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To cite this article: I A Petrenyov *et al* 2018 *J. Phys.: Conf. Ser.* **1124** 022004

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Nanostructural features of anodic zirconia synthesized using different temperature modes

I A Petrenyov¹, R V Kamalov¹, A S Vokhmintsev¹, N A Martemyanov¹,
I A Weinstein^{1,2}

¹NANOTECH Centre, Ural Federal University, Yekaterinburg 620002, Russia

²Institute of Solid State Chemistry, Russian Academy of Sciences, Yekaterinburg 620990, Russia

Abstract. Nanotubular and nanoporous structures of ZrO₂ were synthesized by potentiostatic anodization with varying the temperatures of anode in the range of T_A = 0 – 90 °C and electrolyte in the range of T_{EI} = 20 – 50 °C. It was shown that difference between T_A and T_{EI} had significant influence on growth rate and morphology type of zirconia nanostructures. Optimal parameters of thermal modes for nanotubular ZrO₂ synthesis were discussed.

Introduction

Nanocrystalline ZrO₂ is a promising material for the development of optoelectronic devices, lasers, solar cells, memristors [1-3]. Among various methods of synthesis, for instance, self-propagation high-temperature synthesis, hydrothermal method, laser ablation, etc., anodization of metallic zirconium found wide application as a simple method for obtaining self-oriented and highly ordered arrays of nanotubes [4, 5]. Nanotubular structures of different metal oxides are grown in organic electrolytes containing F-ions [2, 6]. Growth rate of nanostructured anodic oxide layer is governed by kinetic processes of metal oxidation and dissolution of reaction products and depends on temperature [7]. It is known that temperature factor affects morphology and defectiveness of ZrO₂ structure [2], which, in turn, specifies optical and luminescent properties of the material [5]. At the same time, there is no information on the growth features of ZrO₂ nanostructures under conditions of a temperature difference (ΔT) between the anode (T_A) and the electrolyte (T_{EI}). Therefore, the aim of this work is to study the effect of ΔT on the morphological characteristics of anodic zirconia.

Samples and experimental methods

Synthesis routine was performed in a cell with two-circuit thermostatic control (Figure 1) at a constant voltage of 60 V. First circuit maintained the temperature of the anode within the range 10 – 50 °C; second circuit maintained the temperature of the electrolyte within the range of 25 – 50 °C. The value of $\Delta T = T_A - T_{EI}$ was ranged from -25 to 50 °C. A 120 μm thick zirconium foil (99.9 %) served as the anode. The cathode was a stainless steel plate. Zr foil was pretreated in a solution of acids containing HF/HNO₃/H₂O (1:6:20), washed with distilled water and dried in air. ZrO₂ was synthesized by two-stage anodization. The first stage was conducted during 2 hours in the electrolyte (ethylene glycol with adding 0.5 wt. % NH₄F and 5 wt. % H₂O). After removing the primary oxide layer second anodization was carried out under the same conditions.



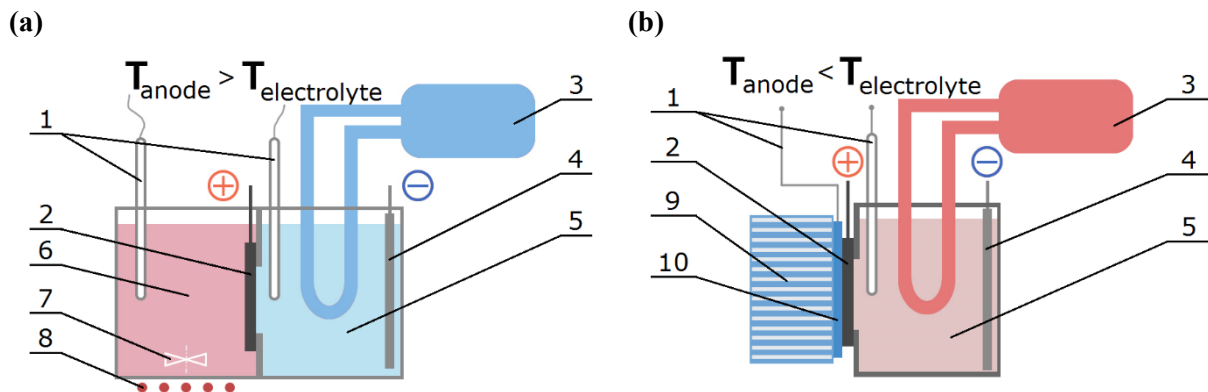


Figure 1 (a, b). Scheme of electrochemical cell for Zr anodization with **(a)** $\Delta T > 0$; **(b)** $\Delta T < 0$; 1 – thermocouples, 2 – anode (Zr foil), 3 – cooling/heating system, 4 – cathode (stainless steel), 5 – electrolyte, 6 – distilled water tank, 7 – stirrer, 8 – heater, 9 – radiator, 10 – thermoelectric cooler.

