Stable, Reliable, and Efficient Tantalum Capacitors

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Ceramic capacitors are rapidly increasing their capacitance and volumetric efficiency CV/cc due to higher dielectric constant and smaller dielectric thickness as well as larger layer count. To compete with ceramic capacitors and meet consumer request for miniaturization, tantalum (Ta) capacitors also need constantly increase their volumetric efficiency. Traditionally, the only way to increase CV/cc in Ta capacitors was reducing particle size in the Ta powder and thereby increasing surface area of the anode (this leaves aside packaging efficiency as a common issue for all types of the capacitors).

Though Ta powder manufacturers continue to increase powder CV, application of newly developed high CV powder is limited to low working voltage (WV) capacitors with very thin dielectric. Higher voltage capacitors can't use high CV powder because they require thicker dielectric than that in the low voltage parts. The thicker dielectric is growing through the "necks" between the powder particles and clogs fine pores between particles, which reduces surface area of anode and, thereby, CV. This means that for mid and high voltage capacitors, which constitute the bulk of the Ta capacitors, the applicable powders have been in use for a long period of time.

This work analyzes utilization of Ta in Ta anodes for creation of the capacitance and explores the possibilities to increase this utilization, providing higher CV/cc to Ta capacitors, while simultaneously improving their stability and reliability. The latter is most critical in special applications of Ta capacitors such as medical, military, and aerospace.

Utilization of Ta in Ta Anodes

Utilization of Ta in Ta anode as a ratio between Ta in dielectric Ta_2O_5 film (Ta*) and Ta in unformed anode (Ta) was calculated using anode weight increase during formation of the Ta_2O_5 film. This weight increase is attributed to weight of oxygen in the anodic oxide film. According to the molecular weight of Ta_2O_5 (181x2 + 16x5), weight of Ta in this oxide is approximately 4.5 times larger than the weight of oxygen. Fig. 1a shows Ta*/Ta and CV/g with 50k CV/g powder as a function of formation voltage. Fig.1a also shows efficient CV/g*, which is a product of Ta*/Ta and CV/g.
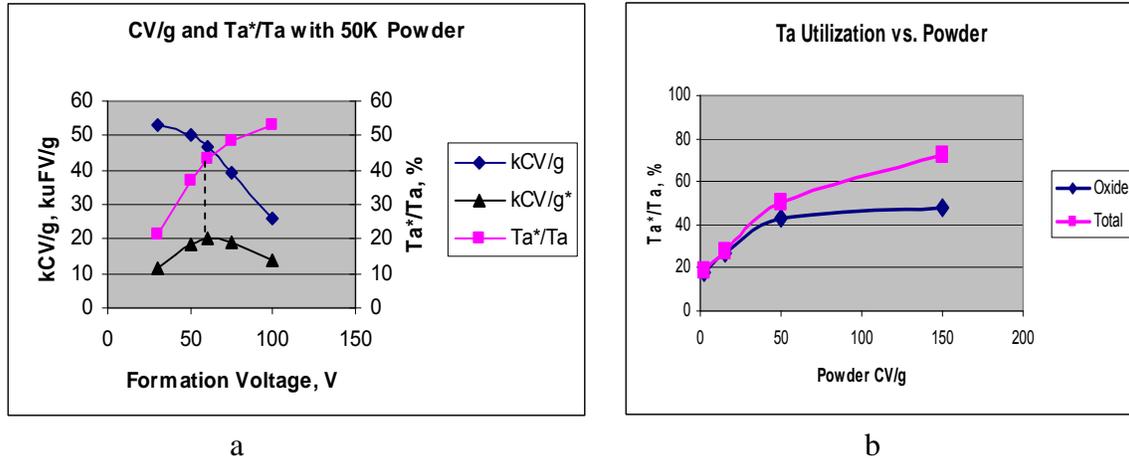
a

b

Fig. 1. Utilization of tantalum (Ta*/Ta) in anodes with 50k CV/g powder (a) and different powders (b).

As one can see from the Fig. 1a, efficient CV/g* achieves maximum at Ta*/Ta about 40%. Similar analysis was performed with different Ta powders. Fig. 1b shows Ta consumption in Ta_2O_5 film (oxide) and combined oxide and 10 nm anode plate (total). According to Fig. 1b, Ta consumption in Ta anodes with low and mid CV/g powders is equal or lower than 50%, while other 50% increase anode weight, volume, and cost, but don't contribute to the capacitance.

