4.1. Flaked Tantalum Powders: High Capacitance Powders for High Reliable Tantalum Capacitors

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ABSTRACT

Tantalum based capacitors are a critical component when electronic devices require reliable performance across a wide variety of environmental conditions. The tantalum capacitor offers stable capacitance over a range of temperatures and voltages, long life with no piezoelectric effect, high reliability, and high volumetric efficiency. These features are particularly attractive for growing applications that are demanding even greater operating voltages and higher reliability under harsher environments including servers, space, and autos. To achieve the higher performance, it is important to choose the proper tantalum powder to produce the capacitor anode. Typical tantalum powders are comprised of spheroidal (nodular) tantalum particles with defined, reproducible, particle size distributions. As the operating voltages of devices increase, the size of the tantalum particles increase to enable thicker dielectrics; however, achieving the performance improvement is to the detriment of the overall volumetric efficiency of the device. Altering the particle shape from nodular to a higher aspect ratio plate-like geometry will exhibit characteristics of higher capacitance at a comparable operating voltage. These high aspect ratio particles found in flaked tantalum powders have historically exhibited attractive performance including high capacitance at high voltage, high breakdown voltage, low DC leakage, and improved ESR, leading to their use in many commercial applications today. The characteristics of these unique tantalum powders are very important to consider when designing capacitors operating at higher voltages or in high reliability applications.

TANTALUM CAPACITOR PRODUCTION

The roots of today's solid electrolyte tantalum capacitor technology trace back to early inventions in the 1950s. Over the past 75 years, many improvements reduced cost and improved the electrical performance of tantalum capacitors; however, the basic capacitor structure has remained consistent. A tantalum capacitor is comprised of a dielectric layer of tantalum pentoxide sandwiched between an anode layer and a cathode layer. The success of the tantalum capacitor resides in the use of a very high surface area tantalum pentoxide dielectric to maximize the capacitance within the capacitor volume.

The tantalum capacitor manufacturing process builds a capacitor from the anode layer to the cathode layer utilizing tantalum as the foundation. An appropriate high purity tantalum powder (primary particle size $< 1\mu m$) is mixed with a polymer system that serves as a binder / lubricant, and the mixture pressed into a mold surrounding a tantalum wire. The polymer system is chosen to aid flow into the press, improve particle-to-particle adhesion, and must exhibit properties that facilitate extraction after pressing. The tantalum compact removed from the press will undergo a binder removal (delube) step that consists of a solvent washing to physically extract the binder or a thermal treatment to decompose and evaporate the binder. The resulting compact becomes a highly porous tantalum pellet after binder removal, but has low compressive strength. The loosely adhered tantalum particles in the pellet are strongly adhered by exposing the pellet to elevated temperatures (> 1000ºC) typically in a vacuum. The high temperature causes some tantalum atomic migration forming necks between the tantalum particles, and resulting in a porous tantalum pellet with high crush strength. An anodization process grows the capacitor dielectric onto the tantalum pellet using an electrolytic cell, converting the outer layer of tantalum into amorphous tantalum oxide. The cathode layer is applied to the dielectric as an MnO_2 layer or by depositing a conductive polymer layer. The coating of a conductive carbon layer followed by a conductive silver layer completes the internals of the capacitor. Figure 1 demonstrates the internal construction of a tantalum capacitor.

All the layers within a tantalum capacitor are critical to the ultimate capacitor electrical performance; however, the dielectric layer controls the majority of the critical electrical design specifications. Tantalum is a valve metal, which means it will form an oxide layer when placed under the right electrical potential. Typically, tantalum pellets are placed within an elevated temperature electrolyte bath containing a weak acid such as phosphoric acid, and voltage is applied across the pellet to anodize the tantalum. Electrochemical reactions convert the tantalum to tantalum pentoxide, with the anodic oxide layer growing inward and growing outward from the surface. The peak voltage used to grow the oxide layer defines the overall oxide layer thickness. Very common electrolytic cell formation conditions follow an initial ramp of voltage at a constant current to a desired formation voltage, and this voltage is then maintained for a set period of time.

