Basic Tantalum Capacitor Technology

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Abstract:
This paper covers the general manufacturing techniques used to make a solid tantalum capacitor. The purpose of this paper is to give the layperson an understanding of current tantalum technology.
1.0 INTRODUCTION

Surface mount technology tantalum capacitors are increasingly being used in new circuit designs because of their volumetric efficiency, basic reliability and process compatibility. Additionally, they are replacing aluminum electrolytics, which use a wet electrolyte. This electrolyte tends to have problems with drying out during the manufacturing reflow of components to a circuit board.

The steady-state and dynamic reliability of a tantalum capacitor are influenced by several factors under the control of the circuit design engineer. These factors are voltage derating, ripple current and voltage conditions, maximum operating temperature and circuit impedance.

It is also of interest that because of the solid nature of the tantalum capacitor’s construction, there is no known wear out mechanism in tantalum capacitors.

This paper has been written to provide the user of tantalum capacitors with an idea of the effect of design criteria on the capacitor and the methods used in their production.

2.0 TANTALUM POWDER

Tantalum capacitors are manufactured from a powder of pure tantalum metal. A typical particle size for a high voltage powder would be 10 µm. By carefully choosing which powder is used to produce each capacitance/voltage code the surface area can be controlled. Powders with large particle size are used to produce high voltage capacitors. This is because when the dielectric is produced, it grows out of the surface of the Tantalum powder by about one third of the thickness and into the powder by around two thirds, thus if small particle size powders were used, each particle would quickly become consumed and isolated.

The production of the dielectric will be discussed in more detail later.

Since capacitance is proportional to surface area, the larger the surface area the more final capacitance. Over the past ten years the powder CV (capacitance/voltage product), which is a measure of the volumetric efficiency, has increased steadily through joint development programs between AVX and the powder suppliers. This increase has been brought about by changing the particle shape from spheres to flakes, and in recent years to a coral type structure, as shown in the stylized drawings in Figure 1. Figure 2 shows scanning electron microscope (SEM) photographs of a low CV, a medium CV and a high CV powder. The change in particle size is easily apparent.

3.0 MANUFACTURE

(a) Pressing

The powder is mixed with a suitable binder/lubricant to ensure that the particles will adhere to each other when pressed to form the anode, and flow easily into the press tool. The powder is then compressed under high pressure around a Tantalum wire to make a Tantalum “slug”. The term “slug” is used in the Tantalum capacitor manufacturing industry to refer to the Tantalum anode element.

The riser wire will eventually become the anode connection to the capacitor. Figure 3 shows an SEM picture showing how the particles have been bound together.
The binder/lubricant is driven off by heating the slugs under vacuum at temperatures around 150°C for several minutes.

(b) Sintering

This is followed by sintering at high temperature (typically 1500°C-2000°C) under vacuum. This causes the individual particles to join together to form a sponge-like structure. This structure is of high mechanical strength and density, but is also highly porous giving a large internal surface area.

If the anodes are sintered for too long or at too high a temperature, the particles fuse together too much, and thus the final capacitance of the anode will be too low. Similarly if the anodes are sintered for too short a time, or the furnace temperature is too low, the capacitance will be too high.

A verification is made on each sinter lot by anodizing several quality control anodes and performing a wet capacitance check.

To illustrate how much surface area is inside a common value tantalum capacitor, let us take the example of a typical 22μF 25 volt rated part.

\[
C = \frac{E E_0 A}{d}
\]

where

- \(E\) is the dielectric constant for tantalum pentoxide (about 27)
- \(E_0\) is the dielectric constant for free space (8.855 x 10^{-12} Farads / m)
- \(A\) is the surface area in m² and
- \(d\) is the dielectric thickness in m

The dielectric thickness is given by the equation,

\[
d = \text{Typical formation ratio} \times \text{Rated voltage} \times \text{Dielectric growth rate in meters} / V
\]

\[
= 4 \times 25 \times 1.7 \times 10^{-9}
\]

\[
= 0.17 \mu m
\]

Substituting this value into equation 1 and rearranging gives,

\[
A = \frac{(Cd)}{E_0}
\]

\[
= \frac{(22 \times 10^{-6} \times 0.17 \times 10^{-9})}{(27 \times 8.855 \times 10^{-12})}
\]

\[
= 0.0156 \text{ m}^2 \text{ or } 156 \text{ cm}^2
\]

which is the same size as a standard 6”x 4” photograph or birthday card.