Anode CV vs. Powder Sintering Conditions

Press density (**d**) and sintering temperature (**Ts**) of Ta powder are the two major parameters that influence utilization of Ta in Ta anodes. As an example, Fig. 2a shows CV/g as a function of **d** and **Ts** with 23 CV/g powder.
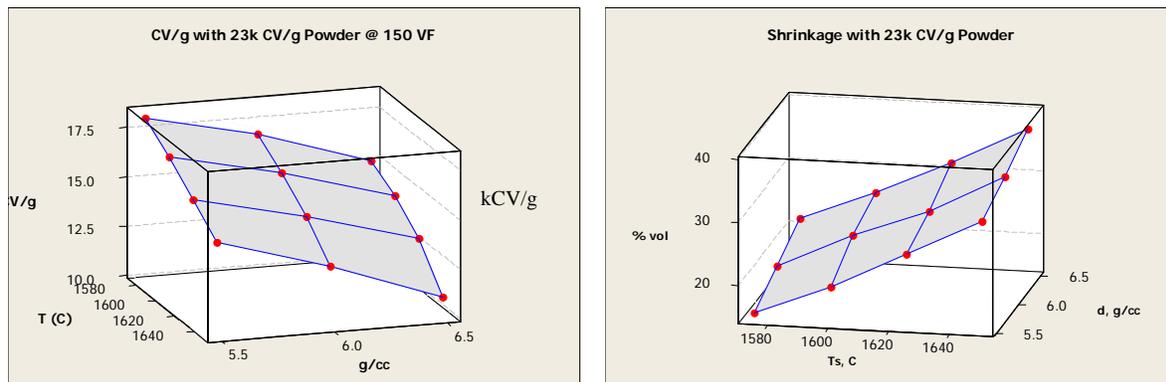

Fig. 2. CV/g (a) and shrinkage (b) in anode with 23 k CV/g powder as a function of press density and sintering temperature.

According to Fig. 2a, CV/g rolls down with increasing of both **d** and **Ts**. This reflects increase of shrinkage of Ta anodes with increasing **d** and **Ts** (Fig. 2b). At the same time, reducing of **d** and **Ts** results in thinner "necks" between powder particles and, thereby, a more rapid CV decrease and DCL increase at higher formation voltages (Fig. 3).
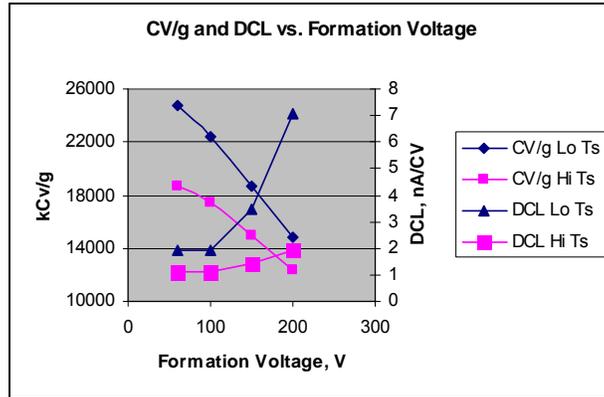
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Fig. 3.CV/g and DCL in anode with 23k CV/g powder as a function of. formation voltage

Volumetric efficiency CV/cc dependence on **d** and **Ts** is different from shown on Fig. 2a weight efficiency CV/g dependence on **d** and **Ts**. As an example, Fig. 4 shows CV/cc as a function on **d** and **Ts** in anodes sintered with 23k CV/g Ta powder.
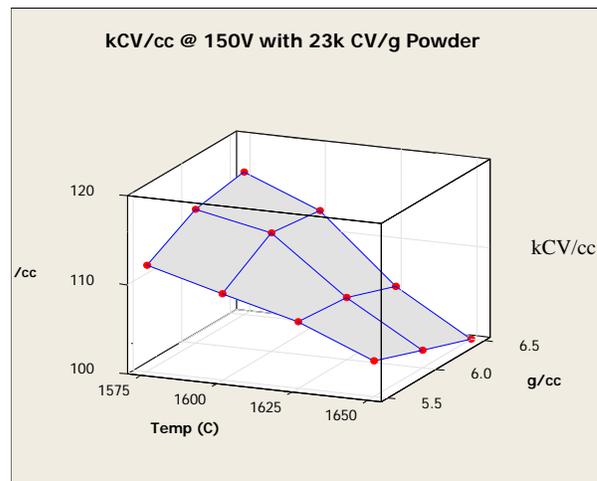

