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ELECTRON MICROSCOPIC STUDY OF ANODIC FILMS ON ALUMINIUM

by

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Adstract: *The structure of anodic films formed in various acid or alkaline media at relatively low cds has been studied, as a function of the pH condition of the electrolyte, using electron microscopy. The structure of anodized Al_2O_3 films depends mainly on the pH of the solution and very little on the nature of the electrolyte. For $pH > 3$ and $pH < 9$ the appearance of the films is almost the same, i.e. they are eontinuous, without pores, containing micrograins. For $pH < 3$ local film dissolution compete with the film - forming reaction producing typical porous films, while for $pH > 11$ besides the slight dissolution of the films, we observe a multilayer formation of anodic films due probably to the high solubility of Al.*

INTRODUCTION

Anodization of *Al* has been extensively used in producing ultrathin and thick oxide films for capacitors, protective layers etc.

It has already been shown that the anodization of *Al* depends largely on the nature of electrolyte1), the oxide film present prior to anodization2) and the electrolyte concentration of the solution3). Electrolytic breakdown experiments combined with electron microscopy observations have also been reported4).

The anodization of *Al* under controlled current density (cd) conditions in acidic enviroment which exert some solvent action on the oxide, leads to the formation of a porous anodic oxide film e.g. such acids as sulphuric acid, chromic acid, oxalic acid etc. The structure of porous anodic oxide films has been extensively investigated by a number of workers. Various authors5–9) have demonstrated by electron - optical techniques that the film is composed of an amorphous oxide with a large number of vertical pores extending through the oxide, almost to the metal/oxide interface. At the bottom of the pore there is a thin layer of non - porous oxide, ∼15 - 200 nm9) — the barrier layer. The exact mechanism of this localized dissolution i.e. the formation of pores, seems to be unknown[10].

Besides acids, alkaline electrolytes also show some solvent action on the anodic oxide. According to Franklin[11], the basic process is the same for the two types of oxide formation and the porosity is a secondary result arising from oxide dissolution.

In the present paper, an attempt is made to examine the anodic oxide films on *Al*, formed by using different electrolytes and under various pH conditions, covering almost the whole range of pH values at relatively low cds by means of electron microscopy.

The difference in the structure of the anodic aluminium oxides due to electrolytic breakdown has also been investigated using electron microscopy observations.

EXPERIMENTAL TECHNIQUE

Material

The material used was 99,99 % pure aluminium foil, 0.2 mm thick, in the form of elongated strips (~5 mm wide, ~3 cm long). The strips were cleaned and degreased in baths of acetone, thichloethylene and alcohol. Any residual oxide formed on the foil during handling was removed by dipping it in a solution of 70 ml orthophosphoric acid (density 1.70 gr/cm³), 25 ml sulphuric acid (density 1.84 gr/cm³) and 3 - 8 ml nitric acid (density 1.50 gr/cm³) at 85 - 110° C and rinsing it in distilled water.

Electrolytes and electrical control.

The electrolytes used were

1. Sulphuric acid : pH = 3, pH = 1, pH = 0.1, pH < 0.
2. Phosphoric acid : pH = 3, pH = 1.5, pH = 0.5
3. Oxalic acid : pH = 3, pH = ~1.5, pH = 0,5
4. Na_2HPO_4 : pH = 9
5. Na_3PO_4 : pH = 12
6. NaOH : pH = 13

where the pH varied by changing the concetration of the acid.

The usual temperature of the electrolytic bath was 25° C.

Anodization was carried out at a constant cd using a Keithley current source supply. The cathode of the electrolytic cell was an inox cylinder with an inside diameter of 6 cm and a height of 8 cm. The *Al* strip was suspended in the axis of the cylinder.

Electron Microscopy

In this investigation the electron microscope was used exclusively because of the extreme fineness of the investigated structures. The films were stripped from the metal using the iodine - methanol or bromine - methanol[12–13] technique, or the «celotape» technique for direct stripping.

