Corrosion Inhibition of Magnesium by Anodizing In Safe and Unsafe Alkaline Electrolytes

Mahmoud Abbas, Salah Salman, Shaimaa Ali Abou El Ela

Abstract: Magnesium has high strength to weight ratio , good machinability , high creep stress and high impact resistance . Such properties make the magnesium an excellent choice in many applications . Disadvantages of magnesium represented in low corrosion resistance in most environments and ignites easily in air . Surface modification techniques which are used to improve surface properties of Magnesium are conversion surface treatments like chromating , phosphating , galvanizing electroplating such as Cu , Zn , Ni , Cr , electroless metal plating and cladding by Aluminum foil .

Anodizing in an electrolyte (with pH>12) is considered a passivation process that produces chemical stable protective oxide film on magnesium surface . Usually unsafe electrolytes such as KOH are frequently used . Anodizing of commercial magnesium (ASTM 9980A) was carried out in 3M KOH(unsafe) , 1M Na₂SiO₃ and 0.6M K₂SiO₃(safe) electrolytes for time periods ranging from 10 to 50 minutes at constant voltage of 5V .The anode was magnesium specimen where the cathode was stainless steel type AISI 304 . Energy Dispersive X-Ray(EDX) and X Ray Diffraction (XRD) approved that magnesium Oxide (MgO) is the anodic film when using 3M potassium hydroxide electrolyte and a magnesium Silicate with a glassy morphology formed in the anodic film using safe electrolytes of 0.6M potassium silicate and 1M sodium silicate . Maximum film thickness reaches to 46 , 27,47 µm after anodizing at 30 min using 3M potassium hydroxide ,1M Sodium silicate , 0.6M Potassium Silicate respectively . It was found that the corrosion rate of commercially pure magnesium decreased from 37 to 7 , 2.2 , 1.3 mpy when using 3M potassium hydroxide , 1M sodium silicate , 0.6M potassium silicate respectively . At the same time the contact angle increases from 70 degrees to 114º, 105º , 113º degrees using the same electrolytes . An increase in microhardness of the anodic films was observed in 3M potassium hydroxide , 1M sodium silicate and 1M potassium silicate respectively . The adhesion of the anodic film measures according to ASTM D3359 method 13 for thickness <125 µm was classified in 3B which denote that the amount of the layer released by the adhesive tape lies from 5-15% of the formed layers using the three electrolytes.

Keywords : anodizing , corrosion , corrosion inhibition , alkaline solutions.

I. INTRODUCTION:

Magnesium has attractive combinations of properties such as high thermal conductivity, dimensional stability, good electromagnetic shielding characteristics and good machining characteristics [1] . These desirable properties make Magnesium an attractive target in a number of applications, especially in the fields where weight reducing is important[2,3]. Despite of these competitive advantages over rival conventional materials , the applications are still restricted due to high corrosion susceptibility [4]. Moreover , effective protection against galvanic and general corrosion is difficult to achieve only by continuing alloy development of Magnesium. Anodizing process is used to protect magnesium and its alloys by forming chemically stable protective layer on surface using alkaline electrolytes with or without various additives[2]. Anodizing of AZ31 and AZ91 using different electrolytes and potentials were carried out and described by N.A El Mahllawy, Basheer Ahmed , Yun-II Chio , Salah Salman,K.Kurada , Salih Durdu , A. K Ehmeda , Z.P.Cai. [1-11] while anodizing of commercial pure magnesium ,Salih Durdu [10] found that oxide coatings were produced on magnesium using micro-arc oxidation in different aqueous solutions of Na_2SiO_3 and Na_3PO_4.

In this study three types of alkaline solutions were used . Sodium silicate and potassium silicate are considered as a safe chemical electrolyte while potassium hydroxide is not safe. Effect of anodizing time on thickness, hardness , adhesion ,microstructure and electrochemical behavior of the anodized layer were investigated.

2-Experimental Work :

2-1 Materials :

Chemical composition of used magnesium ASTM (9980A) was conducted by X-ray fluorescence (XRF) Spectrometer Model NITON XL3 T980 GOLD, as shown in Table 1.

Table 1:Chemical composition of pure Mg used in wt%.

IDS Avg of two runs each ID	Magnesium	Aluminum	Silicon	Vanadium	Chrome
Magnesium(841)	99.54	0.211	0.1	0.087	0.052

The specimens were cut from the block with area of 1 cm² cross section and 1 cm height .