The holding period at the formation voltage helps to ensure the dielectric achieves the desired thickness and more importantly the uniformity.[1]

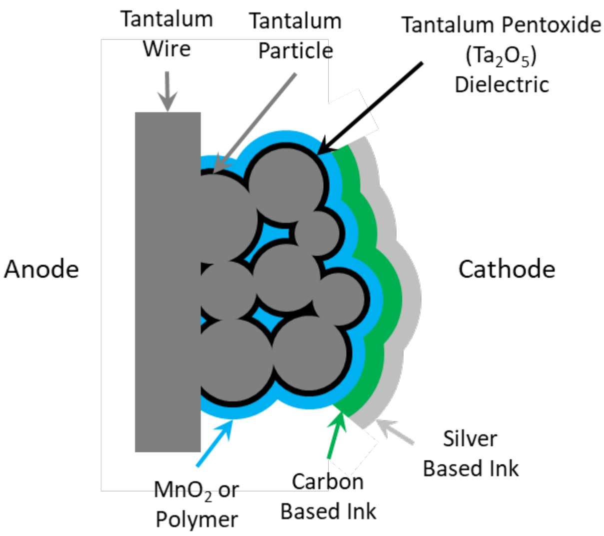

Fig. 1. Tantalum Capacitor Internals

The peak formation voltage (Vf) determines the final dielectric thickness, which defines the ultimate electrical operating conditions for the capacitor. The thickness of the tantalum pentoxide dielectric is directly proportional to the formation voltage with a constant of proportionality between 1.6nm/V and 2.0nm/V, with higher formation temperatures depositing thicker dielectric films.[2] The well-known capacitance equation relates capacitance to the tantalum pentoxide film (here noted for a parallel plate capacitor):

$$C = \kappa \varepsilon_0 \frac{A}{d}$$

where κ is the dielectric constant of tantalum pentoxide, ε_0 is the permittivity of free space, A is the surface area of the capacitor plates, and d is the distance between the capacitor plates. The capacitance of the dielectric layer varies inversely with the dielectric thickness; lower capacitance results as the oxide film grows. Higher formation voltages result in thicker dielectrics, producing lower capacitance. The tantalum capacitor operating voltages are a fraction of the formation voltage. Typically, the Vf used to create the capacitor anode is 2.5x – 4.0x the final capacitor rated voltage (Vr). Creating capacitors capable of operating at higher voltages requires higher formation voltages, thicker dielectric layers, and tantalum powders that can enable these thick films. Higher quality powders that can produce higher quality dielectric films could enable lowering the forming ratio (Vf/Vr) thereby increasing the capacitance or energy of the capacitors.

TANTALUM CAPACITOR POWDERS

The particle size distribution of the tantalum powder controls the ultimate capacitance of a capacitor. There is one ideal particle size that would optimize the capacitance of an anode structure for a given formation voltage. If the particles are too small, very little tantalum metal remains after the formation process, or in the extreme case, particles "form through" where no tantalum exists and no electrical pathway can carry charge to the remainder of the anode, resulting in no contribution to the capacitance. If particles are too large, then the formed pellet will contain large areas of tantalum that take up volume, add weight, and do not contribute to capacitance. Developing the preferred tantalum capacitor powder requires optimizing the particle shape and size distribution of the powder.

The morphology of tantalum powders has changed over the decades to maximize the electrically connected surface area per unit volume within the capacitor and hence increase capacitance. Some of the earliest tantalum powders consisted of roughly crushed tantalum producing very irregular shaped particles. These "angular" powders had large and broad primary particle size distributions with particles containing rough edges and tipped structures. The irregular shapes contributed to inefficiencies in formation where small particles or sharp edges would form through during the growing of the anodic oxide layer, and lead to elevated leakage due to mechanical stress cracking on the dielectric film around the sharp edges. In addition, the broad particle size distributions contain very large particles that would disproportionally not contribute to the capacitance due to large tantalum cores within the network. Powder development into “nodular” powders better controlled the particle size distributions giving narrower distributions with defined average primary particle size and better controlled pore size distribution that further benefited cathode impregnation. Most tantalum powders used today fall under the nodular powder lineage and find use from formation voltages of < 10Vf to in excess of 400Vf. To produce the highest capacitance at very low formation voltages of < 10Vf, nano-particle size tantalum powders have been developed. These powders offer “dendritic” structures with primary particle size < 100nm and produce the highest capacitance tantalum capacitors in low voltage and small profile applications. Finally, “flaked” powders are a variant produced from both angular and nodular powders.[3] These powders offer many of the advantages of nodular powders while also imparting an increase in capacitance due to the unique platelet geometry of the particles. These powders have found to be very successful in use for high voltage, high reliability applications. Figure 2 demonstrates the different morphology of common tantalum capacitor powders.

