Advanced Materials Research *Online: 2012-05-14*
ISSN: 1662-8985, Vols. 518-523, pp 249-254
doi:10.4028/www.scientific.net/AMR.518-523.249

Synergistic inhibition effect of sodium oleate and sodium vanadate on the corrosion of pure aluminum in NaCl solution

Yuhong Zhou[1,a], Shuqing Chen[1,b], Changhong Li[2,c]

[1]Department of Inorganic Chemistry, School of Science, Harbin Institute of Technology, Harbin 150001,China

[2] Harbin Institute of Large Electrical, Harbin 150040,China

[a]yuhong806@yahoo.com.cn, [b]shuqing0113@126.com, [c]Leechanghong@sohu.com

Keywords: Inhibitor; Aluminum; Corrosion; EIS

Abstract. Synergistic inhibition effect of sodium oleate and sodium vanadate on the corrosion of pure aluminum in NaCl solution has been investigated by open circuit potential, potentiodynamic polarization curve, and electrochemical impedance spectroscopy(EIS). Experiment results show that the pure aluminum has the lowest corrosion current density under the optimum technological conditions at room temperature, which can be expressed as follows: the 3.5wt.% NaCl solution contains two inhibitors of sodium oleate and sodium vanadium, and their mole concentration ratio is 1:2, solution pH value is 8.0~8.5. In addition, these two inhibitors have played the major role of corrosion inhibition at different stage respectively, which can be attributed to the formation of continuous phase on the surface of pure aluminum.

Introduction

Pure aluminum is a high activity and light metal, with a electrochemical equivalent up to 2.98 Ah/g, the equilibrium potential of -2.35V. The theoretical specific energy of the aluminum-air battery is up to 100 Wh/kg[1]. It even is 6.67-8.33 times than lead-acid batteries[2]. But in terms of alkaline, acidic or neutral electrolyte, the pure aluminum will be corroded severely, which not only causes the waste of aluminum, and decrease the specific energy of it. Adding the appropriate corrosion inhibitor can solve this problem.

In the neutral chloride medium, authors used to use inorganic compounds as corrosion inhibitors of aluminum, such as chromate and nitrite[3-4]. but this kind of corrosion inhibitors is toxic, can cause serious environmental pollution, so it is prohibited today.

Sodium oleate(SO) has many advantages when used as corrosion inhibitor, such as high inhibition efficiency, easy production, low price and low toxicity[5]. Xianghong Li[6] studied the SO as corrosion inhibitor and its synergistic inhibition effect incorporate with rare earth cerium(IV) ion. The results showed that SO was a moderate effective corrosion inhibitor when single used and exhibits synergistic inhibition effect between the SO and rare earth cerium(IV) ion.

Sodium vanadate is also a high inhibition efficiency, easy production, low price and low toxicity corrosion inhibitor. M. Iannuzzi[7-9] had used the split cell technique, EIS, polarization curves, and adsorption isotherms methods to study the mechanisms of corrosion inhibition of AA2024-T3 by vanadates, and find that the clear metavanadate solutions(contain monovanadate (V1), divanadate (V2), tetravanadate (V4) and pentavanadate (V5) species [10-12]) were shown to be good inhibitors of the oxygen reduction reaction(ORR) by adsorbing on the surface and blocking sites rather than

by a reduction process, and the main corrosion inhibition composition is metavanadate(V1) . While the orange solutions(main contain decavanadates[10, 13]) were shown to be poor inhibitors of the ORR.

At present, people have studied the synergy between inhibitors and find the combined inhibitors have a inhibition efficiency much higher than the sum of all single inhibitor. Synergism is an effective method to diversify the application of inhibitor, to improve the inhibitive force of inhibitor and to decrease the amount of usage[14]. There is a study about the synergistic inhibition effect between sodium vanadate and SO in this work.

Experiment

Pretreatment of aluminum. Material tested was commercial purity aluminum from Beijing Francis Aluminum Co., Ltd., the trademark is 1A97, and state is H19, the elements of the mass fraction of aluminum is 99.986%. Before experiment, the aluminum was polished to ensure the consistency of experimental conditions and the reproducibility. The main processes: sandpaper polished, degreasing, electric polishing, and wash.

Orthogonal experimental design. Use the total concentration of 0.5g/L of SO and sodium vanadate together as the corrosion inhibitors. An orthogonal experimental design $L_{25}(5^3)$ in triplicate was used to evaluate effects of immersed temperature, the mole concentration ratio of SO and sodium vanadate, and pH value of the solution on potentiodynamic polarization curve after immersed for 15 minutes.