The sintering process also helps to drive off the majority of the impurities within the powder by migration to the surface. Figure 4 shows the same powder type anode as previously seen in Figure 3, after it has been sintered. The joints between particles are clearly visible.

The Tantalum slugs are now welded onto a metal carrier strip to enable subsequent processes of manufacture, and a teflon washer is added to the riser wire, which will prevent the manganese dioxide counter electrode passing up the wire and causing short circuits during manufacture. When the slugs have been welded on to the carrier strip they are then referred to as a “stringer” of anodes.

(c) Dielectric Formation

The next stage is the production of the dielectric layer of tantalum pentoxide. This is produced by the electrochemical process of anodization. The slugs are dipped into a very weak solution of acid, for example phosphoric acid, at an elevated temperature, for example 85°C, and the voltage and current are controlled to form the pentoxide layer.

Tantalum is valve metal, and the amorphous pentoxide grown is able to form a uniform, closely coupled layer over the tantalum surface. Figure 5 shows an SEM picture of a slug which has been cracked into two pieces to show the dielectric layer.

The dielectric thickness is controlled by the voltage applied during the formation process. Initially the power supply is kept at a constant current until the required formation voltage has been reached. The power supply is then kept at a constant voltage to ensure the correct dielectric thickness is formed all over the Tantalum slug’s surface, and therefore the forming current decays. Figure 6 shows the typical voltage and current profiles measured during the formation process.
The chemical equations describing the anodization process are as follows:

**Anode:**

\[ 2 \text{Ta} \rightarrow 2 \text{Ta}^5+ + 10 \text{e}^- \]  
\[ 2 \text{Ta}^5+ + 10 \text{OH}^- \rightarrow \text{Ta}_2\text{O}_5 + 5 \text{H}_2\text{O} \]

**Cathode:**

\[ 10 \text{H}_2\text{O} + 10 \text{e}^- \rightarrow 5\text{H}_2 \uparrow + 10 \text{OH}^- \]

As was stated earlier, the oxide forms on the surface of the Tantalum, but it also grows into the metal. For each unit of oxide one-third grows out and two-thirds grow in. Intrinsic to the dielectric are a low ppm level of impurity sites that are evenly distributed over the anode. The impurity sites give a characteristic leakage signature for the capacitor; for a given dielectric thickness their statistical distribution will give a characteristic per square, so a capacitor having twice the capacitance value of another of the same voltage rating will typically have twice the leakage current. Because the pentoxide grows into the anode as well as upon its surface, these impurities can be partially isolated as shown in Figure 7 if the formation voltage is increased. There is a limit of how far the formation voltage can be increased, since the capacitance of the part falls as the dielectric thickens.

The formation voltage can be checked visually by examining the color of the slug. This is because different thicknesses of dielectric create different interference patterns when light is shown onto them, similar to an oil film on water. For example, a light green color could mean a formation voltage in the range 100 to 104 volts and a light purple color to a range of 72 to 76 volts.

The capacitor’s formation voltage is typically 3 to 4 times the capacitor’s rated voltage, this is to ensure good reliability. It is also because when forming the dielectric, one actually produces a semiconducting Tantalum oxide region between the wanted pentoxide and the Tantalum metal. This region is kept to a minimum by removing the stringers from the formation bath when approximately 90% of the final formation voltage is reached, and placing the stringers in an oven at approximately 350°C to 400°C.

This semiconducting region is why Tantalum capacitors are polar devices. Figure 8 shows the reverse leakage characteristics of several different voltage rated parts, note the similarity to the behavior of a diode.

Dielectric will be subjected to very large electric field strengths in the finished capacitor. It is for this reason that Tantalum capacitor manufacturers recommend derating of at least 50% to further improve the reliability of the product. Consider again a 22μF 25V part.

\[
\text{Formation voltage} = \text{Typical formation Ratio} \times \text{Rated Voltage} = 4 \times 25 = 100 \text{ Volts}
\]

The pentoxide (Ta2O5) dielectric grows at a rate of 1.7 × 10⁻⁹ m/V

\[
\text{Dielectric thickness (d)} = 100 \times 1.7 \times 10^{-9} = 0.17 \mu\text{m}
\]

\[
\text{Electric Field strength} = \frac{\text{Working Voltage}}{d} = \frac{25}{0.17 \times 10^{-6}} = 147 \text{ kV/mm}
\]

**Manganizing**

The next stage of manufacture is the production of the cathode electrode plate. This is achieved by pyrolysis of manganese nitrate into manganese dioxide.

