R 316 *Philips Res. Rep.* **12**, *240-248, 1957*

SOME PROPERTIES OF OXIDE LAYERS PRODUCED ON ALUMINIUM BY ELECTROLYTIC OXIDATION

by W. Ch. van GEEL and B. J. J. SCHELEN

53.08: 669.718.915

Summary

A description is given of measurements of the thickness (d), dielectric constant (ε) and density (ϱ) of oxide layers produced on Al by electrolytic oxidation. The X-ray investigation of the structure of these layers was also undertaken. Two different values were found for the thickness of the layer, viz. $d = 13{\cdot}7$ Å/volt and $d = 12{\cdot}7$ Å/volt. The former value was found after chemical cleaning, the latter without any prior removal of the oxide layer formed by reaction with the air. The cleaning probably causes an increase of about 7% in the surface area. If this is correct, then $d = 12{\cdot}7$ Å/volt is the more acceptable value. For ϱ we found the value 3·1 g/cm^3, for ε the value 8·7. When it is formed at room temperature, the oxide is completely amorphous, except when a layer of boehmite has been produced on the Al by boiling it in water. In the latter case $\gamma'\text{-Al}_2\text{O}_3$ is also formed. Oxidation at 100 °C always gives some $\gamma'\text{-Al}_2\text{O}_3$ as well as amorphous Al_2O_3.

Résumé

Dans cet article on décrit des mesures sur l'épaisseur (d), la constante diélectrique (ε) et la densité (ϱ) de la couche d'oxyde produite par oxydation électrolytique sur de l'Al. On donne aussi les résultats des recherches au moyen des rayons X sur la structure cristalline de la couche. On a trouvé deux valeurs différentes pour l'épaisseur de la couche d'oxyde, $d = 13{,}7$ Å/volt et $d = 12{,}7$ Å/volt. La première valeur a été trouvée après un nettoyage chimique de la plaque d'Al, la dernière est la valeur trouvée sans avoir enlevé la couche d'oxyde formée dans l'air. Il est probable que le nettoyage chimique provoque un agrandissement de la surface de 7%. Alors la valeur de $d = 12{,}7$ Å/volt est la plus probable; pour ϱ on a trouvé la valeur 3,1 g/cm^3, pour ε la valeur 8,7. Lorsqu'il est formé à la température ambiante l'oxyde est complètement amorphe, sauf dans le cas où une couche de boehmite a été formée au préalable sur l'Al dans un milieu d'eau bouillante. Il se forme alors aussi du $\gamma'\text{-Al}_2\text{O}_3$. De même l'oxydation à 100 °C donne toujours du $\gamma'\text{-Al}_2\text{O}_3$ en plus de l'oxyde amorphe.

Zusammenfassung

In diesem Artikel wird über Messungen bezüglich der Dicke (d), der Dielektrizitätskonstante (ε) und der Dichte (ϱ) der durch elektrolytische Oxydation auf Al angebrachten Oxydschicht berichtet. Zugleich wurde mit Hilfe von Röntgenuntersuchung die Struktur ermittelt. Zwei verschiedene Werte für die Dicke der Oxydschicht wurden gefunden, $d = 13{,}7$ Å/Volt und $d = 12{,}7$ Å/Volt. Der erste Wert wurde gemessen, nachdem die Platte chemisch gereinigt worden war; der letztere ohne Entfernung der immer vorhandenen Luft-Oxydschicht. Wahrscheinlich verursacht die chemische Reinigung eine Oberflächenzunahme von 7%. Der Wert $d = 12{,}7$ Å/Volt ist der meist wahrscheinliche. Für ϱ wurde der Wert 3,1 g/cm^3 gefunden, für ε der Wert 8,7. Wird das Oxyd bei Zimmertemperatur gebildet, so ist es völlig amorph, ausser wenn durch Kochen im Wasser zuerst eine Boehmit-Schicht auf dem Aluminium angebracht worden war. In diesem Fall entsteht auch $\gamma'\text{-Al}_2\text{O}_3$. Oxydation bei 100 °C ergibt stets ausser dem amorphen Oxyd auch $\gamma'\text{-Al}_2\text{O}_3$.

1. Introduction

The thickness of oxide layers produced on Al by electrolytic oxidation has been determined by various investigators [1]). It can be found in several ways. Firstly, the amount of oxygen taken up by a plate during oxidation can be determined by weighing, and from it the amount of Al_2O_3 formed can be calculated. For this calculation it is necessary to know the density of the Al_2O_3 produced. To determine the density, the aluminium is dissolved; the density of the residual oxide layer is then determined by the suspension method or the pycnometric method.