Electrochemical test. Electrochemical including EIS, open circuit potential time curve(OCP), and Tafel curves which carried out under three-electrode system. EIS measurements were done in the frequency interval of 0.01-10000 Hz with an amplitude of ±1 mV at the free corrosion potential.

Surface morphology. The surface of the specimens are characterized by scanning electron microscopy(SEM) (S3700N) to observe the morphology and analyzed by the energy dispersive spectrometer(EDS) (Apollox) after immersed in inhibitors solution.

Results and Discussions

OCP test results. Fig.1 shows the OCP curves of pure aluminum electrode in 3.5wt.% NaCl solution with and without 0.5g/L inhibitors at 25℃. It tells that the SO and the sodium vanadate all performed as good corrosion inhibition and have a higher OCP than in the blank solution. In-depth analysis, we can find that before immersed for 17 hours, SO performed as a better corrosion inhibition than sodium vanadate. It may because that the adsorption activation energy of SO was significantly lower than the activation energy of oxidation-reduction reaction which sodium vanadate participates in. After 17 hours, sodium vanadate plays better than SO. Then a try of both using SO and sodium vanadate as the corrosion inhibitors was carried out. Compare the “2”curve to “4”find that there is a significantly increase when together use SO and sodium vanadat. That is to say there is a good synergistic inhibition effect between SO and sodium vanadate.

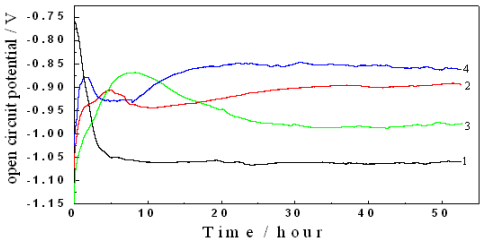


Fig. 1 The OCP curves of pure aluminum electrode in solution with single and inhibitor.

1, blank; 2, $NaVO_3$; 3, $C_{17}H_{35}COONa$; 4, $NaVO_3$+ $C_{17}H_{35}COONa$

Orthogonal test results. After immersed in the solution for 15 minutes, take a Tafel curve of pure aluminum, calculate and record of the corrosion current density. According to the value of the corrosion current density to determine the best technological conditions. Fig. 2 shows the three facts impact on the corrosion inhibition. In Fig. 2(a), Corrosion current density both have a lower value at the mole concentration ratio of 3:1 and 2:1. And the corrosion current density at 2:1 is lower than at 3:1. So the best mole concentration ratio is 2:1. Fig. 2(b) shows the impact of the temperature. Influence of temperature mainly in three aspects. The first is that the processes of cathode diffusion and anodic electrochemical reaction are both accelerated with the increase of the temperature. The second is that the oxidation-reduction reaction which sodium vanadate participates in is increased with the increase of the temperature. The third is that the adsorption rate of SO reduce with the increase of the temperature. Because of all the above facts, Corrosion current density was the lowest under 20℃. Fig. 2(c), we can see that when the pH value of 8.0 to 8.5, the corrosion current density is lowest. So the best technological conditions is that: the 3.5wt.% NaCl solution contains two inhibitors of sodium oleate and vanadium sodium and their mole concentration ratio is 1:2, solution pH value is 8.0~8.5, and the temperature is 20℃.

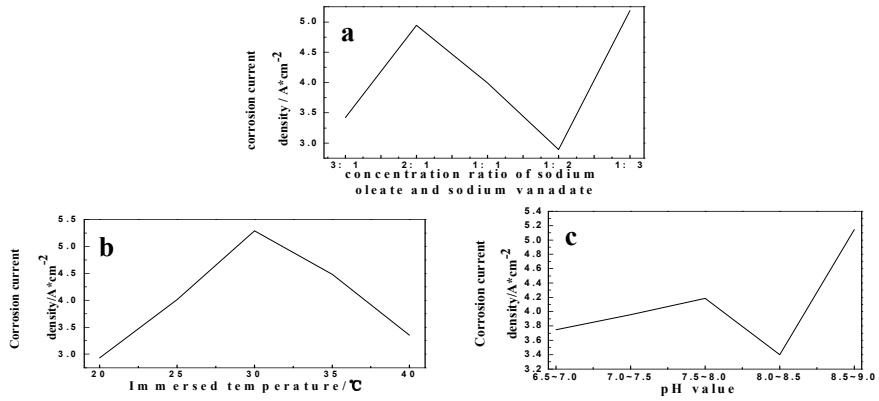


Fig. 2 The the mole concentration ratio(A), temperature(B) and pH value(C) performance on the corrosion inhibition.

