Sains Malaysiana 43(6)(2014): 935–940

Surface Morphology Study on Aluminum Alloy after Treated with Silicate-Based Corrosion Inhibitor from Paddy Residue

(Kajian Morfologi Aloi Aluminium Selepas Dirawat dengan Perencat Kakisan Berasaskan Sisa Padi)

N. MOHAMAD, A. JALAR & N.K. OTHMAN*

ABSTRACT

Aluminum alloys have extensive applications in engineering structures like aircraft due to their high strength-to-weight ratio. However, these alloys are very reactive and prone to corrosion attack. Paddy waste is one of the beneficial natural sources that have a potential contribution on inhibiting the corrosion attack. At 600°C, silica was obtained from rice husk ash. The chemical reaction between silica powders with concentrated alkali generates formulation of potential silicate-based corrosion inhibitor. The potentiodynamic polarization, optical microscope (OM), infinite focus microscope (IFM) and scanning electron microscopy (SEM) were employed to investigate the corrosion behaviour of Al 6061 through electrochemical and surface study. The electrochemical measurement showed that the existence of silicate-based corrosion inhibitor in 0.5 M hydrochloric acid medium significantly mitigates the corrosion rates. SEM, IFM and OM showed that the morphology of untreated Al 6061 contributes more damage on the sample surface than that of Al 6061 treated with silicate-base corrosion inhibitor. The aim of this study was to attain better understanding of surface study on corrosion behaviour of aluminum alloy in acidic medium after treated and untreated with silicate-based corrosion inhibitor from paddy residue.

Keywords: Aluminum alloy; corrosion inhibitor; silicate

ABSTRAK

Aloi aluminium mempunyai aplikasi yang luas dalam bidang kejuruteraan struktur seperti pesawat kerana mempunyai nisbah kekuatan-kepada-berat yang tinggi. Walau bagaimanapun, aloi ini adalah sangat reaktif dan cenderung kepada serangan kakisan. Sisa padi adalah salah satu sumber semula jadi yang bermanfaat dan mampu memberi sumbangan yang berpotensi menghalang serangan kakisan. Pada 600°C, silika diperoleh daripada abu sekam padi. Tindak balas kimia antara serbuk silika dengan alkali pekat menjana formulasi berpotensi bertindak sebagai perencat kakisan berasaskan silikat. Pengutuban potentiodinamik, optik mikroskop (OM), infiniti fokus mikroskop (IFM) dan imbasan elektron mikroskop (SEM) telah digunakan untuk mengkaji perilaku kakisan Al 6061 melalui kajian elektrokimia dan permukaan. Pengukuran elektrokimia menunjukkan bahawa kewujudan perencat kakisan berasaskan silikat dalam medium 0.5 M asid hidroklorik menyebabkan kadar kakisan berkurangan secara ketara. SEM, IFM dan OM menunjukkan bahawa morfologi Al 6061 yang tidak dirawat menyumbang lebih banyak kerosakan pada permukaan sampel berbanding Al 6061 yang dirawat dengan perencat kakisan berasaskan silikat. Tujuan kajian ini adalah untuk mencapai pemahaman yang lebih jelas melalui kajian permukaan berdasarkan kelakuan kakisan aloi aluminium dalam medium berasid setelah dirawat dan tidak dirawat dengan perencat kakisan berasaskan silikat daripada sisa padi.

Kata kunci: Aloi aluminium; kakisan perencat; silikat

INTRODUCTION

Aluminum and its alloy normally signified as materials that appropriately applied in aerospace, household industries, automotive, transportation and marine technology (Szklarska-Smialowska 1999). This is attributable to their good specific strength, excellent formability and corrosion resistance. There are several types of aluminum alloys series which are 1 xxx – 8 xxx series. The 6 xxx series of aluminum alloys attained relatively good corrosion resistance. This aluminum alloys comprised of silicon and magnesium alloying elements, which are approximately in the proportions.

Corrosion is a phenomenon occurred on engineering materials. Several conditions such as in hydrocarbon production, processing industries and the chemical industry caused the occurrence of corrosion. Frequently, corrosion hits the headlines because of some particularly dramatic failure and corresponds towards the loss of lives and properties. Thus, corrosion brings a cost and impacts profits significantly.