The thickness of such layers can also be determined by the optical method. Here the product of the refractive index and the thickness is found from the interference. In order to ascertain the thickness, the refractive index has to be determined. This is done by suspending the Al_2O_3 layer in a liquid with the same refractive index [2]). It is also possible to measure the refractive index of the oxide layer on the Al directly by determining the Brewster angle (Deryagin [1])).

A third method is to measure the capacitance of the system in a bridge. This gives the relationship between the thickness and the dielectric constant, and knowing the latter, the former can be found. There is no simple method for the direct determination of the dielectric constant, hence the measurement of the capacitance is more suitable for determining the dielectric constant when the thickness is already known.

Lastly, the product of thickness and density of the oxide coat can be determined by measuring the change in resistance of a thin aluminium wire during electrolytic oxidation. The method is very accurate and has been employed by us. The same method was used by Güntherschulze who, however, was not concerned with the thickness of the oxide coat, but rather with the dielectric constant which he determined from it.

It remains to mention the method followed by Nagase [1]), in which a piece of the oxide film left on dissolving the Al was mounted on a plane plate of glass. Both the oxide film and the glass plate were then covered with a layer of silver and a second silvered glass plate was placed on the first. The thickness of the layer of air which was exactly the same as the thickness of the layer of oxide was then determined directly by an interference method developed by Tolansky [3]).

In this paper we shall deal in turn with measurements of the increase in weight of an aluminium plate during oxidation as a function of the voltage up to which the plate is oxidized. When the aluminium had been dissolved, the weight of the residual oxide film was likewise determined. The density of the oxide film was determined by the suspension method and the pycnometric method; the thickness of the oxide layer was then found from the previous (weight) measurements. Next, the resistance of a thin aluminium wire was measured during oxidation; using the density, which was already known, it was again possible to find the thickness.

In addition, the ratio of the dielectric constant to the thickness was determined from capacitance measurements, and since the thickness was known, it was possible to calculate the dielectric constant.

The distance between interference bands occurring with wedge-shaped oxide layers in monochromatic light was also measured. From the known refractive index the thickness was determined in this way also.

Finally, an X-ray investigation was carried out to determine the structure of the oxide film.

It should be pointed out that the designation of the thickness d in Å/volt commonly found in the literature is not strictly correct. If an aluminium plate is oxidized with a constant current to a certain voltage, and the current is then decreased with the voltage left constant, the thickness of the layer still continues to increase. If the leakage current has become very small, this increase in thickness is negligible and the thickness can be regarded as constant. With greater leakage currents, however, the current should also be indicated when stating the thickness. We have always oxidized until very low currents were reached. Unless otherwise stated, the oxidations were carried out at room temperature.

2. Experimental

The experiments were performed on Al with a purity of 99·99%. An electrolyte solution of 40 grams of boric acid and 10 grams of borax per litre of water was used. The Al was cleaned in one of three different ways prior to oxidation.

(1) To a mixture of equal parts by volume of water and concentrated sulphuric acid 5 grams of potassium bichromate per litre was added. The Al was immersed in this liquid for at least $1^1/_2$ minutes at 90 °C. This was found to be the best method of cleaning.

(2) The Al was cleaned in alcohol only. The oxide layer, 60 Å thick, formed in the air was not removed in this case.

(3) The Al was immersed for at least 1 minute in a bath at 60 °C, containing 200 grams of KOH per litre of water. After having been rinsed, the Al was dipped alternately in baths of dilute acids and bases. Finally the Al was put in boiling water. This method produces a layer of boehmite on the Al.

3. Determination of the density of the Al_2O_3

The suspension method

An aluminium plate was oxidized up to 340 volts and then cut into pieces, which were put in a solution of bromine in anhydrous methanol

(1 : 12) in which the Al dissolved. The Al_2O_3 film fragments were washed and dried and their density was determined by the suspension method (Burgers [1])). The difficulty with this method is that minute air bubbles readily attach themselves to the fragments. Moreover, there is the risk that the pieces of film will not be sufficiently wetted by the liquid in which they are suspended. Further, small differences in temperature in the liquid give rise to convection, so that it is difficult to keep the particles in suspension. We found the average density to be $\varrho = 2{\cdot}97 \pm 0{\cdot}15$ g/cm³. Burgers and coworkers found $\varrho = 3{\cdot}1 \pm 0{\cdot}05$ g/cm³.

The pycnometric method

The second method used was the pycnometric method, in which the same liquid was used as had served as the electrolyte in the oxidation. This liquid had a good wetting action on the film. However, this method, like the first, is not very accurate. The value for ϱ was $3{\cdot}1 \pm 0{\cdot}2$ g/cm³ and 3·1 was taken to be the best value for the density.

