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The Gaseous Anodisation of Tantalum

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Circuit arrangements for the anodisation of tantalum foil in an oxygen gas plasma are discussed. It is shown that the process can be explained in electrochemical terms. Using constant current anodisation, the thickness of oxide formed in the voltage range 0 to 20 V is in the region of 24 to 28 Å/V. The results indicate that the gaseous process, which has both a low current efficiency and a poor throwing power, is most suitably applied to smooth, vacuum-deposited materials.

1. Introduction

The principal requirement for anodising is the provision of a system, adjoining the metal phase, which is both oxidising and relatively conductive. The latter condition is essential in order that the extremely high field strength (10^6 to 10^7 V/cm), necessary for sustained film growth, may be applied across the oxide layer. In gaseous anodising, the liquid electrolyte of the conventional wet process is replaced by a low-pressure oxygen glow discharge. As originally demonstrated by Miles and Smith [1] with aluminium, the metal specimen to be anodised is positioned in the most conductive region of the discharge and is positively polarised with respect to the anode.

The gaseous process offers considerable advantages over the wet system, since, in principle, thin-film capacitors can be prepared entirely in the vacuum chamber. Apart from experimental convenience, it is evident that this procedure may entail a marked reduction in contamination and an associated improvement in capacitor quality. Additionally, gaseous anodisation may have an application to the preparation of reactively sputtered oxide dielectrics, in which a major problem is the presence of pin-holes. One method of partly overcoming these defects, provided a valve metal is used as the base electrode, is to wet anodise prior to depositing the counter-electrode [2]. Since the sputtering is accomplished in an oxygen discharge, it should also be possible to seal the pin-holes by gaseous anodising, either after completion of or during sputtering. Furthermore, the anodisation could also be used to ensure complete oxidation of the dielectric itself.

Several recent papers have dealt with the gaseous anodisation of aluminium [3-6], tantalum [7], or lanthanum-titanium specimens [8]. Although considerable success has been achieved, notably with aluminium capacitors, other workers in this field have expressed doubts as to the electrochemical nature of the process, and thermal oxidation has been proposed as an alternative mechanism. In the present study, which has been directed towards establishing a better understanding of the underlying processes, tantalum foil has been used throughout.

2. Apparatus

The essential features of the vacuum system are shown in fig. 1. The purpose of the baffle, which separated the anodising chamber from the main vacuum system, was to facilitate the stabilisation of an oxygen pressure. For the initial work, both of the main discharge electrodes were made of duralumin, a separation of 8 cm being employed. Subsequently, the anode was replaced by a platinum electrode. The discharge was operated at a current of 50 mA in a pressure of 5×10^{-2} torr of oxygen. The potential between the main electrodes was 500 V. Under these conditions the dark space was extremely narrow, and constituted a very thin layer adjoining the cathode. The electrical connector for the tantalum foil was a length of anodised tantalum wire, the upper end of which was wound into a tight coil and positioned close to the rim of the discharge anode. Exposed metal at the lower end

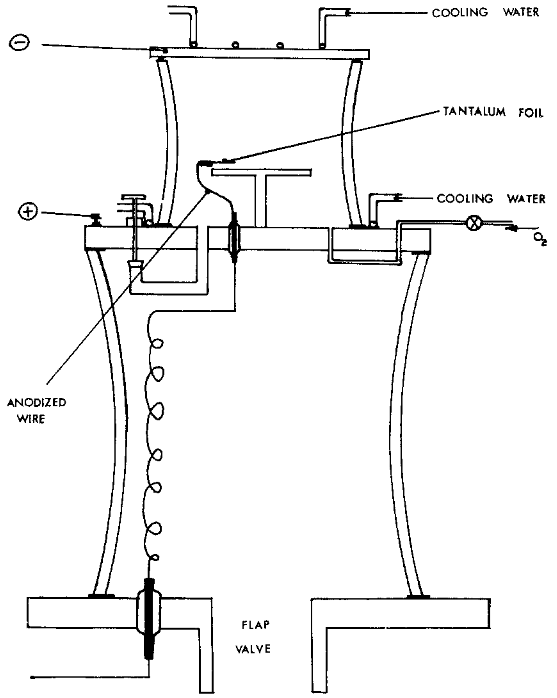

Figure 1 Gaseous anodising apparatus.

where the wire was led in through the base plate was coated with a thin layer of epoxy resin to avoid leakage of current during anodising.

