Distribution of Nickel across the Thickness of Al Anodic Oxide Films Sealed in Nickel Sulphate Solutions

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(Received February 23, 1970)

The distribution of nickel across the thickness of Al anodic oxide films, produced in 15.5% w/v H_2SO_4 as electrolyte and sealed in nickel sulphate solutions, is determined and an approximate confirmation of the conical shape of pores is obtained.

As is well known, anodizing of Al in sulphuric acid electrolyte yields porous films of oxide which are usually sealed before being used. On being sealed, anhydrous oxide is hydrated, swells and fills up the hollow of its pores by the transformation into boehmite ($Al_2O_3 \cdot H_2O$), a less dense phase than the preexisting anhydrous alumina. The usual technique of sealing includes immersion in boiling distilled water, hot water vapour, boiling solutions of chromates, dichromates and salts, such as Ni or Co acetate or sulphate, or capillary active organic compound.[1] The use of nickel and cobalt salts is particularly convenient as they prevent the harmful action of silicates and phosphates, always contained in tap water, so that it can be used in place of distilled water as a sealing medium.[2] Nickel and cobalt salts are adsorbed in the film, where they are hydrolized and precipitated as almost colourless hydroxides. This technique of sealing is also very useful for dyed layers. In this case, according to Speiser,[3] three different reactions occur: 1) hydration of films, as in the case of sealing in boiling distilled water, 2) precipitation of the hydroxide in the pores with consequent blocking-in of the dye, 3) chemical reaction between the nickel (or cobalt) compound and the dye to form a new metal complex.

However, the functions of nickel (or cobalt) in the sealing process are not very clear and need further investigation. This paper deals with the distribution of nickel across the full thickness of Al anodic oxides sealed in nickel sulphate solutions.

The study was performed with the aim of improving the knowledge of sealing mechanism, particularly concerning the functions of nickel salts in sealing solutions and the shape of the pores present in the anodic oxide.

Experimental

a) 99.99% Al samples ($5 \times 10 \times 0.1$ cm) were freed from grease with toluene and polished both mechanically and chemically (in 20 g/*l* NaOH solutions), then rinsed successively in distilled water, 1 : 1 HNO_3 solution, and distilled water again. After drying they were anodized in 15.5% w/v H_2SO_4 solution, at 25.0 ± 0.5°C, 1.3 A/dm^2, for 40 min. Stirring and symmetry of the electrolytic bath were warranted by means of rotating anode and the presence of two bored cathodes, larger than the anodized samples (surface area ratio 1 : 3), equidistant from the central anode.

b) Sealing: The anodized samples were washed with running distilled water and immersed for 30 min in boiling $NiSO_4 \cdot 7H_2O$ 15 g/*l* solution.

c) Cationic exchanger Dowex 50-X 8 (100—200 mesh), H^+ form, medium porosity, total capacity approximately 5.0 ± 0.3 meq/g dry, moisture content 50—56% by weight.

Anionic exchanger Dowex 1-X 4 (100—200 mesh), Cl^- form, high porosity, total capacity approximately 3.3 ± 0.3 meq/g dry, moisture 54—60% by weight.

The two ionic exchangers were contained in columns each 30 cm long and 20 mm internal diameter, which were washed before use: the cationic one with 12M HCl and distilled water (flux rate 2 m*l*/min) and the anionic one with only distilled water (flux rate as above).

d) Spectrophotometer Beckman DU

e) Amel, mod. 461, polarograph.

The anodized sample is kept for a long time in a solution which can dissolve the oxide and nickel is determined in the corroding solution. In order to get consistent information, we assume that chemical attacks proceed uniformly from a layer to the next inner one and that no localized pitting corrosion takes place. The at tacking solutions were Edwards mixture (35 m*l*/*l* H_3PO_4 85% and 20 g/*l* CrO_3) acting for 0—20 min and 1.5M HCl acting for a prolonged time.

Quantitative determination of nickel was performed by four different methods for nickel solutions in the presence of aluminium.

