

FAILURE MECHANISMS IN SOLID ELECTROLYTIC CAPACITORS

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The failure mechanism of solid tantalum and aluminium capacitors have been investigated using a combination of electrical measurements and electron microscopy. The capacitor dielectric was examined before and after life testing and changes correlated with electrical measurements.

The basic mechanism of failure of solid tantalum capacitors is found to be field crystallisation of the essentially amorphous dielectric oxide. The growth of higher conductivity crystalline oxide during operation of the capacitors causes an increase in leakage current and may result in catastrophic failure. The effect of field crystallisation can be minimised by using high purity tantalum to reduce the number of crystallisation nucleation sites. Since crystalline growth is primarily dependant on applied voltage, high voltage capacitors are much more susceptible to failure than low voltage units.

There appears to be no long term failure mechanism in solid aluminium capacitors. However, a particular problem with these units is that they are difficult to make. This is because the anodic layer is chemically less stable in the case of aluminium than in the case of tantalum. The attack is initiated during the deposition of manganese oxide by pyrolysis from manganese nitrate solution and developed by the reform process. Solid aluminium capacitors often have a lower capacitance and higher initial leakage current than comparable solid tantalum units; however, the leakage current decreases on life tests and their reliability is high.

1 INTRODUCTION

In solid electrolytic capacitors the liquid electrolyte of conventional liquid filled types is replaced by a solid conductor of manganese oxide.^{1,5} The higher conductivity of manganese oxide imparts significant improvements in performance, especially under conditions of low temperature and high frequency. Tantalum capacitors constitute the majority of solid types, only a small proportion being made from aluminium.

Although liquid filled tantalum capacitors have a reputation for high reliability,² it is general experience that solid tantalum units have a tendency to undergo a sudden and catastrophic failure. When the capacitor is used in a low impedance circuit, failure rate may be particularly high. Earlier studies in these laboratories of field crystallisation of anodised tantalum in aqueous electrolytes³ prompted a belief that the same process might be the principal cause of failure in solid capacitors, although it has been shown that at least for aqueous electrolytes, other failure mechanisms are possible.⁴

The significant features of field crystallisation relevant to this reasoning are:

a) The crystalline form of the oxide is more conductive than the amorphous form.

b) The crystalline form grows within the amorphous film and may rupture the dielectric.

c) In contact with a liquid electrolyte sufficient crystalline material may eventually grow by anodisation to limit the leakage current; no such mechanism may be present with a solid electrolyte.

The present work attempts to determine whether field crystallisation is responsible for the observed failures in solid tantalum capacitors and the mechanism by which such failures occur.

Failure processes in solid aluminium capacitors, the dielectric of which is known not to undergo field crystallisation, have also been examined. The work has principally involved a study of the changes in the physical, chemical and electrical properties of the dielectric of experimental capacitors during storage at elevated temperature with voltage applied.

2 EXPERIMENTAL CAPACITOR CONSTRUCTION

In order to facilitate the examination of the dielectric layers, wound foil electrodes were used. Since field crystallisation is known to be promoted by impurities in the foil³ most of the work was performed with relatively low purity anode foil. In the case of

tantalum, degreased capacitor grade foil of thickness 0.0013 cm was used, previous work having established that foils cleaned in this way had a surface impurity level of approximately 10^7 particles cm^{-2} .³

Aluminium anodes were prepared from degreased 99.8% foil of thickness 0.005 cm. A brief description of the constructional features of the capacitors is given in this section; specific details of processing are given in paragraph 3.1 and 4.1.

Tantalum and aluminium foils were cut to a width of 1 cm and a length of 7 cm. Riser wires of the same material as the anode were attached at one end. After cleaning, the foils were anodised, washed and dried, and then wound tightly with an etched aluminium cathode and a fibreglass spacer, using the riser wire of the aluminium cathode as a mandrel. The wound structure was secured with chloride free adhesive tape and then reanodised to heal damage caused to the dielectric during assembly.

The unit was coated with manganese oxide using standard impregnation procedures with manganese nitrate followed by high temperature pyrolysis.¹ Anodisation (reforming) in a liquid electrolyte was applied at intervals during coating. This process is usually known as reforming, since the nature of the electrochemical reaction is not fully understood and it is useful to distinguish it from normal anodisation. No encapsulation was employed. In most cases capacitors were tested using a low impedance lead-acid battery as a voltage source.

3 TANTALUM CAPACITORS

Capacitors were constructed using anodes prepared in three different ways:

- 1) anodised to 150 V,
- 2) anodised to 24 V,
- 3) anodised to 150 V on specially purified tantalum.

Foil for 1) and 2) was degreased before anodising by immersion in warm propan-2-ol. For 3), the standard foil was vacuum annealed at 1950°C for 30 minutes at a pressure of 10^{-4} torr.

3.1 Preparation

The anode foil was formed to the appropriate voltage in 1% phosphoric acid at 90°C using a current density of 0.1 mA cm^{-2} , followed by a period of 60 minutes at constant voltage. Reanodisation after winding was effected under the same conditions, but the period at

constant voltage was limited to 15 minutes. The coils were impregnated in manganese nitrate solution (s.g. = 1.73 g cm^{-3}) at 50°C and pyrolysed at 300°C for 10 minutes. After three coatings had been applied, the units were reformed in 0.01% phosphoric acid at 85°C. The reform voltage, approximately 40% of the original voltage, was attained by applying a current of 0.1 mA cm^{-2} and then holding at constant voltage for 30 minutes. After final washing the capacitors were dried for 1 hour at 125°C. Dry capacitance values were approximately 80% of the initial wet values. Typical unit characteristics at room temperature were as follows: High voltage capacitors (150 V), capacitance = $0.8 \mu\text{F}$, $\tan \delta = 2.5\%$ (50 Hz), leakage current $< 1 \mu\text{A}$ (10 V); Low voltage capacitors (24 V), capacitance $< 3.3 \mu\text{F}$, $\tan \delta = 6\%$ (50 Hz), leakage current = $15 \mu\text{A}$ (6 V).

The thickness of oxide would have been approximately 240 nm and 38 nm respectively.

3.2 Life Test Results

Foils anodised under the conditions described in the preceding section were made up into capacitors and tested at 125°C. Units anodised at 150 V were initially tested at 40 V; because of rapid failures, this was reduced to 30 V. Units anodised at 24 V were tested at 4.8 V, i.e. at the same field strength ($\sim 1.25 \times 10^8 \text{ V/m}$) as the higher voltage units at the reduced level. Figure 1 shows the form of the leakage current/time plot for the three types of capacitor. It can be seen that low voltage capacitors and capacitors using purified foil have low and constant leakage currents, whereas high voltage capacitors exhibited a sharply rising leakage current which peaked early in the life test and slowly declines thereafter. In addition to the normal high leakage currents, current surges often occurred in this type of capacitor which could blow 100 mA safety fuses placed in series with each capacitor. The capacitor often recovered on replacement of the fuse, but the latter was sometimes blown again at a later date.

