Formation of Foreign Element-Stabilized Amorphous Anodic Titania with High Permittivity

H. Habazaki*, M. Uozumi*, T. Onodera*, H. Konno*, K. Shimizu*[1], S. Nagata*[2], K. Takayama*[3], Y. Oda*[3], P. Skeldon*[4], G.E. Thompson*[4]
*Graduate School of Engineering, Hokkaido University, N13-W8, Sapporo 060-8628, Japan
*[1]University Chemical Laboratory, Keio University, 4-1-1 Hiyoshi, Yokohama 223-8521, Japan
*[2]Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
*[3]Cabot Supermetals, Co. Ltd., Kawahigashi-machi, Fukushima-Pref. 969-3431, Japan
*[4]Corrosion and Protection Centre, UMIST, P.O.Box 88, Manchester M60 1QD, UK

Titanium has been received attention as a material for electrolytic capacitors, due to relatively high permittivity of its oxide. However, large leakage current of the anodic titania films, associated with an amorphous-to-crystalline transition of the anodic oxide and subsequent oxygen gas generation, have hampered the development of titanium capacitors. The amorphous-to-crystalline transition, which occurs during film growth at low voltages, induces an electron conducting path in the oxide films, enabling oxygen gas formation on the crystalline regions[1]. Recently, the authors have found that the crystalline oxides are formed in the inner 60% of the film thickness, where the film material is developed at the metal/film interface by migration of oxygen species inwards[2]. Further, we have revealed that incorporation of foreign species in the inner part of the film from substrate by alloying of titanium suppresses effectively the crystallization of the anodic oxide, allowing growth of uniform amorphous films to high voltages[3]. However, incorporation of foreign species, such as aluminum, molybdenum, silicon and zirconium species, examine so far results in the decrease in the permittivities of the anodic oxides. In this paper, we have examined the influence of niobium and tungsten additions to titanium on the structure and dielectric properties of the anodic oxide films, since these metals form anodic oxides with high permittivity similar to anodic titania.

The Ti-Nb and Ti-W bcc solid solution alloys, as well as titanium metal, prepared by magnetron sputtering were anodized at a constant current density of 50 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte. The alloys containing more than 10 at% tungsten or 25 at% niobium reveals a linear voltage increase with anodizing time up to more than 100 V, in contrast to significant reduction of the slope at about 20 V for titanium. The change in slope for titanium is associated with reduction of current efficiency for the film growth owing to oxygen evolution.

The formation of uniform anodic films with amorphous structure on the alloys was confirmed directly by TEM observation of the ultramicrotomed sections. The anodic films are two layers, comprising an outer relatively pure titania layer and an inner layer containing both titanium and alloying element species. The relative thickness of the outer layer is larger for the tungsten-containing films than for the niobium-containing films. The different migration rates of the cation species during film growth under the high electric field lead to the formation of such layered anodic films, and their migration rates are related to their strengths of the single metal-oxygen bonds.

The reciprocal capacitances of the anodic films formed on these alloys were changes linearly with formation voltages during uniform film growth. Figure 2 shows change in capacitance of the anodic films formed to 100 V on the Ti-Nb and Ti-W alloys with alloy composition. The capacitances of other titanium alloys are also shown for comparison. In contrast to the Ti-Al, Ti-Mo and Ti-Zr alloys showing a decrease in capacitance with increasing alloying element content, the capacitances of the anodic films on the Ti-Nb and Ti-W alloys are almost independent of alloy composition, revealing high capacitance for the alloys with high contents of alloying elements.

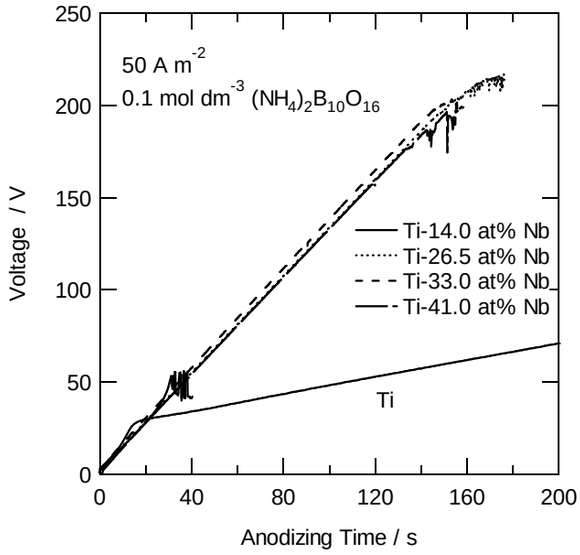

Fig. 1 Voltage-time curves of the sputter-deposited Ti-Nb alloys during anodizing at 50 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte.

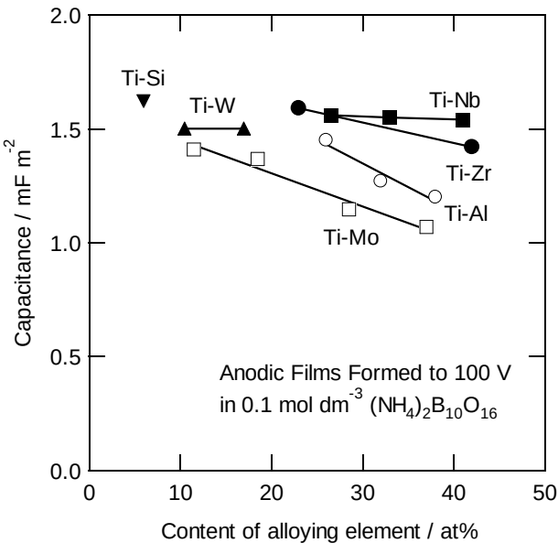

Fig. 2 Change in capacitance of the anodic films formed on the titanium alloys to 100 V with alloy composition.

References

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