EIS results. Within 14d, take a EIS spectroscopy of pure aluminum under the best technological conditions every half an hour. Fig. 3 shows several representative EIS spectrums. In this Fig., there are four stages the of the EIS spectrums. At the first stage, the impedance increase after immersed for 0.5h to 57h, due to the adsorption of SO, because adsorption process is more likely to occur than oxidation process caused by vanadate. The second stage, the impedance decrease from 57h till 144h. It may because of the unstable of the unstable adsorbed film of sodium oleate. The third stage, the impedance again to increase from 144h to 222h, it due to the vanadate passive film caused from oxidation process. The last stage, the impedance decrease from 222h. After 222h, the solution start to lose effectiveness because of the reduced concentration of inhibitor, the change of pH value and the increase of corrosion products. Till 362h, the solution have no inhibitor efficiency.

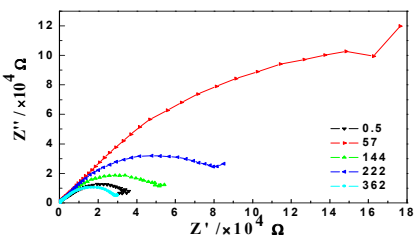
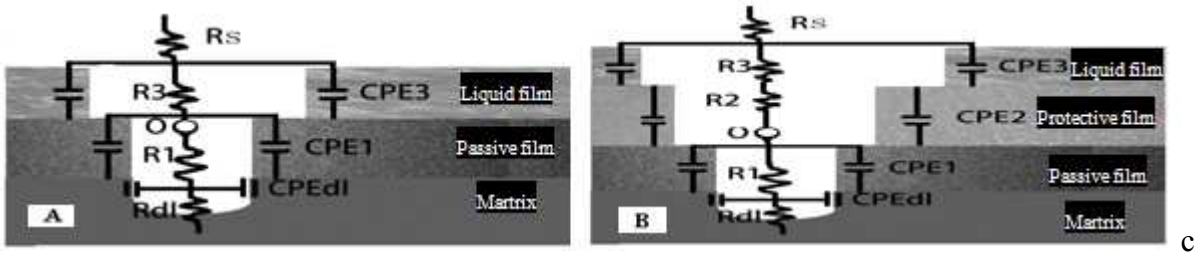


Fig. 3 EIS of aluminum immersed in inhibitors solutions under the best technological conditions.

Modle of the aluminum surface. Only after a short-term immersed, the corrosion inhibitors protective film didn't form on the aluminum surface. At the time the model of the aluminum surface includes aluminum martrix, passive film and liquid film as show in Fig. 4(A), and it's equivalent circuit(R(QR)(Q(RO))(QR)). Because of the long-term immersed, there is a inhibitor protective film formed on the surface of the aluminum, so the model of it contain aluminum martrix, passive film, protective film and liquid film as show in Fig. 4(B), and it's equivalent circuit(R(QR)(Q(R(Q(RO))))(QR)). Fig. 5(a) and Fig. 5(b) was EIS fitting results corresponding with the Fig. 4(A) and Fig. 4(B). Fig. 5(a) shows the fitting result is very well in the high and middle frequency. But it is not very well in the low frequency, it may due to the instable of the initial immersion process. Fig. 5(b) shows the effect of fitting result is very well both in the high frequency and the low frequency, which proved the right model showed in Fig. 4(B).



c

Fig. 4 Short-term(A) and Long-term(B) immersed aluminum surface model and there are equivalent circuit R(QR)(Q(RO))(QR) and R(QR)(Q(R(Q(RO))))(QR).

Fig. 5 Simulation results of EIS after immersed in inhibitors solution for 1.5h(a) and 222h(b) under the best technological conditions.

Surface morphology. Fig. 6 and Fig. 7 show the SEM of the aluminum after immersed in inhibitor solutions for 57 h and 107h under the best technological conditions. Both Fig. 6 and Fig. 7 show that there is a inhibitor protective film formed in the surface of pure aluminum. Table 1 are the Carbon elemental analysis of the "A" and "B" selected area. In this table, we can find that there are a large proportion of the carbon, which tells the SO adsorption film have formed. Fig. 7(A&B) shows that there is a thick inhibitors protective film formed on the surface, and the EDS result tells that both SO and vanadate take part of it. Fig. 6 and Fig. 7 prove the EIS result. Fig. 8(A&B) show the SEM of pure aluminum and the EDS(B) analysis of the "D" selected area after immersed in blank solution for 107h. the result shows that the aluminum has serious pittings, and compare to the Fig. 7(A&B), prove the inhibitors play a good corrosion inhibition.

