Influence of aluminium microstructure on corrosion and Corrosion inhibitor performance in acidic medium

S. A. Umoren [a, b], Y. Li [a*], F. H. Wang [a]

[a] *State Key Laboratory for corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, 62 Wencui Road, Shenyang 110016, P. R. China.*
[b]*Department of Chemistry, Faculty of Science, University of Uyo, P.M.B 1017, Uyo, Nigeria*

Received in 19 Oct 2010, Revised 22 Nov, Accepted 26 Nov 2010.

* For correspondence: Email: liying@imr.ac.cn (Y. Li), Phone: +862423925323, Fax: +862423893624

Abstract

The corrosion behaviour of aluminium with two different microstructures namely polycrystalline (pc-Al) and microcrystalline aluminium coating (mc-Al) fabricated from the polycrystalline Al target by magnetron sputtering in 0.1 M H_2SO_4 solution was studied. The corrosion inhibiting effect of polyacrylamide (PA) was also investigated. Results show that surface microcrystallization increases the corrosion susceptibility of aluminium leading to increase in the kinetics of the anodic dissolution. PA was found to reduce the corrosion rates of both Al samples. Inhibition efficiency of PA was concentration dependent and was more pronounced on the mc-Al specimen.

Keywords: Aluminium; Polyacrylamide; microcrostructure

1. Introduction

The high technological value and wide range of industrial applications of aluminium and its alloy is attributed to its excellent properties such as low density, good appearance, thermal and electrical conductivity, lightness and corrosion immunity due to the formation of a compact adherent passive film oxide on its surface. However, it is known that aluminium is susceptible to corrosion especially pitting corrosion in aggressive electrolytes and consequently a number of studies have been carried out on the corrosion behaviour of aluminium and its alloy in various environments [1].

Some practical steps have been taken towards finding ways of improving corrosion resistance of metals and it has been shown that various means such as reduction of the metal impurity content, application of several surface modification techniques as well as incorporation of suitable alloying elements has yielded significant results [2]. In recent times, grain size modification by nanocrystallization/microcrystallization has become a useful way of improving materials performance. Microcrystalline/nanocrystalline metals have been extensively studied because of the need for better understanding of microsturcture/nanostructure, vis-à-vis the structural and chemical stability as well as potential technological applications. However, there is no general consensus as to the precise relationship between grain size and corrosion resistance at a fundamental level, as the effect of microcrystallization/nanocrystallization on corrosion performance is neither uniform nor definite [3] but varies according to nature of the material and environment and could lead to either improved [4 – 7] or reduced [8 – 10] corrosion resistance.

Addition of corrosion inhibitor to corrosive medium to retard corrosion and reduce acid consumption has long been recognized a practical and effective means of preventing corrosion of metals in acidic media. Generally, it has been assumed that the first step in the mechanism of the inhibitors action in aggressive acid solution is the adsorption of the inhibitors onto the metal surface, which isolate the metal from the anions present in the corrosive medium and hinder further corrosion attack. The use of polymers as corrosion inhibitors has gained wide acceptance in recent times. This is attributed to the fact that they are cost effective, environmentally friendly and possess multiple adsorption sites for bonding with metal surface. Moreso, through their functional groups, they form complexes with metal ions and on the metal surface these complexes occupy a large area, thereby blanketing the surface and protecting the metal from corrosive agents present in the solution [11–13]. Polyacrylamide, polyacrylic acid, polyvinylpyrrolidone, polyethylene glycol, polyvinyl alcohol and gum arabic have been reported as effective corrosion inhibitors for aluminium in acidic and alkaline media [14–17].

Some studies have been focused on the corrosion inhibition of aluminium and its alloy in acidic environments but there is no information available on the corrosion inhibition of their microcrystalline/nanocrystalline counterparts. Although, scanty information on corrosion inhibition and synergistic effect of corrosion inhibiting additives on nanocrystalline iron and its alloy can be found in the literature [2,3,18-21]. It will be of great interest to know the effect of the microcrystalline microstructure on the corrosion inhibitor performance which hitherto has not received attention. The objective of this present study therefore is to assess the effect of a microcrystalline surface fabricated on pure cast aluminium by magnetron sputtering technique, on the corrosion of pure aluminium in 0.1 M H_2SO_4 solution. The inhibiting effect of polyacrylamide on the corrosion behaviour was also studied.

