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Short communication

Characteristics and production of tantalum powders for solid-electrolyte capacitors

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Abstract

The effects of using K_2TaF_7 as the raw material and sodium as the reducing agent on the characteristics of tantalum powder are investigated. Batch-type metallothermic reduction (BTMR) is used to charge the reactor with the raw material and the reducing agent, and external continuous supply metallothermic reduction (ESMR) is used to supply the raw material and the reducing agent at a constant rate at the temperature of the reduction reaction. In the case of ESMR, the yield increases by several tens of percent because of the uniform reaction between the raw material and the reducing agent. It is possible to obtain a powder of over 99.5% purity. The powder particles obtained with BTMR are relatively large (4–6 μm) and have a coarse lamellar shape, while those prepared via ESMR are of uniform 1–2 μm size with a coral-like shape. Measurements of the electric properties show that the leakage current and the dielectric dissipation are low with higher reliability in ESMR than in BTMR, and the capacitance is 26,000 and 8400 CV for ESMR and in BTMR, respectively.

Keywords: Batch-type metallothermic reduction; Leakage current; Dielectric dissipation; Solid-electrolyte capacitor; External continuous supply; Tantalum powder

1. Introduction

Tantalum is a silver white metal belonging to Group V of the Periodic Table but is usually bluish because of the oxide film on its surface. The oxide film is formed through anode oxidation of tantalum and has a rectifying function and high permittivity, and it is electrically stable. Tantalum electrolytic capacitors have been used in various mobile electronic products such as mobile phones, personal digital assistants, laptop computers, controllers in airplanes, and vehicles. With an increasing demand for high reliability and small size in electronic products, technologies are still being developed for tantalum as a material meeting these requirements.

The tantalum capacitor is an electrolytic capacitor that uses tantalum as the material of the electrodes. Similar to an aluminum electrolytic capacitor, it can attain a relatively large capacity. The tantalum electrolytic capacitor is superior to the aluminum electrolytic capacitor both in its temperature characteristic (i.e., the capacity changes according to temperature) and in its frequency characteristic. Unlike aluminum electrolytic capacitors that are made by wrapping kraft soaked in an electrolytic solution and use metal aluminum, tantalum electrolytic capacitors use an opening made when tantalum powder is sintered and hardened, so their electric features are outstanding. Tantalum capacitors have polarity and, in general, a capacitor itself has a (+) mark indicating the polarity. Connection must be made to the correct electrodes. In addition, tantalum capacitors are used in circuits that strictly control the changes in capacity caused by temperature and have somewhat high frequency.

In the present study, tantalum powder is manufactured through metallothermic reduction [1–3] using metallic sodium as a reductant. The characteristics of the tantalum powder as well as the capacitance leakage current and permittivity loss of tantalum electrolytic capacitors are investigated.

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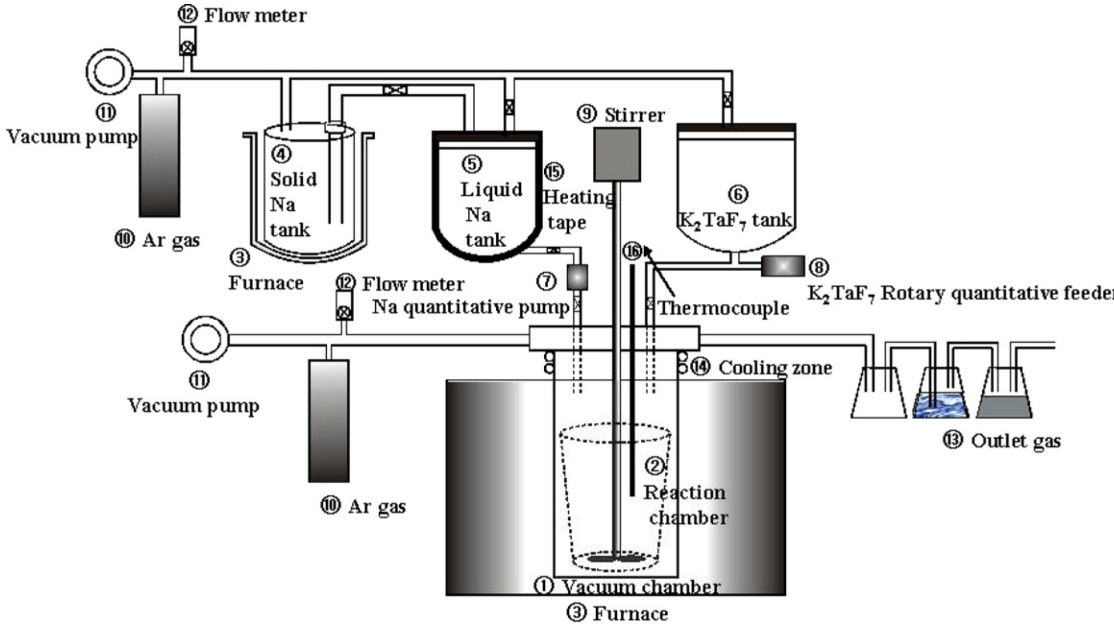

