Journal of Engineering Science and Technology
Vol. 13, No. 6 (2018) 1713 - 1721

ALUMINUM ALLOY AA2024 COATED WITH ZrO_2 USING A SOL-GEL-ASSISTED DIP-COATING TECHNIQUE AND ITS CORROSION PERFORMANCE

VEANUGA GANAPATHY[1], TEDI KURNIAWAN[1,*], H. MAS AYU[2], YULI PANCA ASMARA[1], ROSDI DAUD[2], NIKI PRASTOMO[3], ASEP BAYU DANI NANDIYANTO[4]

[1]Structural Materials Degradation Focus Group, Universiti Malaysia Pahang, Pekan 26600 Pahang, Malaysia
[2]Manufacturing Focus Group, Universiti Malaysia Pahang, Pekan 26600 Pahang, Malaysia
[3]Department of Physics-Energy Engineering, Engineering Faculty, Surya University, Grand Serpong Mall, Jl. M.H. Thamrin Km 2.7 Tangerang, Banten 15143 Indonesia
[4]Departemen Kimia, Universitas Pendidikan Indonesia, Jl. Dr. Setiabudhi No.229, Bandung, Jawa Barat 40154, Indonesia
*Corresponding Author: tedikurniawan@ump.edu.my

Abstract

Aluminum alloys has been widely used in most of engineering applications, such as marine industries and aerospace, due to its light weight and durability properties. In the aggressive environment, aluminum alloy becomes chemically reactive and losses its corrosion resistance that can significantly limit to its applications. One of the approaches that have been studied in this research is to improve the corrosion resistance of aluminum alloy by adding zirconium oxide (ZrO_2) film coating. In the experimental procedure, aluminum alloy was dip-coated into the solution containing zirconium butoxide (as a precursor) in a specific solvent (consisting of acetone, ethanol, and nitric acid). Dipping process was conducted at different dipping-numbers, which are 3, 5, and 7 dipping number. After dip-coating process, the coated aluminum was annealed at 350°C for 3 hours. X-ray diffraction analysis confirmed that the coating film consists of tetragonal ZrO_2. Then, increases in dipping number improved the surface quality of the coating layer, where number of cracks and black spots reduced continuously with higher dipping number. This condition gave positive impacts on the corrosion performance of the aluminum, where higher dipping number brings better corrosion protection in NaCl solution.

Keywords: AA2024, Corrosion, Aluminium alloy, Sol-gel dip coating.

1. Introduction

Aluminum alloys have been widely used in many applications, such as major materials in constructions, automotive, aerospace industries, and marine platforms. Pure aluminum has good corrosion resistance, soft, ductile and high thermal conductivity [1, 2]. But pure aluminum is rarely used in most of the applications due to its low mechanical strength. Alloying with other metals, such as copper, manganese, silicon, and magnesium can improve its mechanical strength and also bring other excellent properties that are required for the engineering applications. AA2024 is one of the examples of aluminum alloy, where the main alloying element is copper with noticeable quantities of alloy silicone, manganese, magnesium, nickel and titanium [2, 3]. This material has high mechanical strength and good fatigue resistance, making this type of alloy being used for aerospace and aircraft applications. In term of corrosion properties, even though aluminum alloy remains stable in nature, aggressive environment makes this material chemically reactive. Indeed, losses in corrosion resistance cannot be avoided, which significantly limits to its application [3-7]. Thus, understanding how to improve the corrosion resistance of aluminum-related material is important, specifically for increasing its life span and reducing the material waste and cost of replacement.

To improve the corrosion resistance, aluminum alloys are usually coated with a paint containing a conversion layer. Chromium conversion coating has been suggested because this coating has excellent adhesion, associating with good barrier properties. Chromate conversion coatings also exhibit self-healing abilities [8, 9]. However, many countries impose severe restrictions on the use of chromate due to its toxicity and environmental hazards. These severe restrictions also stimulated the research and development of new environment-friendly surface treatments. One of the best proposed method as an alternative to chromium coating is by additional inorganic material as a main coating agent. This inorganic material can be easily obtained via a sol-gel technique [9-11].

