

Corrosion Behaviour of Hypereutectic Al-Si Automotive Alloy in Different pH Environment

M. Al Nur, M. S. Kaiser

Abstract—Corrosion behaviour of hypereutectic Al-19Si automotive alloy in different pH=1, 3, 5, 7, 9, 11, and 13 environments was carried out using conventional gravimetric measurements and was complemented by resistivity, optical micrograph, scanning electron microscopy (SEM) and X-ray analyzer (EDX) investigations. Gravimetric analysis confirmed that the highest corrosion rate is shown at pH 13 followed by pH 1. Minimum corrosion occurs in the pH range of 3.0 to 11 due to establishment of passive layer on the surface. The highest corrosion rate at pH 13 is due to the presence of sodium hydroxide in the solution which dissolves the surface oxide film at a steady rate. At pH 1, it can be attributed that the presence of aggressive chloride ions serves to pick up the damage of the passive films at localized regions. With varying exposure periods by both, the environment complies with the normal corrosion rate profile that is an initial steep rise followed by a nearly constant value of corrosion rate. Resistivity increases in case of pH 1 solution for the higher pit formation and decreases at pH 13 due to formation of thin film. The SEM image of corroded samples immersed in pH 1 solution clearly shows pores on the surface and in pH 13 solution, and the corrosion layer seems more compact and homogenous and not porous.

Keywords—Al-Si alloy, corrosion, pH, resistivity, SEM.

I. INTRODUCTION

IN recent years, the understanding of different behavior of Eutectic Al-Si based casting alloys has drawn a great attention to many researchers [1]-[3]. Because of its high strength to weight ratio, excellent castability as well as improved mechanical properties, Al-Si based casting alloys have become candidate materials for many applications in the automobile industries [4]-[6]. Corrosion is a usual course of action, which changes refined metal to their more stable oxide [7]. These oxides are formed by the gradual destruction of the surface of the material by chemical process, viz, atomic molecular or ionic transport. These processes are usually complex and may have a few advantageous steps. The slowest step however is the most important one that controls the rate of overall corrosion [8]. The corrosion rate mainly depends on both the metal type and corrosive media. There are also many factors affecting on the corrosion rate, like pH, temperature and time of immersion. The choices of material parts or the time gaps between their uses determine the corrosion rate [9]. Also, the effect of pH, i.e. the concentration of hydrogen ions

makes the process rather a complex one [10]. Generally, standard type of coolants as recommended by the engine manufacturers is not used in most of the country. The users of the engines use simple tap water as coolant. Most of the time, they do not have a pH value of 7.

The aim of the present study was to study the effect of pH environment on the corrosion behavior of hypereutectic Al-19Si automotive alloy. The research has been directed towards studying the characteristics, formation of oxides, or chlorides as well as the nature and pattern of corrosion on alloy.

II. EXPERIMENTAL DETAILS

Commercially used aluminum engine block was melted at 750 ± 15 °C in a clay-graphite crucible in an electrical resistance furnace under the suitable flux cover (degasser, borax, etc.) and then cast in a cast iron metal mould preheated to 200 °C at pouring temperature of 700 °C. Mould sizes were 16 x 150 x 300 in millimeter. Chemical composition of the alloy was analysed by wet chemical and spectrochemical methods simultaneously and the composition of the studied alloy is listed in Table I. The cast alloy was homogenized at 400 °C for 18 hours in a Muffle furnace and naturally air cooled to relieve internal stresses. The homogenized samples were solution treated at 530 °C for 2 hours and immediately salt ice water quenched to get a super saturated single phase region. The samples of $55 \times 15 \times 3$ mm³ size obtained and were artificially aged at 175 °C for 240 minutes to conduct the tests for studying the corrosion behaviour. The samples were mechanically ground with 220 and 1200 grades of SiC emery paper, then degreased with ethanol of 99% purity and dried. Afterwards, they were weighted which was the initial weight before immersion (W_{int}). A stagnant solution of different pH was used as the aggressive medium. Solutions of pH 1, pH 3 and pH 5 were prepared by adding 10N HCl of 20 mL, 0.2 mL and 0.002 mL respectively into 2000 mL of distilled water solution and for pH 9, pH 11, and pH 13 were prepared by adding 1N NaOH of 0.02 mL, 2 mL and 200 mL respectively into 2000mL of distilled water solution. Distilled water was used as the pH 7 solution. The solution was used at room temperature. Weight loss of the samples was determined, at various time intervals up to 27 days. After the designated exposure in the solution medium, the samples were clean with distilled water and naturally dried using tissue papers. They were weighted again to get the final weight (W_{fin}). Weight loss and corrosion rate were calculated according to the following equations [11]. Three samples were used for every test by taking an average of these values.