Morphological parameters of the synthesized samples of nanostructural ZrO_2 were studied using the Carl Zeiss SIGMA VP scanning electron microscope (SEM). SEM images were processed using SIAMS 700 software, inner (d_{in}) diameters of nanotubes and nanoporous, outer (d_{out}) diameter of nanotubes, oxide layer thickness (h) were evaluated.

Results and discussions

Figure 2 shows the SEM images of anodic ZrO_2 , synthesized at different temperature modes. Reports show that the morphological changes of zirconia layer occurred under the variation of ΔT . For instance, Figure 2a,b shows nanotubular structure corresponding to $\Delta T = -15^\circ\text{C}$. The synthesized oxide layer has $h = 3\ \mu\text{m}$ and consists of self-ordered nanotubes with $d_{in} = 35\ \text{nm}$ and $d_{out} = 55\ \text{nm}$. It is noted that the nt- ZrO_2 structure is formed when $T_A < T_{El}$. When $\Delta T = 0^\circ\text{C}$ the oxide layer is characterized with random nanoporous structure with $h \approx 6\ \mu\text{m}$ and $d_{np} \approx 25\ \text{nm}$, see Figure 2c. Any regularity of the structure practically disappears (Figure 2d) and the oxide layer becomes more disordered at $\Delta T > 15^\circ\text{C}$. These structures are referred to the nanoporous type. The oxide layers are thicker about 2-3 fold than the nanotubular ones. Estimations of the morphological characteristics for all synthesized structures are given in the Table 1.

Table 1. The parameters of synthesized nanostructures of anodic ZrO_2 .

№	Temperature, $^\circ\text{C}$			Geometric parameters			Structure type
	ΔT	T_A	T_{El}	$h, \pm 0.2\ \mu\text{m}$	$d_{in}, \pm 5\ \text{nm}$	$d_{out}, \pm 10\ \text{nm}$	
1		0	20	3.4	27	75	
2	< 0	10	25	5.1	35	55	nanotubular
3		20	25	5.2	30	45	
4		25	25	5.9	25	45	nanotubular
5	0	50	50	6.2	25	–	nanoporous
6		50	35	8.2	–	–	
7	> 0	70	40	9.1	–	–	nanoporous
8		90	40	9.9	–	–	