The sol-gel process and its parameters have been actively studied for the past decades. This process can be employed for the production of oxide films on different metal substrates [12-14]. The coating can form a continuous oxide structure during the deposition procedure. Sol-gel technology also enables the formation of highly adherent and chemically inert oxide films on metal substrates.

Zirconium dioxide (ZrO_2) has been well-known for being used in various applications due to its excellent mechanical properties, such as low thermal conductivity and high resistance to corrosion and high melting point [15-20]. The properties of ZrO_2 are also compatible with the main requirements for a corrosion-resistant coating, e.g., chemical durability and good thermal shock characteristics. Moreover, this oxide has a high mechanical toughness.

Here, the purpose of this study was to investigate the corrosion resistance of aluminum alloy before and after additional zirconium oxide (ZrO_2) film coating. In the experimental procedure, aluminum alloy was dip-coated into the solution containing zirconium butoxide (as a precursor) in a specific solvent (consisting of acetone, ethanol, and nitric acid). Then, by adding heat treatment, the zirconium butoxide converts into ZrO_2. The change in the dip-coating procedure can control the oxide thickness and increase the crystallinity of the oxide. Although many papers have shown the successful synthesis of ZrO_2 film, several limitations have still persisted. For example, the difficulties in the production of high quality of ZrO_2

coating are found, in which this is due to some limitation factors, such as crack phenomena, thickness, compatibily of the thermal treatment condition, and shape of substrates [21-22]. To minimize the impact of the limitation factors, the present study is used the dip-coating technique from the sol-gel mixture. The sol-gel composition was fixed to produce high quality coating and increase the life span of the metal substrates based on previous literature [23-24]. As a model of aluminum alloy, the present study used AA2024-typed substrate. Different number of dip-coating processes were applied to control the thin film performance.

To precisely investigate the effect of dip-coating number on the properties of thin film, the coating layers were characterized using an optical microscope, an electron microscope (SEM) equipped with electron diffraction X-ray spectroscope (EDX), and an X-ray diffraction (XRD). Corrosion tests for the dip-coated substrates were also carried out to find out the performance of coating layer as a protection agent to against corrosion. The corrosion test was performed using potentiodynamic polarization in 3.50% NaCl solution.

2. Experimental Procedure

In this study, AA2024-typed aluminum alloy was used as a substrate. The composition of AA2024 is shown in Table 1. In short, AA2024 contained aluminum (Al), copper (Cu), magnesium (Mg), silicon (Si), iron (Fe), manganese (Mn), zinc (Zn), and titanium (Ti) of 90.7; 3.80; 1.20; 0.50; 0.50; 0.30; 0.25; and 0.15 wt%, respectively. The substrate was mechanically sliced with a dimension of 15, 15, and 3 mm for length, width, and thickness, respectively. Prior to dip-coating process, the substrate was washed ultrasonically in acetone for 15 minutes. The schematic illustration of dip-coating process used in this study is presented in Fig. 1.

Table 1. The chemical composition of AA2024.

Element	Percentage of mass (wt %)
Cu	3.80
Fe	0.50
Mg	1.20
Mn	0.30
Si	0.50
Ti	0.15
Zn	0.25
Al	90.70

To prepare the sol-gel solution for coating agent, several chemicals were used: zirconium (IV) butoxide, ethanol, acetylacetone, and nitric acid. All chemicals were purchased from Wako Chemical, Japan and used without further purification process. The preparation of the solution is shown in Fig. 1. Zirconium (IV) butoxide and ethanol were mixed and stirred using a magnetic stirrer at 500 rpm in room temperature for 30 minutes. Then, acetylacetone was added to the mixture and continuously stirred for another 30 minutes. This mixture was followed by the addition of nitric acid in the continuous stirring for 30 minutes. The prepared ZrO_2 solution was deposited on the surface of the polished aluminum alloy substrates using a Dip Coater (PTL-MM01, OptoSense, UK). The substrates were dip coated for 3, 5 and 7 number of coatings. The parameters of the dip coater was set as followed; travel distance of 35 mm and immersion speed of 100mm/s at room temperature. The substrates were fully immersed in the solution for 1 minute. Then the dip-coated substrate was air-dried for another 2 minutes. These steps were repeated according to the number of coatings of each substrate. Once the deposition of the coating was completed, the substrates were thermally treated. During this phase, excess organic compounds found on the surface of coated substrates were evaporated. Annealing was done at 350°C for 2 hours using an electrical furnace. The heating rate of the furnace was adjusted at 5°C/min.