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Then specimens were mounted in epoxy resin and the surface of the specimens were grounded with emery paper up to 2000 grit , the specimens were carefully cleaned with distilled water rinsed with acetone and dried under air.

2-2 Anodizing electrolytes

The electrolyte was prepared at room temperature with distilled water with 3M potassium hydroxide, 1M Sodium Silicate and 0.6M potassium silicate concentrations as PH of 13 .

2-3 Anodizing Cell

Anodizing process was carried out at room temperature using two electrode cell and a DC power supply . The electrolytes of 200 ml volume was contained in a glass cell . The anode was the magnesium specimen while the cathode was a stainless steel bar . The samples were anodized under constant voltage of 5 V for 10 , 20 , 30 , 40 , 50 minutes. The film formed on the surface were rinsed by distilled water and dried in warm air . The surface morphologies and phases of the film were studied using an optical microscope (OPTIKA), a scanning electron microscopy (SEM, FEI Inspect S50) attached with EDX unit , and X-Ray Diffraction device (XRD PANalytical X Pert Pro NC 4022) . The contact angle was measured by Attension Biolin device (Model: Theta Optical Tensiometers), and the drop size was 5 μ litre of double distilled water at ambient temperature. Electrochemical behavior was conducted in 3 wt. % NaCl solution at room temperature via Versa Stat potentiostat device. The corrosion cell was equipped with a standard three-electrode system: platinum electrode was used as the counter electrode, the calomel electrode (SCE) as the reference electrode and magnesium specimen as the working electrode. Before electrochemical experiments, these magnesium specimens were immersed in 3%NaCl solution for 20 minutes to achieve a stable open circuit potential (OCP vs SCE). The potentiodynamic polarization curves were measured between −0.15 V and 0.15 V (vs. OCP) with the scanning rate of 1 mV/s. Thickness measurements were carried out using Coating thickness gage(PosiTest DFT Combo) ASTM B244/B499/D7091/E376, BS3900-C5, SSPC-PA2 and Optical microscope (OPTIKA). And the Adhesion was carried out using Tape adhesion Test ASTM D3359 .

3- Results and Discussion :

3-1 Contact angle measurements:

Contact angle was measured at different anodizing times for 3M potassium hydroxide , 1M sodium silicate and 0.6M potassium silicate solutions . As indicated in figure(1) It reaches $114^o, 105^o, 113^o$ for 30 minutes anodizing in 3M potassium hydroxide , 1M sodium silicate , 0.6M potassium silicate respectively . That's proves that a hydrophobic layer is formed on the surface of the substrate.
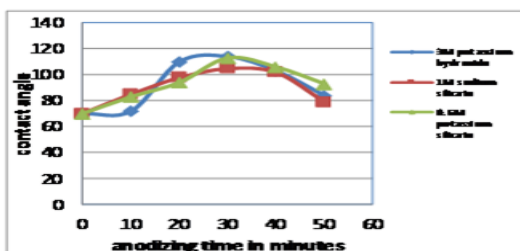
Figure (1) :The effect of anodizing time on the contact angle .

3-2 Polarization measurements :