3.3 Structure of the Anodic Oxides

3.3.1 High voltage capacitor (degreased foil)

a) Before Life Test Figure 2(a) shows the general structure of the oxide. Defects in the film lie in lines along the rolling direction of the foil suggesting that they are initiated from damage induced by rolling or impurities introduced by the rolls. The defects are of three main types: bumps, cracked bumps and pits.³

Figure 2(b) shows a cracked bump in more detail.

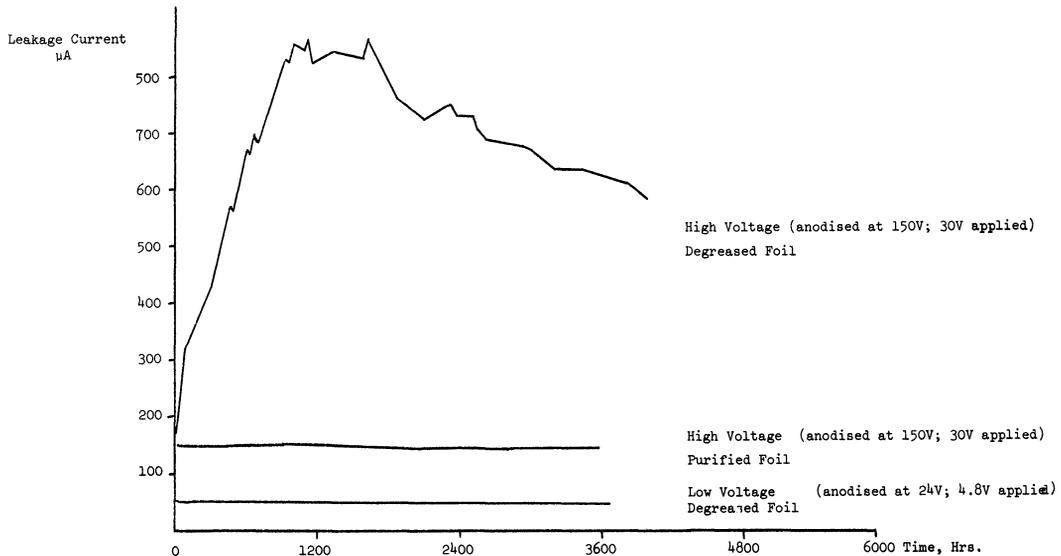


FIGURE 1 Leakage current vs time for solid tantalum capacitors (125°C)

The structure is $\sim 1.5 \mu\text{m}$ across and consists of a pyramidal growth of crystalline oxide cracking open the amorphous oxide to produce a characteristic three branched crack.

The uncracked bumps are somewhat smaller in diameter, generally from $1 \mu\text{m}$ downwards without a visible crystalline body. Low angle examination of these features shows that they are approximately hemispherical in shape. Using transmission electro microscopy the cracked sites appear as dark triangular features and the larger number of uncracked sites as

small circular dark areas with a wide distribution of sizes. Rather indefinite pits lying in the rolling direction can also be seen. When decreasing the microscope accelerating voltage the number of visible pits slowly diminished indicating that they have varying depths. At higher magnification (Figure 3(a)) the trefoil shape of the cracked sites can be clearly seen and small pores can be observed within uncracked bumps. These small pores ($< 0.1 \mu\text{m}$ diameter) show much more clearly if the tantalum oxide is thinned slightly by argon ion bombardment or a few seconds etching in HF; under

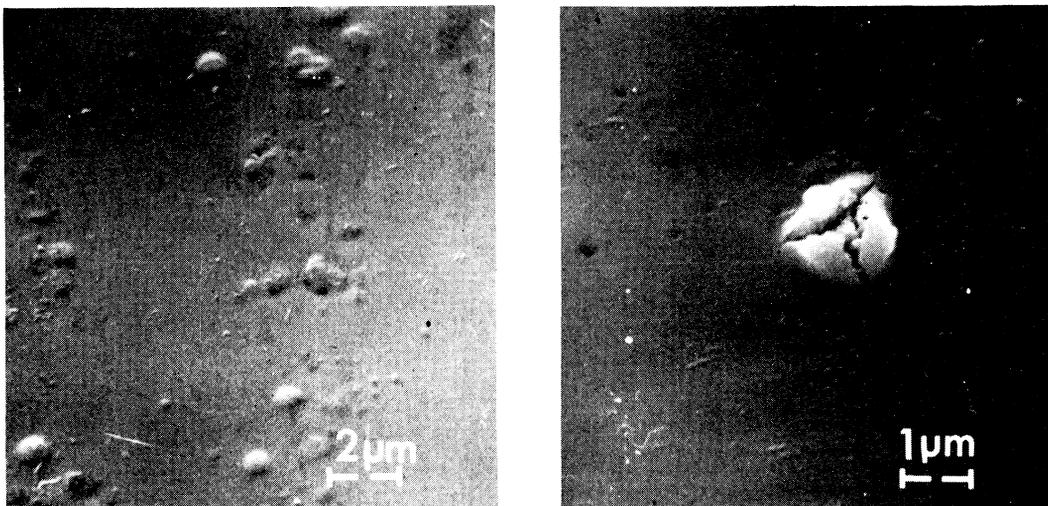


FIGURE 2 Structure of 150 V film prepared on degreased tantalum foil: (a) general structure, (b) cracked bump.