2. Experimental

The material used in this study was pure cast aluminium (99.99%). The aluminium microcrystalline coating (mc-Al) was prepared with SBH-5115D dc magnetron sputtering system using pure cast aluminium (pc-Al) material as target on quartz glass. The details of the magnetron sputtering technique and subsequent characterization of the microstructure of mc-Al have been described in earlier reports [10, 22]. Measurements were also performed on the pure cast aluminium ingot used as the sputtering target for the basis of comparison. Before the experiments, the pure cast aluminium was machined into test coupons of dimension 1 cm × 1 cm × 0.5 cm mounted on PTFE rods by epoxy resin leaving one surface of area $1cm^2$ exposed. They were wet polished with different grades (# 400 to #2000) of SiC abrasive paper, washed with distilled water, rinsed with absolute ethanol and dried in warm air and kept in a desiccator prior to corrosion testing. The corrodent was 0.1 M H_2SO_4 prepared from analar grade concentrated sulphuric acid with distilled water. Polyacrylamide (PA) [$M_n = 3 \times 10^{-6}$ g mol^{-1}] was used as the test inhibitor. Two concentrations 2×10^{-7} M and 1×10^{-8} M were prepared in 0.1 M H_2SO_4 and used in the study.

Electrochemical tests were performed in aerated solutions at 30 ± 1 ^{o}C using a conventional three-electrode glass cell with platinum foil as the counter electrode and saturated calomel electrode (SCE) as the reference electrode connected via Luggins capillary. All the potentials reported in this study are referred to that of the reference electrode. Potentiodynamic polarization experiments were carried out using a PARC Parstat-2273 Advanced Electrochemical System operated with Powercorr software in a potential range from cathodic potential of –250 mV to anodic potential of +250 mV with respect to the corrosion potential (E_{corr}) at a scan rate of 0.5 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) studies were performed using Powersine software at corrosion potentials (E_{corr}) over a frequency range of 100 kHz to 10 mHz with a signal amplitude perturbation of 5 mV. Spectral analyses were performed using Zsimpwin software also supplied by PARC.

3. Results and discussion

3.1. Corrosion behaviour in uninhibited solution

Potentiodynamic polarization experiments were undertaken to distinguish the effect of microcrystallization on the anodic and cathodic corrosion reactions of pure cast aluminium in 0.1 M H_2SO_4. Typical anodic and cathodic polarization curves of the pc-Al and mc-Al in the uninhibited acid solution are shown in Fig.1. Examination of Fig.1 reveals that both samples exhibit active dissolution without any distinctive transition to passivation up to about –0.5 V/SCE. However, it is obvious that surface microcrystallization negatively influenced the polarization behaviour of pure cast aluminium in the test solution. Surface microcrystallization process leads to decrease in cathodic current density and a shift in anodic current density to slightly higher values. The value of corrosion potential (E_{corr}) was lowered from –781 to –999 mV while the corrosion current density (i_{corr}) increased from 515 to 644 μA cm^{-2}. This indicates a higher corrosion susceptibility of the microcrystalline pure aluminium surface. Negative influence of microcrystalline/nanocrystalline surface on corrosion behaviour of metal specimens can be found in the literature. For instance Oguzie *et al.* [2] reported higher corrosion susceptibility of nanocrystalline low carbon steel surface produced by magnetron sputtering technique in sulphuric acid solution while Li *et al.* [23] reported similar behaviour for the same material produced by ultrasonic shot peening in acid sulphate solution.