Acid solution is widely used in industrial acid pickling, acid descaling, acid cleaning and oil well acidizing. Therefore, the use of corrosion inhibitors necessitated in restraining their corrosion attack on metallic materials

(Rani & Bai 2012). Hydrochloric acid, hydrofluoric acid and hydrobromic acid solutions except at concentration below ~0.1% are definitely corrosive to aluminum alloys (Revie 2006). Most aluminum alloys are readily attacked in dilute nitric, sulphuric or hydrochloric acid solutions. In this study, Al 6061 was immersed in a corrosive medium of 0.5 M hydrochloric acid to investigate the corrosion efficiency of silicate inhibitor from paddy residue.

There are several methods to protect the aluminum and its alloys from corrosion such as control of the environment (operating variable i.e. pH, temperature and dissolved oxygen), coatings (inorganic, metallic, conversion and organic coatings) and corrosion inhibitors (organic and inorganic additives). Among these methods, corrosion inhibitor is a preferable method by recent research studies. It is because of their low cost and easy handling, compared with other corrosion prevention methods (Nik et al. 2010). The silicate is one of the common effective molecular used to protect aluminum similar to chromatic, polyphosphates, soluble oils and other inhibitors (Amutha et al. 2010). Inhibitors protect the Al 6061 as it forms a barrier of one or several molecular layers against acid attack (Nik et al. 2010).

The surface morphology study of Al 6061 before and after exposed in 0.5 M HCl with treated or untreated silicate inhibitor examined by the optical microscope (OM), infinite focus microscope (IFM) and scanning electron microscopy (SEM) analysis. This study is carried out to prove the effect of silicate based corrosion inhibitor from rice husk manages to retard the corrosion attack towards Al 6061.

METHODS

The silicate based corrosion inhibitor is formulated from silica, which extracted from rice husk. The Amutha method (Amutha et al. 2010) was applied to yield the silica extract. The rice husk was burnt in a muffle furnace for 2 h at 600°C and generated rice husk ash. This rice husk ash was mixed with 2.5 M NaOH in covered beaker and boiled for 3-4 h in constantly stirred conditions. The mixed solution was filtered by warm distilled water and produced a clear solution in the beaker. Next, this clear solution was titrated with 2.5 M H_2SO_4 at 90-100°C until it reached pH2. A gel-like solution finally produced in beaker. This gel-like solution was filtrated again with warm distilled water. After that, the filtrate residue on filter paper was dried in oven for 15 h at 70ºC and yielded the final product, which was white silica powder. This white silica powder was mixed with NaOH at 90-100°C while constantly stirred for 1 h in covered beaker. Finally, a clear solution of silicate corrosion inhibitor was produced.

The electrochemical method was held using potentiodynamic polarization and Tafel graph was plotted. Potentiodynamic polarization measurement was conducted using potentiostat/galvanostat (model K47 Gamry framework) at 1.0 mV s^{-1} scanning rate, acquired by a potential range of -0.25 mV – 0.25 mV (reaction time is ~15 min). The measurement was carried out in a conventional three-electrode electrolytic cell in 800 mL 0.5 M HCl with Al 6061 working electrodes, a carbon counter electrode and a saturated calomel electrode (SCE) as a reference. The exposed area of Al 6061 coupon is 1 cm^2. The Al 6061 was ground by a series of SiC paper (320, 400, 600, 800 and 1200) before rinsing it with distilled water before use. Surface morphology was analyzed by interfacial force microscopy (IFM), optical microscope (OM) and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

