Materials of Conferences

FORMATION OF OXIDE TUNGSTEN BRONZES ON W – SUBSTRATE BY ELECTROCHEMICAL SYNTHESIS FROM MOLTEN SALTS

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The work is related to the field of high-temperature electrochemistry, in particular, obtaining nanostructural coatings of oxide tungsten bronzes (OTB) by molten salts electrolysis [1–5]. The obtained samples may find application in medicine, electrical engineering, radio engineering, food and chemical industries.

The following melts were used in this study:

1. 0,30 K_2WO_4 – 0,25 Li_2WO_4 – 0,45 WO_3.
2. 0,25K_2WO_4 – 0,25Na_2WO_4 – 0,50WO_3.
3. 0,55 Li_2WO_4– 0,45 WO_3.

The polycrystalline coatings OTB ($K_xLi_yWO_3$) of hexagonal structure were obtained (Fig. 1) during the electrolysis in the 0,30 K_2WO_4 – 0,25 Li_2WO_4 – 0,45 WO_3 melt under pulsed potentiostatic conditions on the textured W-plate. Each microcrystal is an oriented nano-needle structure, in which the needle clusters are linked between each other with the intermediate neck. By increasing the pulse duration up to several seconds the space between the nanoneedles becomes filled by layer-by-layer growth from the needles along the intermediate neck and formation of hexagonal OTB plates with smooth faces occurs (Fig. 2).

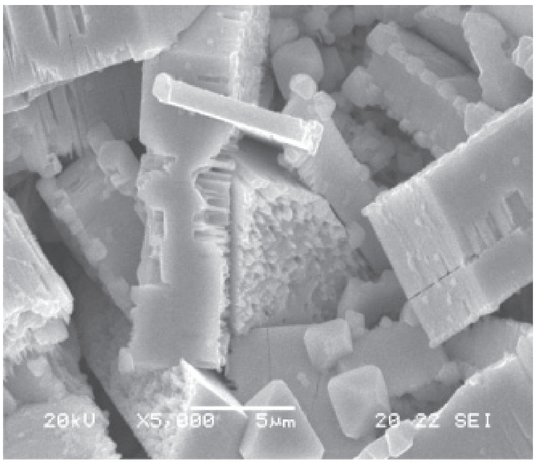

Fig. 1. Morphology of the hexagonal OTB nanocrystalline deposit: T = 700 °C, η = 200 mV, t = 0,5 s

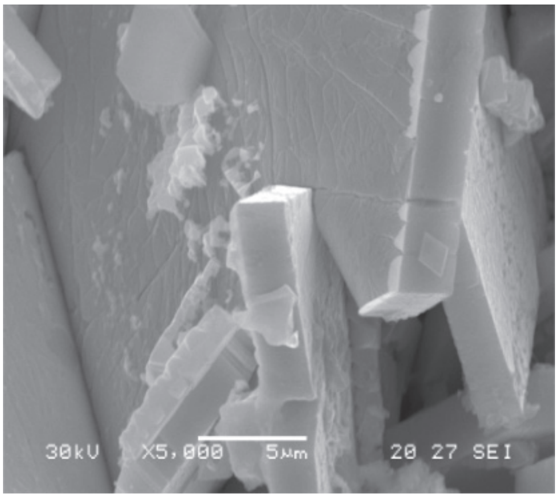

Fig. 2. Morphology of the hexagonal OTB: T = 700 °C, η = 200 mV, t = 15 s

The unformed tetragonal prisms are deposited from the 0,25 K_2WO_4 – 0,25 Na_2WO_4 – 0,50 WO_3 melt (Fig. 3). The tops of individual crystals are composed of needles, having the orientation <001> (the needle thickness at the half-height is 80–150 nm). The process of formation of the regular OTB microcrystal ($K_xNa_yWO_3$) with the tetragonal structure was found to be faster than that of the microcrystal with the hexagonal structure. The formation time is 0,5–1 s.

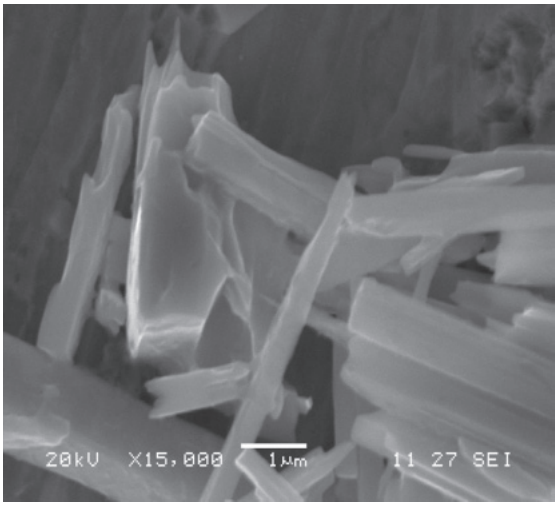

Fig. 3. Morphology of the tetragonal OTB: T = 700 °C, η = 130 mV; t = 0,2 s

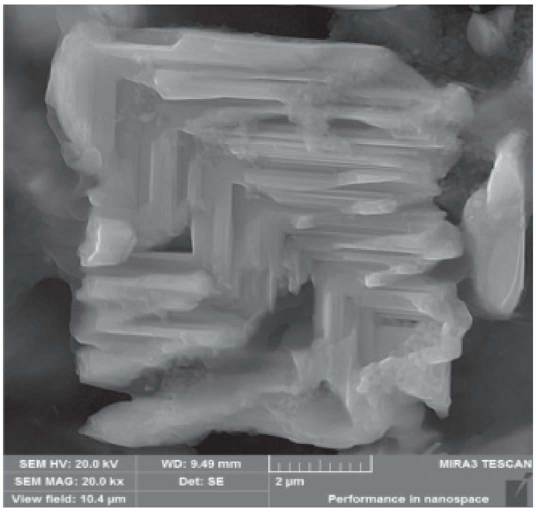

Fig. 4. Microcrystal of the cubic OTB:
T = 800 °C, η = 250 мВ, τ = 0,1 s

During the 0,55 Li_2WO_4– 0,45 WO_3 melt electrolysis the polycrystalline deposits consisting of cubic OTB crystals (Li_xWO_3) are formed. These crystals are formed by the intergrowth of separate needle clusters. The formation mechanism of OTB with different structures (cubic, tetragonal and hexagonal) is assumed to be the same and includes the following stages: the formation of nanoclusters; their interaction with the formation of the intermediate neck; the subsequent filling of the space between the needles. At the same time, these clusters can be positioned both in parallel, as in the case of tetragonal and hexagonal OTB, and perpendicularly to each other, forming stepped structures in the case of cubic OTB (Fig. 4). In the process of growth the stepped structures become porous and then form crystals with smooth faces.

The work was supported by the projects:

1. Nanocrystalline oxide tungsten bronzes obtained by melts electrolysis in catalytic oxidative processes of desulfurization and refining of oil fractions (The program of the Ural Branch of the Russian Academy of Sciences № 12-I-3-2058).

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The work is submitted to the International Scientific Conference «Priority directions of development of science, technologies and techniques», Italy (Roma-Firenze), April 12–19, 2014, came to the editorial office on 05.03.2014.