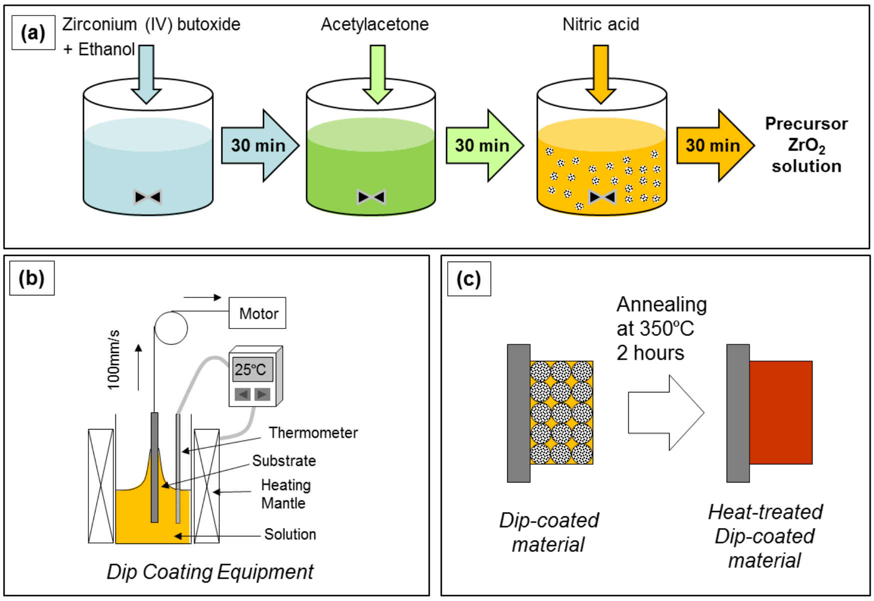

Fig. 1. Schematic illustration of sol-gel-assisted dip-coating process.

The morphology and the thickness of the coated substrates were examined using a Field Emission SEM with back scattered emission gun (JSM-7800F, JEOL, Japan), while the chemical composition was studied using EDX. Meanwhile, the crystal structure of ZrO_2 was examined by an XRD (Miniflex 2, Rigaku, Japan) using Cu-Kα amp radiation at 30 kV and 15 mA. As the coating layer was thin enough to be characterized by XRD, the structure of the coating materials was investigated by drying over night the dipping solution and then annealed it at 350ºC. The powder form the annealing process then observed under XRD.

The corrosion performance of the coated substrates was tested using two methods, which are immersion test and electrochemical test. Immersion test was carried by immersing substrates in 3.50 % of NaCl solution (seawater condition) for 2 weeks at room temperature. Meanwhile, the electrochemical test was conducted in a 3.50% of NaCl solution using a potentio-dynamic polarization method. Three electrodes were used to setup the electrochemical reaction, namely; platinum foil as a counter electrode, saturated calomel electrode (SCE) as a reference for electrode and substrate as a working electrode. At a scan rate of 1 mV/s, the experiment was carried out to reach the required equilibrium. The scanning range for voltage was set between -1.00 to 1.50 volts. The open circuit potential (OCP) was measured for 2 minutes to confirm the condition equilibrium prior to obtaining the potentio-dynamic polarization curve.