Weight loss,

M. Al Nur is with the Department of Mechanical Engineering, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh (phone: 0088-02- 9665636; fax: 0088-02-8613046; e-mail: maglub@me.buet.ac.bd).

M. S. Kaiser is working as a Deputy Director in the Directorate of Advisory, Extension and Research Services, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh (phone: 0088-02-9663129; fax: 0088-02-9665622; e-mail: mskaiser@iat.buet.ac.bd).

$$\Delta W = \frac{(W_{\text{int}} - W_{\text{fin}})}{A} \quad (1)$$

Corrosion Rate,

$$K_{\text{Corr}} = \frac{(K \times \Delta W)}{(A \times T \times D)} \quad (2)$$

where, W_{int} = initial weight before immersion, W_{fin} = final weight after exposure, K = unit conversion constant, ($K = 8.76 \times 10^4$ for the mmpy unit), T = time of exposure (h), A = area in (cm^2), ΔW = Weight loss (g), and D = density of metal (g/cm^3).

To measure the electrical conductivity of the alloy at different conditions, an Electric Conductivity Meter, type 979 was used. Those conductivity data were converted into resistivity for plotting the graph. Optical microscopy of the washed and dried samples after different exposure time was performed using a metallurgical microscope, and some preferred microstructures were taken. To investigate the effects of corrosion on the surface of the sample after their immersions in the pH 1 and pH 13 solution media for 27 days, JEOL SEM coupled energy dispersive X-ray (EDX) and X-ray diffraction analysis (XRD) were used.

TABLE I
CHEMICAL COMPOSITION OF THE EXPERIMENTAL ALLOY (WT.%)

Si	Mg	Cu	Ni	Fe	Zn	Mn	Cr	Al
19.209	0.245	2.826	0.089	0.795	1.117	0.214	0.040	Bal

III. RESULTS AND DISCUSSION

A. Gravimetric Analysis

The weight loss ΔW , mg.cm^{-2} , calculated using (1) for the hypereutectic Al-19Si automotive alloy as a function of pH after immersion for 3 days, is illustrated in Fig. 1. It shows that the weight loss of the alloy is lower in the pH range from 3 to 11. In the range of pH 1 and pH 13, the weight loss is governed largely. The dissolution of Al at pH 1 occurs due to the surface attack by the aggressive chloride ions. The aggressivity of NaOH on aluminum alloy is clearer by comparison of weight loss in HCl. Aluminum is a reactive metal but has a very good corrosion resistance since it forms a thin surface layer of aluminum oxide in air which prevents it from further corrosion. This film is quite stable in neutral and mildly acidic solutions but dissolves more readily in the alkaline pH range. Usually, corrosion behavior of aluminum is directly related to the stability of the oxide film. Typically, the corrosion of aluminum increases exponentially for pH values lower than 3 or higher than about 9 [12].

A plot of the relative corrosion rates K_{Corr} , which were calculated from weight-loss tests using (2) for the experimental alloy at various pH values for 27 days, is presented in Fig. 2. The highest corrosion rate is shown at pH 13 followed by pH 1, while oxides formed in solutions having pH values from 3 to 11 tend to remain on the surface because of the fact that the oxides are not readily soluble in the solution, which causes the minimum corrosion rate. In the case

of pH 13 where the highest rate of corrosion occurs, the sodium hydroxide film on the surface is highly soluble. Thus, the aluminum dissolves uniformly at a steady rate. The results show that, when the pH is decreasing (acidity increase), the corrosion rate is increasing. The low pH solutions make hydrogen ions available, which accelerate corrosion and move up the redox potential of the aqueous solution with a consequent increase in rate [13]. Also, chloride ions have effect on the corrosion behavior of the alloy in acidic solutions, and the increase in chlorine ions increases the corrosion rate [8]. It can be seen that, the K_{Corr} values increased quite abruptly initially until immersion time of 3 days. Afterwards, the K_{Corr} value reaches roughly a constant with immersion time. At higher days of exposure, the accumulation of corrosion products including aluminum oxide and hydroxide, which cover up the surface leading to decrease the weight loss and the uniform weight loss, causes the constant corrosion rate.