The anodic and cathodic reactions occurred at the working electrode (Al 6061) in 0.5 M HCl immersion solution with various concentrations of silicate corrosion inhibitors in the range of 5-25 ppm were studied through polarization measurement. The blank immersion solution plotted graph shifted towards positive value compared with the treated solution with silicate corrosion inhibitor. Nevertheless, the plotted graph shows that the values of corrosion potential were shifted to the negative rate potential value as the silicate corrosion inhibitor concentration increased. Based on Figure 1, the current density of immersion solution without silicate corrosion inhibitor is higher than solution with the addition of silicate corrosion inhibitor. Hence, it verified that the addition of silicate corrosion inhibitor reduced anodic and cathodic current density. However, the cathodic current density reduced extensively compared with anodic current density. According to this result, it suggested that silicate corrosion inhibitor inhibited Al 6061 cathodic reaction slightly more than anodic reaction, whilst, it is a mixed-type of corrosion inhibitor (Ghareba & Omanovic 2011). This result also interpreted that silicate corrosion inhibitor was able to retard the hydrogen evolution reaction and inhibiting the anodic dissolution of Al 6061 (Amin et al. 2009).

The extrapolation of Tafel graph also determines the electrochemical parameter, as shown in Table 1. Based on the electrochemical parameters, E_{corr}, I_{corr}, b_c and b_a are able to be obtained. This result clearly showed that the increased of silicate corrosion inhibitor contributed towards the decreased of current density (I_{corr}) and corrosion potential (E_{corr}). Meanwhile, b_c and b_a values in Table 1 also referred to cathodic and anodic slopes. The changes of both slopes indicate that adsorption of silicate corrosion inhibitor modifies the hydrogen evolution at cathodic as well as the anodic dissolution of Al 6061 (Flores et al. 2011). Moreover, it was notified that there is no definite trend according to E_{corr} values as it demonstrated the small instability value in the range of -722.0 mV and -718.5 mV. This outcome determined that the existence of silicate corrosion inhibitor in immersion solution reduces and protects the aluminum oxidation and hydrogen evolution. The corrosion rate and inhibition efficiency can also be obtained from Table 1. The equation stated in (1) and (2) were applied in order to calculate the corrosion rate and inhibition efficiency by using Tafel plot obtained in Figure 1.

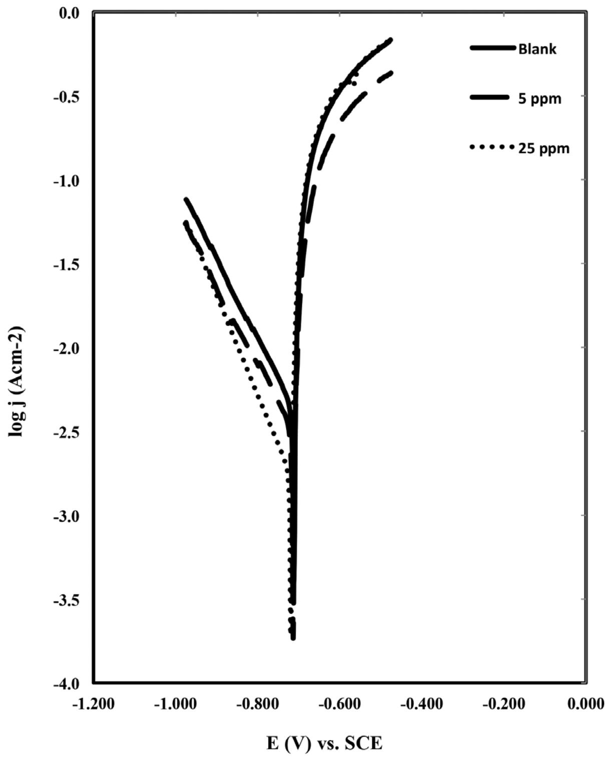

FIGURE 1. Tafel polarization curves of Al 6061: (a) in blank solution where only immersed in 0.5 M HCl, (b) immersed in 0.5 M HCl with 5 ppm silicate corrosion inhibitor and (c) immersed in 0.5 M HCl with 25 ppm silicate sodium silicate

$$\text{CR (mmpy)} = (I_{corr} \times K \times \text{EW})/(dA), \qquad (1)$$

where CR is corrosion rate, I_{corr} is the corrosion current in amps, K is constant (3272), EW is equivalent weight in grams/equivalent, d is density in grams/cm3 and A is sample area in cm^2.