3. Results and Discussion

The optical microscope images from the surface of coated aluminum with different dipping numbers are shown in Fig. 2. It revealed that all substrates have uniform and homogenous coating film. However, in the case of substrates with 3 dipping coating numbers, early initiation of crack was observed and black spots existed on the surface. The cracks were not propagated to the whole substrate. However, in substrate with 5 and 7 dipping numbers, the cracks were not observed and the black spots reduced. Additional layering or coating seems to give positive impact for the improvement of the quality of the coating film.

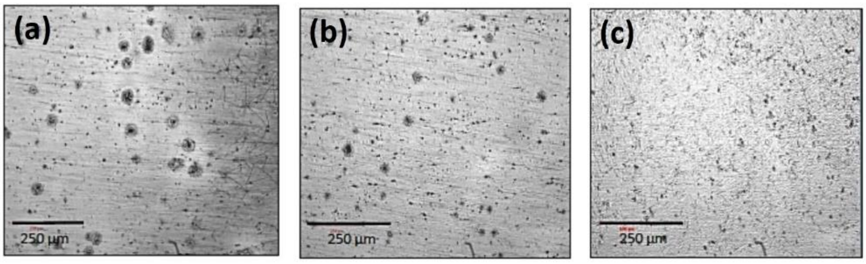

Fig. 2. Microscopic images of the coated substrates at different dipping number: (a) 3, (b) 5, and (c) 7 dipping numbers.

Figure 3 shows FESEM images of the coated film on the surface of substrate produced using various dipping numbers. The Ferret analysis for the average thickness of film with 3, 5, and 7 dipping number was about 3, 5, and 9 µm, respectively. It seems that the change of the thickness was almost proportional to the number of dipping procedure.

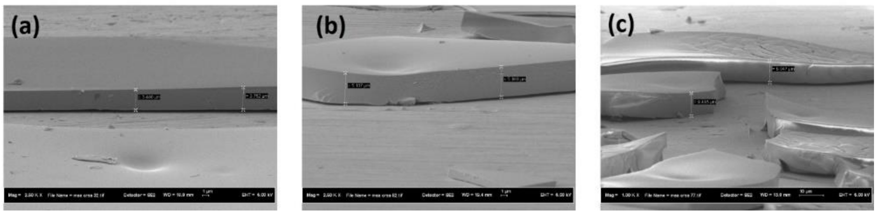

Fig. 3. Thickness of the coated substrates with different dipping number: (a) 3, (b) 5, and (c) 7 dipping number.

Further characterization of the crystal structures of the coating was done by analyzing ZrO_2, obtained by drying and annealed dipping film at 350°C for 2 hours. Then, the prepared fim was characterized using XRD (Fig. 4).

Figure 4 presents the XRD analysis results of the ZrO_2 samples after annealing process. To ensure the structure of the crystal pattern, the XRD pattern was compared to the Join Committe e Powder Difraction System (JCPDS No. 50-108) for ZrO_2 with tetragonal structure. The result showed that the identical pattern was obtained. No other peak was detected. Compared to the JCPDS, the crystal pattern in the figure revealed the existence of material consisting of ZrO_2 with tetragonal crystal structure only.

In the common ZrO_2 procedure, most of the ZrO_2 produced is monoclinic, while ZrO_2 with tetragonal crystal structures can be formed in high temperatures. The existence of tetragonal phase in this type of dip-coating process shows the effectiveness of sol-gel for accommodating the crystallization of ZrO_2 since its lower temperatures. The result is in a good agreement with other work done by Soo et al. [13].