Results of corrosion rate determination by linear polarization techniques table (2) are in good agreement with contact angle measurements i.e condition which gives the highest contact angle showed the lowest corrosion rate. Polarization curves figure (2) of the specimens anodized in 3M potassium hydroxide , 0.6M potassium silicate , 1M sodium silicate solutions for 10 , 20 , 30 , 40 and 50 minutes were shifted to the positive direction i.e it became more noble , and at the same time shifted to the left relative to the unanodized specimen indicating less dissolution .The electrochemical corrosion parameters which are listed in table(2) indicate that the corrosion rate decreased from 36.8 mpy for pure Magnesium to 7 mpy with efficiency of 81.02% for 30 minutes anodizing in 3M potassium hydroxide electrolyte and decreased to 2.27 mpy with efficiency of 93.84% for 30 minutes anodizing in 1M sodium silicate electrolyte also decreased to 1.38 mpy with efficiency of 96.25% for 30 minutes anodizing in 0.6M potassium silicate electrolyte . Potassium silicate electrolyte has given us better corrosion resistance than using sodium silicate electrolyte besides having good safe environmentally friendly properties .
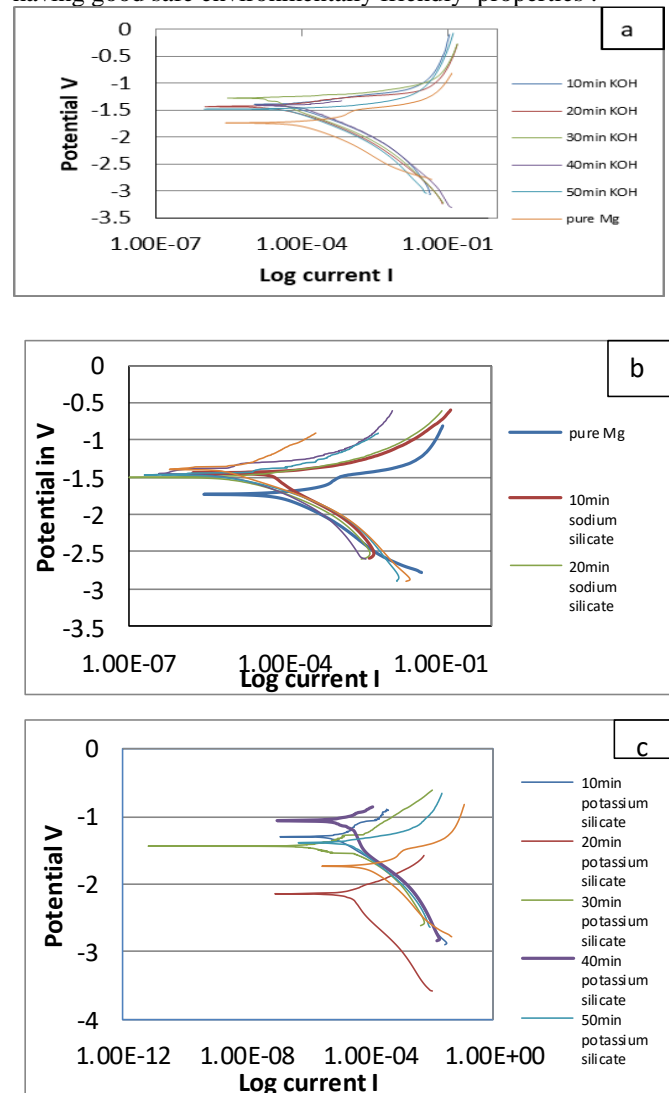
FIGURE(2) : Potentiodynamic Polarization Curves For Pure

Magnesium And AnodizedSpecimens In (A)3M Potassium Hydroxide (B)1M Sodium Silicate (C)0.6M Potassium Silicate Electrolytes For 10,20,30,40 And 50 Minutes.

TABLE(2) : Results of linear polarization experiments for anodized specimens in 3M potassium hydroxide,1M sodium silicate and 0.6M potassium silicate electrolytes for 10,20,30,40 and 50 minutes .

Results of linear polarization experiments of 3M potassium hydroxide .				
Specimen for	E_{corr}, V	R_p, Ω/cm^2	I_{corr}, $\mu A/cm^2$	corrosion rate, mpy	Effeciency,%
pure mg substrate (Blank)	-1.739	650.107	33.439	36.888	-
10min	-1.419	764.008	28.454	25.255	31.53
20min	-1.453	1062	20.464	18.164	50.75
30min	-1.273	2756	7.887	7.0005	81.02
40min	-1.378	1892	11.488	12.673	65.64
50min	-1.483	951.822	22.839	25.195	31.69

Results of linear polarization experiments of 1M sodium silicate.				
Specimen for	E_{corr}, V	R_p, Ω/cm^2	I_{corr}, $\mu A/cm^2$	corrosion rate, mpy	Effeciency,%
pure mg substrate (Blank)	-1.739	650.107	33.439	36.888	-
10min	-1.357	2000.324	9.353	8.4977	76.96
20min	-1.511	2000.691	8.077	7.3385	80.1
30min	-1.427	8000.692	2.5	2.2721	93.84
40min	-1.462	4000.049	5.368	4.8776	86.77
50min	-1.392	3000.747	5.8	5.2695	85.71

| Results of linear polarization experiments of 0.6M potassium silicate .				
Specimen for	E_{corr}, V	R_p, Ω/cm^2	I_{corr}, $\mu A/cm^2$	corrosion rate, mpy	Effeciency,%
pure mg substrate (Blank)	-1.739	650.107	33.439	36.888	-
10min	-1.298	3000.298	6.589	5.9866	83.77
20min	-2.11	4000.908	4.429	4.0237	89.09
30min	-1.44	14000.282	1.522	1.3828	96.25
40min	-1.033	6000.863	3.167	2.8775	92.19
50min	-1.375	2000.605	8.343	7.5798	79.45

3-3 X- ray Diffraction .

