

EFFECT OF Sn⁴⁺ ADDITIVES ON THE MICROSTRUCTURE AND CORROSION RESISTANCE OF ANODIC COATING FORMED ON AZ31 MAGNESIUM ALLOY IN ALKALINE SOLUTION

S. A. Salman^{1,3}, K. Kuroda¹, N. Saito², M. Okido¹

¹Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603 Japan

²EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan

³Graduate School of Engineering, Al-Azhar University, Nasr City, Cairo 11371, Egypt

Keywords: Mg alloy, Anodizing, Sodium Stannate Trihydrate, Alkaline solution.

Abstract

Magnesium is the lightest structural metal with high specific strength and good mechanical properties. However, poor corrosion resistance limits its widespread use in many applications. Magnesium is usually treated with chromate conversion coatings. However, due to changing environmental regulations and pollution prevention requirements, a significant push exists to find new, alternative for poisonous Cr⁶⁺. Therefore, we aim to improve corrosion resistance of anodic coatings on AZ31 alloys using low cost non-chromate electrolyte. Anodizing was carried out in alkaline solutions with tin additives. The effect of tin additives on the coating film was characterized by SEM and XRD. The corrosion resistance was evaluated using anodic and cathodic polarizations and electrochemical impedance spectroscopy (EIS). Corrosion resistance property was improved with tin additives and the best anti-corrosion property was obtained with addition of 0.03 M Na₂SnO₃·3H₂O to anodizing solution.

Introduction

Magnesium is the 8th most abundant element on the earth [1]. It is the lightest metal among all structural metal materials in the practical use with high strength-to-weight ratio. It has also attractive combinations of properties such as high thermal conductivity, dimensional stability, good electromagnetic shielding characteristics, high damping capacity and good machining characteristics. These desirable properties make it an attractive target and excellent choice for a number of applications especially when weight reducing is required. Unfortunately, magnesium has poor corrosion resistance, especially in chloride and all acids except hydrofluoric or chromic acid.

Surface treatment was performed in order to achieve a good corrosion resistance such as electrochemical plating [2], chemical conversion [3], anodizing [4, 5], physical vapor deposition [6], and electroless nickel plating [7].

Magnesium and its alloys are usually treated with chromate conversion coatings, however, hexavalent chromium compounds have been recognized as carcinogenic. Therefore, developing of non-chromate coatings that do not contain hexavalent chromium attracts much attention today [8]. In our previous works, we investigated the anodizing of Mg alloys in NaOH solution at various applied potentials. The film formed at 3 V has a dark gray color with rough surface and it mainly consisted of magnesium hydroxide. Moreover, the film was thicker than all those films formed at higher potential. On the other hand, the anodic film obtained at 100 V has a smooth surface with a white color. The main phase of the coating film was magnesium oxide. The anodic film obtained at 100 V has the lowest hydrogen evolution rate, and it has the best corrosion resistance [9].

Potassium stannate was used for the conversion treatment of magnesium alloy [10]. Moreover, it was reported that addition of tin to conversion coating solution produces a stable film with high corrosion resistance. The conversion coating consisted of hemispherical particles, which were porous and contained nanograins dispersed within the amorphous matrix. The film mainly consisted of tin, magnesium, oxygen and phosphorus species [11, 12]. In the present research, we will investigate the effect of Na₂SnO₃·3H₂O additive to 1 M NaOH alkaline aqueous solution on the microstructure and anti-corrosion property of the anodic film formed on AZ31 Mg alloy at applied potential 100 V. The anti-corrosion behaviors were evaluated using the anodic polarization curves and the electrochemical impedance spectroscopy (EIS). Furthermore, the surface morphologies and phase structure were detected using SEM and XRD.

Experimental

Specimens

Commercially available AZ31 Mg alloys were used as the substrate. The chemical composition of the alloy is listed in Table I. The surface of the alloy was polished up to #2000 emery paper followed by 0.05 μm alumina powders. The specimens were carefully cleaned with water, rinsed with acetone and dried under air. All of the experiment specimens were mounted using polytetrafluoroethylene (PTFE) resin tape, leaving 1 cm² surface area.