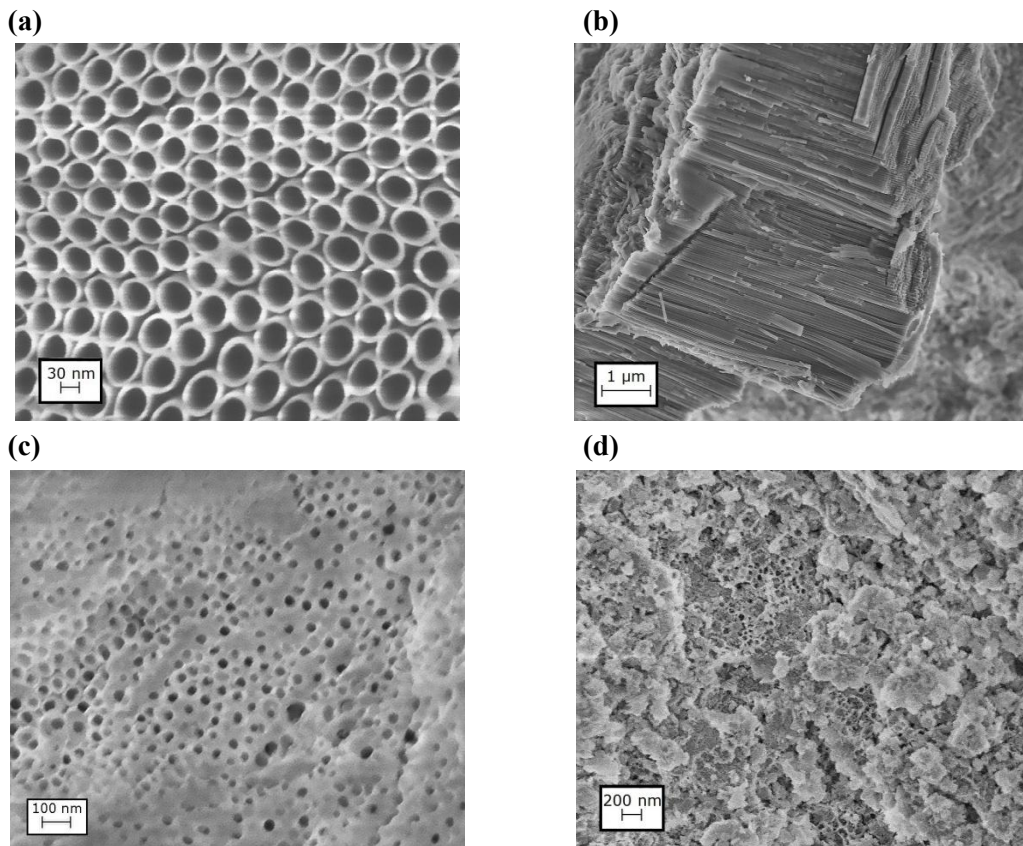


Figure 2 (a, b, c, d). SEM images of the surface **(a, c, d)** and lateral view **(b)** of zirconia layer synthesized at **(a, b)** $\Delta T = -15\text{ }^\circ\text{C}$, **(c)** at $\Delta T = 0\text{ }^\circ\text{C}$, **(d)** $\Delta T = 50\text{ }^\circ\text{C}$.

In order to discuss the influence of the temperature factor (ΔT) on the morphological features of the nanostructured oxide layer formation, major anode processes should be considered. The formation of the ZrO_2 nanostructure is connected to the ratio of the rates of the two competing processes: the anodic oxidation of Zr metal (v_{ox}) at the metal/oxide interface and the dissolution of oxidation products (v_{etch}) at the oxide/electrolyte interface [4, 8, 9] (see Fig. 3).

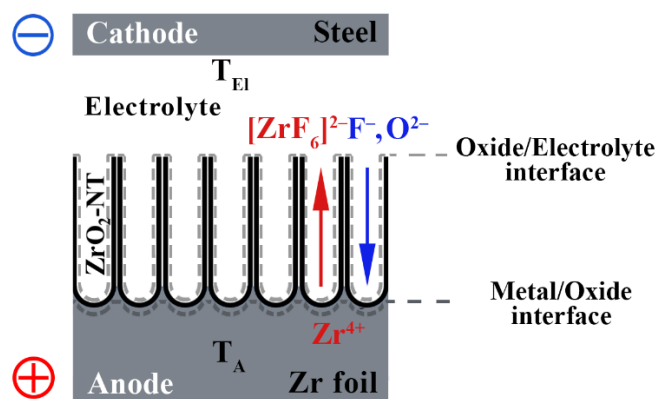
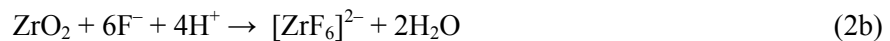


Figure 3. Schematic of the processes occurring during anodization of Zr foil in fluoride containing electrolyte at oxide/electrolyte and metal/oxide interfaces.

On one side, metallic zirconium is oxidized (1a) at the metal/oxide interface. Water molecules are decomposed on the anode surface under the high voltage bias and H^+ and O^{2-} ions (1b) are generated. Oxygen ions interact with the metal to form the zirconium oxide (1c). On the other side, the dissolution process due to the formation of a soluble complex $[ZrF_6]^{2-}$ ion is governed by the migration of Zr^{4+} and F^- ions in the oxide layer under the applied electric field (2a) and (2b) and by chemical etching of the oxide due to the presence of F^- ions in the electrolyte (2c). Described processes can be represented by the following reactions:



On the basis of the described mechanism, the rates of the reactions will be determined by the transport of Zr^{4+} , F^- и O^{2-} ions. Since the temperature influences generation and mobility of ions significantly, a change of T_A and/or T_{El} values leads to a shift of the equilibrium between the two competing processes. Therefore, when $\uparrow\Delta T$ ($T_A > T_{El}$) $\rightarrow v_{ox}\uparrow$ and $v_{etch}\downarrow$. In this case, the oxidation process dominates and leads to the increase in the growth rate of the oxide layer. In turn, when $\downarrow\Delta T$ ($T_A < T_{El}$) $\rightarrow v_{ox}\downarrow$, a $v_{etch}\uparrow$, the oxidation process slows down and the dissolution is intensified.