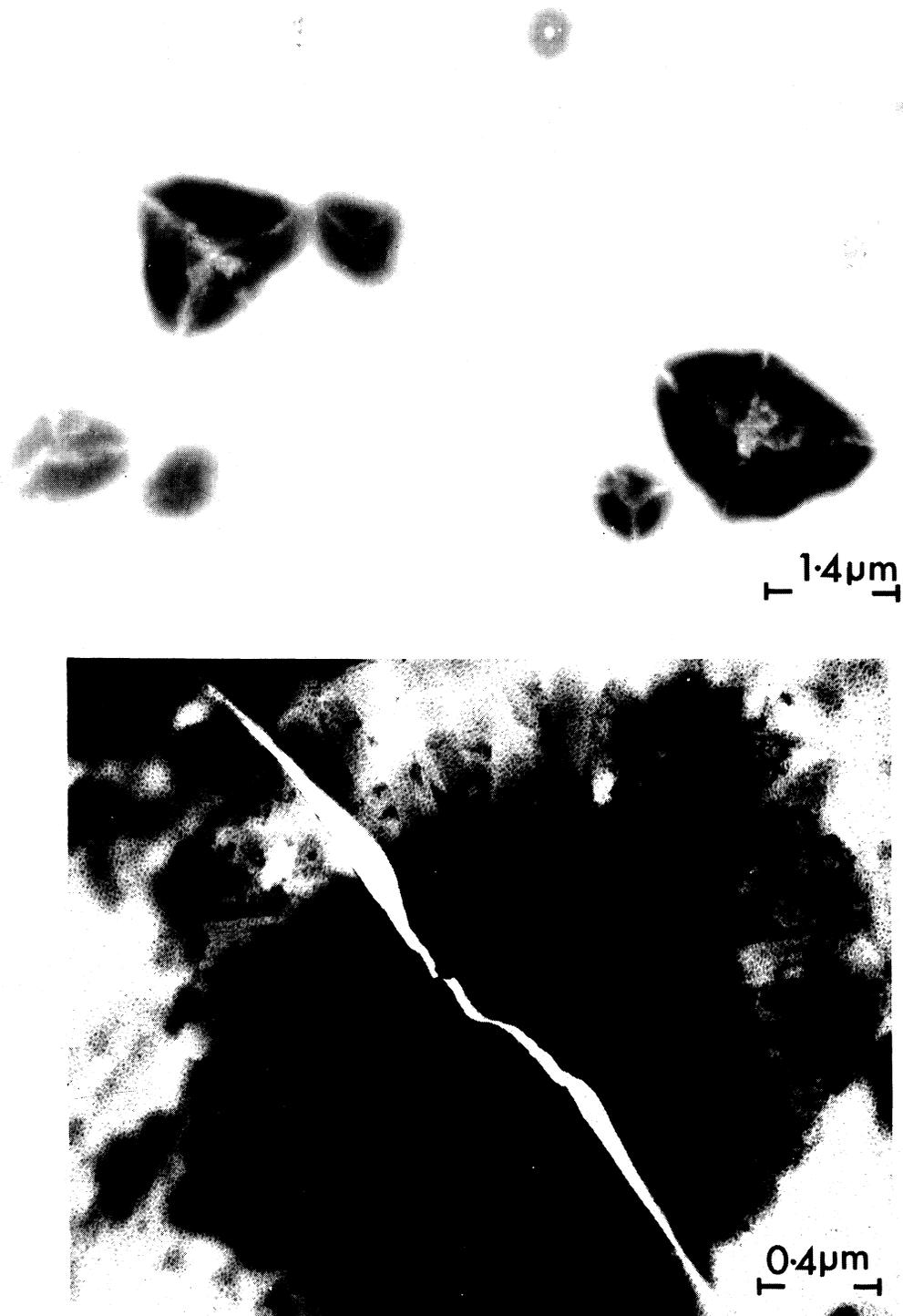


FIGURE 3 Structure of 150 V film prepared on degreased tantalum foil:
(a) transmission micrograph
(b) after argon beam thinning, (the white line across the micrograph is an artefact produced by the film rupturing).

these conditions every bump can be shown to have a central pore. Tilting of the specimen shows that these pores are not spherical but are in fact elongated in the direction of the film thickness. Examination of the under surface of a stripped film shows that bumps are again present lying along the rolling direction; these bumps often have dimples in their surface.

To examine the structures below bumps and cracked bumps argon beam thinning of the stripped oxide film was attempted. A thinned bump is shown in Figure 3(b). The centre of the bump is still dark due to thickness contrast but a fringe of crystalline oxide showing diffraction contrast can be seen.

Selected area electron diffraction shows the crystalline oxide to be $\beta\text{-Ta}_2\text{O}_5$

From the above observations it can be seen that a variety of structures can be observed in the essentially amorphous oxide produced on nominally pure tantalum. From this and earlier work³ it appears that bumps and pits can form at impurity sites in the underlying metal, a number of the bumps become particularly large, crack and reveal a crystalline nucleus below. During prolonged anodisation it has been shown³ that this nucleus can grow and displace the amorphous oxide film with a crystalline film.

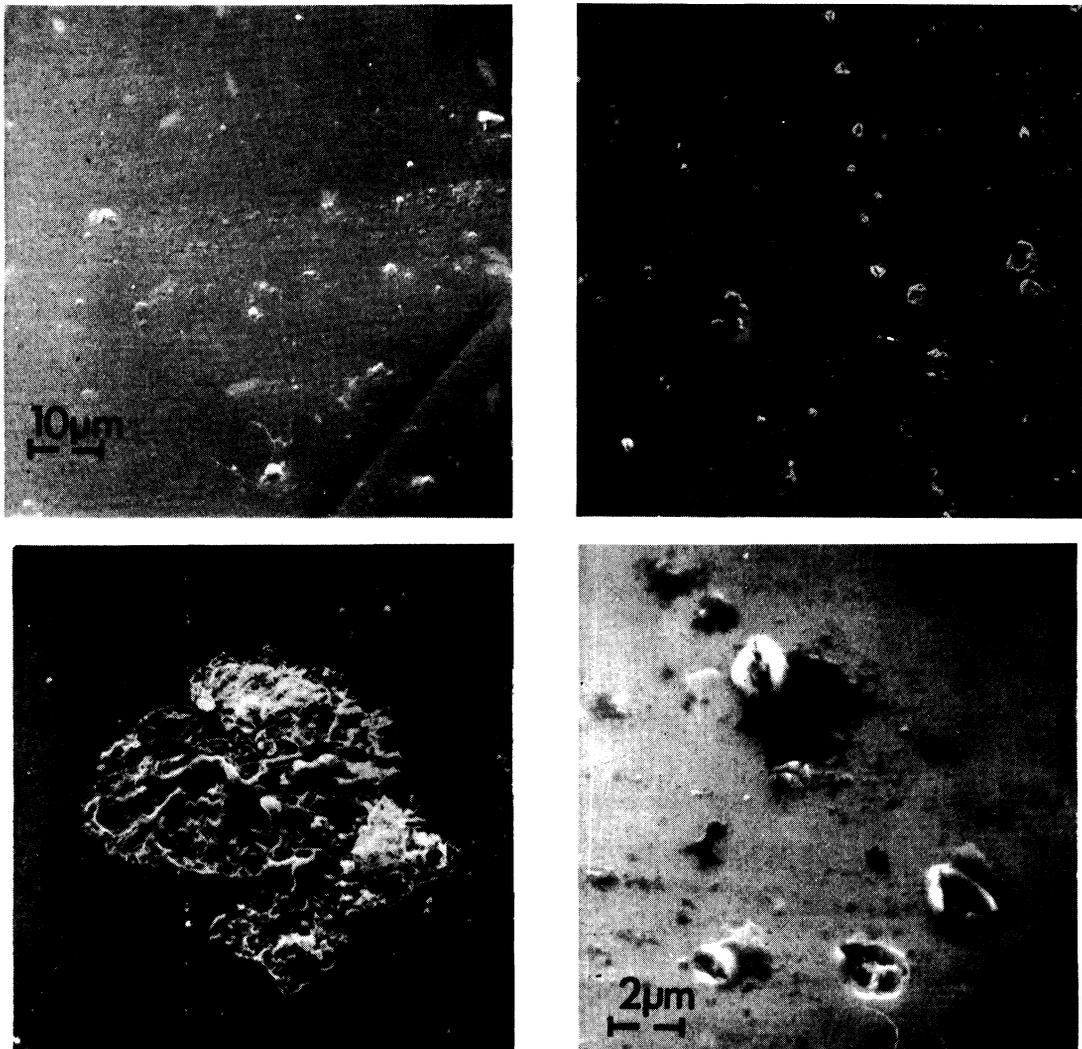


FIGURE 4 Structure of 150 V film prepared on degreased tantalum foil: (a) before life test, (b) after life test (1000 hours), (c) large breakdown site, (d) after extended life test (9000 hours).