Table 1 Carbon elemental analysis of the "A" and "B" selected area

	Element	*Wt%*	*At%*
the "A" selected area	***CK***	22.01	38.15
the "B" selected area	***CK***	15.51	28.71

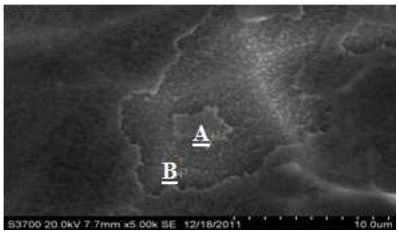


Fig. 6 SEM analysis of pure aluminum after immersed in inhibitor solution for 57h

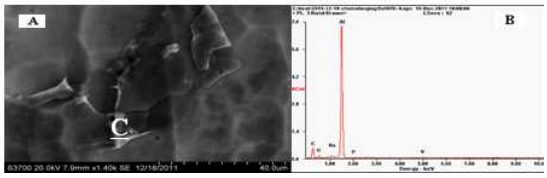


Fig. 7 SEM(A) and EDS(B) analysis of the "C" selected area after immersed in inhibitor solution for 107h.

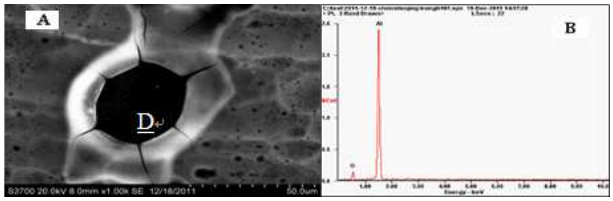


Fig. 8 SEM(A) and EDS(B) analysis of the "D" selected area after immersed in blank solution for 107h.

Conclusions

1, There is a good synergistic inhibition effect of SO and sodium vanadate, and the pure aluminum has the lowest corrosion current density under the best technological conditions at room temperature, which can be expressed as follows: the 3.5wt.% NaCl solution contains two inhibitors of SO and vanadium sodium, and their mole concentration ratio is 1:2, solution pH value is 8.0~8.5.

2, SO and vanadium sodium have played the major role of corrosion inhibition at different stage respectively, which can be attributed to the formation of continuous phase on the surface of pure aluminum.

3, The inhibition under the best technological conditions can do a efficient corrosion inhibition.

Acknowledgment

This research is supported by Heilongjiang Provincial Natural Science Foundation of China (Grant No. B2007-09).

References

[1] ALBERT J M, ANIBU K, GANESAN M, et al. Characterisation ofdifferent grades of commercially pure aluminium as prospective galvanic anodes in saline and alkaline battery electrolyte[J]. J Applied Electrochemical, 1989, 19: 547-551.

[2] Roger A P. The Aminum/Air Battery[J]. Light Metal Age, 2000, 8(3-4):108-110.

[3] Badawy W A, Alkharafi F M, Llarab A S. Inhibition of Contusion of Al,Al-b061 and Al-Cu in Neutral Solution [J].Nullelin of Electrochemistry,1997,13(5):193

[4] Lyberatos G, Kobotialis L. The Inhibition of Aluminium Alloy [J] . Corrosion.1991.47(ll):820

[5] A. Tizpar, Z. Ghasemi, The corrosion inhibition and gas evolution studies of some surfactants and citric acid on lead alloy in 12.5 M H2SO4 solution, Appl. Surf. Sci. 252 (2006) 8630-8634.

[6] Xianghong Li, Shuduan Deng, Hui Fu, et al. Synergistic inhibition effect of rare earth cerium(IV) ion and sodium oleate on the corrosion of cold rolled steel in phosphoric acid solution[J]. Corrosion Science. 52 (2010) 1167-1178.

[7] M. Iannuzzi, G.S. Frankel. Mechanisms of corrosion inhibition of AA2024-T3 by vanadates[J]. Corrosion Science. 49 (2007) 2371-2391

[8] M. Iannuzzi, Inhibition of Al Alloy 2024-T3 Corrosion by Vanadates, PhD Dissertation, The Ohio State University, 2006.

[9] M. Iannuzzi, G.S. Frankel, Electrochim. Acta, in press.

[10] A. Gorzsas, K. Getty, I. Andersson, et al. Chem., Dalton Trans. (2004) 2873.

[11] A.S. Tracey, Coord. Chem. Rev. 237 (2003) 113-121.

[12] A.S. Tracey, C.H. Leon-Lai, Inorg. Chem. 30 (1991) 3200-3209.

[13] J.W. Larson, J. Chem. Eng. Data 40 (1995) 1276-1280.

[14] G.N. Mu, X.M. Li, F. Li. Synergistic inhibition between o-phenanthroline and chloride ion on cold rolled steel corrosion in phosphoric acid, Mater. Chem. Phys. 86 (2004) 59-68.