$$\eta i = \left[1 - \frac{j_{corr}}{j_{corr^\circ}}\right] \times 100, \qquad (2)$$

where j_{corr} and j_{corr° are the corrosion current densities with and without the existence of corrosion inhibitor, respectively. Based on Table 1, it shows that the increasing of silicate corrosion inhibitor caused the Al 6061 corrosion rate to decrease. Hence, it leads to the increase in inhibition efficiency of silicate corrosion inhibitor. The results showed that 25 ppm of silicate corrosion inhibitor attained the highest inhibition efficiency which is 67%. This attribute proved the effect of silicate corrosion inhibitor concentration on Al 6061 corrosion attack. The increase of silicate corrosion inhibitor concentration assigned the adsorbed amount and increased the coverage on Al 6061 (Rosliza & Wan Nik 2010).

The optical microscope images of Al 6061 before and after immersing in 0.5 M HCl with and without the addition of silicate corrosion inhibitor are shown in Figure 2. Figure 2(a) shows the unexposed morphology image of Al 6061 under optical microscope (OM). It shows that the surface was not corroded before immersed in 0.5 M HCl and proved there are no corrosion attack occurred. Meanwhile, Figure 2(b) shows Al 6061 sample was immersed in 0.5 M HCl without the addition of silicate

TABLE 1. Electrochemical parameters obtained by the Tafel-extrapolation for Al 6061 immersed in 0.5 M HCl with and without silicate corrosion inhibitor

Concentration (ppm)	E_{corr} (mV)	I_{corr} (A/cm^2)	b_c (mV dec^{-1})	b_a (mV dec^{-1})	Rp (Ω cm^2)	Corr. Rate (mmpy)	IE (%)
Blank	-711.7	8.842	342.1	110.4	4.100	96.548	-
5	-712.9	7.341	415.9	117.6	5.425	80.149	17
10	-714.1	6.120	261.4	82.4	4.446	66.824	31
15	-716.7	5.002	279.4	101.6	6.470	54.620	44
20	-722.0	3.362	257.7	103.0	9.509	36.705	62
25	-718.5	2.910	218.2	91.5	9.618	31.777	67

corrosion inhibitor. This image observed that Al 6061 surface totally different from the unexposed sample in Figure 2(a). It was noticed that the surface become rough compared with the unexposed sample. This shows that the corrosion reaction has occurred in this sample. Thus, caused almost sample surface covered by the corrosion product. On the other hand, Figure 2(c) shows the Al6061 immersed in 0.5 M HCl with the addition of 25 ppm of silicate corrosion inhibitor. Both Figure 2(b) and 2(c) presents the optical microscope images of corroded Al 6061 surfaces. Both images observed different surface morphology of corrosion product. The corrosion product obtained in Figure 2(b) grown throughout the surface of Al 6061 greater that Figure 2(c). In comparison between Figure 2(b) and 2(c), the morphological analysis showed that there were two regions; base Al 6061 and corrosion product. Compared with Figure 2(c), the corrosion product region dominates the surface of Al 6061 in Figure 2(b). There is only tiny region of base Al 6061 while region of base Al 6061 in Figure 2(c) expands and dominates the Al 6061 surface compared with its corrosion product region. These comparisons are based on the changes of base Al 6061 region occurred on the sample surface. The broadness of Al 6061 region is referring to the Al 6061 surface being covered by silicate corrosion inhibitor. Thus, the occurrence of Al 6061 surface shows that silicate inhibitor managed to prevent sample from corrosion attacked by the 0.5 M HCl. It also clearly stated that the damage caused by this corrosion attack was accentuated in solutions without the addition of silicate corrosion inhibitor suggesting that anodic activity in the immersed solution became intense in acidic solution (Zaid et al. 2008).