The “slug” is dipped into an aqueous solution of manganese nitrate and then baked in an oven at approximately 250°C to produce a Dioxide coat.

The chemical equation, simplified, is:

\[
\text{Mn (NO}_3\text{)}_2 \rightarrow \text{Mn O}_2 + 2 \text{NO}_2 \uparrow
\]
This process is repeated several times through varying concentrations of nitrate solution to ensure good penetration of the anode, and to build up a thick outer coat on the surface of the capacitor. Figure 9 shows a manganized anode, the flake-like outer layer is the manganese dioxide.

This has a resistivity of about 1 to 10 $\Omega$/cm.

![SEM of manganized anode]

**Figure 9**

SEM of manganized anode

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(e) Reform

The stringers are now dipped into an acid bath, generally of acetic acid, and a voltage applied of approximately half the original forming voltage. This removes manganese from high leakage current areas within the slug and grows a dielectric layer to plug the site.

(f) External contact layers

The stringer is then dipped into a graphite dispersion and transferred to an oven where it is heated to ensure good adherence to the slug.

The process is then repeated with a silver dispersion to provide the final connection layer to the cathode terminal. Figure 10 shows a section through the capacitor with all the external contact layers labeled.

![External contact layers]

**Figure 10**

External contact layers

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and the silver would be oxidized to high resistivity silver oxide, and the manganese dioxide reduced to manganese (III) oxide, which again has a high resistivity. The part would therefore become high resistance, and the capacitor cease to function adequately.

$$\text{Ag} + 2 \text{MnO}_2 \rightarrow \text{AgO} + \text{Mn}_2\text{O}_3$$

The stringer now contains up to 70 finished processed anodes, also known as elements, which can be assembled into the appropriate package. The available packages are many and varied. The two most common are covered here.

4.0 PACKAGING

a) Surface mount package

The elements cathode terminals are joined to the cathode leadframe tab using silver loaded epoxy resin, and the anode riser wire is welded to the anode leadframe tab.

The stringer is then cut away leaving the element attached to the leadframe. The silver glue is cured and the element is then molded into an epoxy resin case. This ensures excellent pick-and-placeability, and tight control over the components dimensions.

The molded body is finally coded with its capacitance and rated voltage values, and then tested for all its electrical parameters; capacitance, leakage current, impedance and ESR.

Figure 11 shows a sectioned capacitor, with all the areas of interest highlighted.

![Section of SMD tantalum chip]

**Figure 11**

Section of SMD tantalum chip

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b) Resin dipped package

The anode riser wire is welded onto the anode lead wire, and cut away from the stringer. The cathode lead termination is soldered to the silvered anode by dipping the silvered anode and cathode lead wire into a solder bath. The unit is then dipped into an epoxy based encapsulant, and transferred to an oven for curing.

The encapsulation is coded with the capacitor’s capacitance and rated voltage values. Finally the capacitor is tested for all its electrical parameters; capacitance, leakage current, impedance and ESR.

Figure 12 shows a sectioned finished unit. Areas of interest are highlighted.
5.0 ELECTRICAL CHARACTERISTICS

The electrical characteristics of a tantalum capacitor are determined by its structure, for example the ESR of a tantalum capacitor is very dependent on the tantalum pentoxide dielectric at low frequencies and on the internal manganese dioxide at higher frequencies.

There are several papers published by AVX which explain in detail the factors affecting capacitor behavior. These include:

1. “Equivalent series resistance of tantalum capacitors” by R. W. Franklin
2. “Thermal management of surface mounted tantalum capacitors” by I. Salisbury
3. “Surge in solid tantalum capacitors” by J. A. Gill
4. “An exploration of leakage current” by R. W. Franklin
5. “Capacitance tolerances for solid tantalum capacitors” by R. W. Franklin

These papers are available through the AVX worldwide sales offices.

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