 3.5% NaCl solution. The study was done by conventional gravimetric measurements and complemented by scanning electron microscopy (SEM) and X-ray analyzer (EDX) investigations. The results obtained indicate that the alloys suffers a process of corrosion localized to the area surrounding the precipitates of the Al (Si, Mg) and Al-Mg, which resulted in hemispherical pits. No evidence was found of the formation of crystallographic pitting for exposure times up to 54 days. Gravimetric analysis confirmed that with varying exposure periods the weight loss of the alloys increases and the normal corrosion rate profile of an initial steep rise followed by subsequent fall were observed for both alloys. The rate of corrosion of piston was found to be lower than that of engine block due to presence of Ni and lower percentages of Fe in aluminium piston alloy.

KEYWORDS

Localized corrosion, gravimetric analysis, aluminium-silicon alloys, SEM, EDX

1. INTRODUCTION

Aluminium alloys are widely used in structures where a high strength to weight ratio is important, such as in the transportation industry. Aluminium has a natural corrosion protection from its oxide layer, but if exposed to aggressive environments it may corrode [1]. Still, if correctly fabricated, constructions of aluminium may be reliable and have long service life. Corrosion as the gradual chemical or electrochemical attack on a metal by its surroundings such that the metal is converted in to an oxide, salt or some other compound which result to loss of strength, hardness, toughness and other desirable mechanical properties which metal posses[2]. The corrosion resistance of aluminum is attributed to an exceptionally stable oxide film that forms on its surface. This film is resistant to attack from water and oxygen in a wide range of temperatures and pH levels, making aluminum alloys useful in a variety of environments. Corrosion by pitting is aluminium alloys is a complex process that can be affected by diverse experimental factors such as the pH, the temperature, the type of anion present in the solution or the physic-chemical characteristics of the passive layer [3]. The adsorption of aggressive ions such as Cl^- into the faults in the protective film, and their penetration and accumulation in these imperfections is considered one of the triggering factors of the process of nucleation of pitting [4, 5]. Other studies have suggested that pits may develop as a result of a process of hydrolysis which gives rise to a local reduction of the pH which, in turn, impedes the subsequent process of repassivation [6].

In the present paper, the processes of corrosion of a commercially available aluminium alloy engine block and piston in 3.5% NaCl solution are studied. The research has been directed towards studying the characteristics, condition of formation and morphology of attack. The corrosion data was taken after 54 days immersion in the solution and was investigated using weight-loss data and complemented by SEM/EDX investigations.

2. EXPERIMENTAL DETAILS

The material used in the current study is a commercially used aluminum alloy engine block and piston. The alloys were analyzed both by wet chemical and spectrochemical methods. The chemical compositions of the alloys are given in Table 1. The samples of 25 x 10 x 3 mm^3 size obtained from the aluminium alloy block and piston were used to conduct the tests for studying the corrosion behaviour. The samples were wet-sanded mechanically with SiC papers of 220 and 1200 grit. Before use, the samples were de-greased with ethanol of 99% purity and then rinsed with plenty of water. Afterwards, they were dried, weighted (initial) different exposure periods up to 54 days. A stagnant solution of 3.5% NaCl at pH 5.5 was used as the aggressive medium. Solution was prepared by dissolving 3.5±0.1 parts by weight NaCl in 96.5±0.1 parts of distilled water. The solution was heated at 80oC for three hours every day. After the designated exposure in the solution medium, the samples were rinsed with distilled water, dried between two tissue papers, and weighted again (final weight, Wfin). Weight-loss measurements were made in triplicate and weight loss was calculated by taking an average of these values [4].

Weight loss, $$\Delta W = \frac{(W_{\text{int}} - W_{fin})}{A} \qquad (1)$$

Corrosion Rate, $$K_{Corr} = \frac{(K \times \Delta W)}{(A \times T \times D)} \qquad (2)$$

Where, Wint = initial weight before immersion, Wfin = final weight after exposure, K = unit conversion constant (K = 8.76 x 104 for the mmpy unit), T = time of exposure (hrs), A = area in (cm^2), ΔW = Weight loss (g) and D = density of metal (g/cm^3)

The specimens for microstructural observation were prepared using standard metallographic techniques; final polishing was done with fine alumina. The etching was done using Keller's reagent (HNO_3 -2.5 cc, HCl-1.5 cc, HF-1.0 cc and H_2O-95.0 cc). The washed and dried samples were observed carefully in OPTIKA Microscope and some selected photomicrographs were taken. The SEM investigation and EDX analysis were obtained for the surface of aluminium alloy engine block and piston specimens after their immersions in the solution medium for 54 days. The SEM images were collected by using a JEOL scanning electron microscope with an energy dispersive X-ray analyzer (Model: Link AN - 10000) attached.