1) After having acted for the specified time, the Edwards mixture was passed on an anionic exchanger in order to eliminate phosphate and chromate anions. In this operation a reduction of Cr(VI) to Cr(III) by the resin was observed and a green solution resulted at the end of the column, the intensity of this colour not being possible to be accounted for by the presence of Ni(II) ions. Al(III) was separated by passage through the cation exchanger and elution with 1.5M HCl.[4] Nickel was determined gravimetrically by dimethylglyoxime, having masked Cr(III) by adding citrate.[5]

2) After the necessary lapse of time for the dissolution reaction the 1.5M HCl solution was evaporated to dryness and the residue was dissolved in distilled water. Nickel was determined in the resulting solution a) spectrophotometrically by complexing it with α-furildioxime[6-8] and extraction

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2) H. Richaud, Conference on Anodising, University of Nottingham, Session VI, paper XVI, 12—14 Sept. (1961).

3) C. T. Speiser, Electropl. and Met. Finishing, 9, n.4, 109—116, 128 (1956).

4) C. Michaelis, N.S. Tarlano, J. Clune, and R. Yolles, *Anal. Chem.*, **34**, 1425 (1962).

5) A. J. Vogel, "A Text-book of Quantitative Inorganic Analysis," Longmans, London (1961), p. 479.

6) E. N. Pollock and L. P. Zopatti, *Anal. Chim. Acta*, **28**, 68 (1963).

7) J. S. Forrester and L. J. Jones, *Anal. Chem.*, **32**, 1443 (1960).

8) G. C. Taylor, *Analyst*, **81**, 369 (1959).

of the complex with $CHCl_3$, having previously masked Al(III) by citrate or tartrate; b) by back-titration at pH=10 with EDTA and standard Zn(II) solution, using NET as indicator and masking Al by fluoride;[9-11] c) amperometrically in deoxygenated 0.1M NH_4Cl and 0.5M NH_4OH as supporting electrolyte at −1.7 V *vs.* SCE, using dimethylglyoxime as titrating agent: as both nickel and dimethylglyoxime give diffusion currents, a sharp V shaped titration curve was obtained;[12,13] Al was eliminated by the technique described in 1), just above.

Each measurement was carried out for at least three different samples. The results are given by mean values.

Results

In Table 1 the data of the gravimetric determination are given. In Fig. 1 the calibration curve used for the spectrophotometric titration with α-furildioxime is reported: 2, 2.5, 3, 3.5, 4 m*l* of a standard solution of $NiSO_4 \cdot 7H_2O$, at concentration 14.6 μg Ni/m*l*, were taken, put into a volumetric flask and diluted to 25m*l* with distilled water, so obtaining concentration values 29.2, 36.5, 43.8, 51.1, 58.4 μg Ni/25 m*l*, for which the respective optical densities were measured at 435 mμ (Table 2). In Table 3 the results of the spectrophotometric determination are given; they are determined on the basis of the calibration curve previously drawn. In order to calculate the values of the last column, the dilution ratios must also be considered. This ratio was controlled in the different experiments in order to bring optical densities in the range observed during calibration, thus avoiding extrapolating approximations.

Table 1. Data of gravimetric analysis

Time of acting of Edwards mixture (min)	Weight of nickel-dimethylglyoxime (mg/dm²)	weight of nickel (mg/dm²)
3	5.41	1.10
5	6.99	1.42
8	8.81	1.79
10	9.45	1.92
15	9.60	1.95
20	10.00	2.03

Table 2. Data of the calibration curve

m*l* of standard solution diluted to 25 m*l*	Optical density (at 435 mμ)
2.0	0.395
2.5	0.495
3.0	0.600
3.5	0.695
4.0	0.790

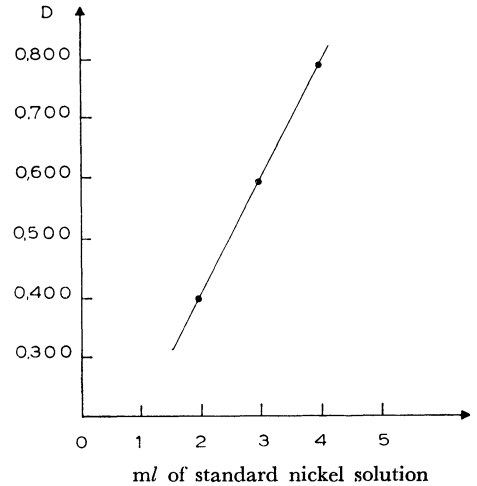

Fig. 1.