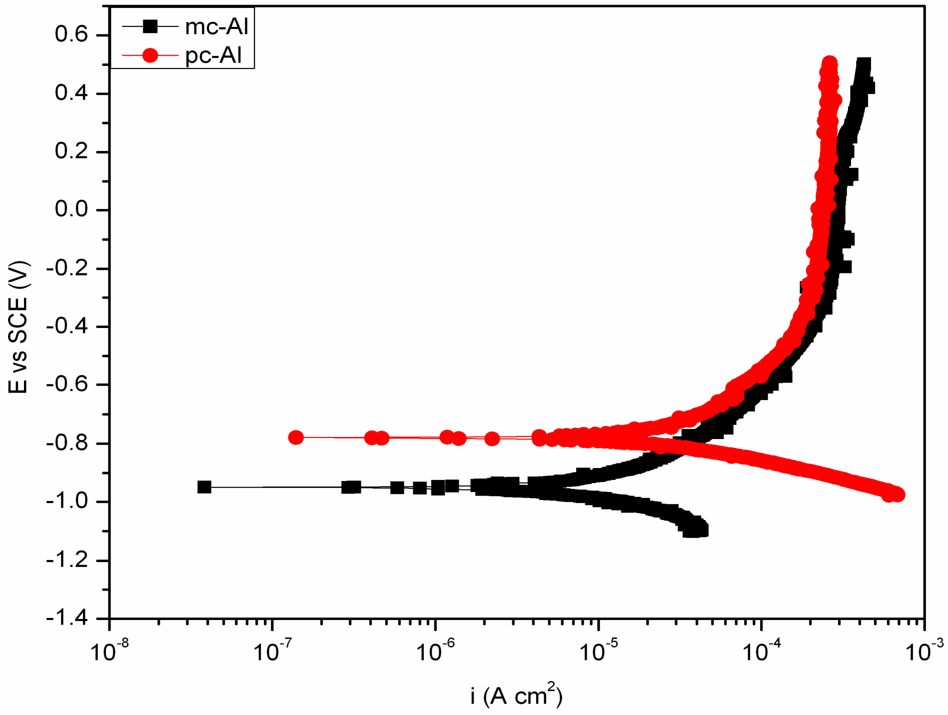

Figure1: Polarization curves of pc-Al and mc-Al in 0.1 M H_2SO_4 in the absence of inhibitor (PA)

Specimens' microstructure characterization using XRD analysis in previous reports [10,22] indicated identical composition for mc-Al and pc-Al, it is therefore pertinent to say that the differences in corrosion behaviour is mainly due to the differences in grain size and the ensuing surface structural modification. The microcrystalline surface with mean grain size in micrometre scale provides both high population active sites and greater surface area for the corrosion reaction. In addition, the considerable volume of grain boundaries enhances the diffusion of the corrodent within the surface [2]. These factors could be responsible for the observed high dissolution kinetics of mc-Al compared to pc-Al. As could also be rightly observed in Fig.1, the effect of microcrystallization was more pronounced on the anodic dissolution reaction and cathodic reaction was less affected. This suggests a predominant influence of the increased number of active sites, which could accelerate the kinetics of the anodic reaction by forming several micro-electrochemical corrosion cells. In a related study by Jung and Alfantazi [24], they observed identical anodic polarization behaviour for nano and micro Co in 0.1 M H_2SO_4, whereas the cathodic kinetics of the nano increased. The increase in the cathodic kinetics was attributed to increased hydrogen evolution reaction rate due to substantial quantity of crystalline defects in the nanocrystalline electrode.

The impedance behaviour is well suited for determining the characteristics and kinetics of electrochemical processes occurring at mc-Al/0.5 M H_2SO_4 and pc-Al/0.5 M H_2SO_4 interfaces. The impedance plots for both mc-Al and pc-Al in 0.1 M H_2SO_4 is illustrated as Nyquist plots in Fig.2. It is observed that the plots for the two specimens are identical indicating the same corrosion characteristics. However, the decrease in the size of the semicircle for mc-Al compared to pc-Al indicates that mc-Al is more susceptible to corrosion in the acidic environment. The Nyquist plots are characterized by three time constants consisting a large capacitive loop at high frequencies(HF), an inductive loop at medium frequencies (MF) followed by the second capacitive loop at low frequencies (LF). The impedance data was analyzed using the equivalent circuit (EC) previously reported [25]. Results obtained showed that microcrystallization lowered charge transfer resistance from 615 to 603 Ω cm^2 and polarization resistance from 1566 to 1552 Ω cm^2. The lower values of charge transfer resistance and polarization resistance for mc-Al may suggest that it is more vulnerable to corrosion in the acidic medium which is consistent with the results of polarization technique.