b) **After Life Test** Standard, high voltage capacitors which had been on life test for several thousand hours and which were therefore showing large leakage currents were removed from life test, the manganese dioxide removed with $\text{HNO}_3/\text{H}_2\text{O}_2$ reagent and the anodic oxide re-examined using the microscopical methods described earlier. On stripping film for transmission electron microscopy it was immediately obvious that the film was very much more fragile than the untested film. The reason for this was apparent on examination: many large cracked bump sites were present after testing, the centre of the defect often being lost, so leaving a hole in the film. All stages of defect growth could be seen, in contrast to untested film where either uncracked bumps or bumps in a late stage of crack development were more usual.

To obtain more quantitative information on the morphological changes occurring during life testing random areas of life tested and untested foil were examined by scanning electron microscopy and the numbers of cracked and uncracked bumps compared. Figures 4(a) (untested) and 4(b) (lifetested) are a comparison of typical areas. It was found that the number of large cracked bump sites approximately

doubled on life testing. A much larger change, 1–2 order of magnitude, was seen in the number of uncracked bumps. Generally these bumps were larger, more distinct and more difficult to distinguish from the cracked bumps in the lifetested case than in the untested case; a less strict definition of what was taken as a cracked site would have produced a much larger ratio than the doubling reported above. In addition to the defect sites much larger failure sites (Figure 4(c)) were observed. The probable sequence of events is that bumps grow in size during life test and finally crack open; a number of these cracked sites then suffer electrical breakdown resulting in the structure shown.

Capacitors which had been on test for much longer periods were also examined. These had suffered a slow gradual decline in leakage current from the early high value. Figure 4(d) shows a typical area of oxide film in such a unit; it appears that the cracked bump sites had become damaged. All stages of damage could be seen, from the lip of the site being partly broken away, through the "cap" of the site being removed exposing the underlying crystal to the crystal being removed. It appears possible, therefore, that the

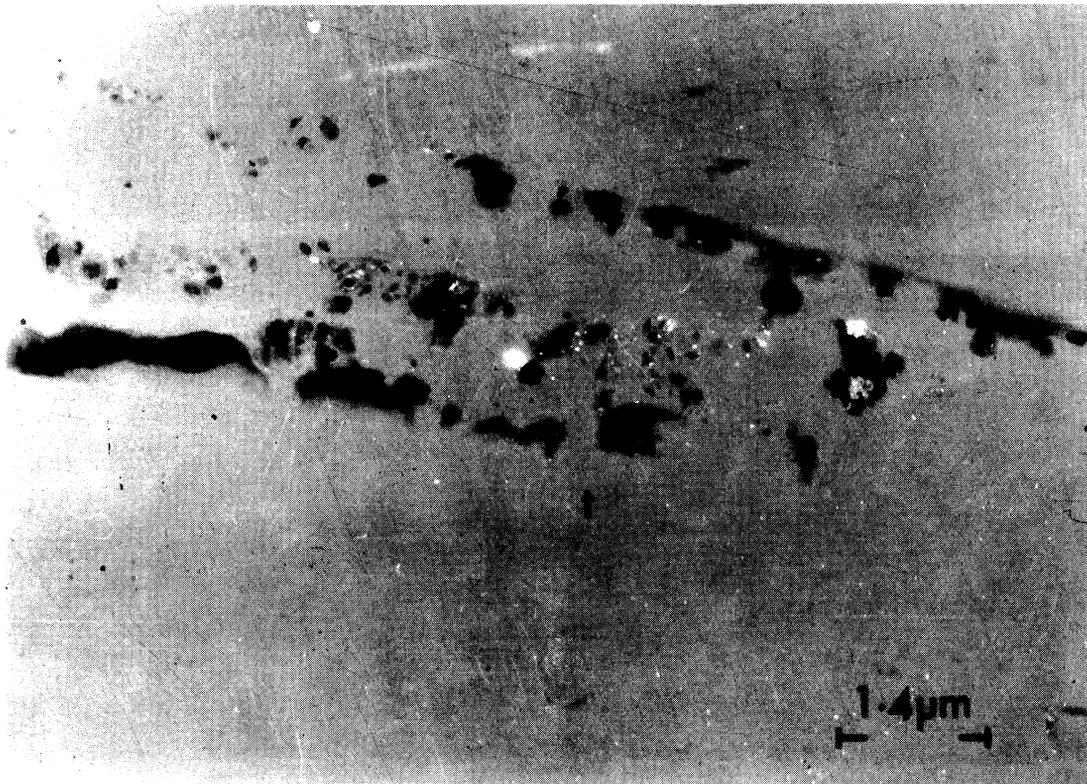


FIGURE 5 Structure of 24 V film prepared on degreased tantalum foil.

decrease in leakage current later in the life test may be due to conducting crystallisation sites mechanically detaching from either the manganese oxide or the tantalum, thus lowering the current.

3.3.2 Low voltage capacitors In contrast to the high voltage oxide, no differences in structure were apparent between films examined before and after life test.

Scanning electron microscopy showed that none of the pit, bump or cracked bump features previously observed could now be seen. However because the film had consumed such a thin layer of tantalum during anodisation (~ 20 nm)⁶ the original surface of the tantalum was effectively replicated resulting in a rough looking oxide. The close replication of the surface allowed the extraction of surface impurities by the oxide (Figure 5). The dark areas are tantalum metal retained in the folds of the rough oxide, the bright particles being crystalline impurities shown up by the dark field conditions employed in the electron microscope. It has proved difficult to analyse these particles sufficiently well by selected area diffraction

to identify them unequivocally; however it can be shown that they are not Ta_2O_5 .

Examination of low voltage anodic oxide has therefore shown that the structures present in higher voltage oxides are absent but that impurities from the underlying tantalum are incorporated in the growing oxide.