Figure (3) illustrates X-ray diffraction patterns results of formed films after anodizing for 30 minutes using anodizing electrolytes 3M potassium hydroxide , 1M sodium silicate and 1M silicate respectively . As shown in figure (3) MgO and $Mg(OH)_2$ were the main phases formed during anodizing; It is clear that the MgO amount was larger than that of $Mg(OH)_2$. The intensity of the peaks of MgO produced in the potassium hydroxide solution was strong owing to the thick film produced . While in the case of 1M Sodium Silicate solution the dominating phase is $Mg_2SiO_4(2MgO.SiO_2)$. For 0.6M potassium silicate solution the dominating phase is also Mg_2SiO_4 $(2MgO.SiO_2)$. Both anodized films using sodium silicate and potassium silicate are partially structured with a glassy morphology as indicated in figure (3). The intensity of the peaks of $Mg_2SiO_4(2MgO.SiO_2)$ produced in sodium silicate solution was similar to that produced in 0.6M potassium silicate solution but for 0.6M potassium silicate solution some peaks show amorphous structure . The occurrence of these phases indicate that the substrate and the solution both contribute in forming the anodic film.
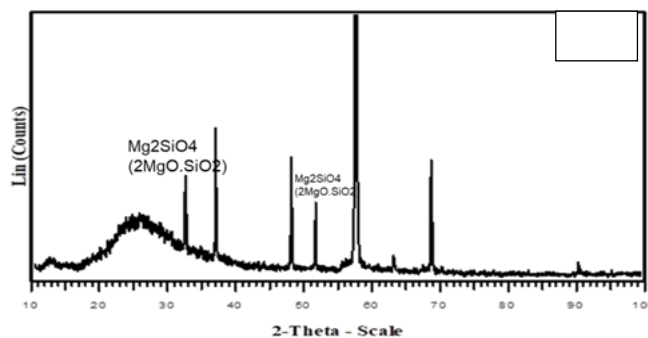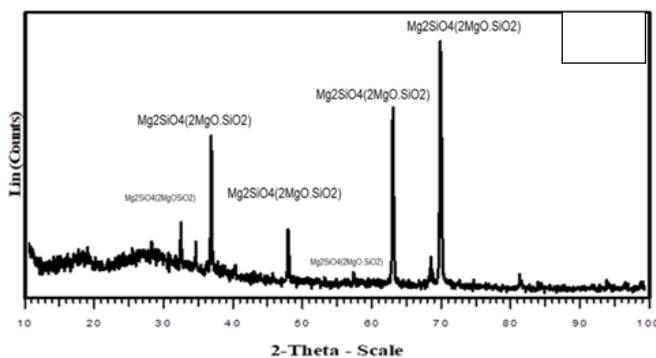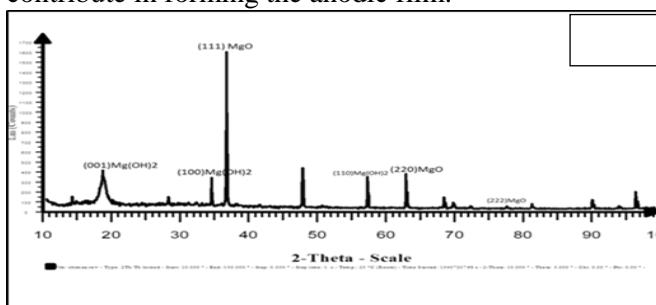
FIGURE(3):XRD SPECTRA OF 30 MINUTES ANODIZED SPECIMENS (A) 3M POTASSIUM HYDROXIDE ELECTROLYTE (B)1M SODIUM SILICATE ELECTROLYTE (C) 0.6M POTASSIUM SILICATE ELECTROLYTE.

