C- RESULTS

Fig (3) shows representation galvanostatic cyclic polarization curves of the pure Al electrode in 0.1M Na_2SO_4 solution with a polarizing current density of 20.715 $\mu A/cm^2$. Figs (4-7) represents the galvanostatic cyclic polarization curves of alloy samples I, II, III and IV respectively in 0.1M Na_2SO_4 aqueous solutions. The polarizing current densities are respectively, 20.715 $\mu A/cm^2$, 18.349 $\mu A/cm^2$, 19.479 $\mu A/cm^2$ and 18.349 $\mu A/cm^2$.

In all above mentioned figures (Figs. 3-7), the curves marked (A) are the anodic parts, while those labeled (C) are the cathodic parts of the galvanostatic cycles. (AD) is the characteristic anodic-decay curves obtained at the end of the cycles by switching-off the polarizing current when the potential of the electrode was at the oxygen evolution value at the end of the third polarization cycle.

The effect of addition of increasing concentrations of the aggressive Cl^- ion on the stability of the anodically formed passive-film on the surface was also examined in 0.1M Na_2SO_4 solutions.

The curves of Fig (8) show the effect of increasing concentrations of Cl^- ions on the characteristics of the galvanostatic anodic polarization curves of pure Al in 0.1M Na_2SO_4 solution at a constant current density of 20.715 $\mu A/cm^2$. Figs. (9-12) show the corresponding galvanostatic polarization curves for the four alloys (samples I, II, III and IV) , respectively , at the current densities given before.

The curves of Figs. (13-16) represent, successively, the effect of addition of increasing concentrations of the sodium salts of chromate, bicarbonate, molybdate and mono-hydrogen phosphate as inhibiting agents on the galvanostatic anodic polarization curves of pure Al electrode in 0.1M Na_2SO_4 +0.002M NaCl solution at a constant current density of 20.715 $\mu A/cm^2$.

Figs (17-32) represent, the effect of addition of increasing concentrations of the above mentioned salts on the galvanostatic anodic polarization curves for the four alloys (samples I, II, III and IV), respectively, in 0.1M Na_2SO_4 + 0.002M NaCl solutions at the current densities mentioned before.

D- DISCUSSION

Results of the cyclic galvanostatic measurements of the pure aluminium electrode and the four alloys in 0.1M Na_2SO_4 solutions at a constant current densities are shown in Figs. (3-7). Inspection of these figures reveals that the general features of all the curves are the same.

Fig. (3) shows the behaviour of pure aluminium electrode in 0.1M Na_2SO_4 solution at the current density 20.715 $\mu A/cm^2$ at 25°C. In the anodic half-cycle (A) the potential rises immediately from the begining of polarization. The charging curve is characterized by a non-linear rapid rise of potential with time extending to high potential values. The potential range over which this takes place amounts to 2 volts.

Trace analysis using the alizarin test(93) during anodic polarization of Al in H_3PO_4 and Na_2HPO_4 solutions indicated the presence of Al^{3+} ions (13). The results led to the assumption that, deviation from linearity at high potentials is associated with an increase of metal ion concentration in solution. It appears, therefore, that the behaviour at the begining of the charging curves is related to the occurence of more than one electrochemical process (94). Since free oxygen evolution does not take place, it is likely that, in addition to charging of the double layer anodic dissolution as well as oxide formation occur simultaneously from the begining. The efficiency for either process is not constant in the same electrolyte, but varies with the time of polarization at constant current density, and with the type of electrode at a fixed polarization period.

Hence, the potential rise with time occured is indicative of more oxide formation on the electrode surface. Anodic dissolution can still occur with a lower efficiency through the pores of the yet incomplete film. When the film becomes complete, the efficiency for film growth approaches 100%, and the anodic current density is mainly utilized to deposite other layers of oxide. Once this stage is reached, the oxide thickness increases linearly with time at a constant current density.

Since the deviation from linearity at high potentials is accompained by an increase of the concentration of the metal ion in solution and an extended oxygen evolution on the surface, it appears, therefore, that this behaviour may be related to structural changes in the oxide film. These changes may occur as a result of either: (i) crystallization of the amorphous oxide(15) which becomes less protecting, thus allowing the access of electrolyte to the bare metal through cracks, or (ii) dielectric breakdown of the oxide film by means of the avalanch type of breakdown. joule heating or internal compressive stress(95,7). Previous results(7) indicated that the breakdown voltage for the anodic film on Al depends on the nature of electrolyte.

