Conf-920402-45

MICROWAVE PROCESSING OF TANTALUM CAPACITOR ANODES*

R. J. LAUF*, C. HAMBY*, C. E. HOLCOMBE*, AND W. F. VIEROW**

*Martin Marietta Energy Systems, Inc., Oak Ridge, Tennessee 37831-6087
**AVX Tantalum Corp., 69 Landry St., Biddeford, ME 04005

ABSTRACT

Porous tantalum anodes were sintered at temperatures from 1600 to 1900°C using a conventional high-vacuum furnace as well as both 2.45 GHz fixed-frequency and 4-8 GHz variable-frequency microwave furnaces. Various insulation and casketing techniques were used to couple the microwave power to the tantalum compacts. Several types of tantalum powder were used to assess the effect of microwave processing on sintered surface area and impurity levels.

Some microwave sintered anodes have an unusual surface rippling not seen on conventionally fired parts. The rippling suggests that a microscopic arcing or plasma might have been generated. Two important effects could be exploited if this phenomenon can be controlled. First, the effective tantalum surface area could be increased, yielding higher capacitance per volume. Second, surface impurities might be cleaned away, allowing the formation of a better dielectric film during the anodization process and, ultimately, higher working voltage.

INTRODUCTION

Tantalum capacitors are widely used in electronics where high reliability is needed, such as cardiac pacemakers and other implants, hearing aids, pagers, diagnostic equipment, and military products. Tantalum capacitors are manufactured from a powder of pure Ta metal pressed to form a pellet and vacuum sintered. The spongelike pellet, although of high mechanical strength and density, is still highly porous giving a large internal surface area. This forms the positive "plate" of the capacitor.

A dielectric layer of tantalum pentoxide is formed on the porous tantalum by anodizing, covering all available surface area. The cathode is formed by infiltrating the anodized pellet with layers of manganese dioxide. Electrical contact is established by deposition of carbon and silver onto the surface of the pellet. Cathode connection is then made by means of conductive contact to a lead frame. Packaging is carried out to meet individual specification and customer requirements.

Two types of Ta powder are used commercially depending on specific requirements. Sodium reduced powder has the highest surface area but somewhat lower purity. Electron beam refined powder has the highest purity for higher working voltages but at the expense of somewhat lower surface area. It is interesting to note that because the dielectric is an anodic oxide film grown directly on the Ta, damage can, to some extent, be self-healing. Conversely, failure can occur at weak spots in the oxide, possibly where impurities have accumulated.

The long term goal of this work is to explore several possible aspects of microwave processing: 1. Microwave-generated plasmas or arcing at particle surfaces might clean away surface impurities such as sulfur that are deleterious to the formation of a good dielectric oxide film. 2. Lower processing temperatures and/or shorter cycles could improve process economics and provide tighter control over the microstructure. 3. Observation of surface chemistry and morphology can give fundamental insights into the actual mechanisms of microwave sintering, which are still poorly understood.

EXPERIMENTAL

Four batches of Ta anodes were pressed from representative commercial Ta powders, two each of sodium reduced and electron beam purified. The pressed compacts contained a small amount of organic binder, which was removed by holding 30 min at

* Work supported by the U.S. Department of Energy, Office of Energy Research, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

480°C in vacuum. The parts were sintered in either a conventional Brew vacuum furnace, a 2.45 GHz fixed-frequency microwave furnace [1], or a 4-8 GHz variable-frequency microwave furnace [2]. In order to initiate microwave heating as well as provide thermal insulation at high temperatures, various casketing arrangements [3] were used in the microwave furnaces. Sintering conditions are summarized in Table 1.

Table I. Sintering Conditions for Tantalum Capacitors.

Run	Powder*	Furnace**	T, °C	Atm.	Casketing
1	Na-1	C	1600	Vac.	
2	Na-2	C	1600	Vac.	
3	EB-1	C	1600	Vac.	
4	EB-2	C	1600	Vac.	
5	Na-1	C	1600	Vac.	
6	Na-2	C	1700	Vac.	
7	EB-1	C	1700	Vac.	
8	EB-2	C	1700	Vac.	
9	Na-1	C	1800	Vac.	
10	Na-2	C	1800	Vac.	
11	EB-1	C	1800	Vac.	
12	EB-2	C	1800	Vac.	
13	Na-1	C	1900	Vac.	
14	Na-2	C	1900	Vac.	
15	EB-1	C	1900	Vac.	
16	EB-2	C	1900	Vac.	
17	Na-2	M	1700	Vac.	Y_2O_3 grit
18	Na-2	M	1700	Ar	Y_2O_3 grit
19	Na-2	M	1700	Ar	Y_2O_3 grit, parts coated with BN
20	Na-2	M	1500-1600	Vac.	ZrO_2 fiber
21	Na-2	M	1700	Vac.	ZrO_2 fiber: Y_2O_3 grit 50:50
22	Na-2	M	1600	Vac.	ZrO2 bubbles, BN casket
23	Na-2	M	1700	Vac.	ZrO2 bubbles, BN casket
24	Na-2	V	~1450	N_2	ZrO2 fiber, BN casket
25	Na-2	M	1800	Vac.	ZrO_2 bubbles, BN casket

**C = Conventional, M = 2.45 GHz, V = Variable frequency
*Na = Na reduced, EB = electron beam purified
All samples sintered 30 min. except #24 which was sintered 90 min.