The tantalum foil, 0.1 mm thick, was 99.89% pure and contained 0.1% niobium. Specimens were cut having sides 1 cm × 1 cm and with tags 2 mm wide and 3 cm long. The foils were chemically polished by immersing for 10 sec in a solution containing 2 volumes of 40% hydrofluoric acid, 2 volumes of 70% nitric acid, and 5 volumes of 98% sulphuric acid. The end of the tag was bent at right-angles and inserted into the coiled end of the tantalum wire. The tantalum specimen was positioned parallel to, and approximately 1 cm above the surface of the discharge anode, quite close to the rim. For experiments in which the current density of anodising was controlled, the tag was pre-anodised in a glycol-borate electrolyte at 120 V at room temperature. Unless used directly after preparation, specimens were given a 1 min clean in chromic acid prior to use. The vacuum chamber was evacuated to a pressure of about 5×10^{-5} torr prior to leaking in the oxygen and starting the discharge.

3. Experimental

With the glow discharge applied, the open-circuit potential between a clean tantalum specimen and the duralumin anode was in the region of −25 V. On polarising the tantalum anodically with respect to the duralumin electrode, a voltage-current relationship of the form shown in curve A (fig. 2) was obtained. If the current was held constant at a few milliamps, the voltage slowly increased (i.e. became more positive) with time, but the oxide film formed at the surface of the tantalum had a distinctly non-uniform appearance. Films of a relatively uniform thickness were produced when the duralumin surface was freshly machined before use. This also resulted in a substantial increase in the initial open-circuit potential to −1 to −2 V. However, the improvement was only temporary, since after a short time in the plasma a fairly rapid reversion towards the original conditions was observed.

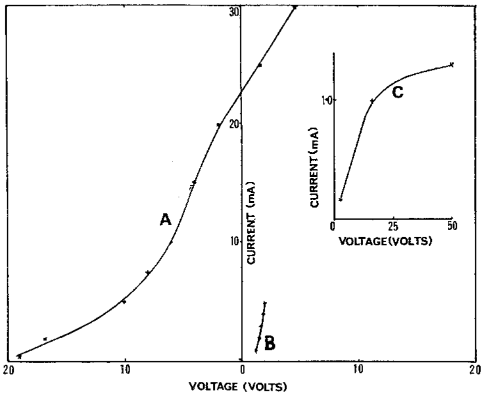

Figure 2 Voltage-current relationship between tantalum and either the discharge anode (A and B) or an auxiliary platinum electrode (C). (Approximate surface area of tantalum = 2 cm².) A. Duralumin anode. B. Platinum anode and platinum wire reference electrode; resistor (20 kΩ) in anodising circuit. C. Auxiliary platinum electrode; both tantalum and platinum isolated from the plasma electrodes.

It was evident from the preliminary experiments that an inert electrode, which did not form a surface film of high resistance in the plasma, was required for the discharge anode. When the duralumin was replaced by platinum foil, the open-circuit potential between the tantalum and the platinum was in the region of −4 V. As a further refinement, a 20 kΩ resistor was inserted in the anodising circuit in order to restrict the amount of plasma current initially by-passed through the tantalum prior to starting the anodisation. In principle, this is equivalent to using an anodising source having a high internal impedance. Consideration was also given to the problem of accurately measuring the anodising voltage. If this is measured between the tantalum and the plasma anode, it is necessary to make allowance for the potential drop in the plasma between the two electrodes and also at the surface of the discharge anode. Since both these potential drops are a function of current density, a floating platinum-wire electrode, the tip of which was disposed close to the tantalum surface, was incorporated in the circuit. The potential between the tantalum and the platinum wire was monitored with a high-impedance meter throughout the subsequent experiments. A schematic diagram of the final circuit arrangement is shown in fig. 3.