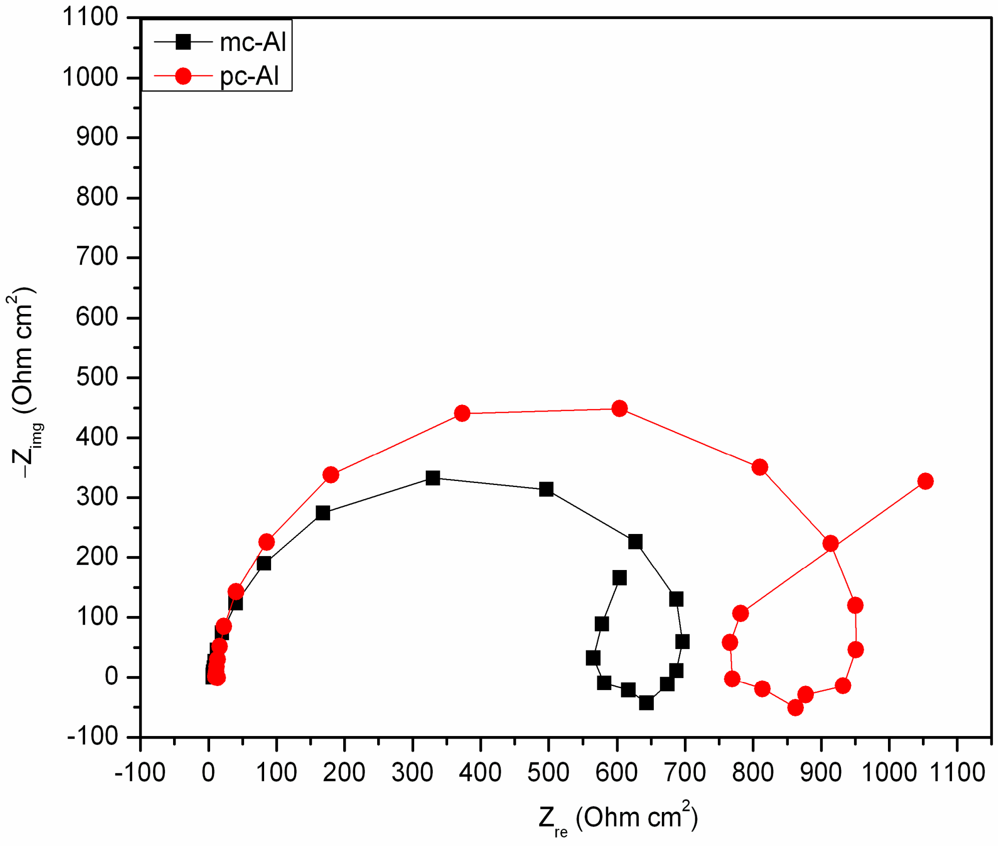

Figure 2: Nyquist plots of pc-Al and mc-Al in 0.1 M H_2SO_4 in the absence of inhibitor (PA)