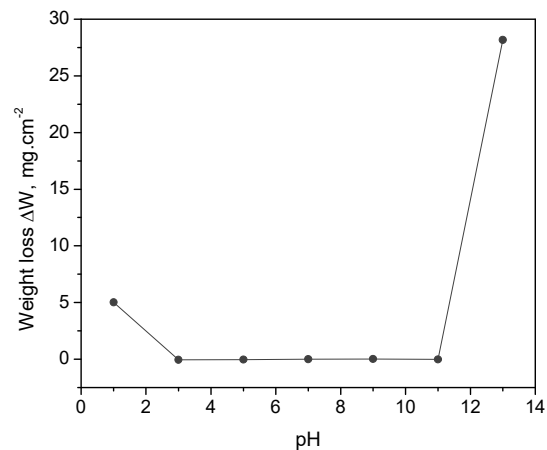


Fig. 1 The variation of the weight loss of Al-19Si automotive alloy as a function of pH environment after immersion time for 3 days

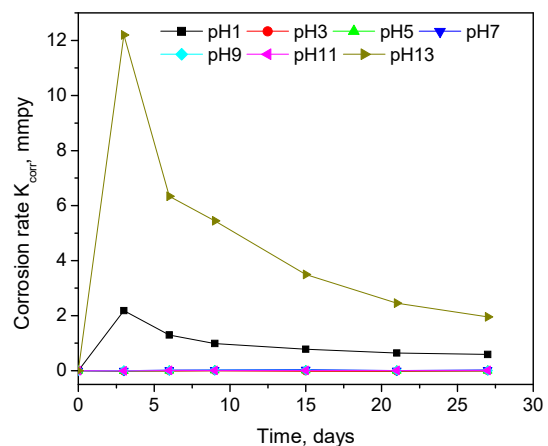


Fig. 2 The variation of the corrosion rate of Al-19Si automotive alloy as a function of immersion time at various pH environments

B. Electrical Resistivity Analysis

The resistivity values of the alloy immersed in different pH

solution for 3 days at room temperature show a general trend of decrease (Fig. 3). At low pH that is in acidic environment, formation of higher pit produces an uneven surface which increases the electrical resistivity of the surface of the experimental alloy. At higher pH environment, aluminum forms a very thin film of aluminum oxide and hydroxide and it has a bond to its surface which reduces the resistivity. The resistivity values of the alloy immersed in different pH solution for 27 days are shown in Fig. 4. At lower pH solution, the resistivity increases with the time but in case of higher pH environment decreases with time. This is due to the fact that it corrodes very quickly. At the pH 1 environment that is in acidic media, continuous degradation of the alloy makes the higher pitting surface which increases the resistivity. At pH 13, aluminum forms a very thin film of aluminum oxide and hydroxide and it has a bond to its surface which affects the resistivity. The thickness of thin film increases after long time exposure and produces the surface cracking. It increases the resistivity of the alloy. At the range from pH 3 to pH 11, the minimum change of resistivity is due to least amount corrosion effects of the alloy.

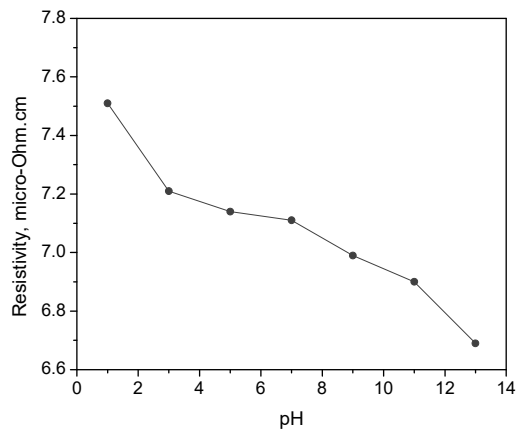


Fig. 3 The change of resistivity of Al-19Si automotive alloy as a function of pH environment after immersion time for 3 days