Table I Chemical composition of AZ31 Mg alloy (mass%)

Al	Zn	Mn	Si	Cu	Ni	Fe	Mg
3.0	1.0	0.43	0.01	<0.01	0.001	<0.003	Bal.

Anodizing

Anodizing was performed at room temperature for 0.5 – 600 s in the aqueous electrolyte of 1 M NaOH using P.R. series power supply (6 A, 500 V, manufactured in Japan) to provide various ranges of constant voltage to the anodizing cell. The applied potential used in this study was adjusted to 100 V. AZ31 magnesium alloy is connected to a positive terminal of a power supply and platinum counter electrode is connected to a negative terminal. Ag/AgCl sat. KCl reference electrode was connected to the cell in order to watch the actual voltage near the surface of the specimen and keep at constant value throughout the anodizing process. After the treatment, the specimens were carefully rinsed using distilled water and dried under air before analysis.

Morphology and Structure of Anodic Film

The morphology and microstructure of the anodic films were observed with a Hitachi S-800 scanning electron microscope (SEM), optical microscopy and digital camera. The phase structure was identified with X-ray diffraction (XRD).

Corrosion Measurements

The potentiodynamic polarization tests were carried out using a Solartron 1285 potentiostat from Solartron Analytical, Farnborough, United Kingdom. The measurements were controlled by Scribner Associates Corrware electrochemical experiment software. The anodic and cathodic polarization curves were measured in 0.1 M NaCl and 0.1 M Na₂SO₄ solution at 298 K with a scanning rate of 1 mVs⁻¹.

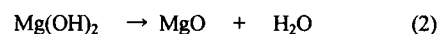
Electrochemical impedance spectroscopy of the immersed samples was measured in 3.5 mass % NaCl solution in order to accelerate the corrosion rate of the anodized specimens. The impedance test was performed at 298 K using a Solartron 1287 electrochemical interface and a Solartron 1260 frequency response analyzer with a frequency range from 100 kHz to 0.01 Hz. The measurements were controlled by Scribner Associates Z plot electrochemical experiment software.

Results and Discussion

Figure 1 shows the change in the current density as a function of time during the anodizing treatment of AZ31 magnesium alloy in 1 M NaOH with various concentrations of Na₂SnO₃·3H₂O additive.

Addition of 0.01 M Na₂SnO₃·3H₂O to 1 M NaOH solution did not affect the anodizing treatment, and it showed the same behaviours as anodizing in 1 M NaOH without Sn additive.

The current density flowed greatly first, the spark was generated, and the current became small afterwards. Moreover, sparking time was longer when 0.01 M Na₂SnO₃·3H₂O was added. The coating film after treatment has a white color similar to that formed without Na₂SnO₃·3H₂O additive. It has been reported that oxygen evolution accompanies with the intense sparking during magnesium anodizing [13]. Magnesium oxide can be formed according to the following reactions.



Addition of 0.02 M Na₂SnO₃·3H₂O made the current continue to flow from beginning to the end of the anodizing treatment with intensive spark and oxygen evolution. The coating film contains a cream color precipitates on the surface. This precipitate was also increased with the increase in Na₂SnO₃·3H₂O concentration in the anodizing solution.

Figure 2 shows the SEM images of the surface after anodizing treatment. The coating film formed in 1 M NaOH solution has a porous structure with small holes. Addition of 0.01 M Na₂SnO₃·3H₂O did not affect the surface structure of the anodic film. However, some parts of the film were destroyed due to the dielectric breakdown of the anodic films with continuous spark