Fig. 4. CV/cc in anodes with 23k CV/g Ta powder as a function of press density and sintering temperature

Fig. 4 shows that there is a possibility to increase CV/cc at high press density and low sintering temperature. However, with conventional sintering in vacuum, low sintering

temperature doesn't provide sufficient bonding between the powder particles and the particles and lead wire, affecting mechanical and electrical properties of sintered anode. This is in part due to oxygen, which dissolves in Ta particles from natural surface oxide during sintering in vacuum and acts as sintering inhibitor.

Sintering in Reducing Atmosphere

When sintering is performed in reducing atmosphere, f.i., in Mg vapor, oxygen is removed from Ta particles.[1] This intensifies diffusion of Ta atoms, allowing growth of "necks" between powder particles at lower temperatures than these at sintering in vacuum. The Y-sintering process, patented by Vishay, also solves a problem of the powder bonding to the lead wire by a short time temperature increase above the deoxidizing temperature but below the regular sintering temperature.[2]

An alternative process of low temperature sintering in deoxidizing atmosphere is under development at Kemet.[3] Initial results of this sintering are presented on Fig. 5 for 50k CV/g Ta powder. This Fig. shows CV/cc, oxygen content, and delta volume in Ta anodes sintered in vacuum (Sintering) and sintered with deoxidizing (D-Sintering)
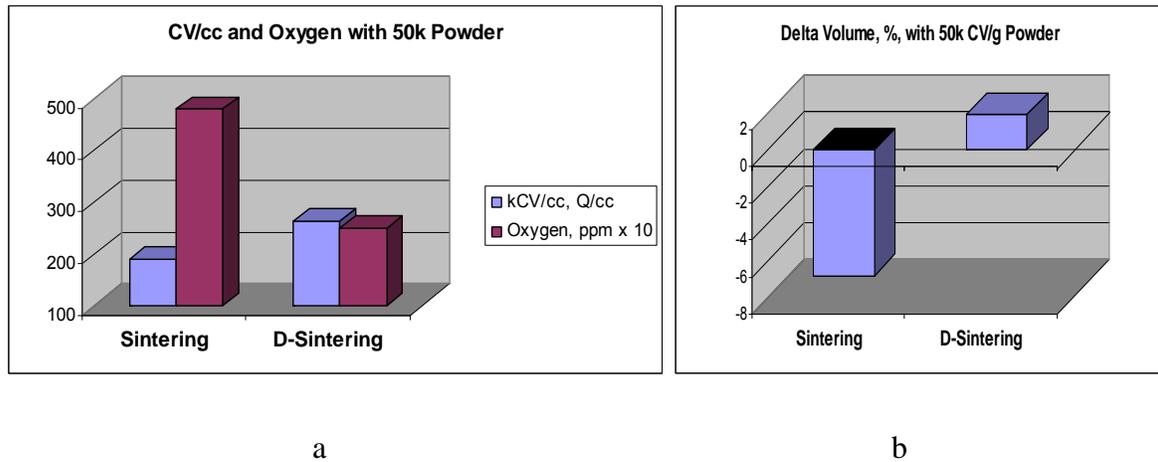
a

b

Fig. 5. CV/cc, oxygen (a) and delta volume (b) in anodes with 50k CV/g powder.

As one can see from the Fig. 5a, D-sintering provides about 35% increase in CV/cc and radical reduction in oxygen content in sintered anodes vs. these with sintering in vacuum. Increase in CV/cc with D-sintering relates to anode expansion, while sintering in vacuum results in anode shrinkage (Fig. 5b). This difference in volume change between regular sintering in vacuum and D-sintering is caused by change in dominant sintering mechanism. With sintering in vacuum, the dominant sintering mechanism is bulk diffusion of Ta atoms, which results in mutual penetration of the powder particles and, thereby, in anode shrinkage. With low temperature D-sintering, the dominant sintering mechanism is surface diffusion of Ta atoms. When Ta atoms flow on the surface of Ta

particles, they build up "necks" between the particles, using fines fraction as a building material. This results in open pores and expanding the anode volume.

