Philips Res. Rep. 2, 313-319, 1947

ON THE AMORPHOUS AND CRYSTALLINE OXIDE. LAYER OF ALUMINIUM

by A. J. DEKKER and W. CH. VAN GEEL

Summary

541.138.2:546.621

Aluminium can be covered electrolytically with a porous layer of aluminium oxide, and oxidation afterwards in boric acid gives rise to the formation of a crystalline layer. The experiments described below show undoubtedly that this layer only fills up the holes of the amorphous Al_2O_3 . Moreover, there is a correlation between the current density in oxalic acid and the porosity of the amorphous layer thus formed.

1. Introduction

By anodic oxidation a piece of aluminium can be covered either with an amorphous or with a crystalline oxide layer.

The amorphous layer obtained in a solution of oxalic, sulphuric 'or phosphoric acid has a porous structure, the pores having a diameter of about 10^{-5} cm and being mainly oriented at right angles to the surface on which the layer is deposited (see electron microscope picture, *fig. 1*). During the process of formation the porous layer is saturated with electrolyte solution and offers only a very slight resistance to the electric current passing through it. Hence, if the oxidation is carried out at a constant voltage, the current, too, will be practically constant, and the layer can be made as thick as we desire; there is only a slight current decrease during the first few seconds of the oxidation.

A crystalline layer of Al_2O_3 can be produced by using an aqueous solution of a borate or boric acid, a succinate or a citrate. This layer has pronounced insulating properties so that during formation at constant voltage the current steadily decreases. Hence, there is a limit to the thickness of a crystalline layer which is determined by the so-called "spark potential" which depends on the specific resistance of the electrolyte solution ¹); for instance, the maximal voltage obtainable in a solution of a borate with specific resistance of 40 Ω cm is about 400 volts giving a maximal thickness of 0.44 μ .

Now, it has been observed by Van Geel and Emmens²) that an insulating crystalline layer can be formed on an aluminium surface that has previously been coated with an amorphous layer. They held the view that the crystalline layer is in this case formed underneath the amorphous layer.

Recent experiments, however, have led us to the conclusion that this is not correct; the formation of a crystalline layer is taking place in the

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pores of the amorphous layer present. These experiments will be described in the present paper.



Fig. 1. Electron-microscope micrograph of a porous layer of 1.8 μ thickness with the electron beam (250 kV) perpendicular to the surface (4200 \times).

2. Experimental results

A) An aluminium plate (purity 99.99%) with an area of 440 cm² was anodically coated with a crystalline layer in boric acid at a constant current of 200 mA. Both the voltage V and the capacity C were measured during the process of formation; we give some of the results here:

Time (min)	Voltage (volts)	1/C (cm ⁻¹)
0	10	1.00)
5	70	2.62 (~10-8
15	210	8.5 (~10
30	375	16.2)
50	575	10 2)

(see fig. 2 and fig. 3, curves I)

dV/dt = 12.2 volts min⁻¹, $d(C^{-1})/dt = 0.54.10^{-8}$ cm⁻¹min⁻¹. The increase of weight after 30 minutes of oxidation appeared to be 28.75 mg; 1 amp. hour giving 298.4 mg of oxygen; the calculated current efficiency becomes 96%. This was in agreement with the fact that no gas development at the anode could be observed. During the formation of the oxide layer both V and 1/C vary linearly with time, as expected. The capacity at t = 0 is due to the oxidation of aluminium by air, and the thickness of this air layer is of the order of 1 m μ .



Fig. 2. Voltage as a function of time for an Al plate of 440 cm² during anodical oxidation in boric acid with 200 mA; curve I without an amorphous layer (A), curve II with an amorphous layer of 3.5μ (B).





By a well-known formula, the capacity of a plate condenser is given by:

$$C=rac{arepsilon S}{4\pi d},$$

where ε stands for the dielectric constant of the oxide layer, S for the surface area, and d for the thickness. Writing ϱ for the specific weight we can express d in the increase of weight, and from this it follows that $\varepsilon \varrho = 24.4$. This is in very good agreement with the numerical values given by Burgers, Claassen and Zernike³), *i.e.* $\varepsilon = 8$ and $\varrho = 3.1$.