Table 3. Data of spectrophotometric analysis

Time of acting of 1.5M HCl (hr)	Optical density	Volume (m*l*)	Dilution ratio	Weight of nickel (mg/dm²)
9.5	0.600	25	1:25	1.1
16	0.710	25	1:25	1.3
24	0.435	25	1:50	1.6
36	0.515	25	1:50	1.9
48	0.545	25	1:50	2.0

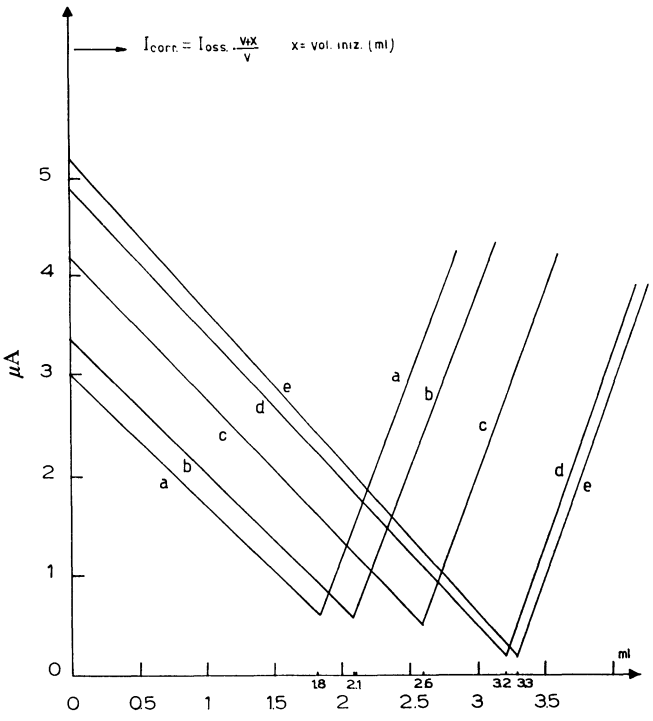

Fig. 2 Curves of amperometric titrations of nickel solutions with ethanolic solution of dimethylglyoxime in ammonia solutions. Nickel content results from the corroding action of HCl 1.5M for the following times:

curve a: 9.5 hr
curve b: 16 hr
curve c: 24 hr
curve d: 36 hr
curve e: 48 hr

9) F. J. Welcher, "The Analytical Uses of EDTA," Van Nostrand, New Jersey (1964), p. 234.
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11) D. H. Williams and L. E. Hibbs, *Anal. Chim. Acta*, **18**, 372 (1958).
12) I. M. Kolthoff and A. Langer, *J. Amer. Chem. Soc.*, **62**, 211 (1960).
13) J. A. Barnard and R. Chayen, "Modern Methods of Chemical Analysis," McGraw Hill, London (1965), p. 45.

TABLE 4. DATA OF AMPEROMETRIC ANALYSIS

Time of acting of 1.5M HCl (hr)	Volume of reactive solution added at the end point (ml)	Weight of nickel-dimethylglyoxime equivalent to ml given in the last column (mg/dm²)	Weight of nickel (mg/dm²)
9.5	1.8	5.4	1.1
16	2.1	6.4	1.3
24	2.6	7.9	1.6
36	3.2	9.3	1.9
48	3.3	9.8	2.0

TABLE 5. DATA OF COMPLEXOMETRIC ANALYSIS

Time of acting of 1.5M HCl (hr)	Volume of EDTA solution added (ml)	Volume of $ZnSO_4$ solution at the end point (ml)	Weight of nickel (mg/dm²)
9.5	4.0	1.88	1.10
16	4.0	1.67	1.31
24	4.0	1.35	1.60
36	4.0	1.04	1.90
48	4.0	0.95	2.01

In Table 4 and Fig. 2 the results of the amperometric determinations of nickel by dimethylglyoxime (609.05 mg in 250 ml 95% ethanol) are reported. In Table 5 the results of the complexometric titration of nickel with 0.0125M EDTA and 0.0170M $ZnSO_4$ are recorded as a function of the time of acting of the corroding solution.