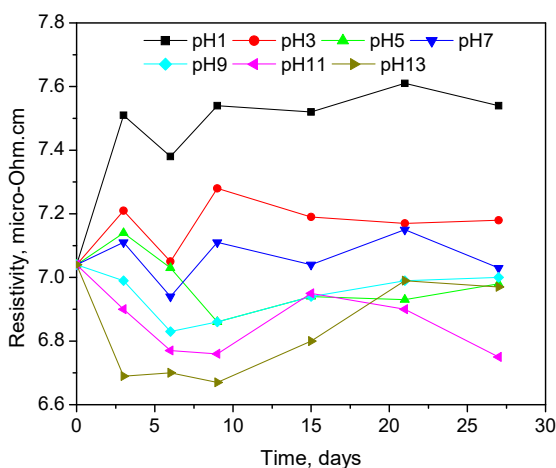


Fig. 4 The change of resistivity of Al-19Si automotive alloy as a function of immersion time at various pH environments

C. Optical Micrographic Observation

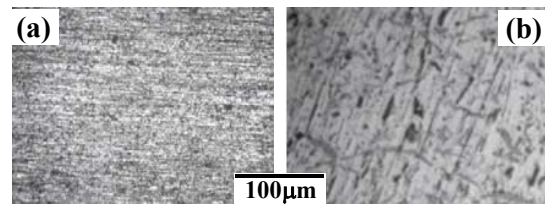


Fig. 5 Microstructure of Al-19Si automotive alloy before corrosion (a) polished (b) etched

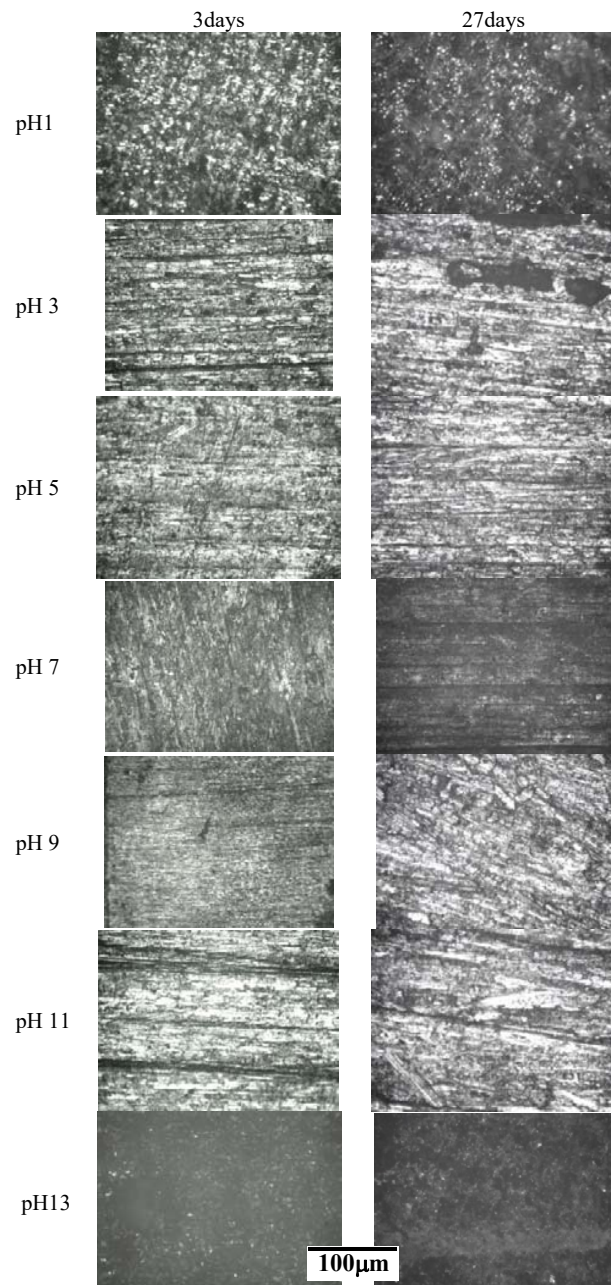


Fig. 6 Microstructure of Al-19Si automotive alloy after corrosion in different pH solution for 3 days and 27 days

Fig. 5 (a) shows the optical micrograph of polished Al-19Si automotive alloy before immersion into the corrosion medium. It consists of dark and lighter regions. The dark region represents the precipitates of Al(Mn, Fe, Cu), and the lighter region represents the Al(Si, Mg) phase. It has been observed in the microstructure that the primary Si and eutectic Si have been finely divided. In the case of hypereutectic as-processed Al-19Si automotive alloy (Fig. 5 (b)), the results of microstructural characterization revealed the presence of primary silicon (Si) and eutectic silicon phases. The primary Si exhibited the blocky morphology, while the eutectic silicon

exhibited needle shape morphology [14], [15].