Table 1. Chemical composition for engine block and piston (wt %)

Alloy	Si	Mg	Cu	Ni	Fe	Zn	Mn	Sn	Ti	Zr	Al
Block	10.783	0.238	2.281	0.083	0.795	0.760	0.256	0.022	0.037	0.006	Bal
Piston	9.764	0.492	2.446	0.278	0.400	0.104	0.495	0.007	0.030	0.001	Bal

3. RESULTS AND DISCUSSION

3.1. Gravimetric Analysis

Figure 1 depicts the change of weight loss ΔW, mg cm^{-2}, calculated using Eq. (1) as a function of immersion time for aluminium alloy engine block and piston immersed in 3.5% NaCl solution. It is clearly seen from Figure 1 that the value of ΔW for the alloy in Cl^- solutions increased with increasing immersion time. This is due to the continuous dissolution under the aggressive action

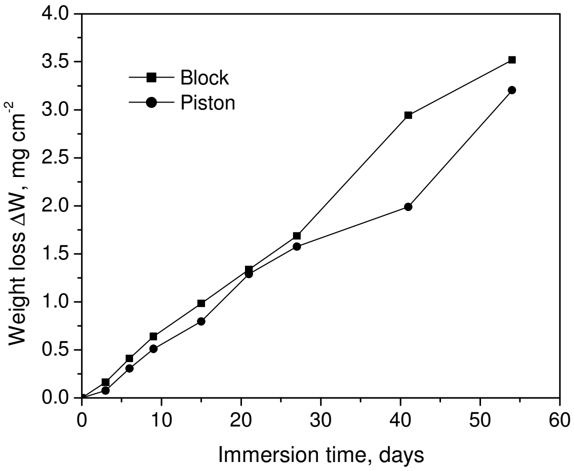

Figure 1. The variation of the weight loss (mg/cm^2) as a function of immersion time (days) for aluminium alloy engine block and piston immersed in 3.5% NaCl solution.

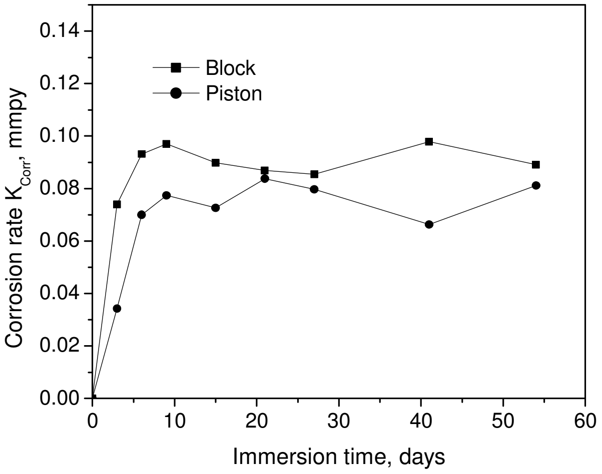

Figure 2. The change of corrosion rate (mmpy) as a function of immersion time (days) for aluminium alloy engine block and piston immersed in 3.5% NaCl solution

of the chloride ions to the alloy surface. Although Al forms Al_2O_3 and $Al(OH)_2$ on its surface, its dissolution rapidly increases with increasing exposure time. This is due to the fact that these forms are not compact and not protective and allow the aggressive ions from NaCl solutions to attack the Al surface. The values of K_{Corr}, which were calculated from weight-loss tests using Eq. (2) for Al alloy in 3.5% NaCl solutions, are plotted against time as shown in Figure 2. It can be seen that, the K_{Corr} values increased quite abruptly initially until immersion time of 10 days. Afterwards, the K_{Corr} value decreased with time and attained roughly a constant value. This is due to the fact that it corrodes (reacts with oxygen molecules) very quickly. Aluminum forms a very thin film of aluminum oxide and hydroxide which is about 2 nm (nanometer or 10^{-9}) thick. And it has a very strong bond to its surface and, if damaged or scratched, reforms immediately in most environments. The cathode reaction of dissolved oxygen and formation of OH^- ions occurs on Al_3Fe particles. These ions react chemically with a protective Al_2O_3 film. The Ni-containing amorphous alloy showed a pitting potential greater than the Ni-free amorphous alloy. Comparing the amorphous alloys, the addition of Ni enhances the pitting potential to a greater extent even though both alloys are amorphous. The effect is pronounced even following devitrification. Although a significant decreases in pitting potential was observed by devitrification of both alloys. The aluminium piston alloy showed a mean pitting potential greater than aluminium engine block [7].

