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Formation of $BaTiO_3$ coatings on titanium by microarc oxidation method

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Barium titanate layers on a titanium surface have been formed with using of microarc oxidation (MAO) method. The formation process was carried out in the aqueous electrolyte containing barium ions. The formation conditions, composition and anomalous properties of surface layers obtained are discussed. Based upon the experimental results the mechanism of metal/dielectric/metal (MDM) structure formation is proposed.

1. Introduction

It is known that $BaTiO_3$ is important ferroelectric material. Applications of it as films on surfaces of metals include a very wide range of technical devices. Many methods used to prepare $BaTiO_3$ thin films require high temperature processing (usually above 500°C) and accordingly are complex techniques. The preparing of $BaTiO_3$ on the titanium substrate under microarc oxidation (MAO) which is rather simple operation is discussed in this paper.

Microarc oxidation (MAO is a historical name of this method) is based on the anodic polarization of processing metals and alloys in aqueous electrolyte solutions under the additional condition of plasma microdischarge on the anode surface [1]. These specific conditions arise after exceeding the critical values of the polarization potential. Localized high temperature, high pressure and high current density, realised for microarc oxidation process of metals and alloys, allow forming the coatings on the surface of an anodizing electrode with special properties different from those of a conventional anodic film. The coatings consist of not only substrate oxides but of the more complex oxide-containing compounds, which include the components present in the electrolyte. The directed search of MAO synthesis conditions [1, 2] allowed production of polycrystalline barium titanate coatings on the surface of technical pure titanium VT1-0 [3–5].

The first information about the synthesis of $BaTiO_3$ by MAO method was published by the present authors in 1990 [3]. The publication of scientific results by other authors (Yoshimura *et al.* —Ref. [6–8] in 1989–1991 and Sviridov *et al.*—Ref. [9] in 1998) is additional independent proof of the trustworthiness of the data presented in [3–5].

2. Experimental conditions

Titanium metal substrates of VT1-0 (Ti, 99.39%; Fe, 0.25%; Si, 0.12%; C, 0.07%; O, 0.12%; N, 0.04%; H, 0.01%) were used as working anodic electrodes. Prior to the MAO treatment, the working electrode was etched in the mixture of acids composed of 25 vol% HF and 75 vol% HNO_3, then washed in distilled water.

The microarc oxidation treatment is described in detail elsewhere [1]. The MAO process was carried out under galvanostatic conditions at anodic current density of 3 A/cm^2 and formation voltage of 100–150 V with use of adjustable power source ($P = 4$ kW). As electrolyte, an aqueous alkaline solution of $Ba(OH)_2 \cdot 8H_2O$ was used ($c = 40$ g/l). Coatings obtained had thickness up to 30 μm and a high adhesion to the titanium substrate.

To determine the barium titanate symmetry and the temperature of possible phase transition, the alterations of X-ray phase composition of the surface layers versus temperature were investigated. For this purpose the X-ray diffractometer (XRD) DRON-2.0 (Cu K_α-radiation) was used. The tests were carried out by heating of samples up to 800°C both in air and vacuum.

To explain the nature of the alteration of the thin-film barium titanate polarization the temperature dependencies of the dielectric constant and conductivity of the MAO-coatings on titanium substrate versus a temperature (t) were investigated. For this purpose, gold spot contacts were sputtered on the samples' surfaces in vacuum and then the capacitance (C) and conductivity (G) measurements of the metal-dielectric-metal (MDM) structure obtained were carried out using alternating current capacitance bridge E7-8 ($\upsilon = 1$ kHz).

The conclusion about the coating's composition was based on X-ray diffractometry data and confirmed by electron probe microanalysis (EPMA).

3. Results and discussion

It is known that at room temperature barium titanate occurs in the polar phase i.e. has a tetragonal symmetry. At the Curie point (equal to 120°C for $BaTiO_3$) the spontaneous electrical polarization characterized by a sharp increase of dielectric constant (ε) takes place in the crystal. When the temperature is higher than the Curie temperature barium titanate transforms to cubic nonpolar phase and stops being a ferroelectric. As a result of this the dielectric constant decreases considerably.