RESULTS

I. Acid Media

Anodizing Al in sulphuric acid

The anodizing of *Al* at different cds varying from 1 mA/cm^2 to 25 mA/cm^2 and with a voltage source of 100 Volts gave cell voltage - time curves as in Fig. 1a, 1b, 1c, 1d, similar to those reported already[14–15]. For all pH values and low cds there was a broad maximum while the electrolytic breakdown voltage for high cds increased as the pH of the solution increased. In adition to the first maximum, a second maximum appeared near the first one.

For electron microscopy examination, samples were prepared by anodizing *Al* for a short time, varying from 1 to 100 sec, and with a voltage source below the breakdown level at a constant cd of 1 mA/cm^2 or 25 mA/cm^2.

Transmission electron microscopy studies of specimens made at the horizontal plateau of the cell voltage - time curves, did not reveal any crystallographic structures. The characteristic appearance of the pores, for a constant time of anodic oxidation, was mainly a function of the pH of the acid solution; e.g. in the case of a cd of 25 mA/cm^2 (oxidation time 10 sec) the surface density of the pores increased as the pH of the solution increased toward the value pH = 3, leading to a continuous anodic film appearance. (Fig. 2a).

Anodic films of the same thickness as the above, formed under a cd of 1 mA/cm^2 and oxidation time 100 sec, have a similar appearance (Fig. 2b).

In addition to the above, in the case of anodic oxidation with a power source of 200 Volts i.e. higher than the electrolytic breakdown voltage, extra pores were noticed on the anodic film, due to electrolytic breakdown (Fig. 3).