3.2. *Corrosion behaviour in inhibited solution*

EIS experiment was undertaken in order to gain insight into the characteristics and kinetics of electrochemical processes which occur at pc-Al/0.1 M H_2SO_4 and mc-Al/0.1 M H_2SO_4 interfaces. Fig. 3 shows the impedance spectra as exemplified by Nyquist plot obtained for pc-Al and mc-Al in the absence and presence of 1×10^{-8} and 2×10^{-7} M PA. The plots revealed that the diameter of the semicircle in the Nyquist plot was increased on the introduction of PA into the corrosive medium for both pc-Al and mc-Al with more pronounced effect on the mc-Al specimen. This phenomenon could be associated with the corrosion inhibiting effect of the PA. The presence of PA increases the impedance but does not change the other aspects of corrosion mechanism for both specimens. The Nyquist plots presented in Fig.3 are characterized by three time constants, namely: (1) a capacitive time constant at high frequency values, (2) an inductive time constant at medium frequencies and (3) a second capacitive time constants at low frequencies. In the literature, there is no consensus about the origin of time constants of the impedance diagram. The time constant at high frequencies is attributed to the formation of the oxide layer or to the oxide layer itself [26]. Brett [27] assigns the high frequency time constant to the reactions involved in the formation of the oxide layer. He suggested that at metal-oxide interface, aluminium is oxidized to Al^+ intermediates. The Al^+ intermediates will subsequently be oxidized to Al^{3+} at the oxide-solution interface where also O^{2-} or OH^- is formed. Simultaneously with the formation of O^{2-} ions, H^+ ions are formed. This results in a local acidification at the oxide-electrolyte interface. Another possible explanation for the capacitive time constant at high frequencies is the oxide film itself which is considered to be a parallel circuit of a resistor due to the ionic conduction in the oxide, and a capacitance due to the dielectric properties of the oxide 16]. The inductive time constant at medium frequencies is often attributed to surface or bulk relaxation of species in the oxide [28]. Adsorption of intermediates (H^+ and SO_4^{2-} ions) in the absence of inhibitor could also cause an inductive loop. But in the presence of PA, the inductor arises from adsorption effects of the oxide film and/or PA molecules and could be defined as ($L = R\tau$) where τ is the relaxation time for adsorption on the aluminium surface [29]. The second capacitive loop observed at LF could be assigned to the metal dissolution [16].

The impedance spectra of the Nyquist plots were analyzed by fitting to the equivalent circuit model consisting of seven elements of the type $R_s(QR_f\{LR_L\})(C_{dl}R_{ct})$ which has been previously reported 25]. In the presence of PA (2×10^{-7} M), the R_{ct} and R_p were observed to increase from 603 and 1552 Ω cm^2 to 2066 and 4254 Ω cm^2 while the C_{dl} was reduced from 39 to 20 mF cm^{-2} for mc-Al. For pc-Al, R_{ct} and R_p increased from 615 and 1566 Ω cm^2 to 1564 and 2870 Ω cm^2 respectively while C_{dl} decreased from 37 to 33 mF cm^{-2}, indicating a retarding of the corrosion reaction. The decrease in C_{dl} values is usually attributed to a decrease in dielectric constant and /or an increase in double layer thickness due to inhibitor adsorption on the metal/electrolyte interface [2, 30]. This implies that the reduction of corrosion rate of the aluminium specimen by PA was afforded by virtue of adsorption on the metal/electrolyte interface, a fact that has been previously established. The protectiveness of PA was measured by comparing the values of charge transfer resistance in the absence and presence of the inhibitor as follows:

$$\eta\% = \left(1 - \frac{R_{ct}^{o}}{R_{ct}}\right) \times 100 \qquad (1)$$

where R^o_{ct} and R_{ct} are the charge transfer resistances in the absence and presence of inhibitor (PA) respectively. The values of inhibition efficiency obtained were 71 and 61% for mc-Al and pc-Al respectively at 2×10^{-7} M PA concentration. This variation in impedance parameters and inhibition efficiency between the two Al specimens is attributed to structural difference namely, there are more available defects, such as grain boundary, to adsorb the inhibitor molecules at the metal-solution interface when the grain sizes become smaller hence the microcrystalline microstructure of mc-Al provides a more favourable surface for PA adsorption in the 0.1 M H_2SO_4 solution. The results obtained in this study collaborates earlier studies [2] which showed that nanocryustalline surface favours inhibitor adsorption. This could imply that the high defect population (grain boundaries, triple junctions, inclusions) which promote metal dissolution, also somehow provides an abundance of acceptor sites for inhibitor [3].