RESULTS AND DISCUSSION

The structures of sintered anodes were characterized by fracturing the pellets and examining the fractured surface by SEM. The results are given in Table 2. In general, all samples were sufficiently sintered to form strong necks between adjacent grains.

Table II. Sintering Results for Tantalum Capacitors.

Run	Surface Reactions	Ripples	Comments
1-16	No	No	Conventional process
17	Yes	No	Well sintered
18	Yes	Yes	Well-sintered without coarsening
19	Yes	Yes	Similar to #18
20	Yes	Yes	
22	Yes	Few	Thick surface crust
23	Yes	Few	
24	Yes	Few	Less sintering than others
25	Yes	--	Reacted w/ZrO_2 bubbles

*All capacitors showed particle-to-particle sintering.

Microstructural development in the controls (Samples, 2, 6, 10, 14, 4, 8, 12, and 16, Fig. 1) illustrates the appearance of "typical" anodes made from the two types of powder. The difference in powder size and surface area is clear because sintering is not carried out to full densification.

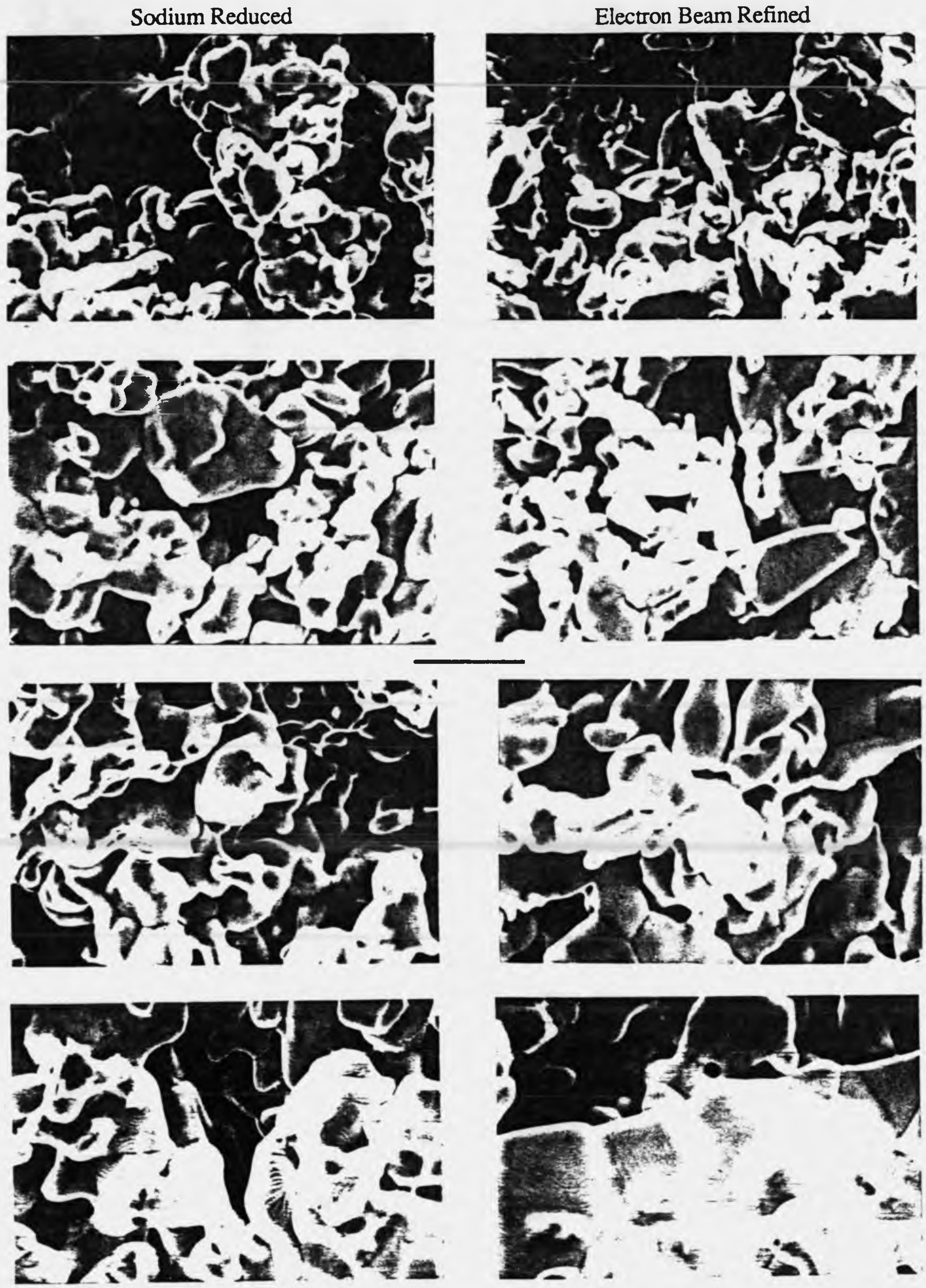

Fig. 1. Ta anodes from two powders conventionally sintered 30 min. in vacuum at (top to bottom): 1600, 1700, 1800, and 1900°C. Bar = 10 μm.