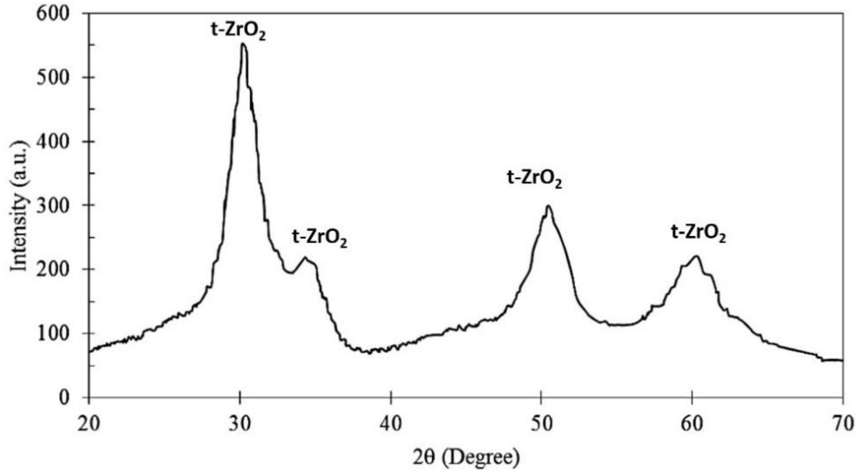

Fig. 4. XRD analysis of ZrO_2 annealed at 350°C with heating rate of 5°C/min for 2 hours.

Figure 5 presents the result of corrosion testing using the immersion test. It is shown that the number coating on the substrates has significant effects to the corrosion rate. The originated aluminum alloy (without additional coating; 0 number of coating) has the highest corrosion rate, and increases in the number of coating have a positive impact to the reduction of corrosion rate. The effects of corrosion kinetic parameters (such as corrosion current (I_{corr}), corrosion potential (E_{corr}), as well as anodic and cathodic Tafel slopes (*ßa* and *ßc*, respectively)) were studied using a potentiodynamic polarization (as shown in Fig. 6).

The result showed that the thickness of ZrO_2 coating has given benefits for improving the corrosion resistance of the coated aluminium alloy. This is shown by the fact that the corrosion potential values are more positive, informing lower corrosion resistance values. Observation of I_{corr}, it shows that I_{corr} and Tafel slopes decrease with the addition of number of coating. From cathodic tafel slopes, there have limitation of current densities, showing diffusion process to occur when materials were coated. In short, this result showed that the number coating on the substrates has significant effects to the corrosion rate [25]. The originated/bare aluminum alloy (without additional coating; 0 number of coating) has the highest corrosion rate, and increases in the number of coating bring positive impact to the reduction of the less corrosion rate.

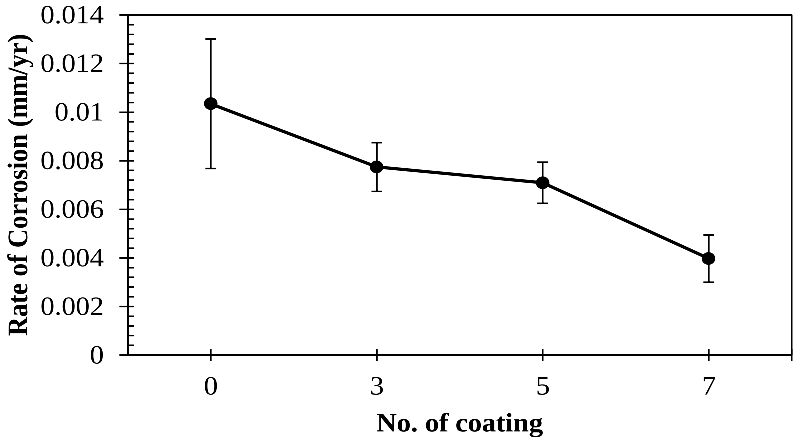

Fig. 5. Rate of corrosion of uncoated and coated substrate.