By analyzing the data given in the Table 1, we can summarize the following. The h thickness of the oxide layer increases from 3 to 10 μm with an increase in ΔT from -20 to 50 $^\circ C$. This fact indicates the shift of anode process in the favor of oxidation. Thus, the higher the anode temperature, the thicker oxide layer can be obtained. However, in this case, the structure becomes more defective and disordered (Fig 2c).

The nanotubular structure of anodic zirconia was formed in the interval of $-20\text{ }^\circ C \leq \Delta T \leq 0^\circ C$. The inner tube diameter of $d_{in} = 30\text{ nm}$ remains constant within the error. This fact corresponds well with the works [10, 11], since d_{in} value mainly depends from the applied voltage [12] and composition of electrolyte [9], that are unchanged in our experiment. The outer diameter d_{out} and the wall thickness $(d_{out} - d_{in})/2$ increase with the lowering of T_A due to suppression of the dissolution process, because of the strong dependence of the solubility of anodization product ions on temperature; this is in agreement with the studies [2, 12]. It should be mentioned that electrolyte temperature remained practically constant when $\Delta T < 0\text{ }^\circ C$ what gives a reason to conclude that only the anode temperature influenced the morphology of the oxide layer. In this case, the migration of ions in the solid phase is probably most crucial for dissolution process in comparison with wet chemical etching. Therefore, anode temperature is a key factor to control the morphology of zirconium oxide layer.

Conclusion

The electrochemical installation with two conditioning circuits was designed. Nanotubular and nanoporous structures of zirconia were synthesized by potentiostatic anodization of Zr foil in the fluoride containing electrolyte. It was shown that the morphology parameters of the grown oxide layer significantly depend on the temperature of anode and electrolyte. Nanotubular type structure was observed at anode temperature range from 0 to 20 $^\circ C$ and at electrolyte temperature of 25 $^\circ C$, nanoporous zirconia with different ordering degree was grown at $0 \leq \Delta T < 15\text{ }^\circ C$ (partially ordered)

and at $\Delta T \geq 15$ °C (disordered). Anodizing rate or the thickness of the oxide layer were increased by ΔT raise. It is shown that the decreasing of T_A leads to rise of the outer diameter of nanotubes. The mechanisms of the nanostructured anodic zirconia growth were discussed with allowing for processes, occurring during anodization at oxide/electrolyte and metal/oxide interfaces.

Acknowledgments

Act 211 Government of the Russian Federation, contract № 02.A03.21.0006, supported the study. R.V.K. thanks RFBR research project № 18-33-01072 for support. A.S.V. and I.A.W. thank Minobrnauki initiative research project № 16.5186.2017/8.9 for support.

References

- [1] Wang X, Zhao J, Du P, Guo L, Xu X, Tang C 2012, *Mater. Res. Bull.*, **47**, 11, 3916
- [2] Hosseini M G, Daneshvari-Esfahlan V, Ordikhani-Seyedlar R 2015, *Corros. Eng. Sci. Technol.*, **50**, 7, 533
- [3] Vokhmintsev A S, Kamalov R V, Kozhevina A V, Petrenyov I A, Weinstein I A, Martemyanov N A 2018, *Proc. 2018 USBEREIT*, **1**
- [4] Amer A W, Mohamed S M, Hafez A M, AlQaradawi S Y, Aljaber A S, Allam N K 2014, *RSC Adv.*, **4**, 68, 36336
- [5] Kozhevina A V, Vokhmintsev A S, Kamalov R V, Martemyanov N A, Chukin A V, Weinstein I A 2017, *J. Phys. Conf. Ser.*, **917**
- [6] Kamalov R, Vokhmintsev A, Dorosheva I, Kravets N, Weinstein I 2016, *Adv. Sci. Lett.*, **22**, 688
- [7] Asgari V, Noormohammadi M, Ramazani A, Kashi M A 2017, *J. Phys. D: Appl. Phys.*, **50**, 375501
- [8] Ghicov A, Schmuki P 2009, *Chem. Commun.*, **20**, 2791
- [9] Lockman Z, Ismail S, Razak K A, Lee L S 2011, *IOP Conf. Ser. Mater. Sci. Eng.*, **18**, 5, 52004
- [10] Ismail S, Ahmad Z A, Berenov A, Lockman Z 2011, *Corros. Sci.*, **53**, 4, 1156
- [11] Berger S, Jakubka F, Schmuki P 2008, *Electrochem. commun.*, **10**, 12, 1916
- [12] Mor G K, Shankar K, Paulose M, Varghese O K, Grimes C A 2005, *Nano Lett.*, **5**, 1, 191