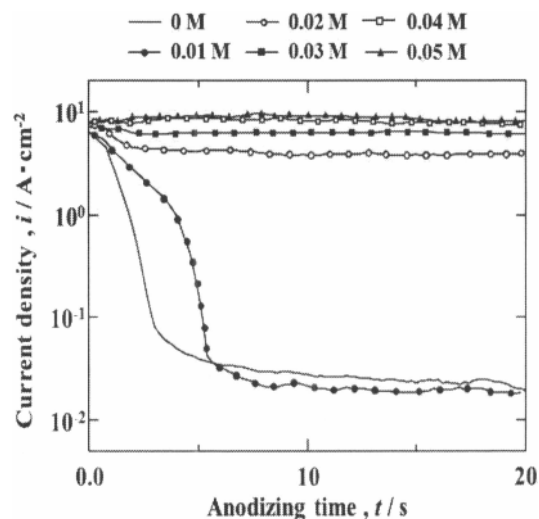


Figure 1 Change in current density with time during anodizing of AZ31 at 100 V for 20 s in 1 M NaOH with various concentrations of Na₂SnO₃·3H₂O at 298 K.

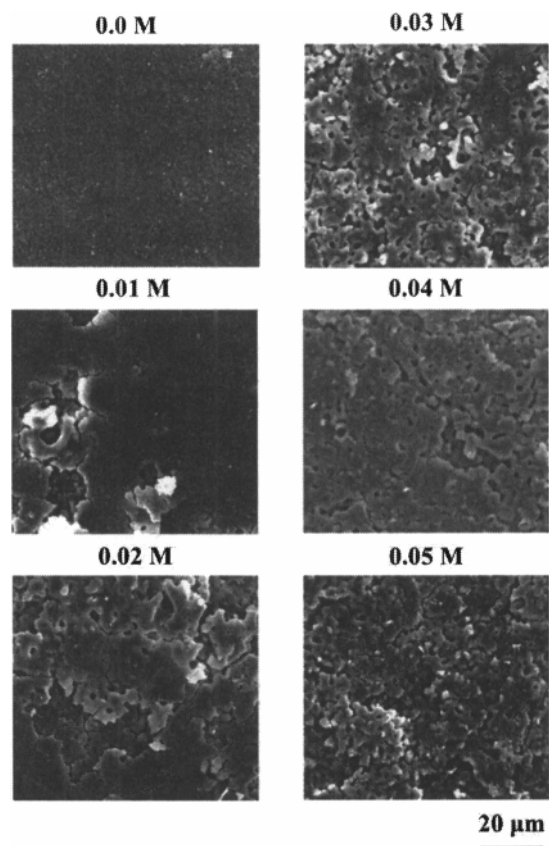


Figure 2 Surface SEM images of AZ31 anodized at 100 V for 20 s in 1 M NaOH with various concentrations of Na₂SnO₃·3H₂O at 298 K.

for long time. The porosity of the anodic films increased with the increase in $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ concentration to 0.02 M. Addition of 0.03 – 0.04 M $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ produced a porous anodic film covers the whole surface and no failure was observed. When 0.05 M $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ was added, some non-adhered powder was observed on the surface due to the increasing of $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ concentration in the anodic solution.

The cross-section of the anodic films was shown in Figure 3. The specimen anodized in 1 M NaOH shows a compact film with thickness of 1.6 μm . Addition of 0.01 $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ leads to a little increase in the film thickness. The anodic film increased to 2.85 μm , 3.55 μm , 5.7 μm , and 4.25 μm with increasing of $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ concentration to 0.02 M, 0.03 M, 0.04 M, and 0.05 M respectively. Moreover, these anodic films show rough surface with observed pores in the cross-section, which suggested that the pores on the surface extend down to the whole films. It is thought that this is an influence where the spark had been always generated throughout the anodizing treatment.

XRD analysis of the anodic films formed in 1 M NaOH solution and 1 M NaOH + 0.01 M $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ solution show two main peaks which have been identified as Mg and MgO as shown in Figure 4. After anodizing in 1 M NaOH + 0.02 M $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ solution, new peaks were detected. These new peaks were identified as Na_2SnO_3 . The intensity of these peaks increased and the peak widths became narrower with increasing the concentration of $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ from 0.02 to 0.05 M. This indicates that the Na_2SnO_3 formed in the anodic films was crystallized into a perfect crystal structure with increasing of $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ concentration in the anodizing solution. Mg_2SnO_4 peaks were detected with addition of 0.03 to 0.05 M $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ to the solution. The intensity of these peaks