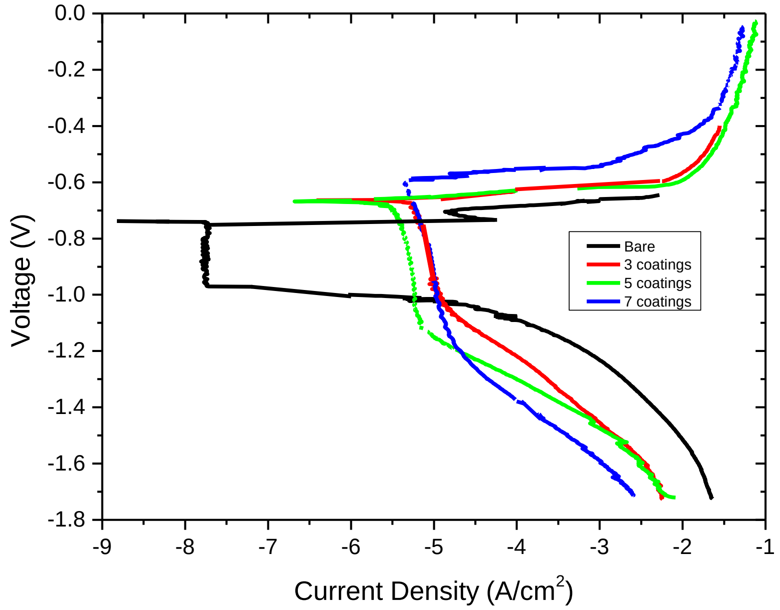

Fig. 6. Potentio-dynamic polarization curve of coated and uncoated substrates.

4. Conclusion

The ZrO_2 thin films has successfully deposited on the surface of AA2024-typed aluminum alloy via sol-gel-assisted dip-coating process. Higher dipping number has produced thicker ZrO_2 coating and reduced cracks and black spots on the surface of the coating. The additional coating number improves the corrosion performance of the coated aluminum. Therefore, ZrO_2 coating can be applied as one of the alternative for a protection barrier towards corrosion of aluminium alloys that exposed to harsh environment, such as seawater condition.

Acknowledgements

This research was fully supported by internal grant from University Malaysia Pahang under grant number RDU1403112. A.B.D.N. acknowledges RISTEK DIKTI for grant in aid Penelitian Terapan Unggulan Perguruan Tinggi Negeri (PTUPT) and Penelitian Unggulan Strategies Nasional (PUSN).

References

1. Hatch, J.E. (1984). *Aluminum: Properties and physical metallurgy*. Ohio:ASM International.
2. Totten, G.E.; and MacKenzie, D.S. (2003). *Handbook of aluminum: Vol. 1: Physical metallurgy and processes*. New York: Marcel Dekker Inc.
3. Hsu, H.C.; and Yen, S. (1998). Evaluation of metal ion release and corrosion resistance of ZrO2 thin coatings on the dental Co-Cr alloys. *Dental Materials*, 14(5), 339.
4. Lee, T.S.; Kain, R.M.; and Oldfield, J.W. (1984). The effect of environmental variables on crevice corrosion of stainless steels in seawater. *Material Performance*, 23(7), 9-15.
5. Kutz, M. (2005). *Handbook of environmental degradation of materials*. New York: William Andrew Inc.
6. Kurniawan, T.; Fauzi, F.A.B.; and Asmara, Y.P. (2016). High-temperature oxidation of Fe-Cr steels in steam condition-A review. *Indonesian Journal of Science and Technology*, 1(1), 107-114.
7. Leong, Y.; Alia, F.; and Kurniawan, T. (2016). High temperature oxidation behavior of T91 steel in dry and humid condition. *Indonesian Journal of Science and Technology*, 1(2), 232-237.
8. Bhargava, G.; and Allen, F. (2012). Self-healing, chromate-free conversion coating for magnesium alloys. *Metal Finishing*, 110, 32-38.
9. Grilli, R.; Baker, M.A.; Castle, J.E.; Dunn, B.; and Watts, J.F. (2011). Corrosion behavior of a 2219 aluminum alloy treated with a chromate conversion coating exposed to a 3.5% NaCl solution. *Corrosion Science*, 53(4), 1214-1223.
10. Osborne, H.H. (2001). Observations on chromate conversion coatings from a sol-gel perspective. *Progress in Organic Coating*, 41, 280-286.
11. Feng, Z.; Liu, Y.T.; and Skeldon, P. (2010). Sol-gel coatings for corrosion protection of 1050 aluminium alloy. *Electrochimica Acta*, 55, 3518-3527.
12. Li, Y.S.; Church, A.L.; Woodhead, N.E.; and Vecchio, J.Y. (2014). Infrared and Raman spectroscopic studies of tris-[3-(trimethoxysilyl)propyl] isocyanurate, its sol-gel process, and coating on aluminum and copper. *Spectrochimica Acta A*, 132, 225-231.
13. Soo, M.T.; Prastomo, N.; Matsuda, A.; Kawamura, G.; Muto, H.; Noor, A.F.M.; and Cheong, K.Y. (2012). Elaboration and characterization of sol-gel derived ZrO2 thin films treated with hot water. *Applied Surface Science*, 258, 5250-5258.
14. Anwar, M.A.; Kurniawan, T.; Asmara, Y.P.; Harun, W.S.W.; Oumar, A.N.; and Nandyanto, A.B.D. (2017). Morphology evaluation of ZrO2 dip coating