B) The same experiment was carried out with an aluminium plate (area 440 cm²) covered with an amorphous layer by oxydation in oxalic acid at 4A during 10 minutes, the thickness of the amorphous layer then being about 3.5μ . Before the second oxidation in boric acid, the plate was

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heated at 450 °C during 15 minutes, to remove residuals of oxalic acid and water. V and C were again determined as a function of time, the current being kept at a constant value of 200 mA. Results follow below (see fig. 2 and fig. 3, curves II):

Time (min)	Voltage ~ (volts)	1/C (cm ⁻¹)	dV/dt = 50 volts min ⁻¹
0	54	2·24.10 ⁻⁸	$d(C^{-1})/dt = 2.04.10^{-8} \text{ cm}^{-1}\text{min}^{-1}.$
6	360	14·5 .10 ⁻⁸	

It may be noticed that, as referred to in the introduction, the oxidation in oxalic acid produces a thin insulating layer which is responsible for the zero-capacity of 49.7 μ F. The increase of weight accompanying the oxidation in boric acid amounted to 6.0 mg, and from this it follows that the current efficiency is just 100%. Comparing the values of dV/dt and d/dt(1/C)of the curves I and II we see that, due to the presence of the amorphous layer, these quantities are about four times as great as in the first experiment.

Calculating the value of $\varepsilon \rho$ for this case, on the assumption that the crystalline layer is formed *underneath* the amorphous layer, we find $\varepsilon \rho = 6.7$, and it is evident that this assumption is wrong. Bearing in mind, however, that the amorphous layer has an open structure containing pores, it is natural to suppose that the much greater velocity of formation, in case an amorphous layer is present, is due to the filling-up of the pores; then only a certain part of the volume has to be filled up with crystalline Al_2O_3 , in order to produce a layer with insulating properties.

This hypothesis can be verified in the following way:

In the experiment just described we used an amorphous layer of about 3.5μ , and the oxidation in boric acid to 350 volts gives rise to a crystalline layer of about 0.35μ ; hence, according to the hypothesis, only a small fraction of the amorphous layer is filled up with crystalline Al_2O_3 . But using, instead, an amorphous layer of, say, 0.2μ we may expect a sudden decrease in the slope of the V(t)-curve during oxidation in boric acid, because at a certain time t the amorphous layer will be wholly filled up, and from this time on the entire surface area has to be covered with crystalline Al_2O_3 .

C) The following experiments were carried out to check this point of view. Five aluminium plates with areas of 165 cm² were covered with an amorphous layer in oxalic acid at a current of 200 mA during 2, 4, 6, 8 and 10 minutes, respectively, and in this way each plate was covered with an amorphous layer of a thickness proportional to the time of oxidation. The plates were again heated at 450 °C during 15 minutes and then anodically oxidized in boric acid at a current of 100 mA to build up

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a crystalline layer; V and C were determined as a function of time; in fig. 4 the results for V have been reproduced, those for 1/C being of the same shape.



Fig. 4. Voltage as a function of time for Al plates of 165 cm² covered with layers of amorphous Al_2O_3 with different thicknesses during anodical oxidation in boric acid at 100 mA (C).

As expected, the slope of the curves are very steep in the start (the period of filling up the holes of the amorphous layer), but after a certain time a marked decrease of the slope takes place.

The two straight portions of the curves in fig. 4 have been extrapolated until they intersect, and the time corresponding to this point of intersection has been taken as the time at which the pores of the amorphous layer are completely filled up with crystalline material. As shown in fig. 5, these time intervals are proportional to the time of oxidation in oxalic acid, as we should expect in virtue of our hypothesis.

From the two extreme values of the slope in fig. 4 one may conclude that the volume of the pores in the amorphous layer amounts to 30% of the total volume. This is in rather good agreement with the specific weights of amorphous and crystalline Al_2O_3 , these values being, respectively, 2.5 and 3.1 from which follows a relative volume of the pores of about 25%.