3.2. Optical micrographic observation

Figure 3a and 3b show the optical micrograph of polished aluminium engine block and piston respectively before immersion into the corrosion medium. The samples has a microstructure characterized by an Al-rich dendritic matrix, α-Al phase and a eutectic mixture in the interdendritic region formed by silicon particles, which are coarse and distributed in plate-like morrphology, set in an Al-rich phase [8]. In this type of image the precipitates of Al(Mn, Fe, Cu) are those that appear in the dark tone while those of Al(Si, Mg) appear in a lighter tone. In Figure 4a and 4b is seen that after removing the samples from the corrosion medium, severe corrosion was observed. These findings primarily suggested that 3.5% NaCl can be an aggressive medium to induce corrosion in the aluminium alloys. Pitting corrosion of aluminium generally occurs at pH values close to neutral.

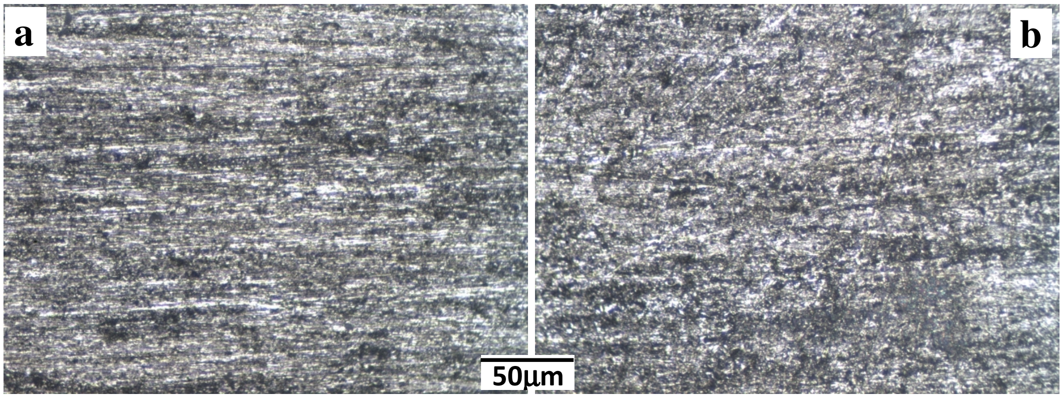

Figure 3. Microstructure of polished aluminium alloy a) engine block and b) piston before corrosion

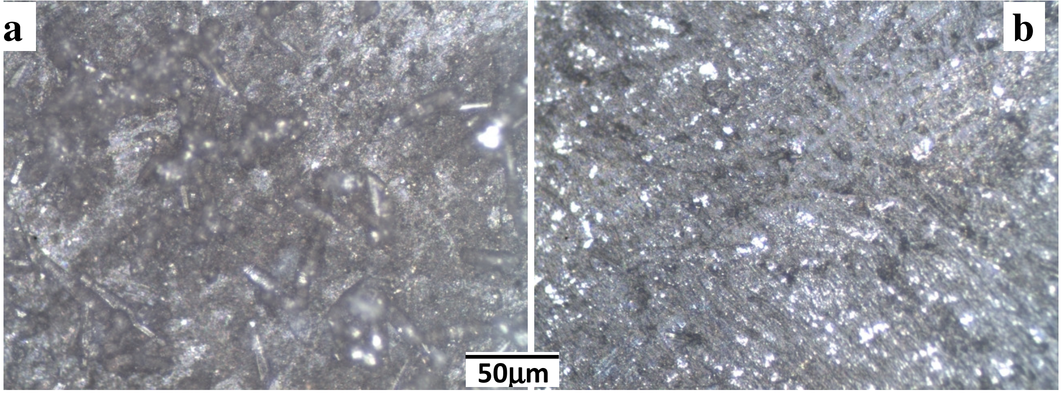

Figure 4. Microstructure of aluminium alloy a) engine block and b) piston after corrosion in 3.5% NaCl solution for 54 days