Figure 3 shows the image from IFM results. From this result, it shows the 3-dimensional (3D) image of Al 6061 surface before and after immersing in 0.5 M HCl. Moreover, the dissimilarity of surface morphology caused by the different concentration of silicate corrosion inhibitor added in immersion solution able to be observed. Figure 3(a) shows that the flat surface of Al 6061 after grinding with series of SiC papers before immersed in acidic immersion solution. Compared to Figure 3(a), the IFM images from Figure 3(b) and 3(c) scanned the rough surface observed on Al 6061. Nevertheless, Figure 3(b) examines rigorous roughness compared with roughness grown on Al 6061 surfaces in Figure 3(c), which was immersed in an acid solution with the addition of silicate corrosion inhibitor. Therefore, it determined that the acidic solution without the addition of silicate corrosion inhibitor caused the severe roughness occurred on Al 6061 surfaces. The presence of roughness surface represented the occurrence of corrosion product on Al 6061 surfaces. It also verified the addition of silicate corrosion inhibitor decreased the corrosion product cultivated on Al 6061 surfaces.

Al 6061 surface morphology is affected by silicate corrosion inhibitor concentration (Figure 4). Figure 4(a) scanned image of Al 6061 surface before immersed in 0.5 M HCl. Based on this image, it shows that Al 6061 surface free from damage with some scratches imprint attributed to the mechanical polishing from SiC papers. Thus, it determined Al 6061 surface free from corrosion attack.

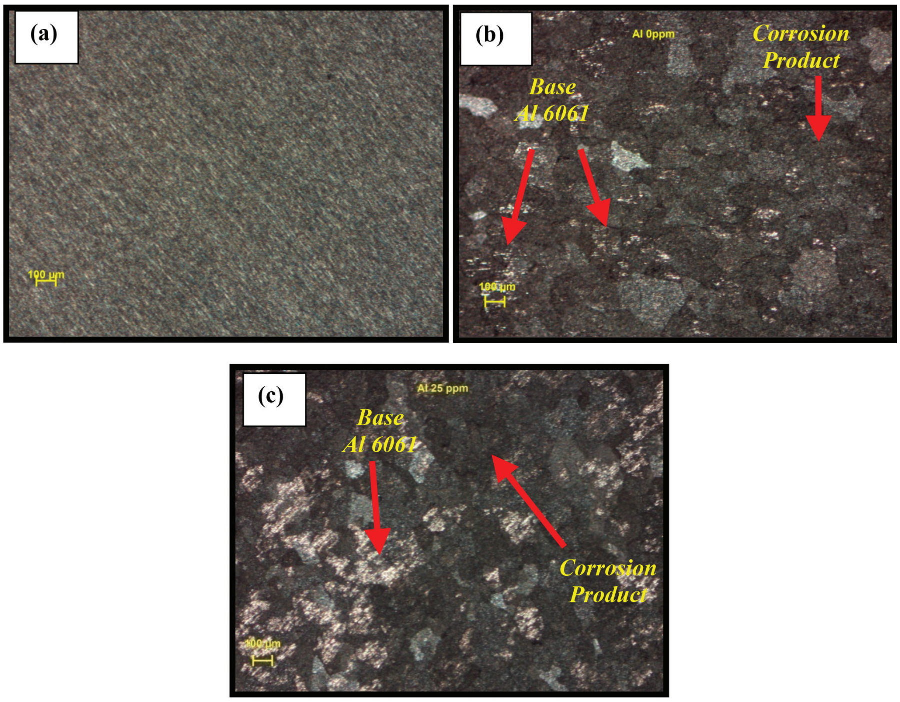

FIGURE 2. Surface morphology images from optical microscope: (a) unexposed Al 6061 before immersed in 0.5 M HCL, (b) immersed in 0.5 M HCl and (c) immersed in 0.5 M HCl with 25 ppm of silicate corrosion inhibitor

