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Extended abstract

EXTENDED ABSTRACT

Effect of electrochemical parameters and working electrode material on the characteristics of bismuth (III) oxide obtained by electrodeposition and thermal oxidation•

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Abstract: Bismuth (III) oxide was obtained by electrodeposition, followed by thermal treatment in air environment. The applied electrodeposition current density and electrode potential affect the surface morphology and chemical composition of the obtained deposit before and after the thermal treatment at 350 C, as well as its crystal structure after the thermal treatment at 350 °C. The listed parameters affect the deposit's morphology after the thermal treatment at 600 °C, but do not affect its chemical composition and crystal structure. The conclusion is that investigated working electrode material does not affect the characteristics of synthesized material.

Keywords: bismuth (III) oxide; current density; potential; electrode; synthesis; control.

INTRODUCTION

Bismuth (III) oxide is an important compound due to its numerous applications, thus various Bi_2O_3 synthetic procedures have been developed, including the electrochemical. By choosing the synthesis procedure and parameters, it is possible to control some important properties of the synthesized Bi_2O_3.[1–7] The aim of this paper is to investigate the influence of electric current density, electrode potential and electrode material on the characteristics of Bi_2O_3 obtained by cathodic electrodeposition, followed by thermal treatment in air environment.

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EXPERIMENTAL

Bi_2O_3 was obtained by cathodic electrodeposition (series 1) at various constant current densities (j) using a) Ti and b) stainless steel as the cathode and deposition (series 2) at various constant potentials (E) using a) Ti and b) stainless steel as a working electrode and saturated calomel electrode (SCE) as the reference electrode (all potentials are referred to SCE). All depositions were done from acidic 0.1 M $Bi(NO_3)_3$ solutions, using Pt as a counter electrode. Thermal treatments were done in air atmosphere. Material characterization was done using SEM, EDX and XRD techniques.

RESULTS AND DISCUSSION

Current density (series 1) and electrode potential (series 2) affect the surface morphology (Figs. 1 and 2). Basically, three different morphologies are observed: polyhedron-like, sheet-like and that of undefined shape. A thermal treatment leads to the morphology transformation in all the cases (Figs. 3 and 4). There are also apparent mutual differences in the morphology of the materials obtained at different j and E values; the main one is the increase of material porosity with the increase of j and decrease of E.

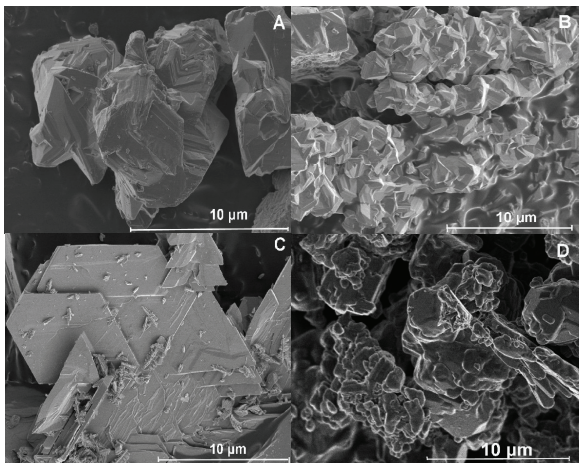

Fig. 1. Morphology of the deposit obtained at constant j of: A) 10; B) 30; C) 50; D) 100 mA cm^{-2}.

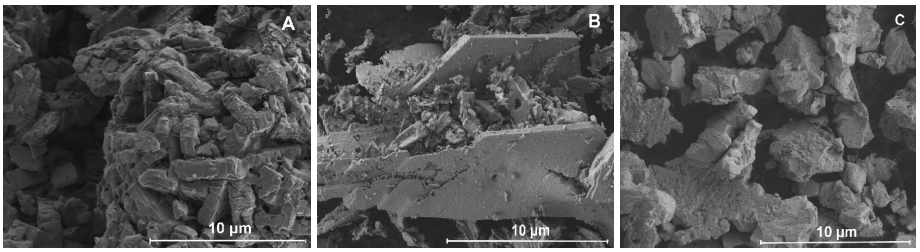

Fig. 2. Morphology of the deposit obtained at constant E of: A) 0.1; B) 0.3; C) 0.6 V.

The chemical composition of the deposit is also affected by the applied j and E (Tables I and II). Material obtained at 10, 30 and 50 mA cm^{-2} and at 0.3 and

0.6 V is metallic Bi, and those obtained at constant j of 100 mA cm^{-2} and constant E of 0.1 V contain a significant amount of O and N, as well. After the thermal treatment at 600 °C, the mass ratio of Bi and O approximately corresponds to the theoretical one in Bi_2O_3 in all the cases, but it seems that bismuth oxide obtained at 100 mA cm^{-2} and at 0.1 V is oxygen deficient.