Discussion

By considering the amounts of nickel found in the corroding solution as function of the attacking time, the distribution curve of nickel across the thickness of the oxide layer can be deduced, assuming that

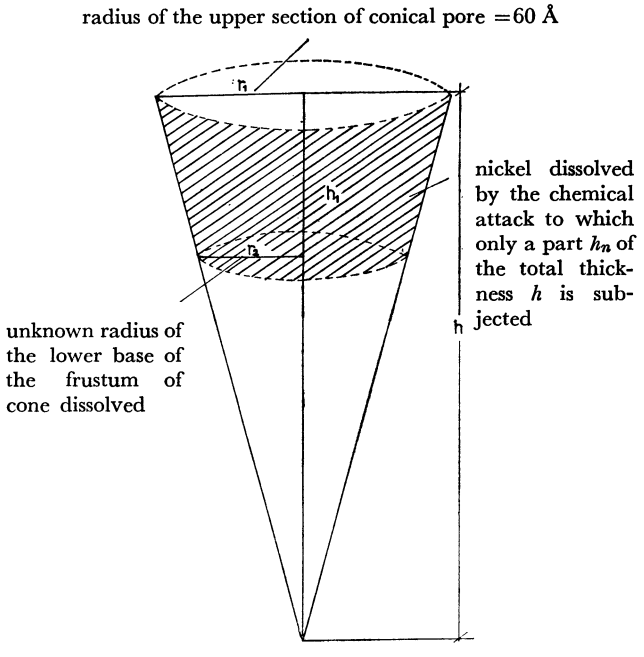

Fig. 3

oxide layers nearer to the basis metal are successively subjected to uniform dissolution. Nickel turns out to be mostly concentrated in the outer portion of the anodic film and the rate of decrease of its concentration through the depth of the oxide supports the conical shape of the pores, as shown in Fig. 3, where nickel content is plotted against percentage of the total thickness (measured by Dermitron, an eddy-currents instrument, manufactured by Unit Process Assemblies Inc., New York).

Considering that the nickel amounts taken off during each attack are those contained in the volumes of the frusta of the cone, which are successively dissolved, and that 2 mg/dm² of nickel are found for the total dissolution of the oxide, a pore can be drawn, taking 120 Å as base diameter[14] and applying the following two equations:

$$r_1^2 h/3 = k m_{tot}$$

$$(r_1^2 + r_n^2 + r_1 r_n) h_n/3 = k m_n$$

where:

- k =a constant term
- r_1 =upper base radius=60 Å
- r_n =lower base radius
- h =height of the cone, taken approximately as 13 μ, that is, the thickness of the oxide layer, measured by Dermitron, neglecting the thickness of the barrier layer which should be subtracted
- h_n =height of the frusta of the cones successively dissolved
- m_n =nickel content of the corroding solution
- m_{tot}=2 mg nickel/dm²

The above system must be applied to each conical frustum equivalent to the varying times of chemical attack. All the frusta have the same upper base. Several values for r_n are calculated, by which Fig. 4 can be

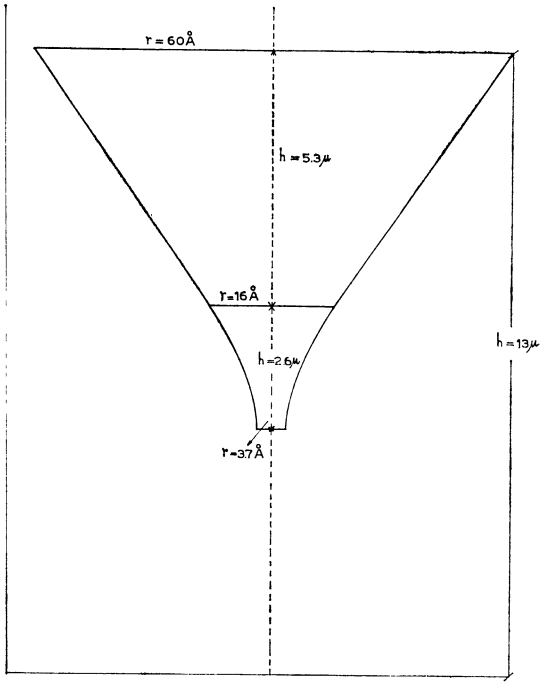

Fig. 4

14) F. Keller, M. S. Hunter, and D. L. Robinson, *J. Electrochem. Soc.*, **100**, 411 (1953); **101**, 335 (1954).

drawn, as representing a pore of the oxide film. The approximations introduced can account for the wider angle we found than ISML researchers.[15]

The present work was carried out with the aid of the Italian National Researches Council.

15) F. Sacchi and G. Paolini, "Indagine sulla struttura fine di strati di ossido anodico su alluminio mediante misure di adsorbimento, micrografia elettronica ed esame gravimetrico," Report of I. S. M. L. (Istituto Sperimentale Metalli Leggeri: Experimental Institute of Light Metals), Novara, Italy (1962—1963).