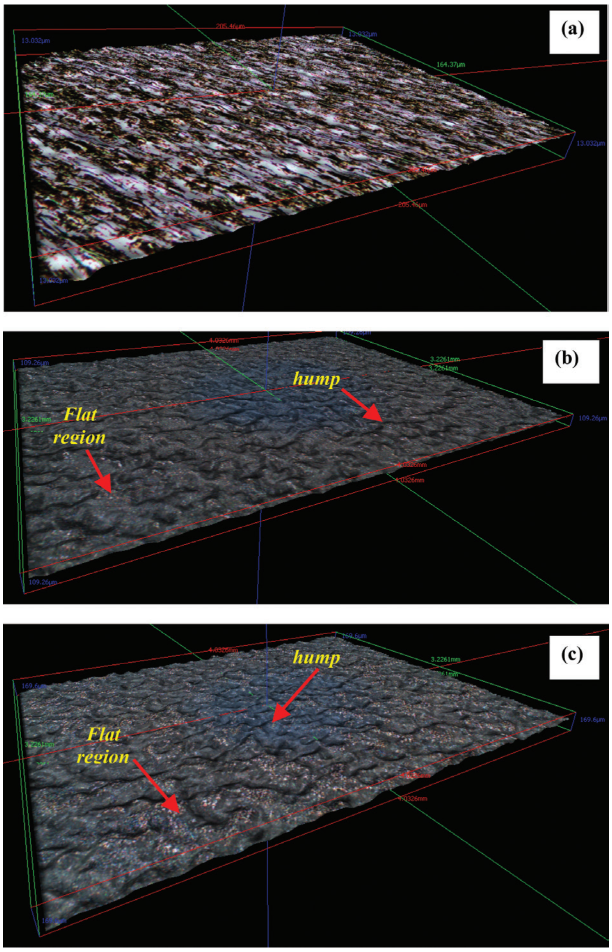

FIGURE 3. IFM images: (a) unexposed Al 6061 before immersed in 0.5 M HCL, (b) Al 6061 exposed in 0.5 M HCl and (c) Al 6061 exposed in 0.5 M HCl with 25 ppm silicate corrosion inhibitor

Figure 4(b) examines Al 6061 surface after immersed in 0.5 M HCl solution. It clearly shows that Al 6061 surfaces damaged severely after immersed in 0.5M HCl for 24 h. The explicit rough surface occurred on its surface represented the Al 6061 corroded significantly. Figure 4(c) shows that Al 6061 surfaces immersed in 0.5 M HCl with 25 ppm silicate based corrosion inhibitor. This SEM micrograph shows the damage of the Al 6061 decreased as the 25 ppm silicate corrosion inhibitor added to the immersion solution. Thus, it clarified that the coverage of silicate corrosion inhibitor protective film on Al 6061 surfaces decreased the corrosion attacked from 0.5 M HCl corrosive medium. Therefore, it notified the dissolution of Al towards HCl medium decreased as the increase of silicate corrosion inhibitor concentration (Phanasgaonkar & Raja 2009).

CONCLUSION

Build upon this research study, a better understanding of surface study on corrosion behaviour of aluminum alloy after treated with silicate-based corrosion inhibitor from paddy residue is accomplished. This silicate corrosion inhibitor proved its potential to retard the corrosion attack from the acidic medium by reducing the damage of Al 6061 surfaces.

