TRENDS IN THE DESIGN AND PERFORMANCE OF TANTALUM CAPACITORS

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This paper shows the type of development that has occurred over recent years in tantalum capacitors, with particular reference to the sintered tantalum powder - liquid electrolyte (wet Ta) system. In the 'wet' system, the various defects that arise, such as silver migration, scintillation and field crystallisation, are illustrated and the effect of improvement in initial particle shapes on final surface area is considered.

INTRODUCTION

Electrolytic capacitors\(^1,2\) are widely used in electronic circuits. Aluminium capacitors have a strong foothold within the commercial and industrial electronic areas, whereas the tantalum family has until recently been specifically aimed at military and avionics requirements. The advantages of tantalum as a capacitor electrode material are: a wide working temperature range, an excellent life due to the stability of the oxide, and an inherently low leakage current over extended periods of storage, with the foil either plain or etched\(^4\) to increase the surface area.

TYPE CONSIDERATIONS

There are three basic types of tantalum capacitors\(^2,3\), wound foil, sintered anode wet and sintered anode solid.\(^5,6\) On first examination, these systems appear to conflict with each other with regard to market requirements, but examination of the influence that the circuit engineer has had upon the design of each of these systems and their subsequent parametric behaviour requires explanation.

As can be seen from Table I, each of the systems has particular advantages and disadvantages. For example, wet tantalum achieves a higher CV than solid tantalum which comes second, with foil tantalum the least efficient. This feature has a significant effect upon the ripple capability of each of these designs, since on the basis of heat dissipation, a foil tantalum unit will carry more current than the solid system, which in turn will carry more than the wet system. The leakage current is lowest in the wet tantalum capacitors, a factor related to the anode processing which permits high quality dielectrics to be formed, with foil tantalum second and solid tantalum third. This leakage current behaviour is

<table>
<thead>
<tr>
<th>Capacitor type</th>
<th>Capacitance (\times) Voltage per unit volume</th>
<th>Working life</th>
<th>Shelf life</th>
<th>Temp. range</th>
<th>Voltage range</th>
<th>Ripple current</th>
<th>Leakage current</th>
<th>Temp. char.</th>
<th>Freq. char.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOIL TANTALUM</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>WET TANTALUM</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>SOLID TANTALUM</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>3</td>
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<td>1</td>
</tr>
</tbody>
</table>

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linked to the voltage range which can be achieved in each of the systems.

Foil tantalum achieves the highest working voltage with wet tantalum marginally lower and solid tantalum generally fulfilling the low voltage requirements. The shelf-life of each type is one of the most significant aspects of their use, as minimal changes in parameters are experienced over periods of years.

Solid tantalum capacitors have the longest working life because there are no manifest wear-out mechanisms. On the other hand, both wet sintered tantalum and foil utilise liquid electrolytes with subsequent vapourisation during working life, which is to a large degree dependent upon the temperature of operation and the severity of use.

The temperature range of the three systems depends to a large extent upon the working electrolyte which is used, and the configuration of the container and seal. The nominal temperature range for the three types of product is $-55$ to $+125^\circ C$, but this can be extended with sintered anode wet systems by utilising a container and seal assembly which will permit the use of the capacitor above the electrolyte boiling point. Several systems which can be used at $200^\circ C$ are in existence, with $150^\circ C$ a general category temperature.

The temperature characteristics of each of the systems are very dissimilar. Solid tantalum capacitors have an essentially linear relationship of capacitance with temperature, but both the sintered anode wet and foil tantalum types show a large reduction in capacitance at lower temperatures when the ion mobility of the electrolyte decreases. This effect is unimportant in many practical applications, e.g. for a heavy duty smoothing capacitor in which the current produces internal heating effects, or in timing applications where the capacitance change which is experienced is limited to the change in dielectric constant rather than the apparent change in impedance measured on an AC capacitance bridge. Not unexpectedly the parametric performance with frequency is a function to a large extent of the electrolyte conductance rather than the electrode system. Hence, solid tantalum once again has the best performance at high frequencies, the ion mobility being a significant factor in the liquid systems.

