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Powder metallurgical processing and metal purity: A case for capacitor grade sintered tantalum

G S UPADHYAYA

Department of Materials and Metallurgical Engineering, Indian Institute of Technology, Kanpur 208 016, India

Abstract. The paper reviews the role of sintered tantalum as volumetric efficient electrical capacitor. Powder characteristics and sintering aspects are discussed. The role of impurities in influencing the electrical properties has been described. Today's driving force behind the Ta market is the use of surface mounted versions known as chip types, for applications requiring a wide range of operational temperature, such as automotive electronics.

Keywords. Tantalum powder; sintering; capacitor.

1. Introduction

Many products and devices are being manufactured through powder metallurgy route, because of many associated advantages (Upadhyaya 1997). The purity of the starting metal or ceramic powder is of significance in controlling the microstructure/properties/processing and performance of such products. The major methods of production of metal powders are: chemical, physical and mechanical.

Tantalum is used mainly as a corrosion resistant metal in the chemical industries, as high temperature heating elements and in electrolytic capacitors as electrodes, which are covered by anodic oxidation with Ta_2O_5 as the dielectric. The latter application is significant, since it has better volumetric efficiency.

Tantalum anodes are of two types, foil type and porous type. The powder metallurgy is relevant for the latter type of capacitor. The porous anode type has a much higher capacity for the same weight of tantalum than has the foil type because of its higher surface area. One of earlier type of cathode Costanet capacitor was manufactured by Plessey using liquid electrolyte and a silver cathode. These elements were assembled in an external nickel container to provide the necessary robust mechanical construction. This is a rather big disadvantage in such types of capacitors, which makes the size big. There are the chances of possible leakage of electrolyte and the disadvantage of large temperature coefficients of capacitance and the power factor associated with liquid electrolyte capacitor, particularly in the low temperature region, which are largely due to the changes in the conductance of the liquid electrolyte. The present solid electrolyte capacitor is the answer of the above limitations, where liquid electrolyte is replaced with a semiconductor (MnO_2).

The production of a solid tantalum capacitor involves making a porous tantalum pellet by pressing and sintering tantalum powder. The pellet, with an attached tantalum lead wire, is electrochemically oxidized to grow a thin layer of insulating tantalum oxide on the surface of the tantalum. Next, the anodized pellet is impregnated with manganese nitrate which is then thermally decomposed to leave or deposit semiconducting manganese dioxide on the tantalum oxide. These processes create the conductor (Ta)/insulator(Ta_2O_5)/conductor(MnO_2) configuration needed for a capacitor. Finally, the unit is encapsulated usually in the chip configuration.

gsu@iitk.ac.in

2. Powder metallurgy of tantalum

Tantalum is a reactive metal with high melting point (2997°C) and hence, powder metallurgy is the usual route of fabrication. One of the most common methods of producing tantalum powder is the reduction of potassium fluoro tantalate, K_2TaF_7, by sodium. The tantalate is obtained by reacting pure fluoro tantalic acid solution by K_2CO_3. This is a typical case of liquid–liquid reduction. One can also prepare tantalum powder by reducing Ta_2O_5, but then the route is through hydriding/dehydriding of tantalum ingot. This method is not common for capacitor grade Ta powder. An excellent review has been done by Gupta (2003).

The quality and electrical performance of capacitor grade powder have improved over the past 40 years because of improvements made in the stirred reactor reduction of potassium fluoro tantalate (K_2TaF_7) with sodium invented by Hellier and Martin (1960) and in the post reduction processing of the primary powder.

The powder must flow well to consistently fill the die cavity in the press and have sufficient green strength. Extremes of bulk density can cause problems during pellet pressing. More usable surface area is required to increase the capacitance of a powder.

Another powder feature to be taken into account is the particle size distribution. A powder with a broad distribution, especially if it contains a high percentage of fine material, will not flow and shall have low crushing strength.

During vacuum sintering of the sodium reduced tantalum powder, following out-gassing stages are noticed: (a) at 400–600°C hydrogen evolution, (b) at 1400–1600°C the reaction of any carbide with oxide forming CO and finally (c) at 2000–2200°C tantalum oxide is generated. It is advisable that the heating rate be rather slow in order to avoid cracking of the pellet. The purification kinetics is, therefore, a function of (a) impurity removal from the surface, (b) sintering temperature and (c) surface area and porosity. As porosity decreases with densification, it is necessary that impurities be removed prior to that. For efficient impurity removal, it is also necessary to give holds at different intermediate temperatures.