Fig. 1. Schematic diagram of external continuous supply system.

2. Experiment

A diagram of the experimental apparatus is shown in Fig. 1. The reductant and raw materials were supplied from outside so that the reaction speed and internal reaction temperature could be controlled according to the feeding rates.

The experimental process can be briefly described as follows. In batch-type metallothermic reduction (BTMR), KCl and KF are prepared as diluents in a weight ratio of 4:1 and a total weight of 2000 g. In addition, 100 g of raw material K_2TaF_7 and 323 g of finely-cut metallic sodium were prepared. Materials were loaded into the reactor in the order: diluent, Na, raw material. The reaction chamber was then evacuated. In external continuous supply metallothermic reduction (ESMR), first 2000 g of diluent was loaded into the reactor and the chamber was then evacuated. At the same time, the raw material tank and Na tank were loaded with 1000 g of raw material and 323 g of Na, respectively, and subjected to a vacuum of 3.99 Pa. In order to minimize the oxygen remaining inside the chamber, vacuuming and argon gas injection were repeated three times. The reaction temperature was raised to 1123 K. In BTMR, reduction was conducted for 3 h. After cooling to room temperature, the reactant was recovered. In ESMR, a reaction temperature of 1123 K was maintained for 1 h, and then the raw material and the reductant were loaded simultaneously from external containers. The raw material was supplied at a constant rate that was adjusted by using the number of screw turnings, while the reductant was supplied constantly using a liquid metering pump. The amounts of the raw material and the reductant used in this experiment were 1000 and 323 g, respectively, and they were loaded at feeding rates of 100 and 33 g mm^{-1}. The materials were agitated to accelerate the reaction among the loaded materials. The agitator was placed 10 mm above the bottom of the reactor, Agitation was performed at a rate of 70–80 rpm, was started 30 min before the supply of the raw material, and was continued for one more hour after the loading was completed. The agitator was then separated from the reactants, and the target temperature was maintained for 1 h for the reactants to settle. Finally, the reactor was cooled to room temperature, and the precipitated sample was recovered from the reactor. The sample obtained through BTMR was post-processed in the same way.

In post-processing, the sample was washed with methanol and distilled water several times to remove the un-reacted Na and salt, and then a pickling process was applied [5]. This consisted of pickling in 20% (HCl + HNO_3) for 1 h, washing with distilled water, pickling in $8\%H_2SO_4 + 8\%Al_2(SO_4)_3$ solution for 3 h, and pickling in $2\%H_2O_2 + 1\%HF$ for 1 h. On completion of the pickling process, the sample was washed several times with distilled water and finally with acetone. Drying was undertaken in a vacuum oven at 353 K for 6 h. Calcium was added as a reductant to the dried powder. De-oxidation was carried out at 1173 K for 5 h followed by vacuum heat-treatment at 1573 K for 3 h.

A tantalum capacitor is made of pure tantalum powder. The typical particle size is 1–3 μm for high voltage, or around 100 μm when clustered. The powder is mixed with an appropriate binder and lubricant, loaded into a moulding tool, and shaped into a pellet. At this stage, tantalum wire is inserted to make an anode. Then, it is sintered in vacuum at a high temperature of 1773–2273 K. The object of this process is to combine separated particles into a sponge-shaped structure. The structure has high mechanical strength and high porosity, which gives a large internal surface area. Finally, heat-treatment and the voltage stability and ageing treatment were performed, and the characteristics of the capacitor such as capacitance, permittivity loss (tan δ) and leakage current (L.C.) were measured.