In Fig. 6, it is seen that after removing the samples from the different pH solutions at room temperature for 3 days and 27 days respectively, severe corrosion was observed. These findings primarily suggested that low pH and high pH environment can be an aggressive medium to induce corrosion in the aluminum alloys. Corrosion on surface is increased specially at pH 1 and pH 13 solutions with increasing the immersion time. In the case of pH 1, the pit formation on the surface is elevated and the thick layer of corrosion forms on the surface of the pH 13 solution.

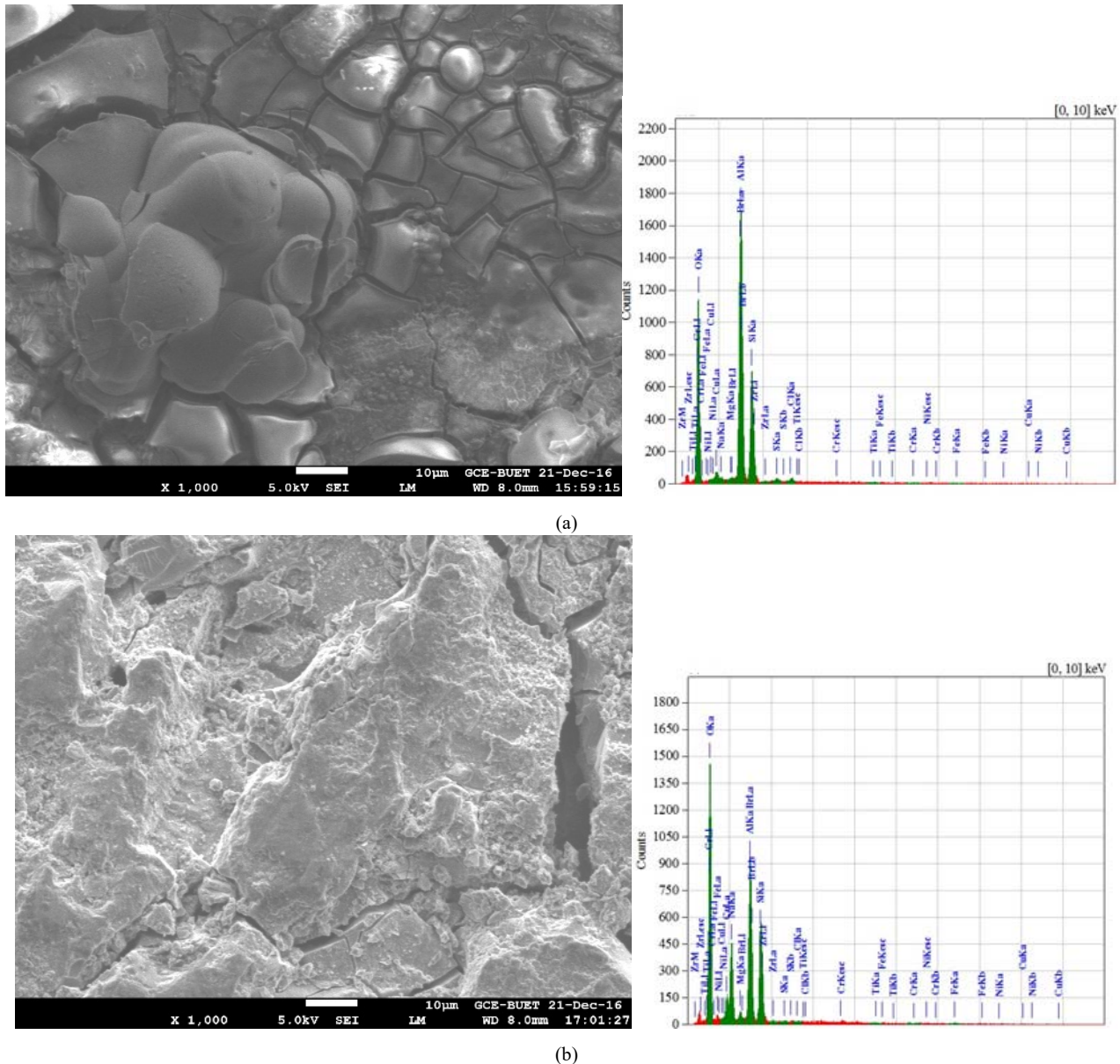


Fig. 7 SEM images and EDX spectra of Al-19Si automotive alloy after exposure for 27 days a) pH1 and b) pH13

The existence of such regions can be accredited to the termination of Al due to the surface attack by the aggressive

chloride ions [16]. The microstructure reveals the presence of sodium hydroxide medium, the increase in the amount of

oxygen can be attributed to the presence of aluminum hydroxide film formed due to the attack of hydroxide ion on the surface of metal [17]. Some corrosion is also observed after 27 days of prolonged exposure in pH 7 solution. Free carbon dioxide exists in the environment. Distilled water contains naturally free carbon dioxide in the form of a dissolved gas. The free carbon dioxide continuously provides water with hydrogen ions and creates acidic water conditions by give up carbonic acid. It is so-called weak acid, but an effective source of acidity resulting in severe corrosion of the experimental alloy.

D.SEM Observation

The SEM images of corroded sample after corrosion tests in pH 1 medium and pH 13 medium for 27 days are given in Figs. 7 (a) and (b), respectively. The SEM image of corroded sample immersed in pH 1 solution clearly shows pores due to the uniform degradation of alloys. High aggressive attack of chloride ions breaks down of the passive film formed on the surface of the alloys [18]. The weight percentages of elements found by corresponding EDX analysis of the SEM are 42.14% O, 0.13% Na, 0.04% Mg, 22.40% Al, 16.63% Si, 0.49% S, 0.58% Cl, 0.29% Ti, 0.22% Cr, 0.61% Fe, 0.09% Ni, 0.98% Cu, 15.02% Br and 0.39% Zr.