4. Determination of the thickness by weighing

Weight of the whole plate

Figure 1 gives the weight G of an Al plate with the dimensions 10 cm × 10 cm × 110 μ as a function of the voltage. The plate was cleaned only with alcohol and was therefore still covered with a layer of oxide formed in the air. We found an increase in weight of 10·9 mg for a surface of 200 cm² on oxidation up to 300 V. This represents the amount of oxygen taken up.

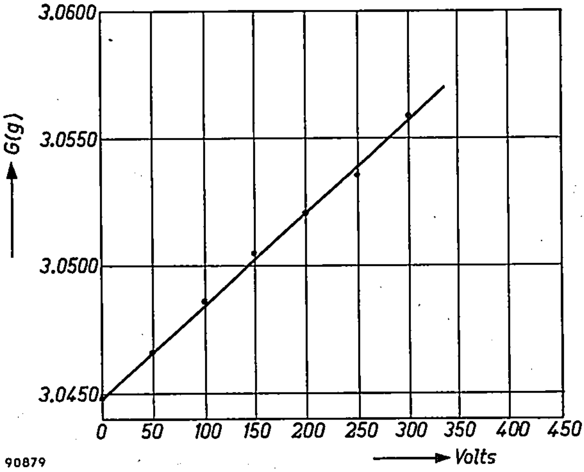

Fig. 1. Increase in weight of an Al plate, 10 cm by 10 cm, as a function of the voltage to which the plate was oxidized.

From this oxygen 23·2 mg of Al_2O_3 is formed. If we calculate from this the thickness of the layer per volt, we find $d = 12{\cdot}5$ Å/volt.

The same determination was carried out on Al which had been cleaned by method 1 with H_2SO_4 and $K_2Cr_2O_7$. Here the oxide layer formed in the air had been completely removed. The value for d was 13·4 Å/volt.

Weighing of the film after dissolving the Al

The weight of the oxide layer was determined after the Al had been dissolved in the manner already described. Here the determination does not depend upon the composition of the oxide. After cleaning by method 1, d was found to be 13·9 Å/volt. After cleaning by method 2, d was found to be 12·6 Å/volt.

5. Determination of the thickness by the resistance method

An Al wire of length l and cross-section O_b is immersed in a bath and oxidized, as a result of which the cross-section of the pure Al part becomes O_e. If the initial resistance is R_b and the final resistance R_e, then $O_e = (R_b/R_e)O_b$.

If the molecular weight of the oxide is given by $M(Al_2O_3)$, the atomic weight of Al by $A(Al)$, the density of the oxide by $\varrho(Al_2O_3)$ and the density of aluminium by $\varrho(Al)$, then the thickness of the oxide layer formed can be calculated simply as follows:

$$d = \frac{M(\mathrm{Al_2O_3})\ \varrho(\mathrm{Al})}{4A(\mathrm{Al})\ \varrho(\mathrm{Al_2O_3})}\ \frac{r}{R_e}\ \Delta R,$$

in which r is the initial radius of the wire and ΔR the increase in resistance.

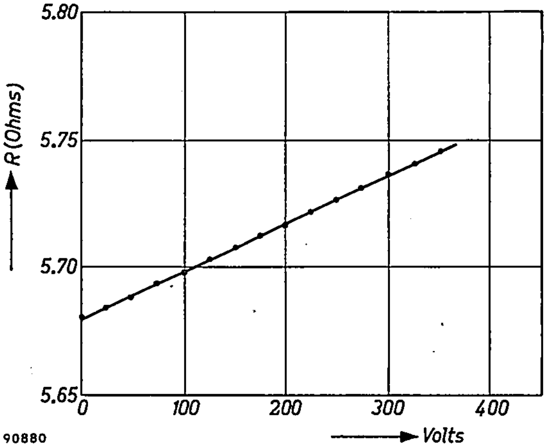

Fig. 2. Increase in the resistance of an Al wire as a function of the oxidation voltage ($r = 46$ μ).

Figure 2 shows the increase in resistance as a function of the voltage to which the wire was oxidized. When the Al was cleaned by method 1 ($K_2Cr_2O_7 + H_2SO_4$), d was found to be 13·8 Å/volt. A constant check was kept to ensure that the voltage increased proportionally with time (fig. 3), since it was found that only in that case was there a linear relationship between resistance and voltage of the type shown in fig. 2.