3-4 Film thickness measurements :

Figure (4) shows variation of film thickness with time using the three different electrolytes 3M potassium hydroxide , 1M sodium silicate and 0.6M potassium silicate electrolytes.
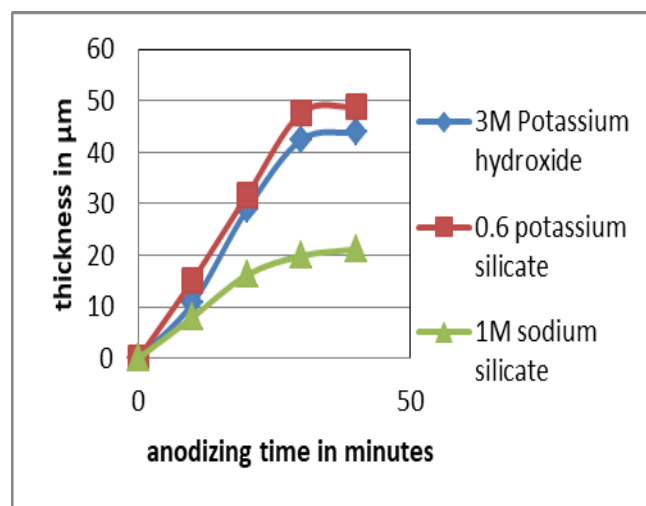
Figure(4):Effect of anodizing time on film thickness by using 3M potassium hydroxide , 1M sodium silicate and 0.6M potassium silicate electrolytes at constant voltage.
The film thickness for the three solutions increases with the anodizing time rapidly in the first 30 minutes with a slow rate after 30 to 40 minutes .

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This behavior is due to the increase in the thickness of the anodized layer acting as barrier to the flow of current which decreases the rate of oxidation of magnesium . From the results the optimum deposition time used to obtain maximum thickness was 30 minutes for 3M potassium hydroxide , 1Msodium silicate , 0.6M potassium silicate electrolytes .The thickness of the anodic film changed according to the type of the electrolyte figure(5). The average thicknesses of formed anodic films which achieve the lowest corrosion resistance of 3M potassium hydroxide , 1M Sodium Silicate and 1M Silicate were measured using optical microscope and Posi Test DFT Combo are 47 µm, 26 µm and 48 µm respectively. Films produced in the 0.6M potassium silicate electrolyte were the thickest in comparison with those produced in 3M potassium hydroxide solution and 1M Sodium Silicate electrolytes for the same volt 5V **.**
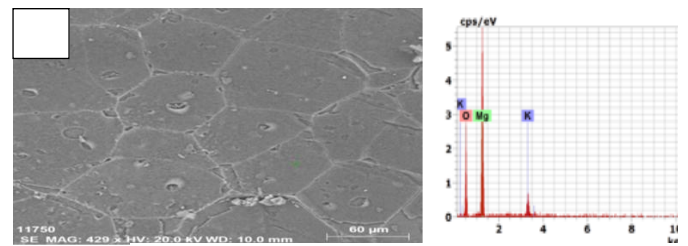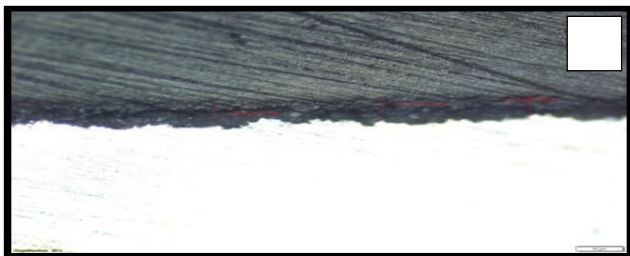

SILICATE ELECTROLYTE (C) 0.6M POTASSIUM SILICATE **.**

3-5 Surface Morphology and EDX results :