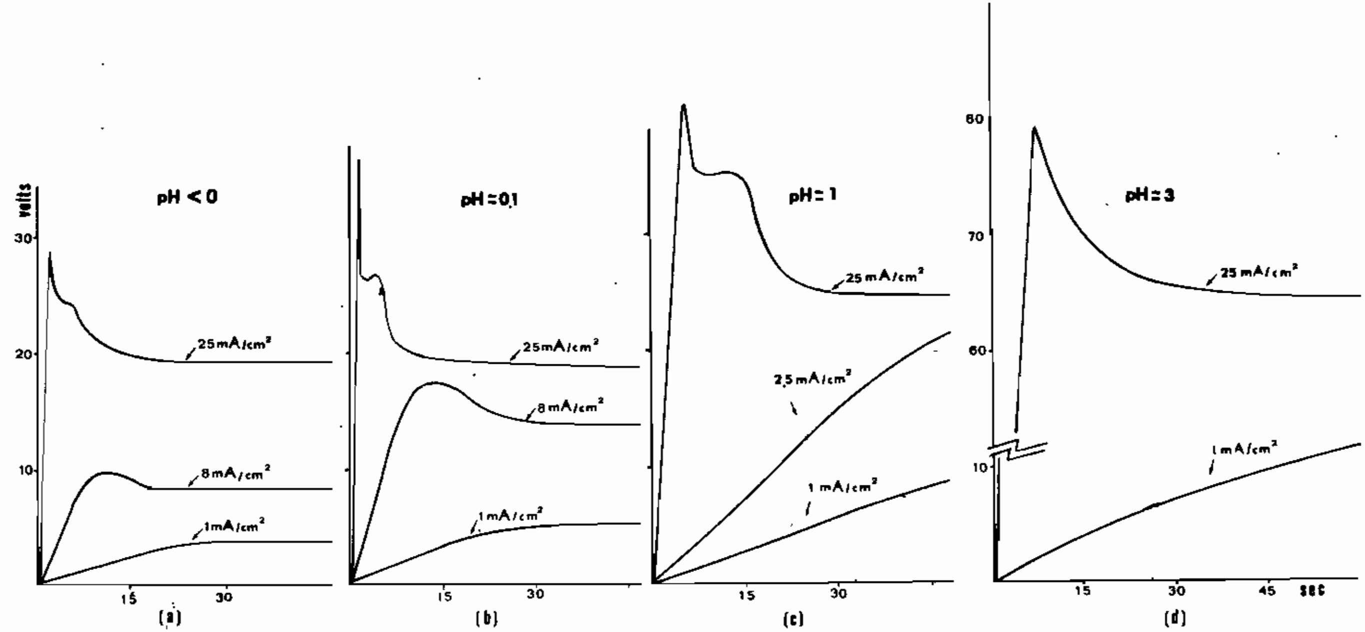

Fig. 1. Cell voltage - time curves of the early stages of anodizing of Al in H_2SO_4 solutions at 25° C at different cds varying from 1 mA/cm² to 25 mA/cm² and pH values of (a) < 0; (b) 0.1; (c) 1.0; (d) 3.0. Voltage source 100 Volts.

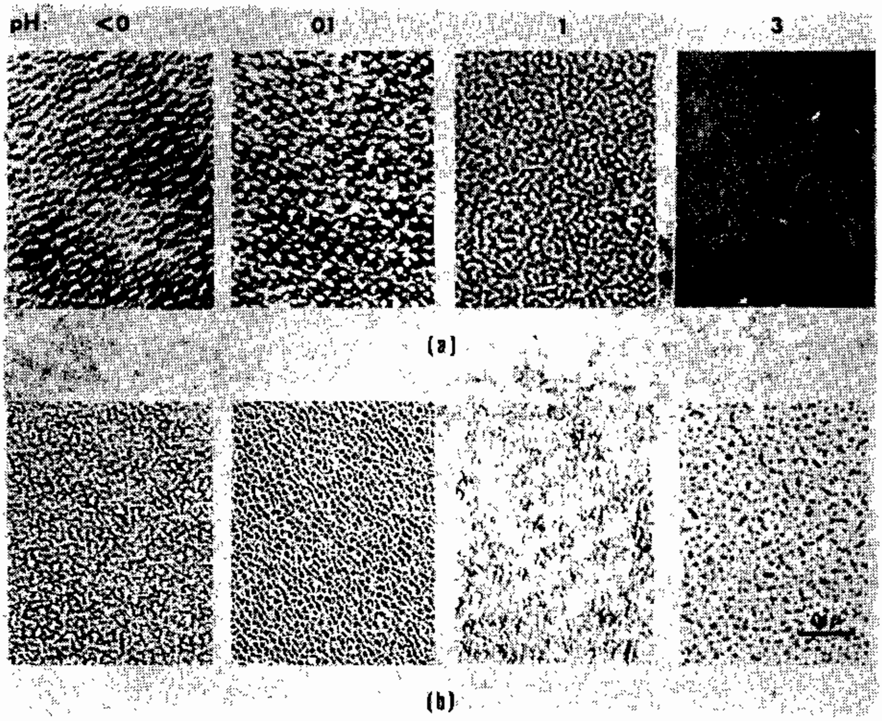

Fig. 2. Transmission electron micrographs of specimens anodized in different pH values of H_2SO_4 solution at 25° C and cd values of (a) 25 mA/cm² and (b) 1 mA/cm².

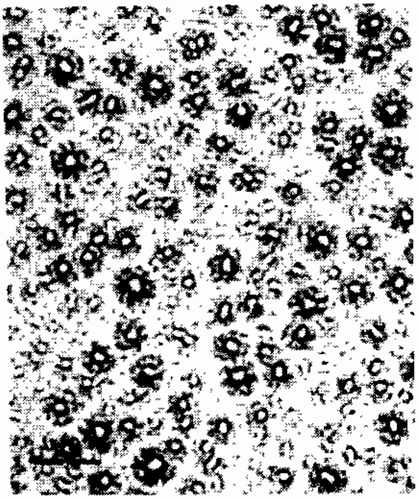

Fig. 3. Transmission electron micrograph of a specimen anodized in H_2SO_4 solution (pH = 0,1) with a power source of 200 Volts at a cd of 25 mA/cm².

Anodizing Al in phosphoric acid.

The films obtained by anodizing *Al* in phosphoric acid were similar in appearance with the ones formed in the sulphuric solution. Thus for low pH values of the solution, the large pores appeared, while they decreased in size as the pH increased, their form becoming elongated at first and finally disappearing (Fig. 4a, b).