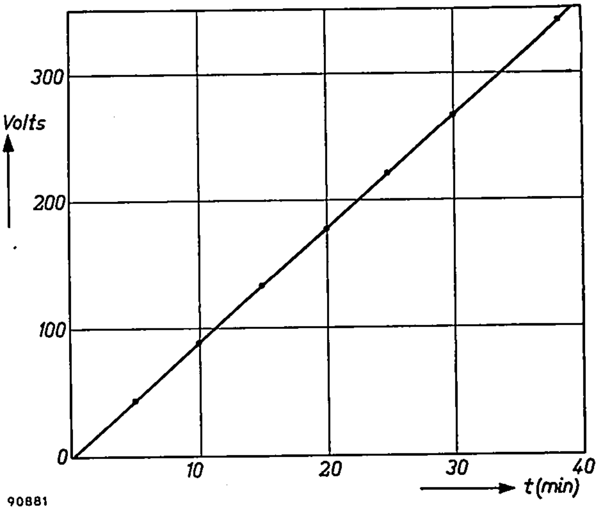

Fig. 3. The linear increase of the voltage as a function of the time for the oxidation of the wire in fig. 2.

It proved difficult to fulfil this latter condition for a wire cleaned by method 2 (alcohol). Such wires were found to have picked up impurities in their surface during drawing, which could only be removed by dissolving away the surface layer. No measurements were made on wires cleaned by method 2.

6. Optical determination of the thickness

A rectangular Al plate was oxidized in sections up till low values of the leakage current. Each successive section was oxidized to a voltage 5 volts higher than that of the preceding section. This was done by withdrawing the plate from the electrolyte by a certain fixed distance for each voltage stage. In this way adjacent layers of various thicknesses were obtained, which together formed a step wedge of oxide. To improve surface reflection, a thin layer of platinum, about 10^{-6} cm thick, was deposited on the oxide layer. Tests were made which showed that the presence of this layer of platinum did not alter the interference colours. If the wedge is viewed in monochromatic light, the dark bands where extinction has occurred can clearly be seen. A refractive index of 1·67 was measured using the suspension method under illumination of a Na lamp. The Al_2O_3 film fragments used were obtained in the same way as described in the earlier density measurements. We found that the best film fragments were obtained after cleaning the Al following method 1. The wedge used for measuring the thickness of the layer was cleaned following method 2 because in this case the colours were more intense. The thickness of the oxide layer was found to be 12·9 Å/volt, a value which is in good agreement with the value found earlier for plates cleaned by method 2. The same results were obtained after cleaning the Al plate following method 1.

It can be understood that the small increase in the surface area, which is produced by method 1, has no influence on the thickness of the layer as measured by the optical method.

Figure 4 gives the positions of the dark bands plotted against their order number for a wedge, 15 cm long, which was oxidized up to 500 volts. This wedge was made by oxidizing the Al plate at constant current density during the withdrawal of the plate from the electrolyte. In this way a wedge of regularly increasing thickness is formed. In fig. 4 we see that the distance between two adjacent bands is constant, which shows that the refractive index does not depend on the thickness of the layer. Weiskirchner [2]) finds that n depends upon the thickness and reports the value 1·59 for n_{Na} for an oxide layer formed at 150 volts. We cannot give an explanation for the discrepancy between Weiskirchner's observation and

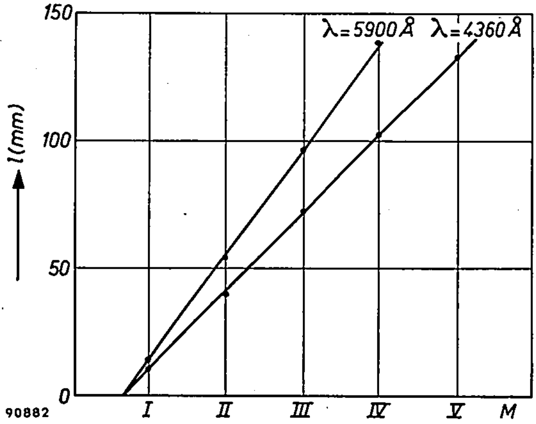

Fig. 4. Position of the interference bands in monochromatic light with a wedge-shaped layer of oxide. Along the abscissa are plotted the order numbers of the dark bands, along the ordinate the positions of the minima.

ours. For a layer formed at 200 volts we found also $n_{\mathrm{Na}} = 1{\cdot}67$. Dr Winkel, of this laboratory, in an independent investigation of the absorption spectrum of the oxide film, obtained a value $n_{\mathrm{Na}} = 1{\cdot}7$.