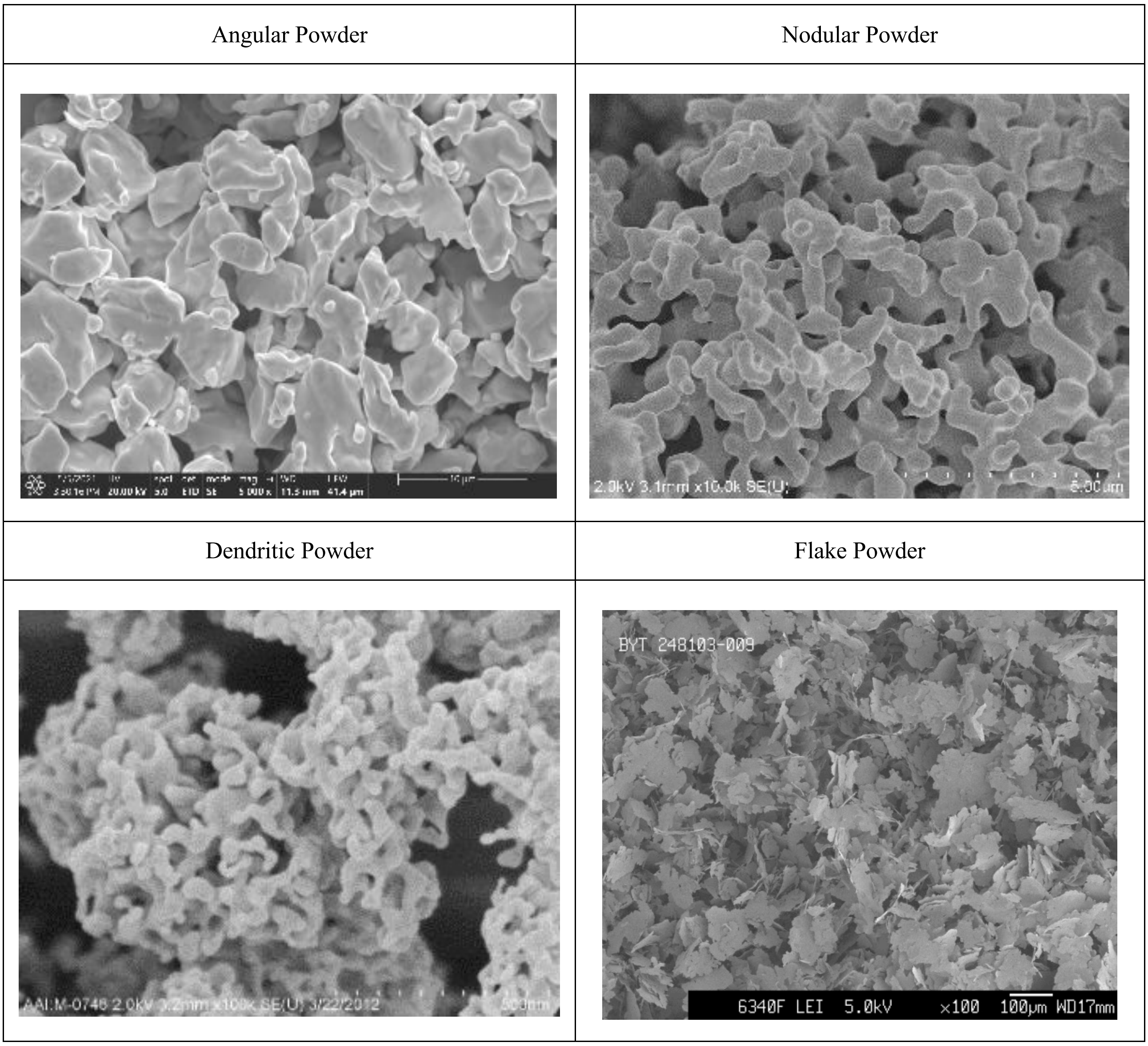

Fig. 2. Morphology of Tantalum Capacitor Powders

TANTALUM POWDER MANUFACTURING METHODS

The production of the majority of tantalum capacitor powders follows a hydrometallurgical extraction and metal reduction process with finishing operations to define unique powder properties. Tantalum contained in ore and recycled scrap is dissolved using hydrofluoric acid to produce hydrogen heptafloroutantalate (H_2TaF_7). The stable pure tantalum salt potassium heptafluorotantalate (K_2TaF_7) is produced by first separating the fluorotantalic acid from other dissolved impurities using a counter current extraction circuit followed by treating the acid with potassium salts. The K_2TaF_7 is reduced to pure tantalum by sodium in a molten salt reactor producing a basic lot of tantalum powder. The reduction conditions define the particle size distribution within a basic lot product. Angular powders are produced by melting and further purifying the basic lot in an electron beam furnace, followed by milling the resulting ingot to a powder. Nodular powders require washing the basic lot with acids, using agglomeration, heat treatments, the addition of low-level chemical additives, and deoxygenation steps to remove oxygen, in order to obtain the desired powder properties. The angular and nodular powders are the source for flake powders.

Producing flake powders from the angular or nodular powders utilizes steps to deform the particles to platelet geometries. Tantalum is a ductal metal with a high elongation at break of approximately 40%, enabling the ability to deform tantalum under pressure without breaking. Converting tantalum powders to flake powders uses various media based milling operations such as ball mills, rod mills, roll mills, or similar methods. The media within the mills are typically metal ball bearings, with the media action of impaction and grinding causing deformation of the tantalum powder. The flaked powder can go through further heat treat, deoxidation, nitriding, and acid washing steps to achieve the desired oxygen level, remove trace contaminations, and meet flow and packing density targets such as Scott density.