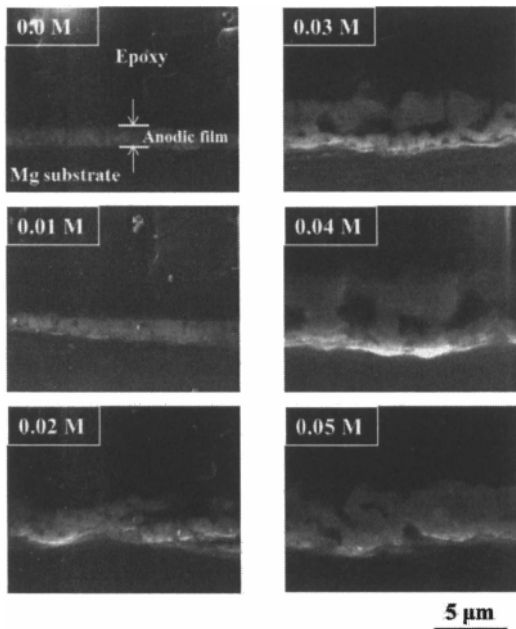


Figure 3 Cross-section SEM images of AZ31 anodized at 100 V for 20 s in 1 M NaOH with various concentrations of $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ at 298 K.

increases with a nearly linear dependence on increasing of $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ concentration in the solution.

In order to evaluate and compare the anti-corrosion properties of anodized specimens, anodic and cathodic polarization curves were measured in 0.1 M NaCl and 0.1 M Na_2SO_4 solution. Generally, the anodic polarization represents the dissolution of magnesium, the cathodic polarization curves are represents the cathodic hydrogen evolution through water reduction. The anodic polarization curves in Figure 5 were revealed clearly that the pitting potentials were moved toward more positive values with

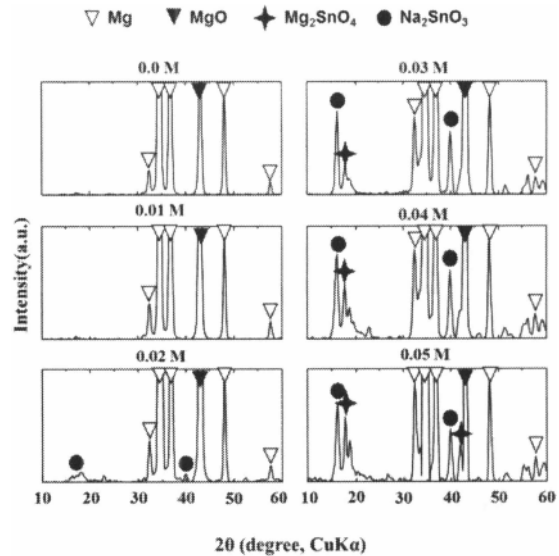


Figure 4 XRD results of AZ31 anodized at 100 V for 20 s in 1 M NaOH with various concentrations of $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ at 298 K.

anodizing in 1 M NaOH solution without $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ additives. Therefore, corrosion resistance has improved with the

anodizing treatment in 1 M NaOH with -1.36 V pitting potential. Addition of 0.01 M $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ has moved the pitting potential values to more negative potential of -1.42. With increasing the concentration of $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, the pitting potential moved to more positive values of -1.22, -1.2, -1.2 and -1.19 V at 0.02, 0.03, 0.05, and 0.04 M $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ respectively. The cathodic polarization curves were measured in order to get more information about the corrosion behaviors of the anodic film. The cathodic potential of all anodized specimens has negatively potentials in comparison to non-treated specimens, which indicate the decreasing of hydrogen evolution by the anodic passive films which mainly formed from magnesium oxide and Mg_2SnO_4 . The hydrogen evolution overpotential of all treated specimens with tin additives was better than those treated in 1 M NaOH solution and non-treated specimens.

Electrochemical impedance spectroscopy measurement (EIS) was performed to ensure the effect of $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ additives on the anti-corrosion property. Corrosion rate determination is associated with the charge transfer resistance (R_{ct}) by using EIS technique. The charge transfer resistance is equal to the diameter of the semicircle in the complex plane graph (nyquist diagram).