Table 1
Chemical compositions (ppm) after heat-treatment for tantalum powder

Sample	Impurity						
	Fe	Cr	Ni	Ca	Na	K	O
Commercial	<50	<10	<10	<20	<10	<50	<3000
BTMR	140	25	20	<20	<10	<50	<3000
ESMR	<50	<10	<10	<20	<10	<50	<3000

3. Results and discussion

3.1. Impurity and morphological analysis

The contents of impurities present in the tantalum powder, are given in Table 1. Those of heavy metals such as Fe, Cr and Ni are much lower in the sample prepared by ESMR that supplied the raw material and the reductant from outside than in the sample made by BTMR that loaded the raw material, reductant and diluent in the mixture. It is considered that, in the BTMR experiment, the heat (Q) generated from the temporary reaction between the raw material and the reductant (Eq. (1)) rapidly increases the temperature inside the furnace rapidly and at this stage the reactants are penetrated by heavy metal impurities from the reactor, through exposure of the agitator to the highly molten salt.

$$K_2TaF_7 + 5Na \rightarrow Ta + 5NaF + 2KF + Q \qquad (1)$$

In the ESMR, however, the sudden rise in reaction temperature is prevented, and the reduction of the raw material takes place uniformly and, as a result, the impurity contents are low. In addition, because of the high-temperature treatment, gases such as oxygen could be controlled to remain below the allowed limit of 3000 ppm [4–6].

According to a report by Izumi [7], trace impurity elements affected the sintering of tantalum particles. That is, it was reported that the high refinement of tantalum was closely related to the characteristic features of the capacitors, and the high level of purity from heavy metals and gas impurities improved the sintering of tantalum powder and its electric properties such as a decrease of leakage current.

Scanning electron micrographs of the tantalum powder manufactured in this study and tantalum powder (c) for commercial capacitors are shown in Fig. 2. The powder from BTMR (Fig. 2(a)) has large coarse globular particles of 5–6 μm, but the granularity distribution is very irregular. This shows that since the BTMR has difficulties in controlling reaction temperature, it is difficult to control granularity and particle shape, which are sensitive to reaction temperature. By contrast, because the raw material and the reductant are supplied from outside at a constant rate in the ESMR, the reaction temperature and the reaction speed can be controlled and the tantalum powder (Fig. 2(b)) has a coral shape with a larger surface area. The granularity of tantalum powder is 1–2 μm, i.e., finer than the particles from BTMR, and the granularity distribution is very uniform.

Particle size can be controlled in various ways. Bose et al. [8] reported that powder granularity is finer when reaction temperature is low, the quantity of diluent, namely, KCl/KF is large, and the quantity of added sodium is small. A low reaction temperature retards nucleation of the precipitated powder particles and a large quantity of diluent suppresses the growth of particles, so that the precipitated powder particles become finer.

3.2. Evaluation of electric characteristics

The granularity distribution of tantalum powder manufactured in this investigation is shown in Fig. 3. The