In case of corroded sample immersed in pH 13 solution, a black corrosion product layer was formed on the surface of the alloy during the corrosion process and it became thicker, compact, homogenous and not leaky particularly at higher NaOH concentrations [19]. The weight percentages of elements found by EDX analysis of the SEM for the alloy at pH 13 solution are 46.57% O, 8.51% Na, 0.80% Mg, 13.54% Al, 13.53% Si, 0.004% S, 0.04% Cl, 0.13% Ti, 2.60% Fe, 1.47% Ni, 3.19% Cu, 9.25% Br and 0.33% Zr.

It is noted from the EDX data that the percent of oxygen means the corrosion of the alloy. The formation of aluminum oxide layer on the surface protects further corrosion of the alloy, which decreases the corrosion of the alloy. In the case of pH 13, the oxide of sodium is visible on the surface of the alloy.

IV. CONCLUSION

The highest corrosion rate is shown at pH 13 followed by pH 1, whereas there is a high protection of surface owing high passivation in the pH range of 3.0 to 11. The highest corrosion rate at pH 13 is due to solubility of the surface oxide film even as the presence of sodium hydroxide in the. At pH 1, it can be attributed to the dissolution of Al due to the surface attack by the aggressive chloride ions. Resistivity decreases in case of alkaline media due to formation of thin film of oxide and increases in acidic media for the higher pit formation on the surface. Corroded samples immersed in pH 1 solution clearly show that pores due to the uniform degradation of the alloy and immersed in pH 13 solution a black corrosion product layer were formed on the surface of the alloy.

ACKNOWLEDGMENT

This work is supported by the Department of Mechanical

Engineering of Bangladesh University of Engineering and Technology. Thanks to Department of Glass and Ceramics Engineering for providing the laboratory facilities.