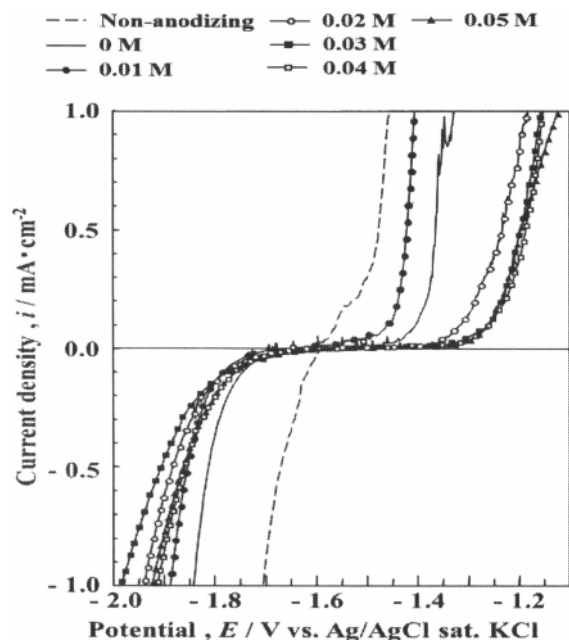


Figure 5 Polarization curves in 0.1 mass% NaCl + 0.1 M Na₂SO₄ solution at 298 K with scan rate of 1 mVs⁻¹ for AZ31 anodized at 100 V for 20 s in 1 M NaOH with various concentrations of Na₂SnO₃·3H₂O at 298 K.

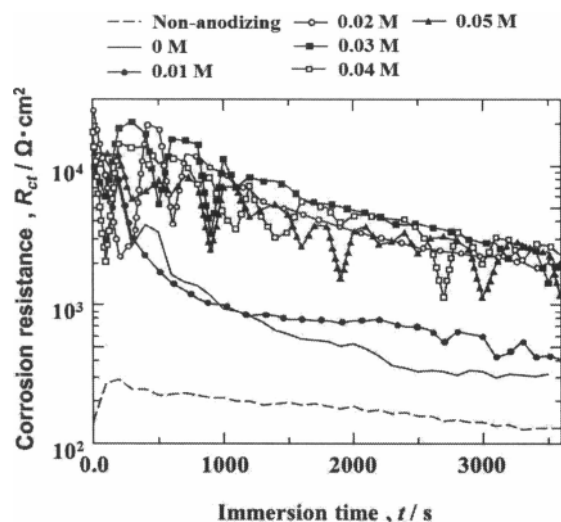


Figure 6 Corrosion resistance in 3.5 mass% NaCl solution for AZ31 before and after anodizing at 100 V in 1 M NaOH with various concentrations of Na₂SnO₃·3H₂O for 20 s at 298 K.

Figure 6 shows the time dependence of the charge transfer resistance, which is corresponding to corrosion rate. The charge transfer resistance increases with anodizing treatment. The non-treated specimen and those anodized in 1 M NaOH with and without 0.01 M Na₂SnO₃·3H₂O additive have the lowest R_{ct} value. On the other hand, the films formed in 1 M NaOH + (0.02 M-0.05 M) Na₂SnO₃·3H₂O have higher R_{ct} values. The highest value was observed with addition of 0.03 M Na₂SnO₃·3H₂O. This result is in agreement with anodic polarization measurements. The reciprocal values of R_{ct} for the anodic films formed at high Na₂SnO₃·3H₂O concentration, it may be results from shifting of the pH to more alkaline side due to the dissociation of the tin contained films.

Conclusions

Anodizing of AZ31 Mg alloy was performed at 100 V constant potential in 1 M NaOH solution with various Na₂SnO₃·3H₂O concentrations. The Thickness of the anodic film increased notably with tin additives to alkaline solution. The anodic film increased from 1.6 μm to, 5.7 μm, with increasing of Na₂SnO₃·3H₂O concentration to 0.04 M. Some tin compounds such as Mg₂SnO₄ were included in the anodic films. The anti-corrosion property was improved with addition of 0.03 M Na₂SnO₃·3H₂O to anodizing solution due to the increasing of film thickness several orders of magnitude and formation of new tin compounds during anodizing process.