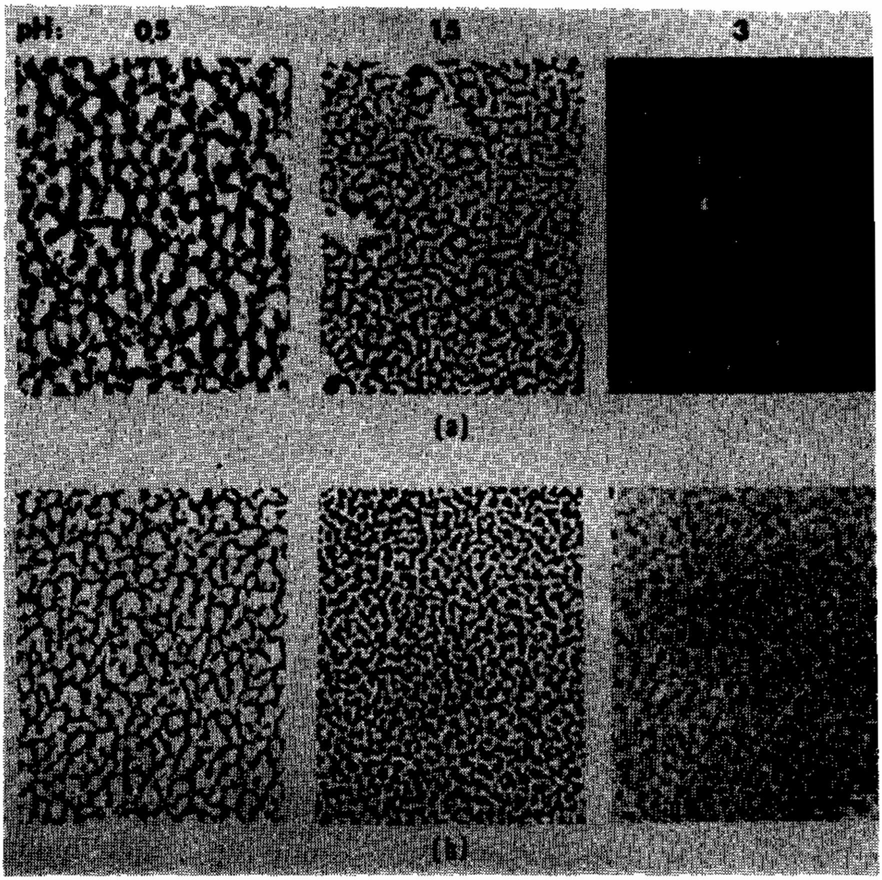

Fig. 4. Transmission electron micrographs of specimens anodized in different pH values of H_3PO_4 solution at 25° C and cd values of (a) 25mA/cm^2 and(b) 1 mA/cm^2.

The only essential difference appears in the cell voltage - time curves where the maximum value of the electrolytic breakdown voltage was ~140 Volts, while in the case of sulphuric acid solutions it was only ~80 Volts.

Anodizing Al in oxalic acid.

By anodizing *Al* in oxalic acid under the same cd and pH conditions similar results were obtained, except for a shift on the decrease of the diameter of the pores toward higher values of pH (Fig. 5a, b).