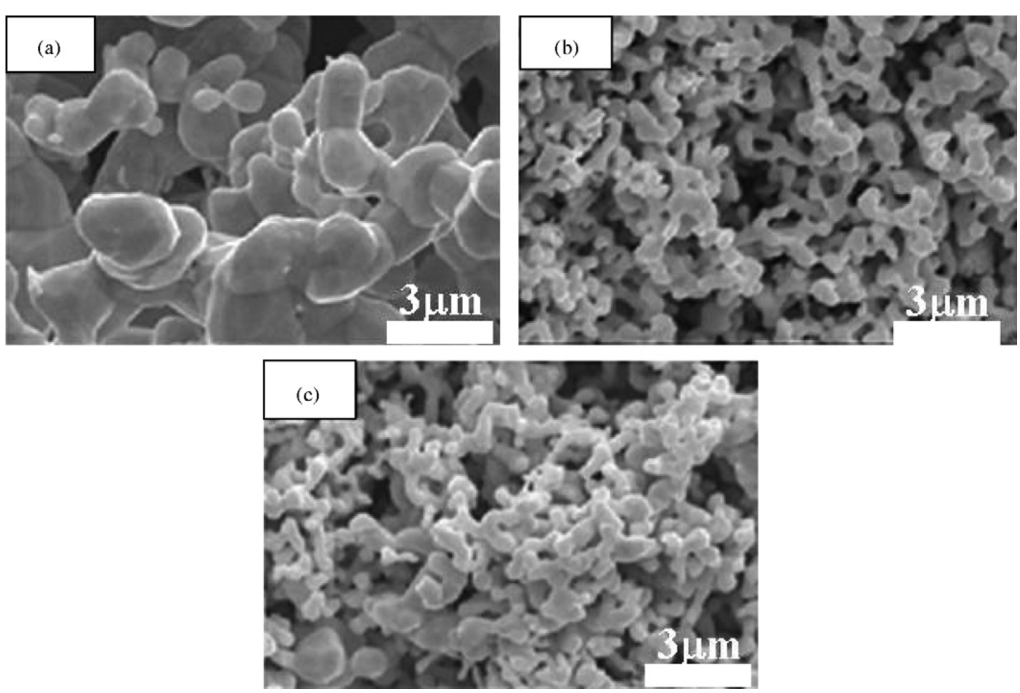

Fig. 2. Scanning electron micrographs of tantalum deposits produced by (a) batch-type process, (b) external supply process and (c) commercial tantalum powder.

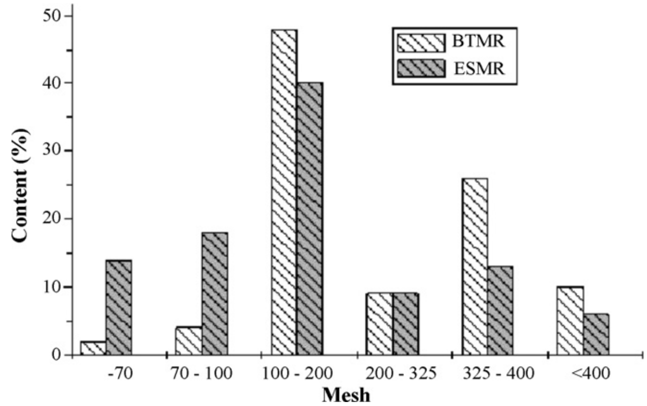

Fig. 3. Particle-size distribution of tantalum powders.

Table 2
Flowability of tantalum powder before and after mixing with binder

Method	Before mixing (Average) (g)	After mixing (Average) (g)	Condition
BTMR	12.4	11.2	Flowability
ESMR	25.0	24.1	20 s and 60 Hz

fluidity before and after mixing with the binder is given in Table 2.

In manufacturing capacitors, a certain quantity of tantalum powder is dropped into a moulding machine and compressed into pellets. Here, fluidity is very important and, depending on the quantity of powder, the volume of pellets before and after sintering changes, which may cause defects in the capacitors.

The globular tantalum powder manufactured with BTMR shows irregular granularity. As a result, the clustering is imperfect, and 40–50% of the particles are smaller than 325 mesh. This lowers the fluidity and increases the defect rate in moulding. On the other hand, tantalum powder manufactured with ESMR contains many coarse and large participles with sizes over 100 mesh, and this improves the fluidity. Thus, the shape of clustered powder is determined by impurities and particle shape.

Data that compare the electric properties with commercial tantalum capacitors are presented in Figs. 4–6. The capacitance of each sample is given in Fig. 4. Pelites of the same size were prepared for each sample and the capacitance (μF) per unit mass (g) of each was measured by applying a constant voltage of 35 V. In the case of BTMR, the capacitance is 0.8 μF in electrolytic solution and around 0.7 μF after ageing treatment. By contrast, higher capacitance is obtained from the capacitors of tantalum powder manufactured with ESMR, i.e., 1.05 μF in electrolytic solution and 0.95 μF after ageing treatment.

The capacitance of the tantalum electrolytic capacitors is dependent on the granularity and particle shape of the tantalum powder. That is, capacitance is high in proportion with the surface area. While the capacitance of tantalum chip capacitors of a specific volume was 1 μF in 1983, that of tantalum chip capacitors of the same volume was 47 μF in 1999. This indictated that, for the same volume of tantalum powder, the capacitance increases with increase in surface area on forming the Ta_2O_5 dielectric after moulding. Accordingly, a higher capacitance is obtained from coral-shaped tantalum powder manufactured with ESMR than from globular tantalum manufactured with BTMR.