It was established that barium titanate contained in the coating has tetragonal symmetry. Besides, tetragonal distortion did not disappear when temperature became higher than Curie point one and remained approximately up to 800°C. Such an effect earlier observed [10] is explained by the small size of the barium titanate particles. When the crystal size is small the phase transition spreads over a wide temperature range and spontaneous tetragonal distortion remains. During the MAO process, abrupt heating of the anode microvolume up to 2000–8000°C and its rapid cooling up to a room temperature as a result of a plasma microdischarge attenuation provide the formation of fine-grained crystals in the coatings. Moreover, each crystal has a surface layer where there are much more deformations than over the bulk of the crystal. The distortion of such layer does not depend on only temperature.

Dielectric constant of the testing material was calculated using the measured values of the capacitance, coatings thickness (d) and square of the sputtered metal contact (S) according to relation: $\varepsilon = \frac{Cd}{\varepsilon_0 S}$ where, ε_0 is a dielectric constant of vacuum.

It was ascertained that the dielectric constant of the coating material, which was not subjected to the previous temperature treatment in vacuum, equals 200 units and conductivity equals to 5×10^{-9} $(\Omega \cdot \mathrm{cm})^{-1}$ at room temperature. As a result of the temperature treatment ε increased up to 1108, and G up to 1.8×10^{-4} $(\Omega \cdot \mathrm{cm})^{-1}$.

Some anomalous features in the behavior of the $BaTiO_3$ thin film were noticed while heating it at a rate of 4.5 K/min. According to Fig. 1, where the temperature dependencies of the dielectric constant and conductivity are shown, the curve $\varepsilon(t)$ maximum is observed at 130°C. That temperature is close to Curie point of the monocrystalline barium titanate. However, by heating up to the largest temperature the dielectric constant within temperature range of 130–290°C did not stabilize and continued to depend on temperature essentially. The considerable increasing of the dielectric constant occurred above 290°C and the ε value at 490°C equaled 8234. Below 290°C in the first degree of approximation the dependence $G(t)$ (Fig. 1b) may be described by an exponential function. The exponential dependence is distorted under a higher temperature.

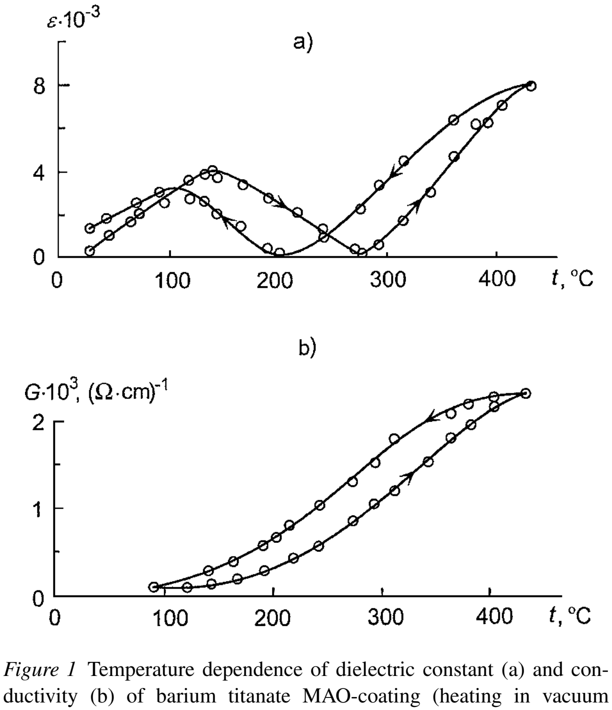

Figure 1 Temperature dependence of dielectric constant (a) and conductivity (b) of barium titanate MAO-coating (heating in vacuum $p = 6.5 \times 10^{-2}$ Pa).

The review of the numerous scientific works concerning anomalous properties of barium titanate is given in Ref. [10]. Above the Curie point the dependence of dielectric constant versus temperature is explained by the presence of a space charge layer on the crystal surface. The thickness of this layer altered by the crystal producing method. The dielectric constant of a space charge layer is very low. The located layer of a space charge forms as a result of a capture of a charge carriers by electron traps. The characteristics of this layer depend on energy of the doping (donors') levels in the bandgap of the semiconductor. The space charge causes the alteration of the electric field strength within the sample bulk and decreases of the material dielectric constant.

