In Situ Doping of Anodic Aluminum Oxide

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Abstract

During anodic oxide growth, anions are attracted to the anode, followed by adsorption on the growing oxide surface and incorporation into the growing oxide. Generally, this phenomenon was found to be hard to avoid, therefore our idea was that it should be turned into something advantageous. During our research it was found that due to this phenomenon, the anodic aluminum oxide may be successfully doped and by way of doping, impart new properties to the anodic oxide. It was shown that successful incorporation of chromates, chelate complexes, organic dyes and nano-sized colloids is possible. In order to successfully incorporate the anions into anodic oxides the incorporated species should be stable in the electrolyte and have small ionic mobility if protonated.

Introduction

Anodic oxides of aluminum and other valve metals formed at certain operating conditions have nanostructured morphology. Nanoporous arrays or nanotubes are frequently obtained using the anodic oxide as a template. Typically, the major point of interest is the morphology of the anodic oxides, or physical properties. However, recent studies show that depending upon the chemical composition of the metallic substrate, or the applied electrolyte, the chemical composition of the nanostructured oxide may be tuned. Such in situ doping can enable the development of new properties to the nanostructured anodic oxides.
Anionic doping

During anodic oxide growth, the anions from the electrolyte bulk are being attracted to the positively polarized anode. As these are adsorbed, the growing oxide incorporates them into the pore walls. Anionic doping is a generally well-known fact, but clear evidence was brought by Arurault’s group in 2010 [1]. In this study, through chemical analyses, they have shown that during anodization of aluminum, phosphate anions are incorporated into anodic alumina. Moreover, it was shown that up to 2.7 at. % of phosphorous was found in the anodic alumina and the majority of the incorporated anions is in the outer part of the oxide, while the inner part comprises mainly of pure alumina [1-2].

![Fig. 1. Scheme of anodic oxide](image)

This phenomenon was used to incorporate chromate anions into anodic alumina [3]. It was found that the greater voltage and electrolyte temperature, the more chromates are incorporated into the AAO. Moreover, photoluminescence spectroscopy revealed that the more chromates (which translates into greater anodizing voltage and greater temperature) the stronger photoluminescence bands attributed to the transitions between split d orbitals [3]. Such incorporation of simple anions into anodic oxides allows the modification or introduction of new properties. Until recently, incorporation allowed the formation of anodic TiO$_2$ with N [4] and Ru [5-6], Ta$_2$O$_5$ with N [7] or WO$_3$ with N [8]. Doping the anodic oxides enabled contributions to catalysis [5-6], photovoltaics [4] and water splitting [8].

More complex anions can also be incorporated into anodic aluminum oxide. However, in this case, prior to the anodizing its stability in acidic electrolyte has to be examined. Our results show that up to 0.2 at.% of Cu may be incorporated into the anodic alumina while copper is in the electrolyte solution in the form of chelate coordination compound with EDTA (ethylene diamine tetraacetic acid) as ligand [9]. [Cu(EDTA)]$^{2+}$ ions are formed and are attracted by the anode. Of course, in the applied electrolyte (2 wt. % sulfuric acid) the anions could partially undergo protonation, despite the effective AAO doping was performed. To confirm the incorporation of Cu$^{2+}$ chelated by the EDTA ligands the photoluminescence studies were performed. According to the ligand field theory, while Cu$^{2+}$ is chelated, visible transitions in the UV-Vis spectrum are being recorded, owing to the d orbitals splitting. Additionally, we have also recorded bands of transition between π bonding and anti-bonding levels at UV range.

Obtained results described above encouraged us to study the incorporation of the organic molecules into AAO. The ideal organic dye for the incorporation should be in anionic form, be stable in acidic electrolyte and have distinct bands to identify with the use of spectroscopy. Indigo carmine, water-soluble organic dye was incorporated into anodic aluminum oxide [10]. The X-ray photoelectron spectroscopy confirmed the presence of the dye in AAO – organic nitrogen and sulfur were noticed (Fig. 2). Despite incorporation of large anions, the nanoporous morphology of the AAO was maintained (Fig. 3). Moreover, the linear relation between pore diameter and anodizing voltage (Al was anodized in 20 wt. % containing 0.0005 M of indigo carmine in the voltage range: 15-25 V),
in addition, the interpore distance and anodizing voltage was maintained [10]. Moreover, like in the case of chromate incorporation, in the case of indigo carmine incorporation, the greatest amount of the incorporated indigo carmine was found for the highest applied voltage. Furthermore, Raman spectroscopy revealed unique set of bands for samples with incorporated indigo carmine (Fig. 4). The most intensive band at 1585 cm\(^{-1}\), attributed to the pyrrolidone rings from the dye confirmed successful incorporation of the dye. Thus, the anionic incorporation of the indigo carmine allowed to form nanoporous AAO with tuned chemical composition and optical properties owed to this dye. Such hybrid organic-inorganic material electrochemically doped may find applications in optical sensing and electronics.

Fig. 2. XPS spectrum of anodic alumina with incorporated indigo carmine.

Fig. 3. Top-view FE-SEM image of anodic aluminum oxide with incorporated indigo carmine.
Fig. 4. Raman spectra of indigo carmine powder, anodic alumina formed in 20 wt. % sulfuric acid with additive of indigo carmine and in 20 wt. % sulfuric acid without indigo carmine (reference sample).

**Cationic doping**

Very often various cations are present as part of the substrate during anodic oxidation. During anodizing, the cations are being repulsed from anode and form nanoporous oxide with OH$^-$ and O$_2^-$ anions at the electrode / electrolyte interface. Alloying elements that are close to the anodized main metal in galvanic series, will also be oxidized, forming a mixed oxide as the result of simultaneous oxidation of the main metal and alloying elements. Schmuki’s Group reported anodization of Ti-Cr alloy. Formed nanotubes consisted of anodic titania doped with chromium [11]. Such composition of the oxide allowed the increase of the photocurrent response of the material, which is crucial in dye sensitized solar cells technology [11].

The next step of research is anodization of ordered intermetallic alloys. Our recent study focuses on the anodic oxidation of FeAl intermetallic alloy [12]. Chemical composition analyses revealed that the oxide is composed of Al, Fe and O, while Fe is in various forms [12]. Moreover, during the oxide growth high current densities, resulting in high oxide growth rates (i.e. 743.0 ± 17.9 µm/h) were noticed for anodization in 20 wt.% sulfuric acid. Despite rapid growth rate, the nanoporous morphology of the oxide was maintained (Fig. 5) and the relationships between the geometrical features and voltage were still linear [12].

**Summary**

During anodic oxide growth in situ doping of the oxide may be performed via two different approaches. Various compounds in anionic form, while added to the electrolyte should be stable, which enables the anions (simple anions, coordination complexes, organic dyes) their attraction to the anode and incorporation into the anodic oxide. Numerous studies revealed the greater voltage and electrolyte temperature the more additive is incorporated into anodic oxide. In situ doping of anodic oxides may be also performed with cationic approach. In this case, alloying element is being oxidized simultaneously with the anodized metal and mixed oxide is formed at the interface.
Despite the doping, the nanoporous and nanotubular morphology of the doped anodic oxides is maintained. Oxides formed by these methods have already found applications in catalysis and energy harvesting. Therefore, such electrochemical in-situ doping is an attractive approach in chemical composition tuning of nanomaterials.

Fig. 5. Top-view FE-SEM images of nanoporous mixed aluminum-iron oxide formed by two-step self-organized anodization of FeAl intermetallic alloy in sulfuric acid.

References