Table 1 gives the general values of impurity levels of tantalum before and after sintering. It is evident that there are considerable changes in the level of some of the metallic and nonmetallic impurities.

3. Effect of powder morphology and purity on electrical properties

Most of the work on capacitance has been related to the morphology of the tantalum powder and the work on leakage has been done on the oxide film. The emphasis has been on the improvement of the dielectric film to lower the leakage and increase the breakdown voltage.

Most finished powders made by the sodium reduction process have a complex nodular morphology. Other work (Fife 1995) showed that plate like or flake like particles have the potential of high volumetric efficiency of the capacitance (figure 1). This fact, however, has not been conclusively established. It is also noticed that as the tantalum particles get finer, they can be treated as rougher, and therefore, possibly have reduced leakage performance (Vermilyea 1963).

In earlier sections, the types of impurities present in the tantalum powder were highlighted. Now, a detailed analysis of their effect on electrical properties is called for (Tripp 1995).

Table 1. Impurity levels of tantalum before and after sintering (after Miller 1959).

Impurity	Before sintering (%)	After sintering (%)
O_2	0·1–0·2	0·005
Fe	0·02	0·01
Si	0·05	< 0·01
Ti	< 0·01	< 0·01
Na	0·01	< 0·002
K	0·01	< 0·002
N_2	0·05	0·003
H_2	0·10	< 0·001
C	0·05	< 0·01
Nb	< 0·10	< 0·10

Oxygen: Oxygen content in a sintered tantalum pellet in excess of 3500–4000 ppm has a detrimental effect on the performance of the capacitor. Even though the initial level of oxygen in the powder is low, further P/M processing does introduce additional oxygen. In order to improve physical properties of powder, they are generally agglomerated. But this heat treatment causes the surface oxygen to dissolve in the bulk. This can be avoided by using a programmed passivation process. Present pellets are heated to remove binder and sometimes they are re-sintered. Each of these processes can add 500–1000 ppm oxygen to the powder. Of late, powder producers have taken steps to control or reduce the oxygen content of capacitor grade powder. H C Starck now vacuum packages tantalum powder to eliminate the pick up of oxygen that otherwise can be of the order of 1 ppm/day. Another method is to manufacture low oxygen nitrided powder. A proprietory process is used to place a small quantity of nitrogen on the powder surface to reduce the amount of oxygen needed for passivation. For example, if a vacuum packed powder has a typical 2300 ppm oxygen, its nitrided version has as little as 1600 ppm oxygen. If a high sintering temperature is required, then nitrogenation becomes desirable for retaining relatively high capacitance values (Clancy 2000).

Carbon: Carbon in the form of tantalum carbide adversely affects the electrical property (Klein 1966). The general carbon content is from 30 to 70 ppm. One of the sources of carbon pick up is from binders and the leaching process is carried out to remove it. The strict control of raw materials cleaning and careful control of plant cleanliness

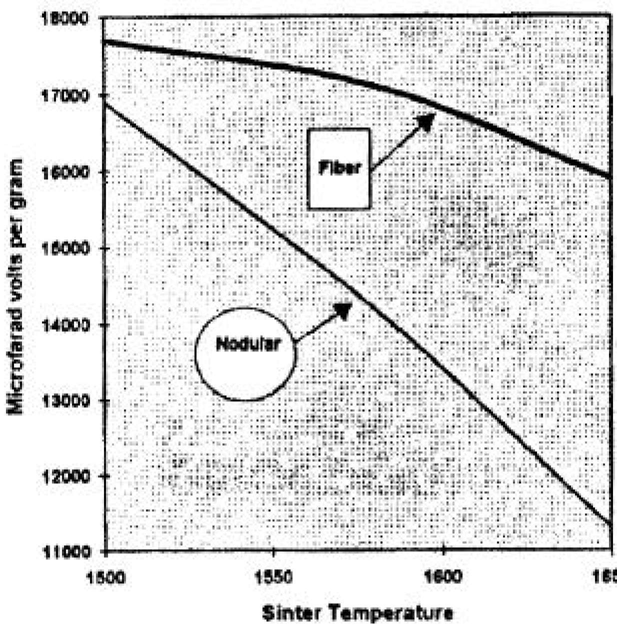

Figure 1. Capacitance comparison of fibre and nodular shaped tantalum powders (after Chang *et al* 1995).