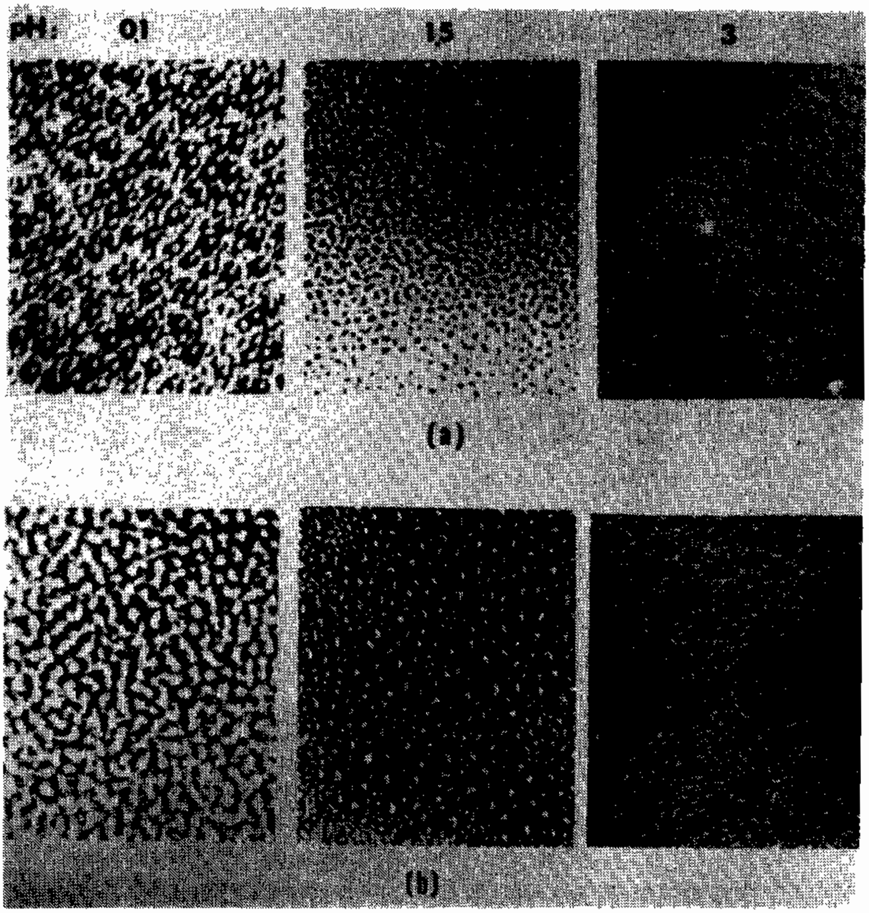

Fig. 5. Transmission electron micrographs of specimens anodized in different pH values of oxalic acid solution at 25° C and cd values of (a) 25 mA/cm^2 and (b) 1 mA/cm^2.

The cell voltage - time curves are closer to those of H_2SO_4, showing an electrolytic breakdown voltage of ~70 Volts at pH $= 0.5$ and ~100 Volts at pH values higher than 1.

II. Alkaline Media

Oxide film formation was carried out at three different alkalinity conditions i.e. at pH $= 9$ (~0.1 M Na_2HPO_4 solution), pH $= 12$ (~0.1 M Na_3PO_4 solution) and pH $= 13$ (~0.1 M $NaOH$ solution). The use of different electrolytes was found necessary because in larger concentrations the anodic oxidation was accompanied by secondary phenomena — e.g. the growth of crystallites on *Al* by dissolved substances — while there was no noticable effect of all three electrolytes on the structure of the films. Indeed during the anodic oxidation of *Al* in concentrations of pH $= 9$ of either Na_3PO_4 or $NaOH$ solution the structure of the film was the same as in the case of a Na_2HPO_4 solution of the same pH.

In following the voltage - time dependence during oxide formation in alkaline media we noticed a peculiar wave form of the cell voltage - time curves (Fig. 6a, b, c) for various electrolytes — or for different pH of the solution — and for different current densities.

I. In «static» solutions of pH $= 9$, a narrow wave - form curve appears at the beginning of anodic axidation with ondulations covering two or three «wave - lengths» (Fig. 6a) after which the potential difference sets to a constant value lower than the breakdown voltage. By stirring the solution no ondulations occur in the voltage - time curve.

II. In «static» solutions of pH $= 12$ and a cd higher than 5 - 10 mA/cm^2 the wave - form curve undergoes only a few ondulations. However, when the cd is lower than 5 ma/cm^2 the wave - form curve ondulates continuously with the amplitude increasing as the mean value increase. (Fig. 6b). The period of the wave - form curve seems to be an inverse function of the cd. By stirring the solution the cell voltage drops to zero and stays there as long as the stirring continuous.