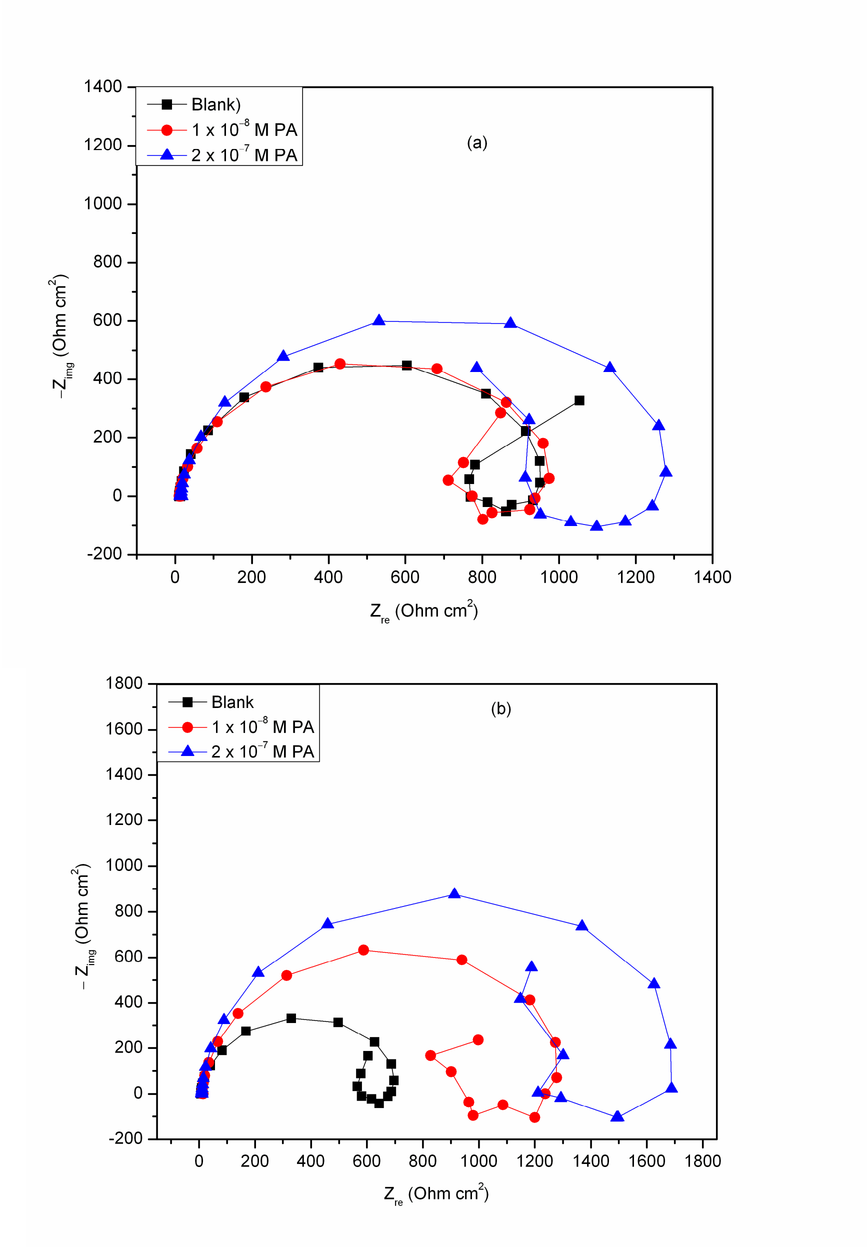

Figure 3: Nyquist plots of pc-Al and mc-Al in 0.1 M H_2SO_4 solution without and with different concentrations of PA for (a) pc-Al and (b) mc-Al.

EIS experiments were also undertaken to assess the effects of Al microstructures on the efficiency of PA (2 × 10^{-7} M) in the presence of iodide ions. The impedance spectra of (a) pc-Al and (b) mc-Al in 0.1 M H_2SO_4 containing 2 × 10^{-7} M PA in combination with 1 and 5 mM KI and PA alone for comparison are shown in Fig.4. The Nyquist plots again revealed that the impedance responses of the two Al specimens do not differ significantly without and with iodide ions. The Nyquist plots were characterized by three time constants and the size of the diameter of the semicircles increases on introduction of iodide ions compared to PA alone and further increased with increase in iodide ion concentration for both mc- Al and pc-Al. The equivalent circuit $R_s(QR_f\{LR_L\})(C_{dl}R_{ct})$ was used to analyze the impedance spectra. Addition of iodide ions resulted in significance increase in R_{ct}, R_p and η% and decrease in C_{dl} values which could be attributed to synergistic effect. The effect was more pronounced for mc-Al compared to pc-Al. For instance in the presence of 5 mM KI, the η% increase from 71 to 92% for mc-Al compared to an increase from 61 to 72% for pc-Al. The mechanism of this synergistic effect has been described in detail in the literature [31-33]. Briefly, the iodide ions are strongly chemisorbed on the corroding Al surface and facilitate PA adsorption by acting as intermediate bridges between the charged metal surface and PA polycation. This stabilizes the adsorption of PA on the Al surface, leading to higher surface coverage hence higher inhibition efficiency.