FLAKE POWDER CHARACTERISTICS

The advantages of using flake powders ultimately relate to the properties that translate into improved capacitor performance. Capacitors of higher value are achieved by enabling higher charge in a given volume and improving long-term reliability to extend the life of an electronic device. Tantalum flake powders can improve these critical characteristics in capacitors, and thus justify the additional processing steps and cost for certain market opportunities.

Volumetric Efficiency

The definition of total charge carried within a capacitor is the product of the capacitance (C) and the applied voltage (V). Similarly, the charge that an anodized tantalum powder can carry is characterized by the product of the capacitance (C) of the tantalum pentoxide film and the formation voltage used for the anodization (Vf). The charge carrying capacity of a tantalum powder is quoted as the specific charge, CVf/g or simply CV/g (charge per unit mass). Similarly, the charge carrying capacity can be quoted as the volumetric efficiency as CVf/cc or simply CV/cc (charge per unit volume). In either case, there is some ambiguity to the values as the ultimate charge carrying capacity depends on how the powder is formed into a pellet, the pellet size, the conditions used for growing the anodic oxide film on the anode, the type and processing conditions of the cathode layer, and finally the aging status of the capacitor. For example, depending on the amount of powder loaded in a press and the pelletizing pressure, the compaction of the tantalum powder will change altering the free surface area available for anodization and hence influence capacitance. It is important when comparing the charge carrying capacity of different tantalum powders that the test anode preparation follows the same processes. Quoting a CV/g for a powder is preferred by powder suppliers due to powders being sold on a mass basis; however, capacitor manufacturers usually prefer quoting CV/cc due to their goal of providing an electronic board level capacitance solution constrained into a given volume. Typically, powders that produce higher CV/g will produce higher CV/cc and vice versa.