7. Determination of the dielectric constant from capacitance measurements

The capacitance of the oxide layer was measured with the aid of a bridge. The way in which this is done has been described earlier [4]). Knowing the thickness d, we can now determine the dielectric constant ε, which was found to be $8{\cdot}7 \pm 0{\cdot}3$.

8. The structure of the oxide layer

Crystal-structure investigation with an X-ray spectrometer showed the oxide layer to be mainly amorphous. In general it can be said that the amorphous Al_2O_3 is made up of oxygen atoms arranged in a close-packed lattice, which is often, but need not necessarily be, cubic. Moreover, the close-packed lattice need not always be strictly periodic. The Al atoms are irregularly distributed over the octahedral and tetrahedral spaces.

After cleaning by method 1 ($K_2Cr_2O_7 + H_2SO_4$), amorphous Al_2O_3 was only formed on oxidation at room temperature. If the oxidation was performed at 100 °C, γ'-Al_2O_3 was also formed [5]). Owing to the higher temperature, crystalline aggregates were produced. The same result was obtained in the oxidation of Al which had only been superficially cleaned and had retained its film of oxide.

Aluminium cleaned by method 3, in which the Al was immersed in boiling water, was always covered during cleaning with a layer of boehmite ($Al_2O_3.H_2O$). This layer does not act as an insulator in the electrolyte. If such a boehmite-coated plate is oxidized and the thickness of the film produced is calculated from the oxygen taken up, and compared with the thickness determined experimentally, then the experimental thickness will be found to be greater than that which follows from the oxygen yield. On weighing the plate before and after oxidation, only a small increase in weight is found. Moreover, in the method described above, in which the increase in resistance was measured during oxidation, a much smaller increase in resistance was found to occur than when there was no boehmite on the wire. The most plausible explanation is that during oxidation part of the boehmite is converted into γ'-Al_2O_3. That γ'-Al_2O_3 is formed during oxidation even at room temperature is evident from the X-ray patterns.

Summing up it can be said that oxidation at 100 °C always gives rise not only to amorphous but also to γ'-Al_2O_3. Oxidation at room temperature gives amorphous oxide only, except when there is a layer of boehmite on the Al prior to oxidation; in this case γ'-Al_2O_3 is also formed.

9. Concluding remarks

The value $d = 10$ Å/volt, found by us earlier[4]), differs considerably from the values reported in this paper. The reason for this lies in the fact that our previous paper related to measurements in which the only method of cleaning used was one in which boehmite was always present on the Al during oxidation. If the methods described in the present paper are applied in the presence of a boehmite layer, we find about the same values as before ($d = 9{\cdot}2$ Å/volt).

The fact that two values are found for d ($d = 13{\cdot}7$ Å/volt and $d = 12{\cdot}7$ Å/volt) is probably due to the fact that the larger value, found after cleaning the surface in $K_2Cr_2O_7 + H_2SO_4$, is the result of a 7% increment in the surface area. The value $d = 12{\cdot}7$ Å/volt, found without chemical cleaning of the surface, is most probably the best one. A difference of about 5·5% was also found between the capacity of the two layers.

Acknowledgments

The authors are greatly indebted to Dr P. Winkel for his help and the interest he showed in their work. They also wish to thank Dr P. B. Braun for making the X-ray diffraction patterns, Mr B. C. Bouma for assisting them with the optical determination of the thickness of the layers and Mr F. Herbschleb for his assistance.

Eindhoven, January 1957

REFERENCES

1) W. G. Burgers, A. Claassen and J. Zernike, Z. Phys. **74**, 593-603, 1932.
A. Güntherschulze and H. Betz, Z. Phys. **73**, 580-586, 596, 1932; **91**, 82, 1934.
B. V. Deryagin and R. M. Friedland, J. tech. Phys. Moscow **18**, 1443-1449, 1948.
W. Walkenhorst, Naturwissenschaften **34**, 373, 1947.
A. J. Dekker and W. Ch. van Geel, Philips Res. Rep. **2**, 313-319, 1947.
G. Hass, J. opt. Soc. Amer. **39**, 532-541, 1949.
K. Nagase, Memoirs of the Institute of Scientific and Industrial Research, Osaka University **10**, 66-71, 1952.

2) W. Weiskirchner, Z. Naturf. **6A**, 509-511, 1951.

3) S. Tolansky, Multiple-beam Interferometry of Surfaces and Films, Oxford, Clarendon Press, 1948, p. 147.

4) W. Ch. van Geel and J. W. A. Scholte, Philips Res. Rep. **6**, 54-74, 1951.

5) E. J. W. Verwey, Z. Kristallogr. **A91**, 317-321, 1935; J. chem. Phys. **3**, 592-594, 1935.