The same result is obtained by noticing that in fig. 5 the slope is just 0.5, and, bearing in mind that the current in oxalic acid was 200 mA and in boric acid 100 mA, we see that a porous layer formed by x amp. minutes is just filled up in boric acid by $\frac{1}{4}$ x amp. minutes; this leads to 25% for the relative pore volume.

3. The rate of change of voltage as a measure of the porosity of the amorphous layer

Let us now compare the rate of change of the voltage during oxidation in boric acid in the various experiments described above. The rate of change in the voltage will, of course, be proportional to the current density, so that to render our data mutually comparable we should divide dV/dt by the current density *i*. It will be easily verified that we then have

experiment A:

$$\frac{\mathrm{d}V/\mathrm{d}t}{i} = 26.4 \frac{V \,\mathrm{min^{-1}}}{\mathrm{mA \ cm^{-2}}},$$
becond stage of experiment C:

$$\frac{\mathrm{d}V/\mathrm{d}t}{i} = 25.6 \frac{V \,\mathrm{min^{-1}}}{\mathrm{mA \ cm^{-2}}},$$

in satisfactory agreement, since in both cases the entire surface area was being coated with a crystalline layer.



Fig. 5. The time necessary for filling up the amorphous layer at 100 mA as a function of the time of oxidation in oxalic acid at 200 mA, *i.e.* as a function of the schickness of the amorphous layer.



Fig. 6. The velocity of oxidation for 100 mA in boric acid as a function of the oxidation current in oxalic acid for Al plates of 165 cm^2 .

On the other hand we have in experiment B:

and in the initial stage of experiment

$$\frac{\mathrm{d}V/\mathrm{d}t}{i} = 110 \frac{V\,\mathrm{min^{-1}}}{\mathrm{mA\,cm^{-2}}},$$

C:
$$\frac{\mathrm{d}V/\mathrm{d}t}{i} = 83 \frac{V\,\mathrm{min^{-1}}}{\mathrm{mA\,cm^{-2}}}.$$

In these two instances the crystalline matter was being formed in the pores of an amorphous layer. The increased rate of change of voltage must then be due to a current density in the pores higher than the current density

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calculated from the apparent surface area. If so, our data lead to the conclusion that the porosity of the amorphous layer was of the order of 25 to 30%. This is in keeping with density observations, the specific weight of an amorphous and a crystalline layer being 2.5 and 3.1 respectively.

The above comparison between experiment B and the initial stage of experiment C also suggest a difference in the degree of porosity in these two cases. This may be a consequence of different current densities used in the formation of the amorphous layer, 9.1 mA/cm² and 1.2 mA/cm² respectively. This has led us to investigate the rate of change $\frac{dV/dt}{i}$ as a function of the current density used in forming the amorphous layer, with the results tabulated below and plotted in fig. 6.

Current density in oxalic acid (mA/cm ²)	$\frac{\mathrm{d}V/\mathrm{d}t}{i}$ in boric acid ($V \min^{-1}/\mathrm{mA~cm^{-2}}$)	
1.21	76	
2.22	89	
3.04	95∙⁵	
6.05	104	
9.10	106	
13.35	106	

There is indeed a marked dependence, a higher current density in oxalic acid producing a denser structure of the amorphous coating.

It may finally be noted that the capacity of an aluminium surface that has wholly been oxidized in boric acid is the same as the capacity of a surface that has first been oxidized in oxalic acid and subsequently in boric acid: This shows that the dielectric constants of amorphous and crystalline Al_2O_3 must be equal.

Eindhoven, June 1947

REFERENCES

1) W. Ch. van Geel, Physica 1, 989-995, 1934.

²) W. Ch. van Geel and H. Emmens, Physica 1, 415-416, 1935.

3) W. G. Burgers, A. Claassen and J. Zernike, Z. Phys. 74, 593-603, 1932.