Figure 2 shows a similar progression for three microwave sintered specimens (samples 22, 23, and 25). It is clear from the high degree of sintering that the third sample experienced a much higher temperature than its nominal 1800°C sinter.

Many microwave sintered anodes show unusual surface ripples on their individual Ta grains, Fig. 3. The origin of this effect is presently unknown, but it suggests the possible existence of microscopic arcing or plasma formation within the pore spaces. Such phenomena could be helpful by encouraging rapid sintering without coarsening and/or by cleaning away surface impurities. Diagnostic tools are presently under development with which we hope to detect microscopic discharge effects as they occur [4].

Fig. 2. Ta anodes from Na reduced powder microwave sintered 30 min in vacuum at (top to bottom): 1600, 1700, and 1800°C (nominal). Bar = 10 μm.

All microwave processed samples had some degree of surface reaction such as a thin (presumably oxide) layer, Fig. 4, or a more catastrophic reaction with the insulation medium, Fig. 5. Because cleanliness of the anode is crucial to the fabrication of a good tantalum capacitor, it is clear that casketing techniques must be improved to minimize material interactions and temperature nonuniformities as well as to facilitate the attainment of the best possible vacuum.

Sample 24 was sintered at 1450°C in nitrogen at 6.7-6.8 GHz in a preliminary test of the variable-frequency furnace [2]. Despite the low temperature, some sintering was observed in the specimens.

Fig. 3. Surface ripples on Ta particles after microwave sintering.

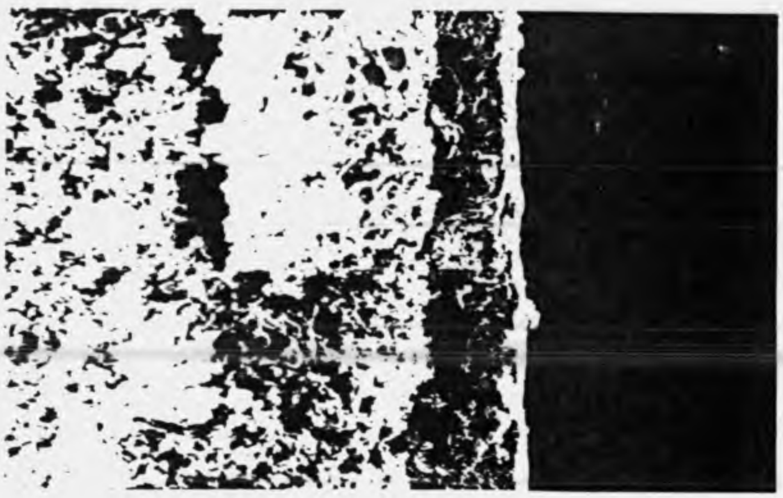

Fig. 4. Layer on outside of microwave sintered pellet.

Fig. 5. Pellet fired at 1800°C (nominal) showing reaction with ZrO_2 bubbles on surface.

CONCLUSIONS

1. Tantalum capacitor anodes can be sintered using microwave heating provided the casket contains lossy materials to initiate heating from ambient temperatures.

2. Microwave sintered anodes often show unusual surface ripples on the individual Ta particles; their exact origin is presently unknown.

3. Casketing techniques must be improved in order to maintain high vacuum, cleanliness, and uniform temperatures within the working volume.

ACKNOWLEDGMENT

This project was supported by the U.S. Department of Energy, Office of Energy Research, Laboratory Technology Transfer Program, and conducted under Cooperative Research and Development Agreement No. ORNL 91-0056 between Martin Marietta Energy Systems, Inc., and AVX Tantalum Corporation.

REFERENCES

1. C. E. Holcombe and N. L. Dykes, "Microwave Sintering of Titanium Diboride," J. Mat. Sci. 26, 3730-38 (1991).

2. D. W. Bible, R. J. Lauf, and C. A. Everleigh, "Multikilowatt Variable Frequency Microwave Furnace," Mat. Res. Soc. Symp. Proc., Vol. 269 (1992).

3. C. E. Holcombe and N. L. Dykes, "Importance of 'Casketing' for Microwave Sintering of Materials," J. Mat. Sci. Lett. 9, 425-8 (1990).

4. D. W. Bible, Oak Ridge National Laboratory, personal communication (1992).