3.3.3 Oxide formed on specially purified tantalum As with the low voltage oxide, life testing had no effect upon the structure. On examination the oxide was found to be smooth and largely defect free. An occasional line of impurities could be discerned following a prior grain boundary in the underlying metal and crystallisation sites were present at a few of these impurities (Figure 6). It can be seen therefore that a purification treatment greatly inhibits the occurrence of defects in the anodic oxide by reducing the number of initiating impurities. Although the starting foil was of 99.99% purity spark mass spectrometry has shown that most impurity elements have concentrations 1–2 orders of magnitude higher at the

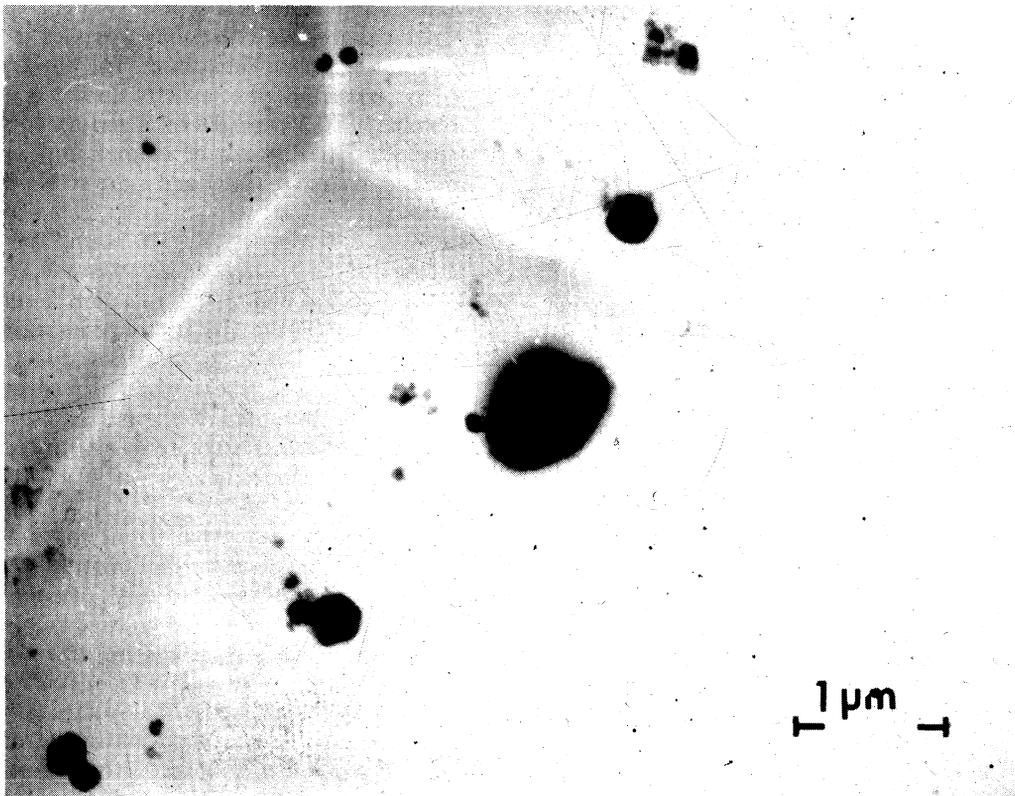


FIGURE 6 Structure of 150 V film prepared on purified tantalum foil.

surface than the bulk. Therefore nominally 99.99% pure material may have only a 99% pure surface layer.

3.4 *Environmental Effects on Solid Tantalum Capacitors*

Early in the life test it became apparent that the leakage current of the capacitors was dependant on environment; large initial changes occurred on "drying out" of the capacitors in the first few hours on test and admitting fresh moist air by opening the oven door later in the test perturbed the leakage current values. It appeared possible that the environment, particularly water vapour, could affect the degradation mechanism. Therefore, the dependance of capacitor characteristics on environment was investigated more systematically.

An all glass vacuum system capable of vacuum drying capacitors at 125°C and $<10^{-3}$ torr was used. Capacitors were held in capsules, dried under dynamic vacuum and backfilled as required with gaseous environments. The capsules could be sealed on the vacuum line, removed, and the capacitors life tested in the sealed capsules. Testing voltages were applied via contacts sealed through the capsule walls. The environments examined were 13 torr of air free water vapour, dry air at 760 torr, dry oxygen at 760 torr and perfluoro-N-Hexane at 234 torr. This last gas is known to inhibit electrical discharges because of its high breakdown strength and could possibly inhibit the formation of large electrical breakdown sites if breakdown through air was involved in their formation. The dry gases had a residual water content estimated at $<5 \times 10^{-5}$ torr.

Of the environments examined only water vapour was found to have any effect on the leakage current/time plots of the capacitors on life test. The effect of water vapour was examined more closely by life testing capacitors in capsules attached to the vacuum line so that known pressures of water vapour could be introduced to, or removed from, the capacitor at will during the test.

It appeared from the observations that two independent processes were occurring. Firstly there was the basic degradation mechanism which caused the leakage current to rise steadily and irreversibly with time, and which was unaffected by water vapour.

Secondly, superimposed on this steady increase in current, short term reversible decreases could be made to occur by introducing water vapour. This effect was in contrast to the effect of liquid water where leakage current rises sharply because water makes electrical contact with damaged areas of oxide previously

uncontacted by manganese dioxide. It appears that water vapour at 125°C probably enters the manganese oxide structure and increases its resistivity, thus lowering leakage current.

3.5 *Circuit Impedance Effects on Solid Tantalum Capacitors*

Commercial experience suggests that solid tantalum capacitors are more stable in service if they have an impedance in series with them than if they have voltages applied from a low impedance source. To check this and investigate the mechanism of the circuit impedance effect, life tests were performed with an added circuit impedance.

A four terminal power supply was adapted with a 1 k Ω series resistor to provide up to 20 mA without voltage drop to the capacitor terminals; from 20 mA to 50 mA the capacitor terminal voltage fell linearly from 30 to 0 V. In this way variations in applied voltage due to variations in steady state leakage current could be avoided while maintaining the ability of the circuit impedance to inhibit large current surges. A series of standard capacitors with voltages applied from this power supply were compared with a series with voltages applied from low impedance lead-acid batteries. The power supply voltage was adjusted to exactly the battery voltage (nominally 30 V) and the tests performed simultaneously. The addition of a circuit impedance resulted in a much lower and more stable leakage current which increased gradually from about 20 μ A to 45 μ A over a period of 1300 hours. The morphology of the oxide surface before and after life test is shown in Figure 7. With a high circuit impedance, bumps in the film, although increasing in number during life test as in the low circuit impedance case, do not generally crack, in contrast to the observations reported in Section 3.3.1. A further important feature was the initial absence of large electrical discharge sites, only one of these being found.