Acknowledgment

The authors gratefully acknowledge the financial support of the Ministry of the Education, Culture, Sports, Science and Technology, Japan. We wish also to acknowledge Professor Ryoichi Ichino of Ecotopia Science Institute, Nagoya University who gave me a lot of valuable discussion and advices during this research. Special thanks go to Ryuzo Mori and Dai Yamamoto of the Department of Material Science and Engineering, Nagoya University for their assistance during the experiments.

References

1. H. Baker et-al., eds., *Metals Handbook: Magnesium and Magnesium Alloys*, (Metals Park, OH: American Society for Metals, 1999), 3-84.
2. J.E. Gray and B. Luan, Protective coatings on magnesium and its alloys – a critical review, *Journal of Alloys and Compounds* 336, 88-113 (2002).
3. S. A. Salman, Ryoichi Ichino, and Masazumi Okido, "Development of Cerium-based Conversion Coating on ZA31 Magnesium Alloy," *Chemistry Letters*, 36 (8) (2007), 1024-1025.
4. S. A. Salman, R. Ichino and M. Okido, "Production of Alumina-Rich Surface Film on AZ31 Magnesium Alloy by Anodizing with Co-Precipitation of Nano-Sized Alumina," *Materials Transactions*, 49 (5) (2008), 1038-1041.
5. S. A. Salman, R. Ichino and M. Okido, "Influence of Calcium Hydroxide and Anodic Solution Temperature on Corrosion Property of Anodizing Coatings Formed on AZ31 Mg Alloys," *Surface Engineering*, 24 (3) (2008), 242-245.
6. B.L. Yu and J.Y. Uan, "Sacrificial Mg film anode for cathodic protection of die cast Mg-9wt. %Al-1wt.%Zn

- alloy in NaCl aqueous solution," *Scripta materialia*, 54 (2006), 1253-1257.
7. W.J. Cheong, B.L. Luan and D.W. Shoesmith, "Protective coating on Mg AZ91D alloy-the effect of electroless nickel (EN) bath stabilizers on corrosion behavior of Ni-P deposit," *Corrosion Science*, 49, (2007), 1777-1798.
 8. H. Umehara, M. Takaya, & Y. Kojima, "An Investigation of the Structure and Corrosion Resistance of Permanganate Conversion Coatings on AZ91D Magnesium Alloy," *Materials Transactions*, 42 (8) (2001), 1691-1699.
 9. S. A. Salman, R. Mori, R. Ichino and M. Okido, "Effect of Anodizing Potential on the Surface Morphology and Corrosion Property of AZ31 Magnesium Alloy," *Materials Transactions*, 51 (6) (2010), 1109- 1113.
 10. A. R. Shashikala, R. Umarani, S. M. Mayanna and A. K. Sharma, "Chemical Conversion Coatings on Magnesium Alloys - A Comparative Study," *International Journal of Electrochemical Science*, (9) (2008), 993-1004.
 11. C.S. Lin, H.C. Lin, K.M. Lin, W.C. Lai, "Formation and properties of stannate conversion coatings on AZ61 magnesium alloys," *Corrosion Science*, 48 (2006), 93-109.
 12. Lihui Yang, Milin Zhang, Junqing Li, Xiang Yu, Zhongyi Niu, "Stannate conversion coatings on Mg-8Li alloy," *Journal of Alloys and Compounds*, 471 (2009), 197-200.
 13. F. A. Bonilla, A. Berkani, Y. Liu, P. Skeldon, G. E. Thompson, H. Habazaki, K. Shimizu, C. John, and K. Stevens, "Formation of Anodic Films on Magnesium Alloys in an Alkaline Phosphate Electrolyte," *Journal of the Electrochemical Society*, 149 (1) (2002), 4-13.