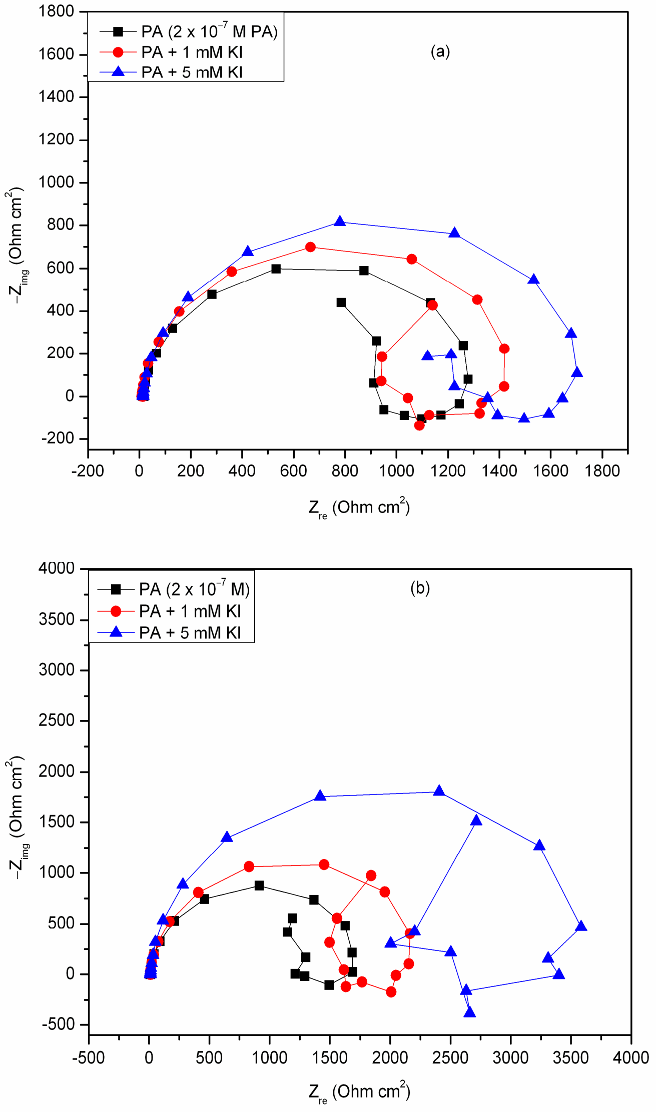

Figure 4: Nyquist plots of (a) pc-Al and (b) mc-Al in 0.1 M H_2SO_4 in the presence of 2×10^{-7} M PA and in combination with 1 and 5 mM KI.

4. Conclusion

A microcrystalline surface was fabricated on pure cast aluminium using magnetron sputtering technique. EIS and potentiodynamic polarization studies revealed that the microcrystalline surface and the polycrystalline counterpart have identical corrosion mechanisms in 0.1 M H_2SO_4 solution and exhibited active dissolution within the range of potential range studied. However, the micrograined microstructure accelerated the corrosion of pure cast aluminium in the acidic medium by shifting the corrosion potential to less noble values and increasing the kinetics of the anodic reaction. Polyacrylamide was found to exert corrosion inhibiting effect on both mc-Al and pc-Al samples with higher inhibition efficiency obtained for mc-Al.