It appears that an added circuit impedance not only prevents the development of large electrical discharge sites but also the growth of uncracked bumps into somewhat larger cracked bumps. The smoothness of the leakage current/time plot in the low impedance case suggests a gradual increase in the number of "leaky" cracked bump sites rather than the sudden appearance of the occasional large electrical discharge site. To investigate the mechanism of the circuit impedance effect more closely some order of magnitude calculations were performed to see

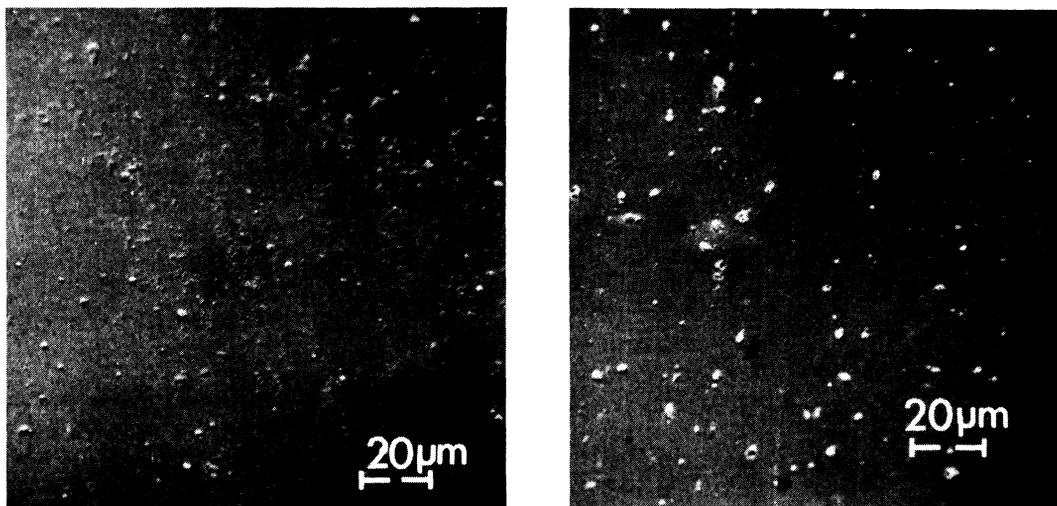


FIGURE 7 Structure of 150 V film prepared on degreased tantalum foil after life testing: (a) high impedance circuit (b) low impedance circuit

what effect current surges could have on the bump and cracked bump sites.

A model for a defect site may be developed by considering it as a disc shaped area of low resistance surrounded by an area of high resistance. The rate of heat input from the power supply minus the rate of heat loss of the disc by conduction to its surroundings gives the net rate of change of heat content of the disc in the form of a differential equation. Approximating the situation by assuming heat is only conducted from the disc through the metal tantalum, a solution can be obtained:

$$t = \frac{\text{d.m.c.}}{kA} \ln \left(\frac{IV}{IV - kAT/d} \right)$$

and

$$T_{\max} = \frac{IVd}{kA}$$

where t = time required to reach temperature T .

d = distance from disc to unheated tantalum substrate.

m = mass of disc

c = specific heat of disc

k = thermal conductivity of tantalum

A = peripheral area of disc

I = power supply current

V = power supply voltage

T_{\max} = maximum temperature attainable.

Substituting suitable values† of these variables for small crystallisation sites and large damage sites allows the response of these sites to current surges from the power supply to be evaluated.

Because of their very small size, surge currents through crystallisation sites lead to extremely high temperatures in extremely short times e.g. 10^4 °C in 3×10^{-8} sec. More realistic results are obtained in applying the calculation to large damage sites e.g. 10^4 °C is reached in 3×10^{-5} sec. suggesting that a circuit impedance which would limit the current passed to much less than the value of 100 mA used in the calculation may act by preventing an excessive temperature rise at such a defect site.

† Values used in the calculations were as follows:—

- | | |
|--------------------------|----------------------------------------------------------------|
| (i) Small Crystal Sites | $I = 10^{-2}$ amps |
| | $c = 0.4$ joules/gm ⁻¹ |
| | $A = 7.85 \times 10^{-3}$ m ² |
| | $m = 1.93 \times 10^{-12}$ gm |
| | $d = 10^{-6}$ m |
| | $K = 5 \times 10^{-3}$ watts m ⁻¹ /°C ⁻¹ |
| (ii) Large Damaged Sites | As for above, except: |
| | $I = 10^{-1}$ amps |
| | $A = 7.85 \times 10^{-9}$ m ² |
| | $m = 1.93 \times 10^{-8}$ gm |

4. ALUMINIUM CAPACITORS

4.1. Preparation

Plain anode foils were formed to 80 V in a borax-phosphoric acid electrolyte at 95°C, using a constant current density of $\sim 6 \text{ mA cm}^{-2}$. The anodes were held at the forming voltage for 30 minutes. Reanodisation after winding, was accomplished at 80 V for 30 minutes in a saturated aqueous solution of ammonium pentaborate (A.P.B.) at room temperature, using the internal cathode of the coil as the counter electrode. Impregnation was performed in manganese nitrate solution (s.g. = 1.61 cm^{-3}) at 50°C, followed by pyrolysis at 350°C for 15 minutes. Reformation was then carried out using the identical conditions to those for reanodisation. Current densities used to attain the reform voltage were chosen to be as low as possible, while still maintaining a reasonable rate of increase of voltage with time up to 80 V. After washing and drying, two further pyrolyses and reformations were given; the level of the final current after reform increased with the number of coatings applied. Three coatings were found to be the maximum possible, since additional applications resulted in little observed reform action and very high leakage currents in the finished capacitors. In general, units after three coatings had dry capacitance values of 70–80% of the initial wet values. Typical unit characteristics at room temperature were: capacitance = $0.5 \mu\text{F}$, $\tan \delta = 4\%$ (50 Hz), leakage current = $1 \mu\text{A}$ to $40 \mu\text{A}$ at 10 V. The film thickness was approximately 11 nm.

4.2. Electrical Measurements

Capacitors were life tested at 125°C with 30 V d.c. applied. Initial leakage currents were similar to the tantalum units but subsequent behaviour was markedly different. In general the leakage current decreased with time up to ~ 1000 hours and then remained essentially constant for test periods up to 9000 hours. The initial decrease in current was found not to be a "drying-out" effect, dependant upon temperatures alone. This was established by storing capacitors at 125°C for 2,500 hours prior to applying the voltage. As shown in Figure 8, the leakage currents decreased in the same way as the control capacitors. It was also observed that if the applied voltage was interrupted for a short period of time when the leakage-current had fallen to the steady value, a significantly lower current was apparent on reconnection. However, a gradual recovery to the steady value occurred over a time period of several tens of hours.

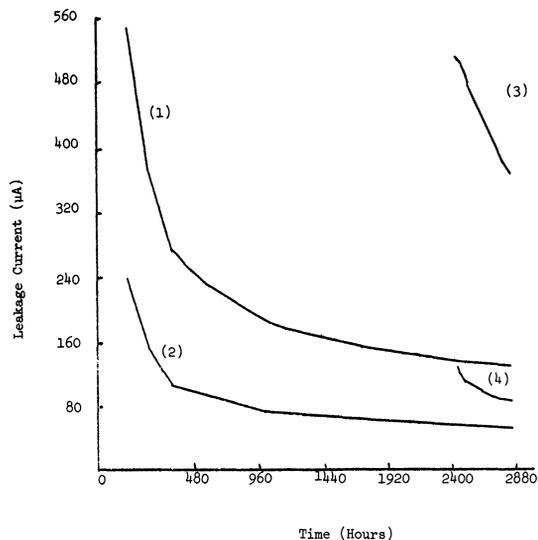


FIGURE 8 Leakage current vs time for solid aluminium capacitors on test at 125°C with 30 V applied. Nos. 1 and 2, testing voltage applied immediately specimens had reached temperature. Nos. 3 and 4 testing voltage applied after 2400 hours at temperature.

