

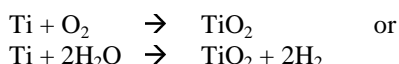
Titanium Sponge Grown on Titanium Substrate

J. Ki, J. Chung, D. McGervey and G. Welsch
 Department of Materials Science & Engineering
 Case Western Reserve University
 Cleveland, OH 44106

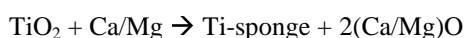
Titanium/TiO₂ is a promising material for electrolytic capacitors. The relative dielectric constant of titanium dioxide is $\epsilon_r = 90$ (at 60Hz) which compares to a value of 28 for tantalum oxide in Ta/Ta₂O₅ of commercially used electrolytic capacitors.

Surface layer titanium sponge can be made by various techniques, e.g., see US patent 6,226,173. One method, applied here, is by oxidation and reduction.

Commercially pure titanium samples were oxidized in the air or steam, respectively, between 400 and 1000°C for 5 minutes to 96 hours to grow titanium oxide scales according to:



The oxidized samples were then placed into sealed titanium retorts and were again encapsulated in stainless steel retorts with magnesium or calcium granules added. The samples were reduced in Ca- or Mg-vapor between 800 and 900°C for 12 to 24 hours.



After opening the retorts CaO/MgO was leached in distilled water for 1 to 15 days. A spongy layer of metallic titanium was obtained in place of the previous oxide scale. It provided the surface enhancement. Anodization at 20 Volt in 1%-H₃PO₄ electrolyte generated a thin (27nm) TiO₂ film on the sponge surface. Capacitance and charge density measurements provided a measure of the increase in surface area. Whereas flat Ti/TiO₂ has a charge density around 50 $\mu\text{C}/\text{cm}^2$ the spongy surface layers had charge densities of as high as 15,000 μC per cm^2 of substrate area, see also Table 1.

Table 1. Processing parameters for titanium sponge layer. Evaluation of surface enhancement from capacitor charge density after anodization to 20V.

Temperature and time of oxidation in air		Reduction temperature, time, and reducing agent		Charge density per substrate area
°C	h	°C	h / Ca, Mg	$\mu\text{C}/\text{cm}^2$
1000	0.25	900	24 / Ca	5579
1000	0.25	900	24 / Mg	1038
1000	0.5	900	12 / Ca	7482
1000	0.5	900	12 / Mg	1532
1000	3.0	900	12 / Ca	4528
1000	3.0	900	12 / Mg	14987

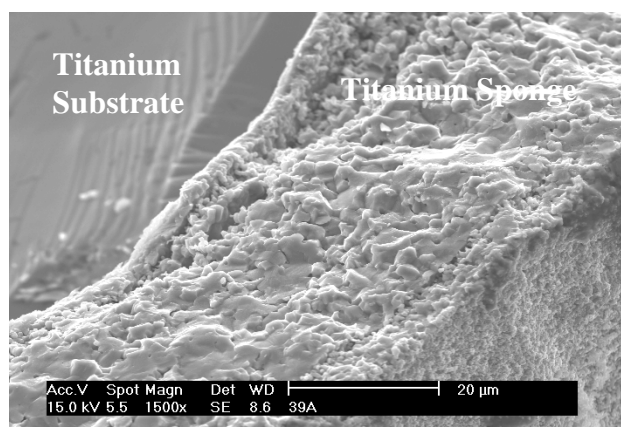


Figure 1. SEM micrograph of cross section of 12h, 900°C magnesium-reduced titanium sponge.