REFERENCES

- [1] M. S. Kaiser and Swagata Dutta, "Corrosive wear behavior of commercial aluminium engine block and piston in 3.5% NaCl solution," *International Journal of Chemical, Material and Environmental Research*, vol. 2, no. 2, pp. 1-9, 2015.
- [2] S. Zor, M. Zeren, H. Ozkazanc and E. Karakulak, "Effect of Cu content on the corrosion of Al-Si eutectic alloys in acidic solutions," *Anti-Corrosion Methods and Materials*, vol. 57, no. 4, pp. 185-191, 2010.
- [3] T. Giulio and F. Alberto, "The effects of microstructure heterogeneities and casting defects on the mechanical properties of high-pressure die-cast AlSi9Cu3(Fe) alloys," *Metallurgical and Materials Transactions A*, vol. 45, no. 12, pp.5486-5498, 2014.
- [4] M. Javidani and D. Larouche, "Application of cast Al-Si alloys in internal combustion engine components," *International Materials Reviews*, vol. 59, no. 3132, pp. 1-27, 2014.
- [5] E. Tillova and M. Chalupova, "Solution treatment effect on microstructure and mechanical properties of automotive cast alloy," *Materials Engineering*, vol. 19, pp. 39-46, 2012.
- [6] M. S. Kaiser and S. Dutta, "Comparison of corrosion behaviour of commercial aluminium engine block and piston in 3.5% NaCl solution" *International Journal of Advances in Materials Science and Engineering*, vol. 1, no. 1, pp. 9-17, 2014.
- [7] J. J. Manappallil, "Basic Dental Materials," 3rd Edition, Published by Jaypee Brothers Medical Publishers (P) Ltd, 2010.
- [8] Z. R. Muslim, H. I. Jaafer and M. Q. Fahem, "The effect of pH level on corrosion rate of aluminium and copper," *International Journal of Basic and Applied Science*, vol. 2, no. 4, pp. 89-92, 2014.
- [9] P. B. Madakson, I. A. Malik, S. K. Laminu and I. G. Bashir, "Effect of anodization on the corrosion behavior of aluminium alloy in HCl acid and NaOH," *International Journal of Materials Engineering*, vol. 2, no. 4, pp. 38-42, 2012.
- [10] Z. R. Muslim and A. A. Abbas, "The effect of pH and temperature on corrosion rate stainless steel 316L used as biomaterial," *International Journal of Basic and Applied Science*, vol. 4, no. 2, pp. 17-20, 2015.
- [11] H. H. Strehblow, "Corrosion mechanism in theory and practice," *Marcel Dekker*, New York, 1995.
- [12] S. Adhikari, "Alkaline dissolution of aluminium: surface chemistry and subsurface interfacial phenomena" *Ph.D thesis*, Iowa State University, Ames, Iowa, USA, 2008.
- [13] L. L. Shreir, "Corrosion: Metal/Environment Reactions," 2nd Edition, Published by Elsevier Science, 2013.
- [14] M. S. Kaiser, "Effects of solution treatment on wear behaviour of Al-12Si-1Mg piston alloy containing trace Zr" *MAYFEB Journal of Materials Science*, vol. 1, pp. 27-38, 2016.
- [15] S. K. Chaudhury, V. Warke, S. Shankar and D. Apelian, "Localized recrystallization in cast Al-Si-Mg alloy during solution heat treatment dilatometric and calorimetric studies," *Metallurgical and Materials Transactions A*, vol. 42, no. 10, 3160-3169, 2011.
- [16] A. A. E. Maghraby, "Surface Investigations of Aluminum in 2M Hydrochloric Acid Solution," *The Open Corrosion Journal*, vol. 3, pp. 54-57, 2010.
- [17] P. Deepa and R. Padmalatha, "Corrosion behaviour of 6063 aluminium alloy in acidic and in alkaline media," *Arabian Journal of Chemistry*, vol. 5, no. 6, pp. 2690-2705, 2013.
- [18] I. Boukerche, S. Djerad, L. Benmansour, L. Tifouti and K. Saleh, "Degradability of aluminum in acidic and alkaline solutions," *Corrosion Science*, vol. 78, pp. 343-352, 2014.
- [19] T. Notoya and T. Ishikawa, "Corrosion of aluminium-copper alloy and inhibition action of benzotriazole, tolyltriazole and hydroquinone in sodium hydroxide solution," *Bulletin of the Faculty of Engineering*, Hokkaido University, vol. 105, pp. 1-7, 1981.