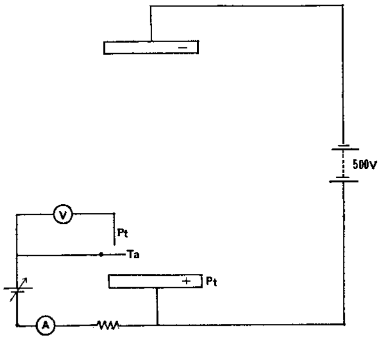

Figure 3 Circuit arrangement for gaseous anodisation.

With the discharge applied, the tantalum was at -0.3 V with respect to the reference electrode. On polarising the tantalum anodically, the voltage-current plot shown in curve B (fig. 2) was obtained. Uniform, oxide film thicknesses were produced when the tantalum was anodised at current densities of a few milliamps per square centimetre. The platinum reference electrode was cleaned between runs by heating in concentrated hydrochloric acid and under these conditions the initial tantalum-platinum potential was usually reproducible in the range -0.1 ± 0.2 V. It was also found necessary to clean occasionally the platinum anode in hydrochloric acid, otherwise slight non-uniformities in oxide thickness were observed. The effect was apparently caused by deposition of a contaminating film at the surface. The results obtained using this circuit are discussed in the next section.

4. Results

Voltage-time plots when chemically polished tantalum foil was anodised, using the circuit arrangement shown in fig. 3 at current densities in the range 0.5 to 4.0 mA/cm^2, are shown in fig. 4. Concomitant current-time curves when the voltage was held constant are shown in fig. 5.

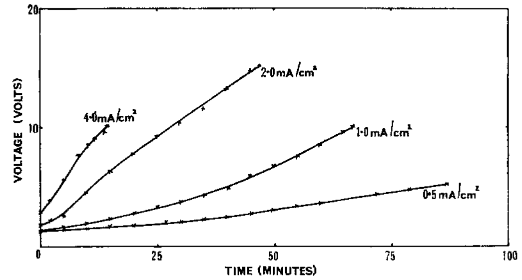

Figure 4 Voltage-time curves during gaseous anodisation of tantalum at current densities between 0.5 and 4.0 mA/cm^2.

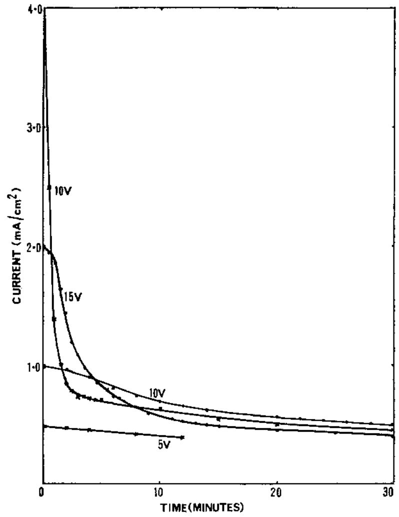

Figure 5 Current-time curves at constant voltage after gaseous anodisation of tantalum at current densities between 0.5 and 4.0 mA/cm^2.

Unlike the films formed at ambient temperatures on chemically polished foil by wet anodising, the oxide layers were found to be quite adherent. At a current density of 2 mA/cm^2, the voltage-time plot was relatively linear between 6 and 15 V, corresponding to a value of 0.25 V/min. This rate of formation is approximately 160 times lower than that achieved by wet anodising in dilute aqueous electrolytes at the same current density at 20° C. Plots at other current densities were non-linear; the overall rates of formation are given in table I. Between 1 and 4 mA/cm^2, the average current efficiency appears to be approximately constant in the voltage ranges studied, but there is a marked drop at 0.5 mA/cm^2. The current efficiency at 2 mA/cm^2 fell between 15 and 20 V and was quite low above 20 V. However, the tantalum continued to anodise and reached 28.5 V in 210 min. With the 20 kΩ resistor removed from the circuit, the average rate of formation at 25 mA/cm^2 was only 0.1 V/min, and at 20 V the film was found to be severely corroded.