III. In «static» solutions of pH $= 13$ the wave - form curve behaves in the same way as in the later case, except for the fact that it is permanent even at relatively high values of cds (Fig. 6c).

The structure of the anodic films depends on the alcalinity of the solution i.e. in a weak base solution (pH ≤ 9) they are almost continuous containing micrograins but without pores (Fig. 7a) and their structure is independent of the cd.

Increasing the alkalinity of the solution (pH $= 12$) the anodic films remain continuous, containing micrograins, but wrinkled, pro-

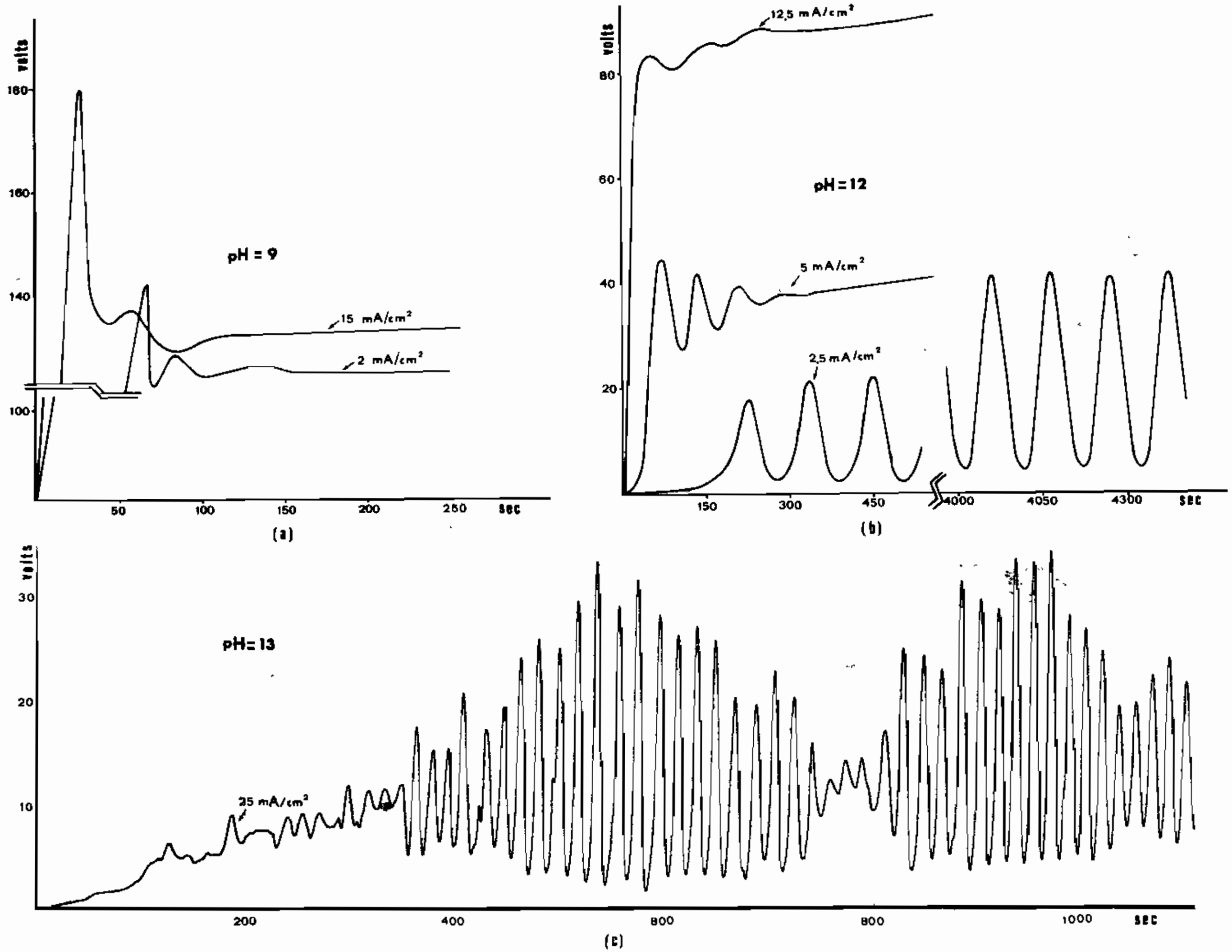

Fig. 6. Cell voltage - time curves of Al anodized in alkaline solutions of different pH values and at different cds