Cathodic polarization half-cycles (C) was obtained by reversing the polarizing current when the electrode was at oxygen evolution potential so as to make the working electrode the cathode. It is clear from Fig. (3) that, the potential drops almost directly to a more negative values, displaying a small dip before levelling up. The second polarization cycle reveals a rapid linear rise of potential in the anodic half-cycle (A). The duration to oxygen evolution (time of passivation) is shorter than of the first cycle. It appears reasonable to attribute this to the presence of some oxide on the electrode surface usually remaining from the first polarization cycle. It is of interest to note that, the potential at which oxygen evolution occurs is higher in the third cycle than the two first and second ones. This may due to the changes be found in the nature of the passive electrode surface as a result of cyclization.

The anodic decay curve (AD) reveals that, upon interrupting the polarization current, the potential of the electrode drops almost directly to more noble value than that required for hydrogen evolution.

From Figs. (4 and 5) representing the cyclic galvanostatic curves of alloys (I and II) in 0.1M Na_2SO_4 solution at current densities of 20.715 and 18.349 $\mu A/cm^2$, respectively, one observes a linear build up of the potential in the first anodic cycle (A). This is due to the decay of the hydrogen overpotential on the electrode surface and the subsequent charging of the anodic double layer at the metal/solution interface. However, free oxygen evolution does not occur during the linear potential rise. As the charging curves deviate from linearity at relatively high potentials, which depend on the type of the electrode and the number of cycle, oxygen evolution commences. It is of interest to mention that, both the first and second anodic half-cycles (A) of alloy (sample I) are characterized by an ill defined potential step. This step may be attributed to the formation of magnesium oxide. However, in alloy (sample II) this step is not observed.

In Figs. (6 and 7) the anodic and cathodic polarization curves of alloys (samples III and IV) in 0.1M Na_2SO_4 solution are shown. The polarizing currents are respectively 19.479 and 18.349 $\mu A/cm^2$. From the variation of the potential of the electrode with time, it can be seen that, at first there is a rapid linear build-up of potential ascribed to the charging of the anodic double layer (96-98). The potential range over which this process occurs amounts to ca. 1.05 V. When this process comes to an end, the potential of the electrode changes more slowly with time, giving rise to two steps, before oxygen evolution commences.

Inspection of the curves of Figs. (6 and 7) shows that, the starting potentials of these two anodic steps are -0.1 and -0.05 V, (against SCE), respectively. The first step seems to be associated with the formation of Cu_2O. The second step in the polarization curves is due to the oxidation of Cu_2O to the higher oxidation state of copper, namely CuO. The quantity of electricity consumed during the two steps (Figs. 6 and 7) are practically the same denoting that the Cu_2O formed during the first step converts to CuO along the second step.

Upon cathodic reduction and anodic oxidation (Figs. 6 and 7) curves were obtained which exhibited the same features as those described above. However, two ill defined anodic steps are detected and the amount of electricity consumed in the passivation of the electrode was smaller than that passed during the first anodic half cycle. This is most probably due to the change of the conditions of the electrode surface, on one hand,

and the presence of corrosion products at the metal/solution interface on the other. In the cathodic half-cycles (C), the potential is first dropped to negative values, but levelled up again giving rise to two well defined steps. The potential then changed more slowly before finally dropping to values characteristics for the evolution of hydrogen.

The two main steps in the cathodic reduction curves are expected to corrospond to the reduction of CuO and Cu_2O, repectively. It is of interest to note that, the quantity of electricity consumed during the two steps (Figs. 6 and 7) are practically the same. These will be explained in details from cyclic voltametry of the different alloys, which gives more information than the galvanostatic curves.

Regarding the oxygen evolution potential for aluminium and its four alloys, it is of interst to note that, the presence of the alloying elements, reduces the values of this potential (Table 2). Since the oxygen evolution potential is associated with the metal ion concentration in the electrolyte, it can be safely concluded that, the presence of these alloying elements affects the rate of the anodic dissolution of aluminium in 0.1M Na_2SO_4 solutions.