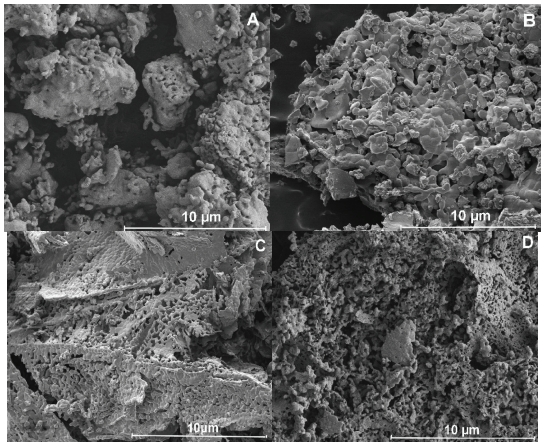

Fig. 3. Morphology of the deposit obtained at constant j of: A) 10; B) 30; C) 50; D) 100 mA cm^{-2}, after thermal treatment at 600 °C.

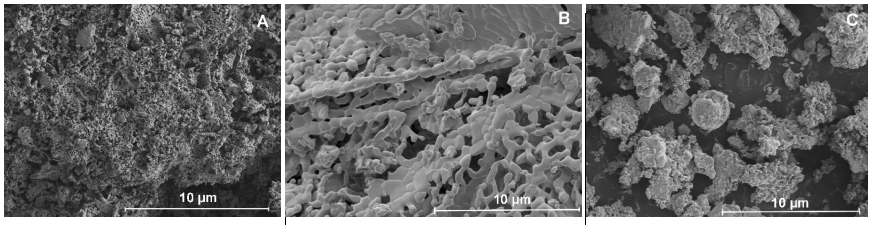

Fig. 4. Morphology of the deposit obtained at constant E of: A) 0.1; B) 0.3; C) 0.6 V, after thermal treatment at 600 °C.

TABLE I. Chemical composition of the material synthesized by galvanostatic electrodeposition before and after thermal treatment at 600 °C

j / mA cm^{-2}	Composition, % Bi + O + N (electrodeposited)	Composition, % Bi + O (electrodeposited + thermally treated)
10	99.79 + 0.21 + 0.0	89.87 + 10.13
30	99.68 + 0.32 + 0.0	90.17 + 9.93
50	99.41 + 0.59 + 0.0	90.81 + 9.19
100	65.29 + 21.72 + 12.99	90.72 + 9.28

XRD analysis (Fig. 5) confirms the formation of pure rhombohedral Bi at constant j of 10, 30 and 50 mA cm^{-2} and at the constant E of 0.3 and 0.6 V. The material obtained at 100 mA cm^{-2} and the one obtained at 0.1 V contains rhombohedral Bi, crystalline bismuth basic nitrates (BBN), and small amount of some amorphous phase.

TABLE II. Chemical composition of the material synthesized by potentiostatic electrode position before and after thermal treatment at 600 °C

E / V	Composition, % Bi + O + N (electrodeposited)	Composition, % Bi + O (electrodeposited + thermally treated)
0.1	58.35 + 27.49 + 14.16	90.79 + 9.21
0.3	98.91+1.09 + 0.0	90.51 + 9.49
0.6	99.1 + 0.9 + 0.0	88.3 + 11.7