Measurements of the angle of permittivity loss (tan δ) and the leakage current (L.C.) are given in Figs. 5 and 6, respectively. The tantalum powder prepared with ESMR is superior in terms of dielectric loss and leakage current. These two parameters are determined by the impurities and the uniformity of granularity when the Ta_2O_5 dielectric is formed after tantalum powder is

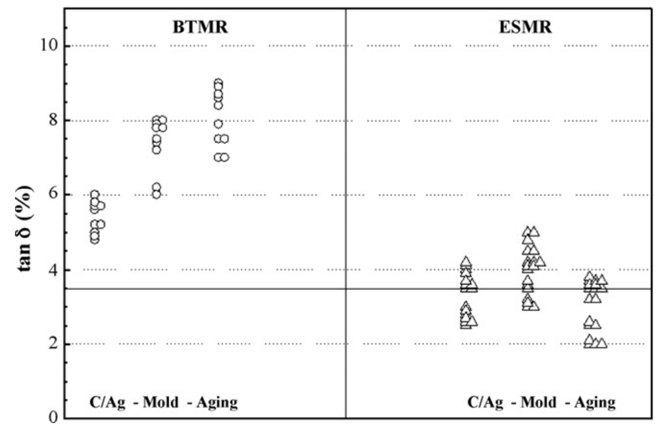

Fig. 5. Distribution of dissipation factor (tan δ).

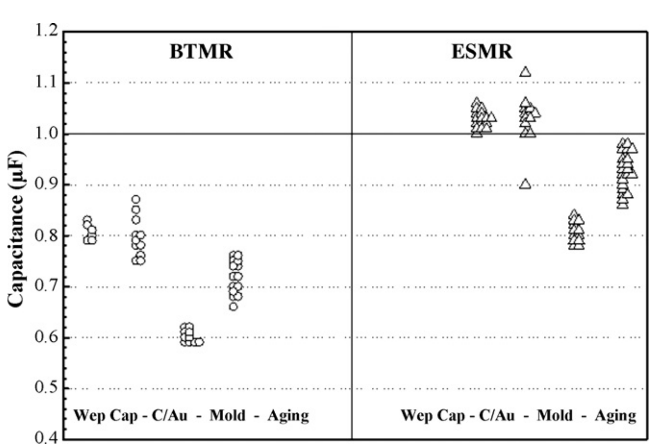

Fig. 4. Distribution of capacitance.

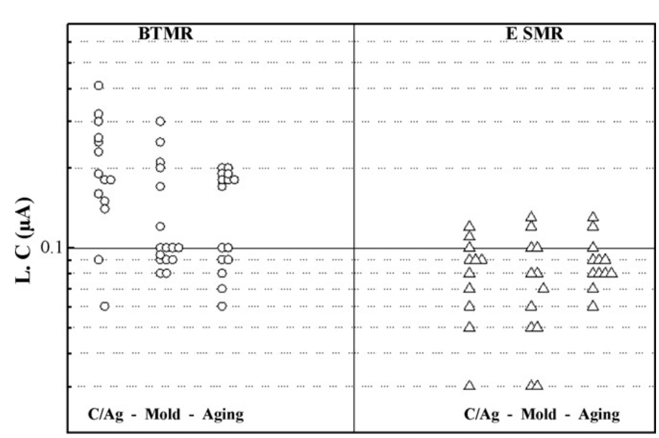

Fig. 6. Distribution of leakage current.

muolded. The impurities are semi-conductive oxides that are generated between the Ta_2O_5 and the tantalum and they lower dielectric loss and powder sintering, which, in turn, increase the leakage current. Accordingly, while the tantalum prepared with BTMR contains a great deal of impurities and shows a high dielectric loss and leakage current, the tantalum from ESMR with low impurity contents exhibits a low dielectric loss and leakage current.

In summary, to increase the capacitance and reduce the dielectric loss and leakage current, it is necessary to improve the granularity, particle shape and purity of tantalum powder.

4. Conclusions

Tantalum powder manufactured with ESMR contains low contents of heavy metals. The contents of Fe, Cr and Ni are lower by tens of ppm than those in the tantalum powder manufactured with BTMR, in which reduction occurres with the raw material, reductant and diluent loaded together. When the reductant and the raw material are supplied at a constant rate at the reduction temperature, the heat generated from the reaction can be controlled and the impurity contents are significantly lower due completion of the reaction. Despite the morphological aspects of tantalum powder, such as shape and granularity that are highly sensitive to reaction temperature, the ESMR process makes it possible to manufacture tantalum powders made up of large coral-shaped globular particles with a uniform granularity of 1–2 μm.

The capacitance of tantalum powder manufactured with BTMR is 8400 CV, whereas that of tantalum powder manufactured with ESMR is 26,000 CV. In addition, the latter powder not only has a low leakage current and permittivity loss but also has low impurity contents and an regular particle shape.

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