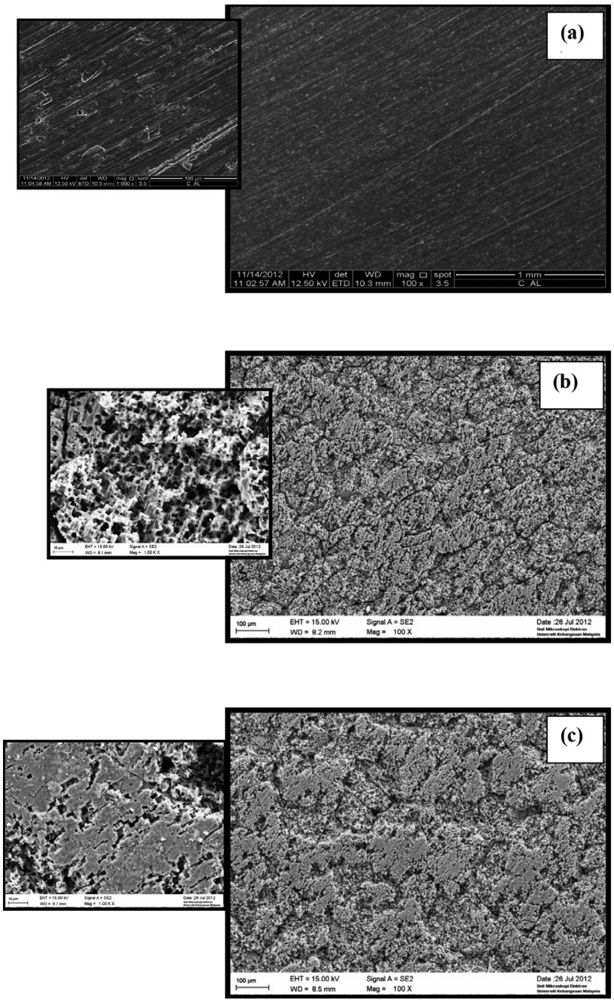

FIGURE 4. Surface morphology images from SEM: (a) unexposed sample before immerse in 0.5 M HCl (b) immersed in 0.5 M HCl and (c) immersed in 0.5 M HCl with 25 ppm of silicate corrosion inhibitor

ACKNOWLEDGEMENTS

The authors express their sincere acknowledgement to the Ministry of Science, Technology & Innovative (MOSTI), Malaysia for the financial support given through the Science Fund Grants Scheme (03-01-02-SF0734), ERGS/1/2012/STG05/UKM/02/2, DIP -2012-2014 and Ministry of Education (MOE), Malaysia with their support through MyBrain15 scholarship.

REFERENCES

Amin, M.A., El-Rehim, S.S.A., El-Sherbini, E.E.F., Hazzazi, O.A. & Abbas, M.N. 2009. Polycrylic acid as a corrosion inhibitor for aluminium in weakly alkaline solutions. Part I: Weight loss, polarization, impedance EFM and EDX studies. *Corrosion Science* 51: 658-667.

Amitha Rani, B.E. & Bharathi Bai, J.B. 2012. Green inhibitors for corrosion protection of metals and alloys: An overview. *International Journal of Corrosion* 2012: 380217.

Amutha, K., Ravibaskar, R. & Sivakumar, G. 2010. Extraction, synthesis and characterization of nanosilica from rice husk ash. *International Journal of Nanotechnology and Applications* 4(1): 61-66.

Flores, E.A., Olivares, O., Likhanova, N.V., Domínguez-Aguilar, M.A., Nava, N., Guzman-Lucero, D. & Corrales, M. 2011. Sodium phthalamates as corrosion inhibitors for carbon steel in aqueous hydrochloric acid solution. *Corrosion Science* 53: 3899-3913.

Ghareba, S. & Omanovic, S. 2011. 12-Aminododecanoic acid as a corrosion inhibitor for carbon steel. *Electrochimica Acta* 56: 3890-3898.

Nik, W.B.W., Sulaiman, O., Fadhli, A. & Rosliza, R. 2010. Corrosion behaviour of aluminum alloy in seawater. *Proceedings of MARTEC 2010. The International Conference on Marine Technology,* Dhaka, Bangladesh. 11-12 December. pp. 175-180.

Phanasgaonkar, A. & Raja, V.S. 2009. Influence of curing temperature, silica nanoparticles- and cerium on surface morphology and corrosion behaviour of hybrid silane coatings on mild steel. *Surface & Coatings Technology* 203(16): 2260-2271.

Revie, R.W. 2006. Ughlig's Corrosion Handbook. In *Aluminum and Aluminum Alloys*. 2nd ed., edited by Ghali, E. Canada: CANMET Materials Technology Laboratory, Ottawa, Ontario. pp. 677-716.

Rosliza, R. & Wan Nik, W.B. 2010. Improvement of corrosion resistance of AA6061 alloy by tapioca starch in seawater. *Current Applied Physics* 10: 221-229.

Szklarska-Smialowska, Z. 1999. Pitting corrosion of aluminum. *Corrosion Science* 41(9): 1743-1767.

Zaid, B., Saidi, D., Benzaid, A. & Hadji, S. 2008. Effect of pH and chloride concentration on pitting corrosion of AA6061 aluminium alloy. *Corrosion Science* 50: 1841-1847.

School of Applied Physics
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor D.E.
Malaysia

*Corresponding author; email: insan@ukm.edu.my

Received: 21 March 2013
Accepted: 1 March 2014