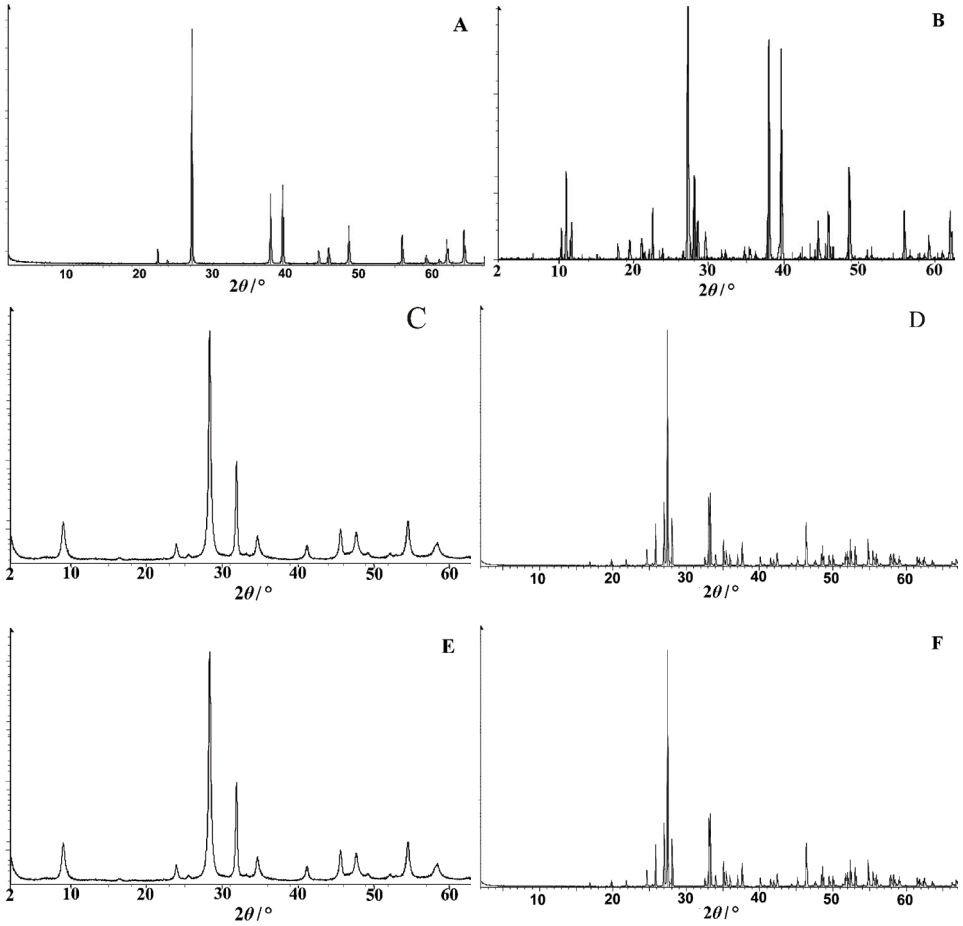

Fig. 5. XRD patterns of the deposits obtained by electrodeposition at A) 30 mA cm^{-2}; B) 100 mA cm^{-2}; C) 0.1 V; D) 30 mA cm^{-2}, and thermal treatment at 350 °C and E) 0.1 V; F) electrodeposition (all) and thermal treatment at 600 °C.

At lower *j* and at the higher *E* the cathodic reaction was the reduction of Bi^{3+} and the formation of metallic Bi. At high *j* and lower *E*, the reduction of H^+ also took place, leading to the local formation of OH^-, which further formed BBNs

with oncoming Bi^{3+} and the present NO_3^-. After the thermal treatment at 350 °C deposits obtained at 10, 30 and 50 mA cm^{-2}, and those obtained at 0.3 and 0.6 V were mixtures of monoclinic (α) Bi_2O_3, rhombohedral Bi, tetragonal (β) Bi_2O_3 and traces of triclinic (ω) Bi_2O_3; the ones obtained at 100 mA cm^{-2} and at 0.1 V were transformed to β-Bi_2O_3, with the significant part of amorphous phase. At 600 °C all the deposits were transformed to α-Bi_2O_3, but the ones with metallic Bi and the ones with BBNs had different transformation paths. The working electrode material did not affect the examined synthesized material characteristics.

CONCLUSION

In the process of electrodeposition from acidic Bi (III) solution, the applied electrodeposition current density and electrode potential affect the surface morphology, chemical composition, mechanical stability and thickness of the obtained material, before and after the thermal treatment at 350 °C, as well as its crystal structure after the thermal treatment at 350 °C. The listed parameters affect the deposit's morphology, mechanical stability and thickness after the thermal treatment at 600 °C, but do not affect its chemical composition and crystal structure. Investigated working electrode material does not affect the examined synthesized material characteristics. By applying the proper electrochemical parameter and thermal treatment, it is possible to control some important material properties, including its crystal structure.

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ИЗВОД

УТИЦАЈ ЕЛЕКТРОХЕМИЈСКИХ ПАРАМЕТАРА И МАТЕРИЈАЛА РАДНЕ ЕЛЕКТРОДЕ НА КАРАКТЕРИСТИКЕ БИЗМУТ(III)-ОКСИДА ДОБИЈЕНОГ ЕЛЕКТРОДЕПОЗИЦИЈОМ И ТЕРМИЧКОМ ОКСИДАЦИЈОМ

МИЛИЦА М. ПЕТРОВИЋ, СЛОБОДАН М. НАЈДАНОВИЋ, МИЛОШ М. КОСТИЋ, МИЉАНА Д. РАДОВИЋ, НЕНА Д. ВЕЛИНОВ, ДАНИЈЕЛА В. БОЈИЋ и АЛЕКСАНДАР Љ. БОЈИЋ

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Бизмут(III)-оксид је добијен електрохемијским таложењем и накнадним термичким третманом у ваздушној атмосфери. Примењена густина струје електрохемијског таложења и потенцијал радне електроде утичу на површинску морфологију и хемијски састав добијеног материјала пре и након термичког третмана на 350 °C, као и на његову кристалну структуру након термичког третман на 350 °C. Исти параметри утичу на морфологију након термичког третмана на 600 °C, али не утичу на хемијски састав и кристалну структуру. Испитивани материјал електроде не утиче на испитиване особине синтетисаног материјала. Применом одговарајућих електрохемијских параметара синтезе и термичког третмана, могуће је контролисати неке важне особине материјала, укључујући кристалну структуру.

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