on mild steel and its corrosion performance in NaOH solution. *IOP Conference Series: Materials Science and Engineering*, 257(1), 012087.

15. Szklarska-Smialowska, Z. (1999). Pitting corrosion of aluminium. *Corrosion Science,* 41(9), 1743-1767.
16. Thim, G.P.; Oliveira, M.S.; Oliveira, E.D.; and Melo, F.C.L. (2000). Sol-gel silica film preparation from aqueous solutions for corrosion protection. *Journal of Non-Crystalline Solids*, 273(1-3), 124-128.
17. Wang, D.; and Bierwagen, G.P. (2009). Sol-gel coatings on metals for corrosion protection. *Progress in Organic Coatings*, 64(4), 327-338.
18. Yang, X.F.; Tallman, D.E.; Gelling, V.J.; Bierwagen, G.P.; Kasten, L.S.; and Berg, J. (2001). Use of a sol-gel conversion coating for aluminum corrosion protection. *Surface and Coatings Technology*, 140(1), 44-50.
19. Mas-Ayu, H.; Izman, S.; Abdul-Kadir, M.R.; Daud, R.; Shah, A.; Yusoff, M.F.M.; and Kamarul, T. (2014). Influence of carbon concentrations in reducing Co and Cr ions release in cobalt based implant: A preliminary report. *Advanced Materials Research*, 845, 462-466
20. Meléndez, C.L. (2012). Evaluation of corrosion resistance of thin films 304 stainless steel deposited by sputtering. *International Journal of Electrochemical Science*, 7, 1149-1159.
21. Yusoff, M.F.M.; Abdul Kadir, M.R.; Iqbal, N.; Hassan, M.A.; and Hussain, R. (2014). Dip coating of poly (caprolactone)/hydroxyapatite composite coating on Ti6Al4V for enhanced corrosion protection. *Surface and Coatings Technology*, 245, 102-107.
22. Diaz, L.; García-Galván, F. R.; Llorente, I.; Jiménez-Morales, A.; Galván, J. C.; and Feliu Jr, S. (2015). Effect of heat treatment of magnesium alloy substrates on corrosion resistance of a hybrid organic - inorganic sol-gel film. *RSC Advances*, 5, 105735-105746.
23. Rezaee, S.; Rashed, G.R.; and Golozar, M.A. (2013). Electrochemical and oxidation behavior of yttria stabilized zirconia coating on zircaloy-4 synthesized via sol-gel process. *International Journal of Corrosion*, 2013, 1-9.
24. Fedrizzi, L.; Rodriguez, F.; Rossi, S.; Deflorian, F.; and Di Maggio, R. (2001). The use of electrochemical techniques to study the corrosion behaviour of organic coatings on steel pretreated with sol-gel zirconia films. *Electrochimica Acta*, 46(24-25), 3715-3727.
25. Hamidah, I.; Solehudin, A.; Setiawan, A.; Hamdani, A.; Hidayat, M.A.S.; Adityawarman, F.; Khoirunnisa, F.; Nandiyanto, A.B.D. (in press). Corrosion study of AISI 304 on KOH, NaOH, and NaCl solution as an electrode on electrolysis proses, *Journal of Engineering, Science and Technology (JESTEC), Special Issue on AASEC'*2017.