Acknowledgement

S.A Umoren acknowledges the Chinese Academy of Sciences (CAS) and Academy of Sciences for the Developing World (TWAS) for the CAS-TWAS Postdoctoral Fellowship

References

1. Khaled, K. F., Qahtani M., *Mater. Chem. Phys.* 113 (2009) 150.
2. Oguzie, E. E., Li, Y., Wang, F. H., *Electrochim. Acta* 52 (2007) 6988
3. Oguzie,E. E., Wang, S. G.., Li,Y., Wang,F. H., *J.Phys.Chem.C* 113 (2009) 8420.
4. Kwok,C.T., Cheng, F.T., Man, H.C., Ding,W.H., *Mater. Lett.* 60 (2006) 2419.
5. Youssef, Kh.M.S., Koch,C.C., Fedkiw,P.S. *Corros. Sci.* 46 (2004) 51.
6. Wang, X.Y., Li,D.Y., *Electrochim. Acta* 47 (2002) 3939.
7. Thorpe,S.J., Ramaswami, B., Aust, K.T., *J. Electrochem. Soc.*135 (1988) 2162.
8. Mishra, R., Balausbramaniam, R., *Corros. Sci.* 46 (2004) 3019.
9. Rofagha,R., Erb,U., Ostrander,D., Palumbo,G., Aust, K.T., *Nanocryst. Mater.* 2 (1993) 1.
10. Zhang, B. Li, Y., Wang, F., *Corros. Sci.* 49 (2007) 2071.
11. Rajendran, S., Sridevi, S. P., Anthony, N., John, A. A., Sundearavadivelu, M., *Anti-corros. Methods Mater.* 52 (2005) 102.
12. Jianguo, J., Lin, W., Otieno-Alego,V., Schweinsberg, D. P., *Corros. Sci.* 37 (1995) 975.
13. Yurt, A., Bütün, V., Duran, B., *Mater. Chem. Phys.* 105 (2007) 114.
14. Umoren, S. A., Ogbobe, O., Ebenso, E.E., Okafor, P. C., *J. Appl. Polym. Sci.* 105 (2007) 3363.
15. Umoren, S. A., Ebenso, E.E., *Ind. J. Chem. Technol.* 15 (2008) 355.
16. Amin,M. A., Abd El-Rehim,S. S., El-Sherbini,E. E. F., Hazzazi, O.A., Abbas,M. N., *Corros. Sci.* 51 (2009) 658.
17. Umoren, S. A., Obot,I.B., Ebenso,E.E., Okafor,P. C., Ogbobe, O., Oguzie, E.E., *Anticorros. Methods Mater.* 53 (2006) 355.
18. Shen,C.B., Wang,S.G., Yang,H.Y., Long,K., Wang, F.H., *Appl. Surf. Sci.* 253 (2006) 2118
19. Shen,C.B., Wang,S.G., Yang,H.Y., Long,K., Wang, F.H., *Electrochim. Acta* 52 (2007) 3950
20. Shen,C.B., Wang,S.G., Yang,H.Y., Long,K., Wang, F.H. *Corros.Sci.* 48 (2006) 1655.
21. Oguzie, E. E., Li, Y., Wang, F. H., *J. Solid State Electrochem.* 12 (2007) 721.
22. Zhang, B., Li,Y., Wang, F., *Corros. Sci*. 51 (2009) 268.
23. Li, Y., Wang, F., Liu, G., *Corrosion* 60 (2004) 891.
24. Jung, H., Alfantazi,A., *Electrochim. Acta* 51 (2006)1806
25. Umoren, S.A., Li,Y., Wang, F.H.,.*J. Solid State Electrochem.* 14 (2010) 2293.
26. Khaled, K.F., Amin, M.A., *J. Appl. Electrochem.* 39 (2009) 2553.
27. Brett, C.M.A., *J. Appl. Electrochem.* 20 (1990) 1000
28. Frers, S.E., Stefenel, M.M., Mayer,C.M., Chierchie,T., *J. Appl. Electrochem*. 20 (1990) 996.
29. Abdel-Gaber, A.M., Khamis,E., Abo-ElDahab,H., Adeel,Sh. *Mater. Chem. Phys*. 109 (2008) 297.
30. Mu,G., Li, X., *J. Colloid interf Sci.* 289 (2005) 184.
31. Umoren,S.A., Ebenso, E.E., *Mater. Chem. Phys*. 106 (2007) 387
32. Umoren, S.A., Li,Y., Wang, F.H., *Corros. Sci.* 52 (2010) 1777.
33. Jeyaprabha,C., Sathiyanarayanan,S., Venkatachari,G., *J. Electroanal. Chem.* 583 (2005) 232.