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SHORT COMMUNICATION

ANODIC OXIDATION OF TITANIUM UP TO 100 V

F. CLIMENT and R. CAPELLADES

Departamento de Matalurgia, Facultad de Químicas, Universidad de Barcelona, Spain

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Abstract—This is a study of the dielectric breakdown of TiO_2 films and of the anodic oxidation of Ti over 50 V, in order to analyze the dielectric properties of the Ti–TiO_2 system. A maximum limit of anodization was found to be around 100 V, thereafter the growth of crystalline areas in the TiO_2 film begins to be produced, causing its electrical properties to deteriorate. Values of effective electric charge close to 14 μFV cm^{-2} were achieved in TiO_2 films, upon carrying out the anodic oxidation of Ti in sodium phosphate and isopropyl phosphate in ethylene glycol.

INTRODUCTION

Anodic oxidation of Ti presents great difficulties compared to that of other valve metals such as Al and Ta, because of an elevated electronic conductivity, which leads to a great oxygen evolution during the reaction, specially at low voltages[1–5].

In a previous paper, we studied the anodization of Ti up to 100 V only[6]. In the present study, the anodic oxidation of Ti above 50 V has been analyzed, to increase application range of the Ti–TiO_2.

EXPERIMENTAL TECHNIQUE

Examinations of dielectric breakdown and anodic oxidation of Ti sheet (MRC), 0.05 mm thick and 99.97% purity have been carried out in different aqueous and non-aqueous electrolytes. The trials of dielectric breakdown were carried out in 15 min with a current density of 5 mA cm^{-2}. The values of initial and final voltage and the oscillations of electrode potential higher than 1 V which are produced throughout the entire process were analyzed.

EXPERIMENTAL RESULTS

Analysis by X-ray diffraction of the TiO_2 films obtained up to 100 V only shows the presence of the microcrystalline anatase variety. Between 102 and 110 V, depending on the electrolytes, the rutile variety starts to nucleate together with anatase, increasing as the formation voltage increases, so that over 150–155 V only rutile exists.

In addition, over 105 V, craters and cracks begin to appear in the structure of the oxide film, as well as the formation of sparks, indicating local breakdowns in the dielectric.

The sparks that are produced in the scintillation stage therefore, are the first indication of the progressive transformation of the anatase to rutile, although the process is accelerated by an intense heating which takes place within the TiO_2 layers, due to a high oxide thickness in this zone of the reaction.

Figure 1 shows the variation of the thickness of the TiO_2 layer in a solution of sodium acetate (2.97%) in ethylene glycol ($\chi = 1$ mS cm^{-1}) at environmental temperature *vs* formation voltage. It shows that the TiO_2 layer linearly increases with the formation voltage at a little more than 25 Å V^{-1} up to 110 V, where the slope of the curve changes and at about 150 V it increases drastically. Over 170 V several colours begin appearing on different parts of the sheet at the same time.

The aforementioned result permits us to establish a maximum oxidation limit to the TiO_2 films of anatase around 100 V, which must not be exceeded if dielectric breakdown is to be avoided. In continuation, the most adequate electrolyte medium permiting the anodization of Ti up to 100 V must be evaluated, with acceptable breakdown values as well as the lowest

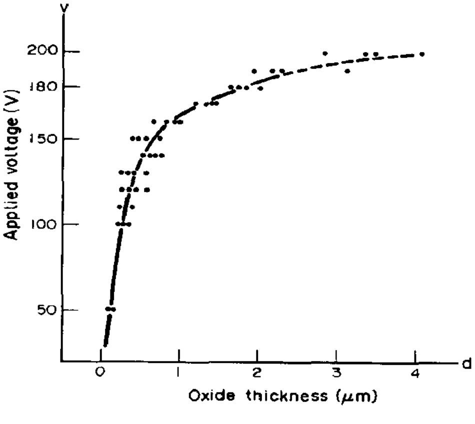

Fig. 1. Variation of TiO_2 thickness *vs* voltage.

Table 1. Breakdown test during anodic oxidation of Ti at constant current 5 mA cm^{-2}; 15 min; environmental temperature

Electrolyte in ethylene glycol	%	χ (mS cm^{-1})	*Vf*	*vf*	Breakdown number
Na Ac O	—	0.146	15	125	448
$C_3H_9O_4P$	sat.	0.175	15	269	415
Na_2HPO_4	0,2	0.106	1	157	105
Na_2HPO_4	0,27	0.133	1	150	98
Na_2HPO_4	0,40	0.217	1	146	97
$Na_2HPO_4 + C_3H_9O_4P$	(0,4) + (10)	0.177	1	160	43
$Na_2HPO_4 + C_3H_9O_4P$	(0,4) + (20)	0.184	2	215	21
$Na_2HPO_4 + C_3H_9O_4P$	(0,4) + (30)	0.201	2	208	18
$Na_2HPO_4 + C_3H_9O_4P$	(0,4) + (40)	0.243	2	173	52
$Na_2HPO_4 + C_3H_9O_4P$	(0,4) + (50)	0.270	1	145	66

Vi, initial voltage; χ: conductivity; *Vf*, final voltage; breakdown number, oscillations of electrode potential higher than 1 V.

possible number of voltage oscillations throughout the process.

Table 1 schematically presents the results obtained with a series of non-aqueous electrolytes in ethylene glycol. It shows clearly that in phosphate mixtures the highest voltage is reached in the case of Na_2HPO_4 (0.4 %) and $C_3H_9O_4P$ (20 %) in ethylene glycol, which also presents few partial breakdowns (> 1 V). Consequently, it is our choice of solution for carrying out the anodic oxidation of Ti up to 100 V.

In spite of obtaining a breakdown voltage of 215 V with this electrolyte, the beginning of the TiO_2 crystalline nucleation becomes evident around 125 V. For that reason we have limited the anodization of Ti up to 100 V.

The effective electric charge of TiO_2 films obtained in the mixture of phosphates is situated between 12.6 and 13.9 μFV cm^{-2} which is very similar to those obtained at low voltage. The values of residual current at the end of the reaction are much lower than those obtained in non-aqueous medium up to 50 V.

From a morphological point of view, the TiO_2 films obtained up to 100 V in the mixture of phosphates are characterized by being uniformly quite porous and very adherent to the substrate. Above 125 V the first structural changes characterized firstly by the appearance of pores, after cracks, then finally dielectric breakdowns may be observed.

CONCLUSIONS

The process of dielectric breakdown in anodic TiO_2 films is due to an effect of electron avalanche which is produced during the scintillation phase and leads to local heating up in the dielectric, partly due to an abnormal increase in thickness in the TiO_2 film at voltages above 150 V.

It is in this region of scintillation where the process of transformation of the anatase to the rutile which becomes predominate at 150 V, begins. A solution in ethylene glycol of Na_2HPO_4 (0.4 %) and $C_3H_9O_4P$ (20 %) is found to be a proper forming solution to obtain stable TiO_2 structures at formation voltages up to 100 V, with dielectric breakdown values higher than 200 V.

The effective electric charge of the films oscillates between 12.6 and 13.9 μFV cm^{-2}. Although the leakage current values are low, they are three times higher than those obtained with the $Ta-Ta_2O_5$ system in the same voltage conditions.

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