Figure(6-a) shows the SEM for unanodized polished specimen. The surface morphology of the anodic film figure (6-b) reveals that homogenous distribution of oxides produced in KOH electrolyte. It contains dark spots which indicate the anodizing process deposited the oxides MgO on the surface of the metal . No cracks were observed in the anodized layer . Film produced in sodium silicate solution in figure(6-c) shows heterogeneous structure with microcracks in the outer layer of the film . Some domains of the anodized layer have amorphous structure and others have ordinary one. It was observed that the Layer produced in potassium silicate solution has more domains of amorphous structures than those produced in the layer of sodium silicate solution . The layer consists of a mixture of both amorphous and ordinary domains causes more micro cracks on the outer layer on the surface figure (6-d) .
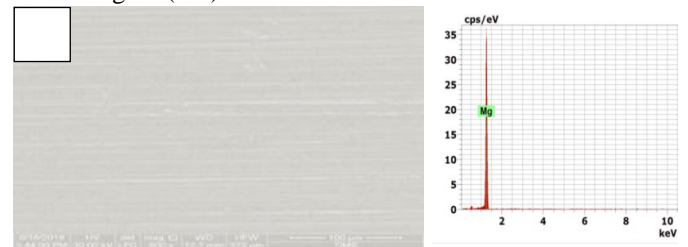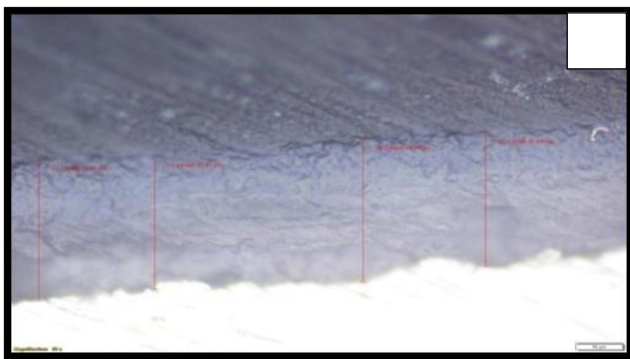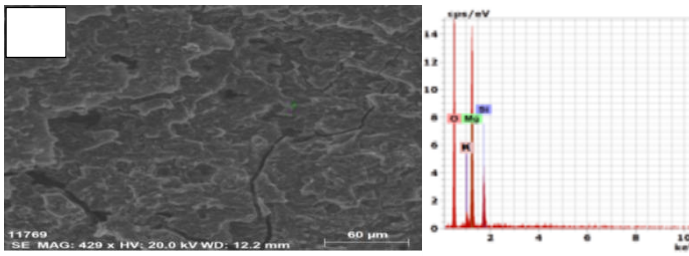

Base metal

3M potassium hydroxide
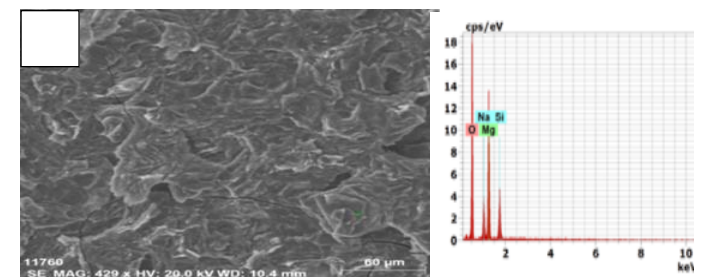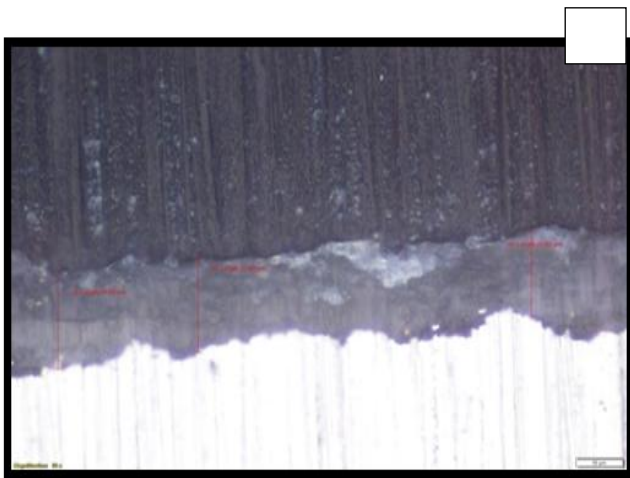
1M sodium silicate

FIGURE(5) : FILM THICKNESS OF 30 MINUTES ANODIZED SPECIMENS USING(A)3M POTASSIUM HYDROXIDE ELECTROLYTE (B)1M SODIUM

0.6M potassium silicate

Figure(6): Surface morphology and spectrum analysis of (a)pure magnesium (b)30minute anodized specimen in 3MKOH electrolyte (c)30mintes anodized specimen in 1M sodium silicate electrolyte (d)30minutes anodized specimen in 0.6M potassium silicate electrolyte.