TABLE I Rate of anodisation (V/min) at current densities between 0.5 and 4.0 mA/cm^2.

Current density (mA/cm^2)	Voltage range (V)	Mean rate of anodisation (V/min)
0.5	1 to 5	0.036
1.0	1 to 10	0.13
2.0	6 to 15	0.25
4.0	3 to 10	0.46

At voltages up to 20 V, the thickness of the film, estimated by comparison with an optical step gauge, was in the region of 24 to 28 Å/V. The corresponding value for wet anodising in dilute aqueous electrolytes at 20° C is about 16 Å/V; a value in the region of 25 Å/V would be expected at an anodising temperature of 180° C. However, the optical thickness of the films is related to the composition of the electrolyte and may be substantially different in non-aqueous solutions. A thermocouple introduced into the discharge at the same position as the tantalum indicated a temperature of 110° C. The observed adherence of the film after gaseous anodisation might be an indication that the actual temperature at the surface of the tantalum is rather higher than this value. Wet-anodised oxide layers become adherent to chemically polished foil on heating at temperatures in the region of 200° C; prolonged treatments at 120° C on the other hand have not been found to affect adherence. It is possible, of course, that ion bombardment prior to anodising could be the important factor in the gaseous system. Consequently, the actual thickness-temperature relationship is at present uncertain, but the general correspondence with wet anodising is apparent. It seems probable that a similar explanation may be advanced for the 23 A/V found with aluminium. [1].

When a sintered, porous, tantalum body, having a surface area of about 70 cm^2, was anodised at a current density of 0.14 mA/cm^2 in the glow discharge, oxide formation apparently proceeded quite rapidly at a rate of 0.04 V/min. At 20 V, the specimen had a uniform film colour and, on holding the voltage constant, the current decreased quite smoothly. However, on breaking open the compact, it was found that oxide formation had not occurred on the inside; the film colour was associated only with a thin surface layer. No improvement was observed on forming down for periods up to 210 min. Accordingly, a foil specimen was bent along one edge to form a cylinder of metal approximately 1 mm in diameter and 1 cm long. When this specimen was anodised, at a current density of 2 mA/cm^2, film was formed over the whole of the outer, or exposed, surfaces. On opening out the cylindrical section, it was found that, except for approximately 0.5 mm at each end, no film had formed on the inner surfaces. In the light of these experiments, it is evident that gaseous anodising has an exceptionally poor throwing power and is unable to form oxide in even quite large cavities. It would seem, therefore, that the most suitable application is to smooth, vacuum-deposited, metallic layers.

5. Discussion

In many respects, the electrical discharge may be considered to behave in a similar manner to the liquid electrolyte in conventional anodising. For example, if a tantalum specimen is short-circuited to the discharge anode, oxide films will grow to a thickness dependent on the open-circuit potential between the two electrodes. In addition, electrically isolated specimens will anodise to low voltages in the plasma by bipolar action, i.e. both anodic and cathodic reactions take place on the same electrode. The bipolar mechanism may be advanced as an alternative explanation to that of essentially field-assisted thermal oxidation for the recently reported growth of an oxide film at a silicon surface supported in a microwave-excited plasma [9].