(*a*) Na_2HPO_4 *solution of* $pH = 9$,
(*b*) Na_3PO_4 *solution of* $pH = 12$, *and*
(*c*) *NaOH solution of* $pH = 13$.

bably because of partial detachment from *Al.* (Fig. 7b).

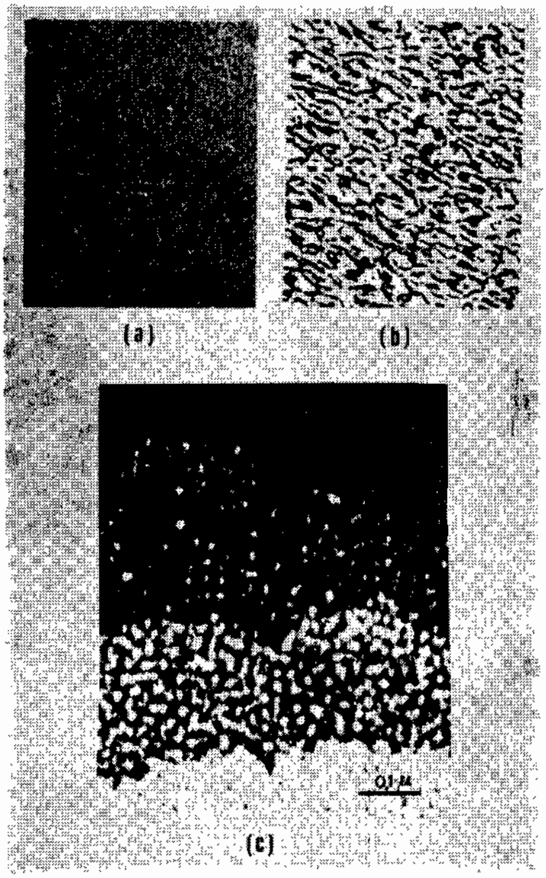

Fig. 7. Transmission electron micrographs of specimens anodized in alkaline solutions with different pH values, (a) pH = 9, (b) pH = 12 and (c) pH = 13.

Finally, at the highest pH value studied the anodic films are porous in multiple layers (Fig. 7c) and their adhension with *Al* is so weak that a single piece of celotape is enough to deatach the anodic film.

DISCUSSION

According to our results the structure of anodic aluminium films, under low current density conditions, depends mainly on the pH of the solutions and very little on the nature of the electrolyte. For pH > 3 and pH < 9 the appearence of the film structure is almost the same.

This is in good agreement with the observations of G. Wood and J. O'Sallivan[3]. Differences appear mostly during the growth of the anodic films in strong acid ($pH < 3$) and in strong base ($pH \geqq 11$) solutions. That could be explained on the basis of the different solubilities of Al and Al_2O_3 in acid or base media respectively. So the formation of pores in acid solutions could be explained as due to the high solubility of Al_2O_3, while the easy detachment of the anodic films in alcaline solution as due to the high solubility of Al.

This latter point of view is supported by the wave - form - like appearance of the cell voltage - time curve. As the anodic oxidation is started, a film layer is formed, while a simultaneous increase in the cell - voltage curve is observed. This is followed by a detachment of the layer and as a consequence a decrease of the cell - voltage is observed. This phenomenon is repeated at almost constant periods, which corresponds to constant film thicknesses and as a result the film formed is a multilayer one. However, in an acid solution the anodic films are subjected mainly to the solubility of the electrolyte and as a consequence we have the formation of the characteristic pores. As to the kinetics of the oxidation, Franklin's[11] view, according to which the basic process in oxide growth is the same for the two types of oxides, and that the porosity is a secondary effect arising from oxide dessolution, seems to be supported. This was concluded by the fact that all the diffraction patterns of the amorphous films, taken with an electron microscope, looked alike and also by the fact that durring electronbeam crystallization the same diffraction patterns, corresponding to γ - Al_2O_3 were obtained, in agreement to observation by P. Neufled et all[15].