Other factors also influence the development and use of each of the types. With the wet system, whilst it has an exceptionally high volumetric efficiency, it is impractical to construct small devices of low capacitance because the seal of the unit becomes the major factor in size. The solid tantalum system is extremely difficult to process in high capacitance values, but readily allows mass production processing and assembly in small anodes values and sizes. The foil tantalum system is ideal for high voltage formation and subsequent high voltage applications where the increased size is not a significant disadvantage. In view of these factors, the circuit engineer when selecting a component for a particular application tends to use a tantalum foil or wet sintered capacitor in the first and second stage smoothing in a power supply and selects the type of component to meet his space, temperature and ripple/frequency requirement. If selecting for a coupling or decoupling application, the requirement for high ripple and high capacitance is not necessary, and he will generally select a solid tantalum. From this it can be seen that the three systems are complementary to each other and not, as many engineers envisage, in competition. Each of the systems will give a comparable performance in the correct application. The circuit designer in general is controlling the development of each of the systems. In solid tantalum his influence is observed in the type of package currently predominant in the industry where the professional package has been abandoned and the device encapsulated in a resin 'dip' system to give adequate environmental performance, while utilising the excellent electrical performance of the tantalum anode. In the wet sintered system, the influence of the circuit designer is felt in requirements for increased capacitance per unit volume. The following micrographs highlight the changes in process and materials which are currently utilised to manufacture these units.

ANODE AND CATHODE STRUCTURES

The anode is a porous structure prepared from sintered tantalum powder (Figure 1(a) and (b)) and the cathode, which in the earliest form of the device is made of silver, also acts as the container. Figure 1(a) shows a scanning electron micrograph of the outside of a sintered anode and Figure 1(b) shows a similar picture of the fractured inside of such a body this time at a higher magnification. It is of interest to note that the layer of oxide prepared by the anodization treatment is clearly visible at the centre of the micrograph, surrounding the fractured tantalum surface. As indicated in the equivalent circuit (Figure 2) the effective capacitance of the unit is the reciprocal sum of the two capacitors formed by the anode and the cathode. In order to obtain the maximum capacitance from the anode, it is important that the cathode capacitance (and hence surface area)
should be as large as possible. For the silver cased units, this is achieved by the use of sintered silver powder prepared from the type of powder shown in Figure 3, or a coating of platinum black (Figure 4). These types were originally developed for use at temperatures up to 150°C and are extremely successful when used in conjunction with sinusoidal wave forms in smoothing applications, or in long time-constant work where good charge retention is essential. As the frequency of operation increased and the
wave-form utilised within the avionics industry changed from sinusoidal to triangular and square, a failure mode within the system was highlighted. This involved the transfer of silver from the cathode to the anode (Figure 5) and resulted in increased leakage current and a subsequent pressurisation, leading to failure. Development work was undertaken to remove the silver cathode and replace it with a similar electrode system to that used in the anode. This necessitated the use of a second porous tantalum electrode utilising the highest possible surface area, together with a low voltage dielectric to give partial reverse voltage protection.

Another problem in the use of liquid systems highlighted by the circuit engineer was the puncturing of the oxide of the anode dielectric due to forward voltage transients. This has led to a great deal of work being carried out on the formulation of electrolytes to minimise the resulting scintillation effect, which is shown in Figure 6. It can be seen that a large area of oxide has been damaged by scintillation.

A major part of the work carried out in research has been aimed at the realisation of higher surface areas, thereby increasing the capacitance available per gram of tantalum powder. One way of effecting this is to lower the sintering temperature. However, this leads to reduced purification and an increase in leakage current through the imperfection centres in the dielectric. In addition, failure processes related to anode purity, e.g. field crystallisation, may be promoted. The radial growth of crystalline oxide related to a high incidence of impurity is illustrated in Figure 7. Relative degrees of initial crystalline growth corresponding to sintering temperatures of 1600°C and 1900°C are shown in Figure 8, where it can be seen that the higher sintering temperature produces far fewer field crystallisation centres. However, developments in powder technology have occurred which also contribute to enlarging the surface area. The most fundamental of these concerns changes in particle shape and size. Early powders (Figure 9(a)) had a wider range of particle size together with
angular features, which produced on sintering the type of structure shown in Figure 9(b). A typical modern high capacitance powder and the anode which is prepared from this by current technology is shown in Figure 10 — the use of such a powder has raised the capacitance from 2000 to over 7000 μF/gm. A great deal of work in both the construction and the purity aspects of the sintered anode system is continuing in order to fulfil the changing requirements of the military and avionics industry. A further aspect that has been considered in relationship to sintered porous structures is the application of electrical transmission line theory to porous bodies filled with electrolyte. It is now possible to describe the frequency dependence of capacitance and dissipation factors successfully.

CONCLUSIONS

This paper has shown the type of development that has occurred over recent years in tantalum capacitors,
with particular reference to the sintered tantalum powder—liquid electrolyte (wet Ta) system. In the "wet" system the various defects that arise such as silver migration, scintillation and field crystallisation have been illustrated and the effect of improvement in initial particles shapes on final surface area has been considered.

REFERENCES