The pits are usually rather obvious as they tend to contain large amounts of hydrated white alumina gel of the type shown in the photographs. In general the pits tend to start within the first few weeks of exposure. Pitting develops as a two stage process with an initiation stage and a propagation stage. During the initiation stage the passive film is penetrated by aggressive ions such as chlorides. The number of initiation sites will exceed mainly thousand per square centimeter. These pits compete amongst themselves and only a very small number eventually propagating. In order to identify the various types of intermetallic compounds present in the alloy, the samples were studied using SEM and EDX spectroscopy.

3.3. SEM and EDX observation

The SEM micrographs of as-received Aluminium alloy engine block and piston are shown in Figure 5a and 5b respectively. The microstructures consisted of mainly primary Al dendrite, eutectic Si, $Al_{15}(Fe, Mn)_3Si_2$, Mg_2Si and a few number of Fe- rich intermetallic phases on α-Al matrix in the inter-dendritic region. It can be seen that the eutectic Si phase is flake-like and acicular morphologies. A number of voids and cavities can be seen in the microstructure of the engine block alloy. From table 1 it can be observed that the piston alloy contains significant amount of Ni. In case of piston alloy two type of Al_3Ni phase are the plate-like and needlelike morphologies [9]. The Ni particles are distributed homogenously in acicular forms inside the Al-

Si matrix without any cracks or voids between them. The Ni particles reacted with Al matrix forming Al_3Ni intermetalics. Addition of Ni particles decreases the Al-Si matrix grain size and eutectic dendritic arms but it increases the amount of α –phase.

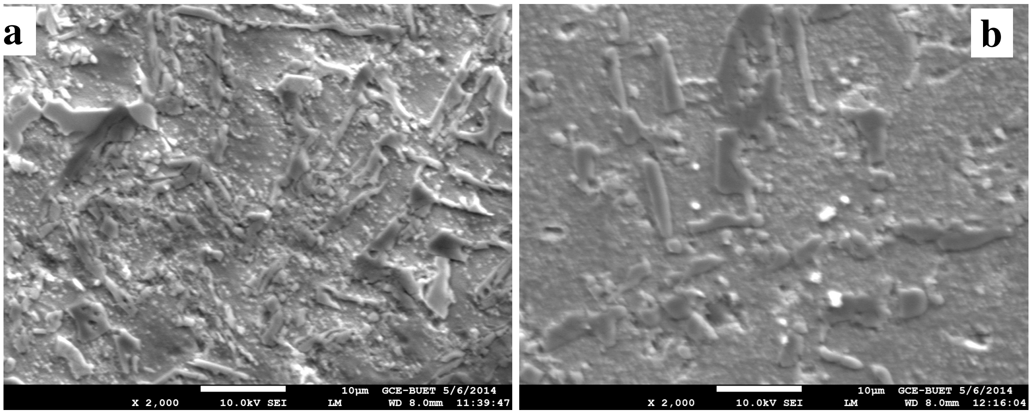

Figure 5. SEM micrographs of as-received aluminium alloy a) engine block and b) piston

The SEM image in the aluminium engine block of the surface after 54 days of prolonged exposure in 3.5% NaCl solution as shown in Figure 6, which indicates that the surface composes of two regions. One is covered with grass like corrosion products from which the mushrooms were formed and the other area is covered with a thin layer of corrosion products. The corresponding EDX profile analyses for the selected square areas of the SEM are shown in Figure 6. The weight percentage of elements found in white area were 81.60% O, .81% Na, 1.78% Mg, 11.03% Al, 2.33% Si, 0.23% Cl, 0.10% Mn, 0.79% Cu, 1.34% Zn and in dark area were 85.54% O, 1.60% Na, 1.52% Mg, 6.82% Al, 2.81% Si, 0.16% Cl, 0.58% Mn, 0.61% Cu, 0.37% Zn.