Observations find the specific charge carrying capacity of flake powders are higher than comparable nodular powders. Figure 3 demonstrates the specific charge comparison over a range of high formation voltage conditions for commercial tantalum powders from Global Advanced Metals (GAM) covering two flake powders, C275 and C255, and a nodular powder, C350. Testing these powders used identical size & weight pellets, identical anodizing conditions, and the same electrical measurement conditions. It is apparent C275 has a higher specific charge than C350, but C255 is lower than C350 over the range of formation voltages. The data illustrates that the powder with highest specific charge will depend on the level of Vf. Clearly, C275 has the highest specific charge, but as formation voltage increases past 200 Vf, the specific charge of C255 will be higher than that for C350. If the data were extended to 250Vf, the specific charge capacity of C275 would fall off and fall below C255 as the thinner flake particles form through. Typically, C275 is recommended for conditions of less than 200Vf, while C255 would be preferred above 200Vf. Even though C275 has higher CV/g at around 200Vf, C255 may be more suited for a particular application due to other properties such as reliability and direct current leakage.

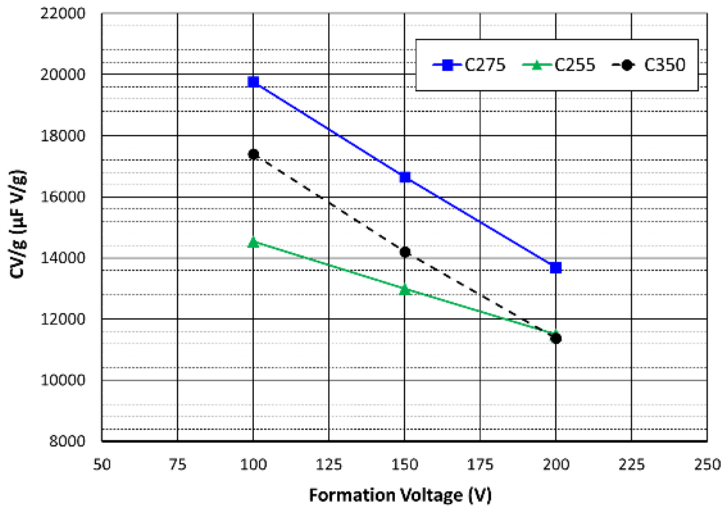

Fig. 3. Specific Charge of Flake and Nodular Powders

Theoretical models support the observation of higher specific charge capacity and higher volumetric efficiency of flake powders. Models for a flake powder can be built considering the distribution of critical flake dimensions, the dielectric thickness at a given voltage, and the oxide growth mechanism in a tantalum particle. Similarly, models for nodular powders can be built considering the same arguments; however, the geometric considerations change from a platelet geometry to a cylinder geometry. Figure 4 gives the results of one of these models demonstrating the theoretical maximum specific charge capacity of a single particle of a flake powder to a nodular powder.

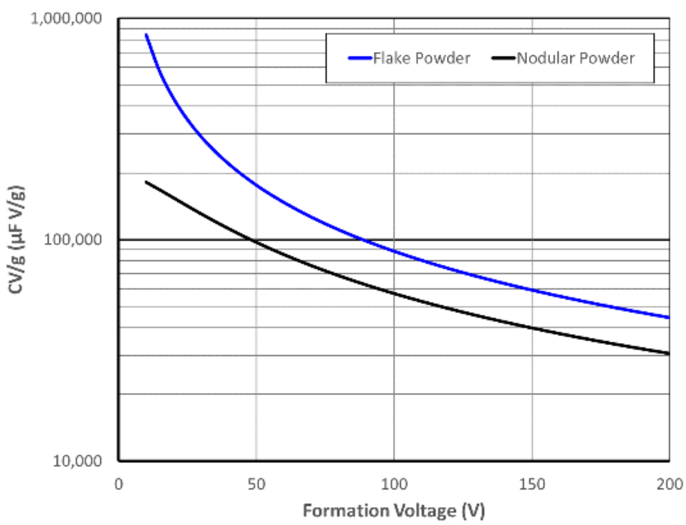

Fig. 4. Modeling Specific Charge of Tantalum Powder

Electrical Reliability

Tantalum capacitors are well known for their long-term reliability over diverse operating conditions. Maintaining a defect free anodic oxide dielectric is important to the long-term stability. As the tantalum pentoxide layer is grown onto tantalum powders, the layer expands increasing the volume of the combined tantalum and dielectric network in the pellet. This volume expansion imparts stresses on the dielectric layer that can create defects that allow electrical leakage through the dielectric, and adversely affect the long-term reliability of the capacitor. Producing tantalum anodes at elevated voltages becomes more challenging due to the thicker dielectrics formed and the potential for defect formation.