Table: (2)

Alloy	Pure Al	Sample I Al-3% Mg	Sample II Al-3%Mg-0.1%Cu	Sample III Al-4.5% Cu	Sample IV Al-4%Cu-0.1% Mg
O_2 evolution	1.55 V	1.375 V	1.25 V	1.35 V	1.25 V

Since anodization of aluminium and its four alloys results in oxide formation on the surface, the thickness of this oxide could be taken as a measure for the extent of passivation. Usually the electrode surface carries a prepolarization oxide of thickness δo which depends on the experimental procedure particularly the method of surface treatment. Anodic polarization increases the thickness according to:

$$\Delta\delta = rit/\sigma,$$

where (r) is the volume of oxide formed per coulomb,

(t) is the time of polarization and (σ) is the roughness factor. The parameter (r) is related to the molecular weight of the oxide (M), its density (S) and the number of faradays required for the formation of one mole of oxide by:

$$r = M/SnF$$

Hence, the thickness becomes :

$$\delta = \delta_o + \Delta\delta$$

Since the prepolarization oxide (δ_o) will have nearly the same thickness for the same experimental conditions, $\Delta\delta$ may be safely taken as a measure of oxide thickness. With M=102 for Al_2O_3, n=6 and S=3.42 gm/cm^3 , the value of r becomes $5.16X10^{-5}$ cm^2/coulomb. It is then possible to calculate $\Delta\delta$ as a function of potential. Table (3) gives the results of such calculations for Al and its four alloys in 0.1M Na_2SO_4 neglecting the density and molecular weight of the oxides of the alloying elements.

It is clear that, at a certain potential (-1.0V) and before the formation of oxides other

Table (3) : Coulometric increase of oxide thickness on $\Delta\delta$ on Al its alloys in 0.1M Na_2SO_4.

Potential (V)	σ	Pure Al	Sample I Al -3% Mg alloy	Sample II Al-3% Mg-0.1% Cu alloy	Sample III Al -4.5% Cu alloy	Sample IV Al-4% Cu -0.1% Mg alloy
-1.0	2	0.000603	0.000201	0.000201	0.000201	0.000201
-0.5	2	0.001407	0.001067	0.000804	0.000804	0.001206
+0.5	2	0.003618	0.002613	0.002412	0.005629	0.005629
+1.0	2	0.005629	0.003417	0.003216	0.006835	0.007237

than Al_2O_3, Δδ for the different alloys is constant and less than pure.

-At -0.5 V, Δδ decreases in the order :

-Al > Al -4% Cu -0.1% Mg > Al -3% Mg > Al -3% Mg -0.1% Cu = Al -4.5% Cu

-At + 0.5 V, Δδ decreases in the order :

Al -4.5% Cu = Al -4% Cu -0.1% Mg > Al > Al -3% Mg > Al -3% Mg -0.1% Cu

-At + 1V, Δδ decreases in the order :

Al -4% Cu -0.1% Mg > Al -4.5% Cu > Al > Al -3% Mg > Al -3% Mg -0.1% Cu.

From these conditions, it may be concluded that , the effect of the alloying elements on the passivation of Al depends upon the potential at which the oxide thickness is calculated. On the other hand, from the orders given above, it can be seen that Cu is superior to Mg (at the percent composition used) as an alloying element for retarding the anodic dissolution of aluminium in 0.1M Na_2SO_4.

The available theories of film growth in aqueous media , as reviewed by a number of authors (99-101) , are based on the migration of the reactant species from the metal and the solution side with the existing film before they react to form more oxide. A high anodic electric field is required across the film to justify the migration of cations and the oxygen containing anions towords each other within the film and away from, respectively the metal and the solution.

Dealing with film formation, the growth of the oxide film during the initial stages of galvanostatic oxidation of Al in H_3PO_4 was shown by Thompson et. al.(102). They suggested the existance of two simultaneous processes for the initial film growth (i) oxide formation near the metal film interface due to the migration of Al^{3+}, ^-OH, O^{2-} (ii) Al^{3+} injection at the film/electrolyte interface with partial deposition of anion-contaminated aluminium. The Al^{3+} injection into the solution has, also, been suggested by Siejka and Ortega(103) after studying the film growth in 15% H_2SO_4 aqueous solution by O^{18} tracing technique.

Chao, Lin and Macdonald's(104) model considered that, cations migrate directly towards the solution with injection at the film/electrolyte interface. However, this theory did not consider oxide precipitation at the interface near the solution, this process being suggested to explain the different textures of the outer part of the anodic film(102) . If this precipitation takes place, the metal would be passivated faster, because there would be two processes leading to oxide formation : anion migration towards the metal(104) and oxide precipitation at the film/electrolyte interface(102).

Furthermore, the anodic oxide film for aluminium alloys appears to be more complicated because of the existance of the alloying elements. Hence, the sequence of events during the oxide film formation in this case, is very defficult to be treated.