A major difference is observed if the tantalum is anodised against an auxiliary platinum electrode, which is electrically isolated from the discharge anode. The form of the voltage-current relationship obtained with this circuit is shown in curve C (fig. 2). A large over-potential, which is presumably associated with the anodising cathode since anodic processes are found to occur satisfactorily in the plasma, is observed. A similar effect has been noted by Fopiano [6] using a platinum probe. Consideration of normal plasma conditions indicates that, owing to pronounced differences in velocity between electrons (the predominant negatively charged species) and positive ions, a large, positive space charge develops at the cathode. Consequently, transport of positive ions to the electrode surface is impeded and, in order to sustain the discharge, a relatively large voltage must be applied at this electrode. It is probable that the same mechanism is operative in the case of the auxiliary cathode. The reason why a cathodic reaction will proceed more easily at the plasma anode could be because this process involves reduction of negative oxygen ions, which are transported to the electrode under the influence of the main discharge voltage and against only a small, negative space charge. Accordingly, the electrode reactions in the plasma may be visualised as follows:

(*a*) *Anode*

$$\epsilon_{(\text{gas})} \rightarrow \epsilon_{(\text{solid})} \qquad (1)$$

$$O^- \rightarrow O^\cdot + \epsilon \qquad (2)$$

(*b*) *Tantalum*

$$\epsilon_{(\text{gas})} \rightarrow \epsilon_{(\text{solid})} \qquad (3)$$

$$2Ta + 5O^- \rightarrow Ta_2O_5 + 5\epsilon \qquad (4)$$

(*c*) *Anode where cathodic to tantalum*

$$O^- + \epsilon \rightarrow O^= \qquad (5)$$

Since electrons are the major, negatively charged species, reactions (1) and (3) are dominant at the anodes, and low current efficiencies of anodisation are apparent. At the discharge cathode, positive oxygen ions predominate.

(*d*) *Cathode*

$$O^+ + \epsilon \rightarrow O^\cdot \qquad (6)$$

It is possible that molecular oxygen contributes, either by reduction to negative ions or oxidation to positive ions, to the reactions at each of the electrodes. For example, at the tantalum surface, a reaction of the following type may take place:

$$2Ta + 5O_2 \rightarrow Ta_2O_5 + 5O^+ + 5\epsilon \qquad (7)$$

Reaction (7) may be compared with the liquid-anodising reaction in acid or neutral aqueous solution:

$$2Ta + 5H_2O \rightarrow Ta_2O_5 + 10H^+ + 10\epsilon \qquad (8)$$

It is apparent that reactions (4) and (7) require only half as much of the quantity of electricity to form a given weight of tantalum pentoxide as reaction (8), and so the theoretical current efficiency of the gaseous process is double that of the wet.

The limited throwing power of the glow discharge is presumably related to an electrostatic shielding effect, which results in only molecular or atomic oxygen penetrating into recessed or porous areas. Owing to the low conductivity of the oxygen, the high field at the oxide, necessary for growth, is absent. It is possible that throwing power might be improved by altering the plasma conditions to give an increased concentration of charged species, but it is doubtful whether the process can be sufficiently modified to enable even moderately porous bodies to be anodised.

The low current efficiency of anodisation may be related, as already indicated, to the predominance of electrons in the discharge. These could channel down defects in the oxide film. However, it should be noted that high-temperature anodisation of tantalum in fused salt electrolytes (circa. 200 to 300° C) has also both a low current efficiency and a low maximum voltage. Possibly at high temperatures, the electronic current through the bulk of the oxide competes effectively with the ionic current, the latter being normally dominant at ambient temperatures.

6. Conclusions

(*a*) Oxide films of non-uniform thickness are formed during gaseous anodisation if the initial open-circuit potential between the tantalum and the plasma anode is large. It is necessary to avoid using reactive metals for the anode as these may themselves form anodic layers of high resistivity.

(*b*) A suitable anodising circuit employs a platinum anode and incorporates a high series resistor. A platinum wire positioned close to the tantalum makes a convenient reference electrode.

(*c*) Constant current anodisation of tantalum foil in the range 0.5 to 4.0 mA/cm^2 indicates a thickness of oxide in the region of 24 to 28 Å/V in the voltage range 0 to 20 V.

(*d*) The higher thickness-voltage relationship found with gaseous anodising can largely be accounted for by the higher temperatures present in the plasma.

(*e*) Gaseous anodising has both a low current efficiency and a poor throwing power. It is most suitably applied to smooth, vacuum-deposited materials.

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