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ΠΕΡΙΛΗΨΙΣ

ΜΕΛΕΤΗ ΑΝΟΔΙΚΩΝ ΟΞΕΙΔΙΩΝ ΤΟΥ ΑΡΓΙΛΛΙΟΥ ΔΙΑ ΤΟΥ ΗΛΕΚΤΡΟΝΙΚΟΥ ΜΙΚΡΟΣΚΟΠΙΟΥ

Ὑπὸ

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Μελετᾶται ἡ μορφὴ ἀνοδικῶν ὑμενίων ἀναπτυχθέντων ἐπὶ τοῦ Al, συναρτήσει τοῦ pH τοῦ ἠλεκτρολύτου, ὡς καὶ ὑπὸ τὴν ἐπίδρασιν διαφορετικῶν ἠλεκτρολυτῶν.

Κατὰ γενομένας παρατηρήσεις μὲ τὴν βοήθειαν τοῦ ἠλεκτρονικοῦ μικροσκοπίου εὑρέθησαν τὰ κάτωθι:

α) Ἡ μορφὴ τῶν ἀναπτυχθέντων ὑμενίων Al_2O_3 διὰ τιμὰς $3 < pH < 9$ εἶναι σχεδὸν ὁμοία, ἤτοι σχηματίζονται ὑαλώδη καὶ ἄνευ πόρων ὑμένια.

β) Διὰ τιμὰς $pH < 3$ τὰ ὑμένια ἐμφανίζονται πορώδη, ἡ δὲ διάμετρος τῶν πόρων αὐξάνεται ὅταν τὸ pH τοῦ ἠλεκτρολύτου γίνεται μικρότερον.

γ) Διὰ τιμὰς $pH > 9$ τὰ ὑμένια ἐμφανίζονται ὄχι μόνον πορώδη ἀλλὰ καὶ πολλαπλῶν στρώσεων. Ἐπὶ πλέον ταῦτα εὐκόλως διαχωρίζονται ἐκ τοῦ Al. Ὁ ἐν λόγω τρόπος ἀναπτύξεως τῶν ὑμενίων εἶναι δυνατὸν νὰ διαπιστωθῇ καὶ ἐκ τῶν ληφθέντων καμπυλῶν τάσεως-ἐντάσεως. Αὗται εἶναι κυματοειδοῦς μορφῆς, καθ' ὅσον ἀρχικῶς μὲν σχηματίζεται ἀνοδικὸν ὑμένιον καὶ συνεπῶς αὐξάνεται ἡ διαφορὰ δυναμικοῦ ἐν συνεχείᾳ ὅμως ἀποκολλᾶται ἐκ τοῦ ὑποβάθρου καὶ συνεπῶς ἐλαττοῦται ἡ διαφορὰ δυναμικοῦ. Τὸ φαινόμενον τοῦτο ἐπαναλαμβάνεται εἰς τρόπον ὥστε νὰ σχηματισθῇ τελικῶς ὑμένιον πολλαπλῶν στρώσεων.

Ὡς πρὸς τὴν κινητικὴν τῆς ὀξειδώσεως θὰ πρέπῃ νὰ δεχθῶμεν τὴν ἄποψιν τοῦ R. Franklin κατὰ τὴν ὁποίαν τὸ μὲν βασικὸν φαινόμενον τῆς ὀξειδώσεως εἶναι τὸ αὐτὸ εἰς ὅλας τὰς περιπτώσεις, πλὴν ὅμως τὸ πορῶδες τῶν ὑμενίων εἶναι δευτερογενὲς φαινόμενον ὀφειλόμενον εἰς τὴν διαλυτότητα τοῦ ὀξειδίου ἐντὸς τοῦ ἠλεκτρολύτου.