Low and Stable DC Leakage

The typical way to reduce and stabilize DCL in Ta capacitors is reducing electrical field in the dielectric. This can be accomplished either by increasing form-factor, which is a ratio between formation voltage and working voltage, or by de-rating, which is a ratio between application voltage and designed working voltage. In both cases DCL reduces exponentially and the rate of degradation processes, provoking DCL increase, also reduces exponentially. The problem with this approach is that volumetric efficiency CV/cc of Ta capacitors is inversely proportional to both formation factor and de-rating. That's why the real challenge for Ta capacitors is combining of high stability and reliability with highest possible volumetric efficiency.

Low oxygen content in the bulk of D-sintered anodes allows suppression of crystallization of amorphous dielectric, which is the major degradation mechanism in mid and high working voltage Ta capacitors. To enhance stabilization of the amorphous dielectric, this sintering technique should be combined with other anode and dielectric manufacturing techniques that provide chemical purity and structural uniformity to Ta anode and oxide dielectric.

When the package of techniques, suppressing growth of crystalline inclusions in amorphous matrix of the dielectric, is implemented, the dielectric remains amorphous during testing and field application. As a result, DCL stays low for long period of time even in conditions, which are much harsher than normal application conditions. As an example, Fig. 6 shows DCL distribution in as manufactured D-case Ta capacitors 22 µF – 20 V (a) and after 2000 hours of life test at 1.32 working voltage (WV) and 85° C (b). The capacitors were made with the crystallization preventing package of techniques (test) and conventional technology (control).
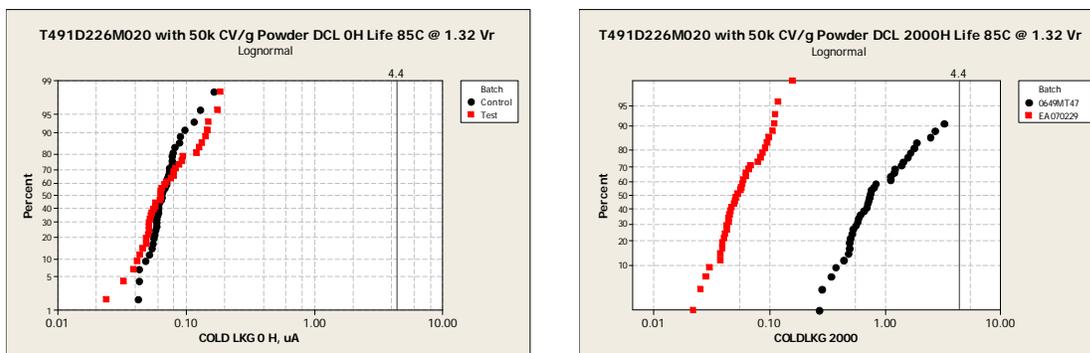

Fig. 6. DCL distribution in D-case Ta capacitors 22 uF – 20V as manufactured (a) and after 2000h life test (b).

As one can see from the Fig. 6, initial DCL was much below limit and practically identical for both test and control parts. At the same time, only parts with the test technology remained low DCL during the life test, while the DCL of control parts increased for more than an order of magnitude. In some of the control parts, DCL exceeded the limit, causing parametric and catastrophic failures of Ta capacitors.

An important feature of the capacitors presented on Fig. 6 was that they were made with 50k CV/g Ta powder. This is the highest in industry CV/g powder applicable for 20 WV capacitors. Using of higher CV powder provides higher volumetric efficiency to Ta capacitors, however, it also promotes crystallization of the dielectric and, thereby, DCL increase during testing and in the field. Nevertheless, even with this powder, capacitors made with the package of the crystallization preventing techniques demonstrated low and stable DCL during long accelerated test.

Conclusion

The package of the crystallization preventing techniques, which includes anode sintering in deoxidizing atmosphere (D-sintering), provides low and stable DCL as well as increased volumetric efficiency to Ta capacitors with mid and high working voltages. When developed by Kemet breakdown simulation screening[4] of the finished capacitors is added to the manufacturing package, Ta capacitors also demonstrate exceptional reliability, which is critical for most applications, especially, medical, military, aerospace, and high temperature ones.

Literature

1. Albrecht et al. US Patent 4,537,641
2. Y. Freeman. US Patent 6,447,570 B1
3. Kemet Provisional PA in process
4. Y. Freeman, R. Hahn, Phil Lessner, J. Prymak, Proceedings of CARTS-Europe'07, P. 111.