The influence of the environment (composition of the gas media) and MDM-structure material on the dimension and properties of the surface charge layer is established in some previous papers. In Ref. [2, 11] for example, it is shown that under specific conditions the coatings formed on valve metals by different methods possess the inhomogeneous distribution of oxygen vacancies through the bulk of the coating. Layers located closer to the coating/metal interface have the oxygen concentration lower as compared to the layers disposed closer to the coating/air phase boundary having excess of an oxygen in the material lattice as compared with the stoichiometric composition.

The presence of the p-n transition causes unipolar conductivity observed both on anodic and on MAO-coatings. Moreover, the nature of plasma-microdischarge provides generation of the pores in the coating material the sizes and quantity of which are controlled by anodization conditions. Thus, the coating material has a rather complex structure. Besides, incorporation of electrolyte components into the coating material magnifies the defectiveness of MAO-layers. The sorption of oxygen containing ions on the defect sites causes the bend of bands on the surface of the coating (at the coating/air phase boundary) and in the most cases leads to the formation of a space charge region possessing own capacitance and capacitance resistance [11].

The presence of such series-connected capacitance can considerably decrease the effective capacitance of the system. Desorption of the ions from the surface and unifying of stoichiometry of the material coating through its bulk (these processes takes place under vacuum annealing of the samples) increases capacitance and conductivity of system that has been observed in practice. Given arguments are coordinated with the experimental data obtained during previous annealing

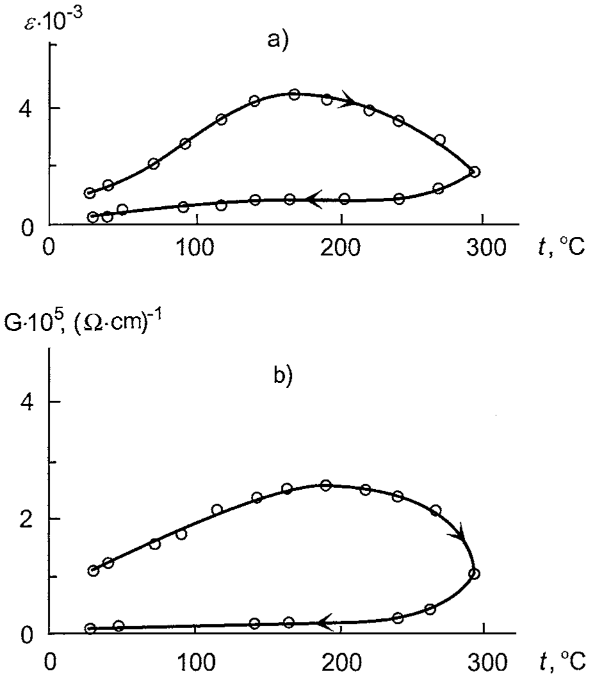

Figure 2 Temperature dependence of dielectric constant (a) and conductivity (b) of barium titanate MAO-coating (heating in air).

of the barium titanate thin film in vacuum (Fig. 1) and a subsequent annealing in air (Fig. 2).

As a result of annealing in air already at 70°C the conductivity of MDM-structure (Fig. 2b) became lower as compared with the film conductivity in vacuum but from 190°C the system conductivity decreases significantly. The function $\varepsilon(t)$ showed no maximum as the temperature is decreased from 190°C to 130°C (Fig. 2b) and dielectric constant values became considerably less than calculated ones under vacuum annealing in this temperature range. The results of this investigation in combination with analyses of literature data suggest the presence of a space charge layer on the surface of each tiny crystal of barium titanate, which were obtained by MAO-method.

4. Conclusions

In this paper the properties of the $BaTiO_3$ thin films which obtained by the MAO-method on titanium substrate in aqueous electrolyte have been demonstrated. The sorption and desorption of oxygen-containing ions on the surface of MAO-coating, which cause an alteration of capacitance and resistance of the space charge region, determine the dependences $\varepsilon(t)$ and $G(t)$ for MDM-structure. Anomalous behavior of the dielectric constant of the coating material consisting of $BaTiO_3$ is connected with the presence of residual material polarization, which is produced as a result of the specific conditions of the MAO-coating formation.

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