Similarly, the SEM image in the aluminium piston of the surface after 54 days of prolonged exposure in 3.5% NaCl solution as shown in Figure 7, which indicates that the surface composes corrosion products similar to that of engine block where the corrosion product is uniformly distributed. The corresponding EDX profile analyses for the selected square areas of the SEM are shown in Figure 7. The weight percentage of elements found in white area were 42.35% O, 0.45% Na, 0.77% Mg, 29.84% Al, 20.57% Si, 0.20% Cl, 1.62% Mn, 1.57% Fe, 0.47% Ni, 1.60% Cu, 0.56% Zn and in dark area were 51.55% O, 0.83% Na, 2.50% Mg, 27.84% Al, 11.45% Si, 0.03% Cl, 2.16% Mn, 1.12% Fe, 1.39% Cu, 1.13% Zn. After 54 days of prolonged exposure in 3.5% NaCl solution, it can be observed that the sample has been descaled as a consequence of fracturing of the surface film. The surface oxide film was observed to develop at an early period and increased in area and in thickness with the passage of time [6].

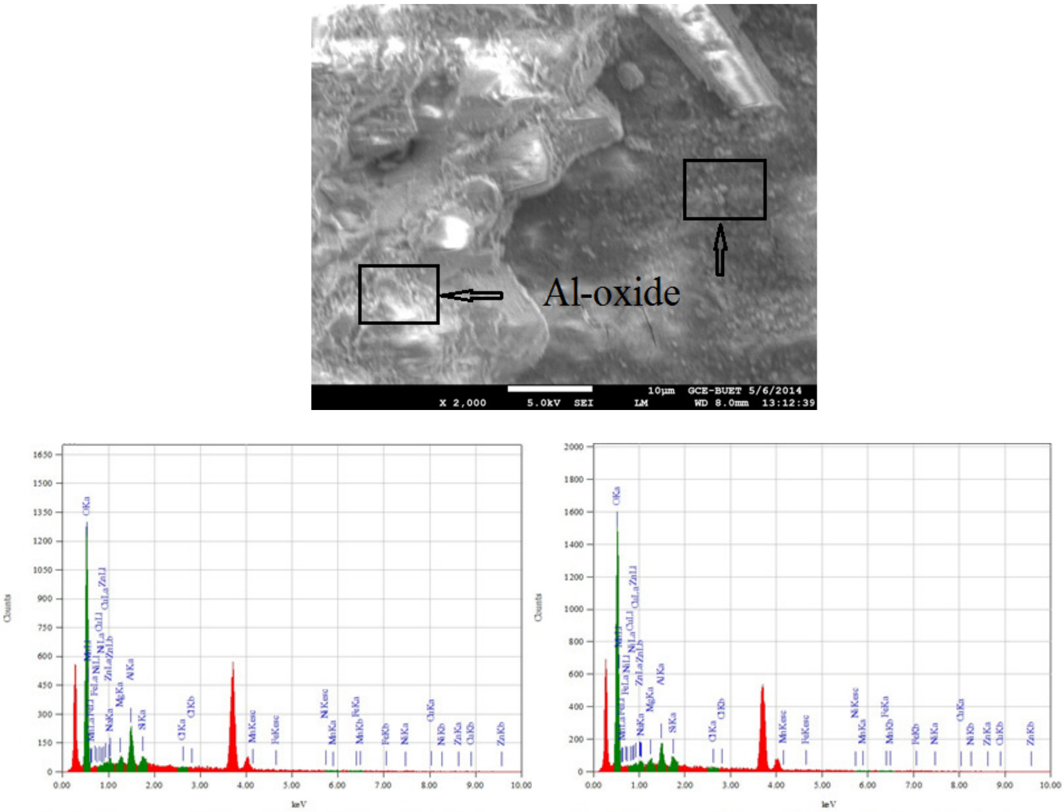

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Figure 6. SEM images and EDX spectra obtained for samples of aluminium alloy Engine block after exposure in a 3.5% NaCl solution for 54 days

The results obtained shows that, the aluminium alloy engine block and piston suffers a process of localized corrosion in a 3.5% NaCl solution. This process affects the zones of the matrix in contact with the intermetallics. The phenomena appear from the first day of exposure. It can be proposed that the presence of metallic inclusions more noble than the matrix reduces the resistance of the alloy to corrosion. These inclusions promote a process of anodic dissolution in the surrounding matrix by acting as cathode. The effect of the presence of Al_3Fe inclusions on the corrosion behavior of the alloys revealed that the presence of Al_3Fe precipitates increases the susceptibility of the alloy to pitting corrosion [10]. The behavior was attributed to the local increase in pH which is produced as a consequence of the reduction reaction of O_2 and is indicated as a possible cause of the formation of pits around the intermetallic compounds. The corrosion product of both aluminium engine block and piston showed similar result where engine block showed higher oxide formation and piston alloy showed less amount of oxide with uniform distribution. The better distribution of piston alloy is due to the presence of Ni. The Ni particles are distributed homogenously in acicular forms inside the Al-Si matrix.