3-6 Microhardness measurements :

Shore hardness test indicate that the micro hardness for the produced film using 3M potassium hydroxide , 0.6M potassium silicate and 1M sodium silicate solutions are 97(85.6RHN) , 88(83.4RHN) and 99(86RHN) respectively .
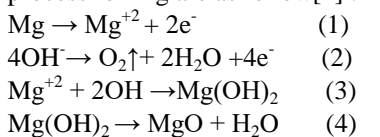
3-7 Film adhesion testing :

The analysis of the anodic obtained film layers showed that they contain Mg- MgO – Mg2SiO4 . This indicates that the metallic substrate has diffused into the anodized film layer resulting in further enhancement of the adhesion . Adhesion was measured according to ASTM D 3359 method 13 , thickness <125 µm . The adhesion of the anodic films classified as 3B which denote that the amount of the layer released by the adhesive tape lies from 5-15% of the formed layer .
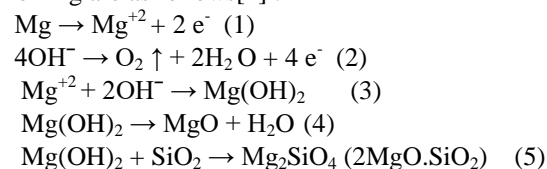
4- Mechanism of anodizing process:

Mechanism of anodizing process could be explained as dissolution and oxygen evolution process [11 -16]. Anions in the electrolyte first need to reach at the anode/electrolyte interface and then enter into anodic coatings [2].

The general reactions using 3M KOH solution in anodizing process for Mg are as follow[2] :

$$Mg \rightarrow Mg^{+2} + 2e^- \qquad (1)$$
$$4OH^- \rightarrow O_2\uparrow + 2H_2O + 4e^- \qquad (2)$$
$$Mg^{+2} + 2OH \rightarrow Mg(OH)_2 \qquad (3)$$
$$Mg(OH)_2 \rightarrow MgO + H_2O \qquad (4)$$

The general reactions occurring in the anodizing process using 1mole sodium silicate and 0.6 mole potassium silicate for Mg are as follows[1] :

$$Mg \rightarrow Mg^{+2} + 2 e^- \quad (1)$$
$$4OH^- \rightarrow O_2 \uparrow + 2H_2O + 4 e^- \quad (2)$$
$$Mg^{+2} + 2OH^- \rightarrow Mg(OH)_2 \quad (3)$$
$$Mg(OH)_2 \rightarrow MgO + H_2O \quad (4)$$
$$Mg(OH)_2 + SiO_2 \rightarrow Mg_2SiO_4 \ (2MgO.SiO_2) \quad (5)$$

During the oxidation process , the Mg ions , produced by reaction(1) combine with the OH^- in the electrolyte solution to form $Mg(OH)_2$ and $Mg_2SiO_4(2MgO.SiO_2)$ reactions(3) and (5) , respectively. The hydroxides change to oxide compounds by the dehydration process , reaction(4). The film formation processes ,reactions(3),(4)and(5) may be promoted by a high concentration of the electrolyte , containing more SiO_2 and OH^- ions .

5- Conclusions :

- The corrosion rate of pure magnesium decreases from about 37 mpy to be 7, 2 ,1.4 mpy with efficiency of 81% , 93.84% , 96.25% for 30 minutes anodized specimens using 3M potassium hydroxide ,1M sodium silicate and 0.6M potassium silicate electrolytes respectively .
- Safe electrolytes (sodium silicate and potassium silicate) used have shown better corrosion resistance than using unsafe electrolyte (potassium hydroxide).
- XRD diffraction & EDX confirms that for 30 minutes anodized specimens the film is mainly consists of magnesium oxide using 3M potassium hydroxide electrolyte and mainly consists of magnesium silicate Mg_2SiO_4 with a partially amorphous structure using 1M sodium silicate and 0.6M potassium silicate .
- The contact angle of pure magnesium changed from 70^0 (hydrophilic) to $114^o,105^o,113^o$ (hydrophobic) for 30 minutes anodized specimens using 3M potassium hydroxide , 1M sodium silicate and 0.6M potassium hydroxide electrolytes respectively.
- Film thickness reaches 48, 26 , 47µm for 30 minutes anodized specimens in 3M potassium hydroxide , 0.6M potassium hydroxide and 1M sodium silicate electrolytes respectively .
- Hardness of the anodic films has increased from 38 to 85.6 , 83.4 and 86 RHN for 30 minutes anodized specimens in 3M potassium hydroxide , 0.6M potassium hydroxide and 1M sodium silicate electrolytes respectively .
- According to ASTM D3359 method 13 for thickness <125 µm .The adhesion of 30 minutes anodic films using the three electrolytes are classified as 3B which denote that the amount of the layer released by the adhesive tape lies from 5-15% of the formed layer .

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