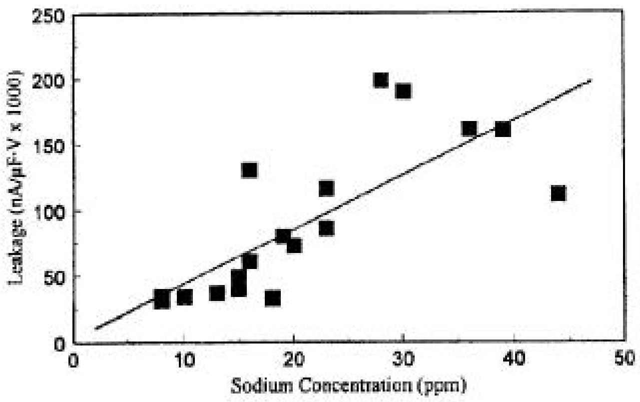

Figure 2. Leakage as a function of sodium concentration in tantalum (after Tripp 1995).

and operating procedures have given rise to as low as 10 ppm carbon level.

Sodium and potassium: The alkali content of the tantalum powder is primarily a function of the reduction conditions. Unfortunately, the conditions best suited to reduce sodium and potassium also reduce the surface area and associated specific capacitance of a tantalum powder. At present the powder has sodium content below about 2 ppm and potassium less than the typical detection limit of 10 ppm. The biggest challenge is to develop methods to achieve further reduction in the alkali concentration while simultaneously making powder with greater specific capacitance. Figure 2 shows the results of the wet test leakage of anodized, sintered tantalum pellets as a function of sodium concentration of the powder.

Phosphorus and sulphur: The role of impurities on the capacitance has been tackled more on their success to keep the open porosity high during sintering, i.e. as shrinkage inhibitors. In this regard two elements are worth mentioning—phosphorus and sulphur. More research is needed in this direction.

Niobium: As niobium is closely associated with tantalum, it is interesting to study its role on the electrical characteristics of the latter. The amount of niobium in the tantalum powder used for tantalum capacitors ranges from the maximum of 100 ppm to a level that cannot be detected, probably < 5 ppm. Of course, the level depends on the size, type and voltage of tantalum capacitor that one desires to make and the sintering temperature used. For small, low voltage ('A' case capacitor with < 10 V), one can probably make a commercial capacitor using a powder with 50 ppm of niobium. For larger capacitors with 35 V, one might require a powder with < 5 ppm niobium (Serjak 2004).

4. Conclusions

The future in tantalum capacitors lies in improving the quality of tantalum powder and the volumetric efficiency, so as to place more capacitance in the standard case sizes. Although from cost point of view, tantalum has difficulties in competing with MLC's and aluminium with their very large volume of production, but it could be mitigated by the continued exploitation of high CV/g powders, taking full advantage of the higher CVs achievable at lower voltages.

References

Chang H, Fife J A and Pathare V M 1995 in *Proceedings of int. symposium on tantalum and niobium* (Brussels: Tantalum–Niobium International Study Centre (TIC)) p. 227

Clancy D J 2000 in *Proceedings of int. symposium on tantalum and niobium* (Brussels: Tantalum–Niobium International Study Centre (TIC)) p. 273

Gupta C K 2003 *Chemical metallurgy* (Weinheim: Wiley-VCH) p. 421

Fife J A 1995 *TIC Bulletin* **81** 5

Hellier E G and Martin G L 1960 Production of tantalum, US Patent 2950185

Klein G P 1966 *J. Electrochem. Soc.* **113** 348

Miller G L 1959 *Tantalum and niobium* (London: Butterworth Scientific Publications)

Serjak B 2004 Consultant TIC, Private Communication

Tripp T B 1995 in *Proceedings of int. symposium on tantalum and niobium* (Brussels: Tantalum–Niobium International Study Centre (TIC)) p. 219

Upadhyaya G S 1997 *Powder metallurgy technology* (Cambridge, UK: Cambridge International Science Publishing)

Vermilyea D A 1963 *J. Electrochem. Soc.* **110** 250