4.3. Structure of Anodic Oxide

Examination of the anodised foil revealed the presence of nodules of non-coherent oxide distributed randomly over the surface (Figure 9(a) and (b).) The nodules were in the region of $1 \mu\text{m}$ to $3 \mu\text{m}$ in diameter and had a population density of $\sim 3 \times 10^6 \text{ cm}^{-2}$. Electron probe microanalysis indicated a high concentration of iron at the nodular sites. After processing and immediately prior to life testing, the surface showed signs of severe corrosion, a particularly bad area containing massive damage being shown in Figure 9(c). After life testing, many of the less damaged sites had become plugged with new oxide growth (Figure 9(d)).

Studies of the changes occurring during processing of the capacitor indicated that little attack was apparent until after the first pyrolysis/reform. It appeared that pyrolysis initiated damage to the oxide layer and these sites then underwent dissolution during the reform process. The nature of the damage to the oxide caused by the pyrolysis could not be established. For example, X-ray diffraction failed to detect the presence of any hydrated oxide, e.g. Boehmite, and there was no apparent correlation with surface impurities. However, examination after pyrolysis revealed a corrosion pattern characteristic of the warp and weft structure of the fibreglass spacer

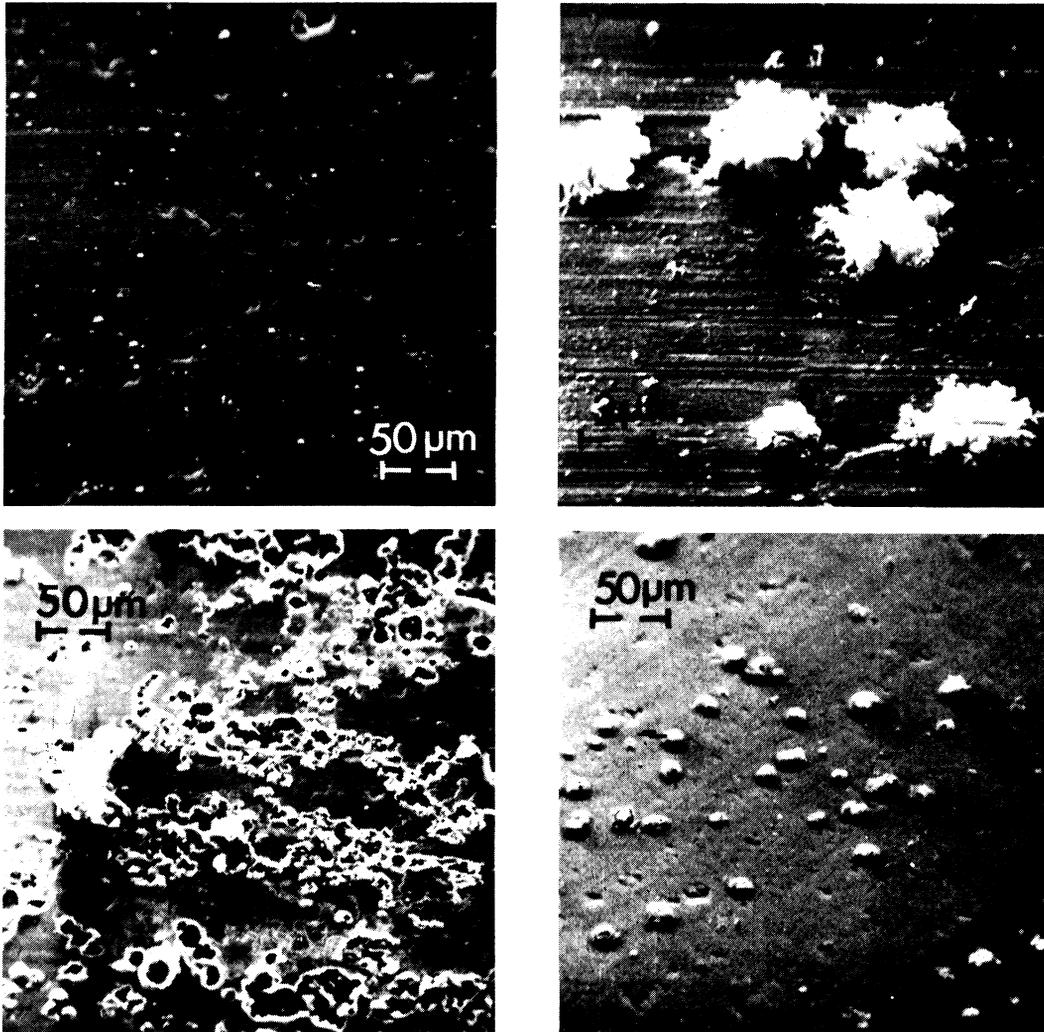


FIGURE 9 Structure of aluminium oxide: (a) & (b) after anodisation, (c) after final reform showing a severely corroded area, (d) after life testing.

and indicated that damage to the anodic oxide was largely confined to those areas where the spacer was in close contact with the surface. This was probably because the decomposition products of pyrolysis, largely oxides of nitrogen and water, could not readily escape from these regions. It was observed that the 'dry' leakage current was always much lower than the 'wet', suggesting that much of the reform effect was due to electrical isolation of the damaged sites rather than a reanodisation of the base aluminium.

4.4. Evaluation of Pyrolysis Damage

The dissolution rate of anodised aluminium in

bromine-methanol may be used for indirectly measuring the damage caused by pyrolysis. The bromine-methanol reagent has been used extensively in this work to strip oxides from the underlying metal. The basis of this technique depends upon the selective solubility of the metal in the reagent. The dissolution of the metal proceeds via defects in the oxide which allow access to the reagent. Thus a measure of the extent of damage after pyrolysis can be readily obtained by determining the weight after immersion under standard conditions. Results for specimens pyrolysed three times without reformation are given in Table I. Pyrolysed specimens were found to show a greater weight loss than untreated specimens.

TABLE I

Weight loss of anodised aluminium specimens in bromine-methanol reagent

Experiment no.	Specimen	Dissolution time (hr)	Wt. Al lost (%)	Ratio of wt. loss
1	Pyrolysed	1.75	8.9	1.9
	Untreated	1.75	4.7	
2	Pyrolysed	3.0	36.3	9.3
	Untreated	3.0	3.9	
3	Pyrolysed	3.0	50.4	4.5
	Untreated	3.0	11.2	

The spread in the results is not unexpected, since there will be an inherent variability in the sizes and the numbers of defects. In addition, problems arise due to differences in the activity of the reagent caused by small variations in the amount of water.