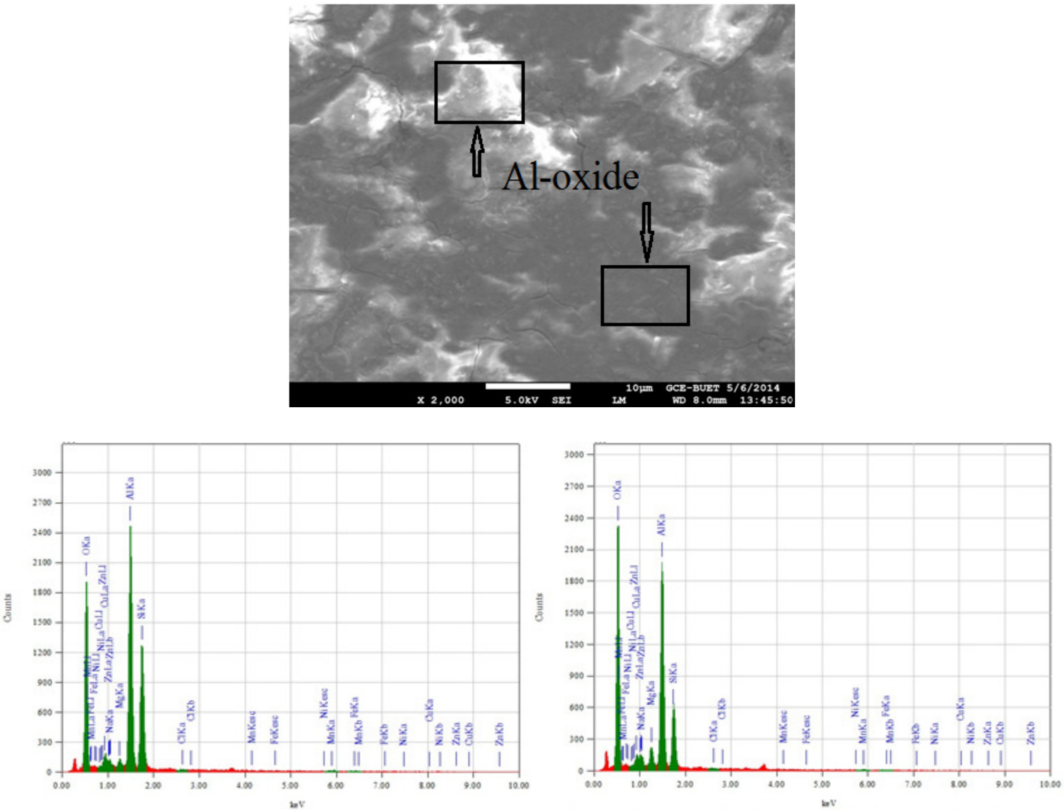

Figure 7. SEM images and EDX spectra obtained for samples of aluminium alloy piston after exposure in a 3.5% NaCl solution for 54 days

4. CONCLUSIONS

Corrosion behaviour of the aluminium alloy engine block and piston suffered localized corrosion process in a 3.5% NaCl solution. The corrosion process was analysed by gravimetric analysis shows that the weight loss of the alloys increases and the corrosion rate decreases with time. The piston alloy showed better corrosion behaviour due to presence of Ni and lower percentages of Fe than that of engine block. The alloy undergoes a process of corrosion localized to the area surrounding the precipitates of the Al (Si, Mg) and Al-Mg. The corrosion may be related to the cathodic activity of these precipitates. The local increase in pH that is produced as a consequence of the reduction reaction would give rise to the local dissolution of the layer of the oxide and to the subsequent dissolution of matrix in contact with the precipitates. Under the condition of exposure, no evidence was found of the formation of crystallographic pitting for exposure times up to 54 days.

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