Flake powders offer advantages in preventing leakage currents due to shape considerations. The primary particles in flake powders have platelet geometries with significantly lower curvature than nodular powders. With lower curvature, the dielectric growth is more uniaxial on a flake powder producing less internal stress. The difference between a dielectric on a nodular powder and a flake powder is evident in Figure 5. Even though the dielectrics appear to be of similar thickness, it is apparent nodular powder dielectrics have a significant change in surface area from the inner tantalum core to the outer surface, while a significant portion of a flake powder maintains the same surface area over similar dimensions.

Comparing the leakage currents of commercial flake powders to nodular powders demonstrates the dramatic reduction in the potential to leak electrical current. Figure 6 demonstrates the direct current leakage normalized to the specific charge over a range of high voltage formation conditions for commercial tantalum powders from Global Advanced Metals (GAM) covering two flake powders, C275 and C255, and a nodular powder, C350. There is a significant reduction in leakage current for the flake powders across the formation voltage range, and furthermore, the relative improvement increases as Vf increases. At 200 Vf, the C350 nodular powder produces a DCL/CV 10X that of the C255 flake powder. Recalling the specific charge for these powders, C275 has a higher CV/g at 200 Vf than C255; however, if the desire is to minimize leakage within this range, C255 would be an improvement over C275.

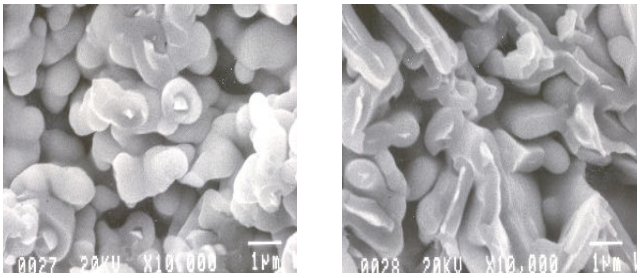

Fig. 5. Dielectric on Nodular and Flake Powders

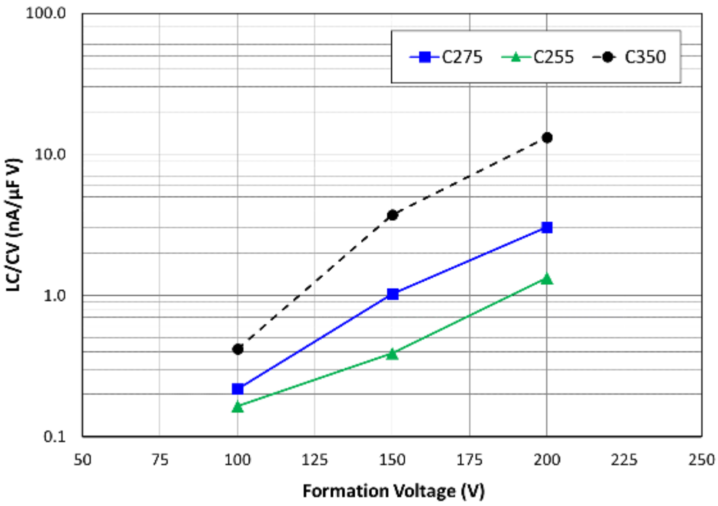

Fig. 6. Leakage Current of Flake and Nodular Powders

SUMMARY AND CONCLUSIONS

Flake tantalum powders provide capacitor manufacturers an answer to the market's need for high reliability, high operating voltage components. In comparison to the more widely used nodular powders, flake powders will produce higher volumetric efficiency and reduced leakage current. The manufacturing technology for flake tantalum powders is well established and the powders have been fully qualified across MnO_2 and polymer capacitor technologies. There are flake powders variants available across different electrical performance characteristics enabling capacitor manufacturers the potential to optimize for end applications.

REFRENCES

[1] Gill, J., Basic Tantalum Capacitor Technology, KYOCERA AVX Components Corporation

[2] Freeman, Y., (2018). Tantalum and Niobium-Based Capacitors, Springer

[3] Getz, M., Maggio, M., & Hitch, B. (1982) US Patent No. 4,441,927. Washington, DC: U.S. Patent and Trademark Office.