5 DISCUSSION

This work has provided evidence that the major cause of failure in solid tantalum capacitors is the growth of crystalline oxide in the amorphous oxide dielectric at localised sites during capacitor operation, so creating low resistance paths through the dielectric. High currents through these sites can lead to catastrophic thermal breakdown of the capacitor. The crystallisation sites lie in longitudinal lines suggesting that they are initiated by mechanical damage or chemical impurities introduced by the foil rolling process. It has been shown that impurities exist at the surface in very much higher concentrations than the bulk but it is difficult to determine the composition of the impurities unequivocally because of their very small size ($<0.1 \mu\text{m}$). The probable dependence of crystallisation site initiation on impurities or mechanical damage immediately suggests that improvements in capacitor reliability may be made by using vacuum heat treated material. This was found to be the case; vacuum purification of tantalum foil at 1950°C for 30 minutes gave anodic films which were largely crystallisation site free and which were stable in capacitors on life test.

Field crystallisation may also be controlled by limiting the anodising voltage. Low voltage capacitors utilising low voltage film do not appear to be subject to failure by field crystallisation. It is known from earlier work that the incidence of field crystallisation decreases as the anodising voltage is

reduced. There does not appear to be a simple relationship between voltage and degree of crystallisation; neither is it possible to define very easily a voltage threshold below which crystallisation will not occur. In the present work however no crystallisation sites could be seen in film formed at 24 V and low voltage capacitors behaved well on life test. It can be seen from this work that the important effect which causes increasing leakage current and failure of solid tantalum capacitors is the presence of crystalline oxide. Relatively more defective, thinner oxide, is much more stable as it does not contain developing crystallisation sites. The best behaviour however is observed with purified foil, where the oxide is largely defect free and smooth.

On life test, capacitors constructed using standard conditions showed a sharply rising leakage current which levelled out after ~ 1000 hours and fell slowly thereafter. Current surges occurred which produced thermal damage sites ~ 0.1 mm diameter in the dielectric, presumably at particularly conductive crystallisation sites. The fact that not all of these thermal damage sites led to fuse failure and that the capacitor was stable after a discharge suggests that the manganese oxide over such a site is either dispersed by the discharge or converted to a lower conductivity oxide. It may be that when this isolation does not take place, current sufficiently large to produce fuse failure can occur.

Examination of oxide before and after life test of standard capacitors showed that the number of defect bumps in the oxide increased considerably and that many uncracked bumps became cracked. No significant changes were seen with low voltage or purified foil. Transmission microscopy showed that crystals under cracked bumps grew to several times the diameter of the cracked site, opening the crack and allowing the crystalline body to be seen. From the calculation it can be seen that if crystalline sites become sufficiently conductive, high temperatures can be obtained allowing growth by purely thermal means. This may be important in the later stages of development of a cracked site but it is likely that, in the earlier stages of uncracked bump development, growth occurs by ion transport in the electric field leading to a continued slow anodisation. It is believed that the slow decline in leakage current later in the life test is due to a loss of adhesion between the high conductivity points in this dielectric and the overlying manganese oxide.

Environmental effects on solid tantalum capacitors were only found to be important in the case of water vapour. The effects were reversible however

and were thought to occur through changes in the manganese oxide. As they were not relevant to the irreversible capacitor degradation mechanism they were not investigated in detail.

It was observed that the addition of a circuit impedance of the order of 1 k Ω prevented the development of large thermal runaway sites. A simple calculation of the temperature developed at such sites during electrical discharge indicated that the inhibition of current surges by the added circuit impedance was a reasonable explanation for these observations. It was also observed however that a high circuit impedance inhibited the development of bumps into cracked bumps, while leaving the increase in number of uncracked bump sites unaffected. This is consistent with the high impedance life tests results where leakage currents stayed relatively low; increases in leakage current are thought to correlate with the development of cracked bumps. The mechanism by which circuit impedance affects bump development is still unclear however as the currents passed at such sites are too small to be significantly affected by the circuit impedance.

A major part of the work on solid aluminium capacitors was concerned with developing and examining the capacitor construction process. Control of the reform stages was the most difficult. Aluminium oxide was found to be much more susceptible to damage than tantalum pentoxide and this made reform more difficult and limited the number of reforms to three. It was often observed that a capacitor which would not initially reform satisfactorily could be "retrieved" by prolonged soaking in ammonium pentaborate solution followed by a second attempt at reform. These observations suggested that diffusion of products from the reform site was an important factor in achieving a successful reform. The current passed is normally much larger than that required to reform damage sites in the oxide; most of the current is consumed in dissolving aluminium to form ions. The low pH environment produced by hydrolysis of these ions persists where washing is inadequate or in crevice situations, i.e. at the contact of the spacer tape and oxide surface. It was found that prolonged washing could be used to mitigate this effect without fear of hydrating the anodic oxide.

Attempts were made to minimise pyrolysis damage while increasing the manganese oxide fill factor by using progressively lower reform voltages and reforming after multiple pyrolyses. These variations on the standard process had limited success however.

Examination of capacitors during the construction process showed that the occurrence of damage was highly variable but mainly developed subsequent to the first pyrolysis and reform treatments. The construction of the capacitors was important, damage being largely confined to areas where the space tape was in close contact with the surface. The bromine-methanol test showed that damage to the oxide was indeed caused by pyrolysis although this was difficult to see by scanning electron microscopy. It should be noted that tests were performed on flat pieces of foil; in the case of a coiled capacitor with spacer tape pyrolysis damage may be expected to be more severe because of the difficulty of pyrolysis products escaping from this construction.

The situation appears to be, therefore, that pyrolysis initiates damage to the sites in the dielectric which subsequently suffer dissolution during the reform. The fact that the "dry" leakage currents of such units are always much lower than "wet" leakage currents suggests that much of the reform effect is due to electrical isolation of damage sites by dissolution of the overlying manganese oxide rather than reanodising of bare aluminium.

Life test results on solid aluminium capacitors showed that they recovered much more slowly from interruption in polarisation than solid tantalum units. In general however their behaviour on life test was much more stable than solid tantalum; no failures occurred and leakage currents tended to fall. The fall was rapid initially and dependant on polarising voltage. Examination of capacitors after test showed why this was so; the damage sites in the dielectric had a plug of oxide over them. It is probable that early in the life test continued anodisation occurs at the defect sites, plugging them with poorly formed oxide, and so reducing the leakage current.

Solid aluminium capacitors appear to be stable on life test compared to solid tantalum units because they have no inherent degradation mechanism such as field crystallisation. They are difficult to manufacture but may be expected to become slightly better in use and relatively immune to catastrophic failure.

6 CONCLUSION

The basic mechanism of failure of solid tantalum capacitors has been shown to be field crystallisation of the dielectric oxide. However, in the case of solid aluminium capacitor it appears that problems are caused by the damage initiated in the dielectric by the

pyrolysis process which is subsequently aggravated by the reformation.

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