Electrochemical deposition of tungsten from tungstate-borate melts

Malyshev V.V., Gab A.I., Shakhnin D.B., Franko M.M.

Institute of Engineering & Technology,
Open International University of Human Development "Ukraine",
23 Lvivska St., Kyiv-03115, Ukraine

E-mail: viktor.malyshev.igic@gmail.com

Introduction and Methods

Acid-base properties of tungstate melts have substantial effect both on electrode processes and composition of cathodic products. Various acceptors of oxygen ions, particularly Li^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, and Al^{3+} cations, PO_3^- anions, and also neutral WO_3, MoO_3, and CO_2 molecules, were used to modify acidity of the melts. The cations of alkali and alkaline-earth metals form cationized electrochemically active species, while PO_3^- and indicated oxides produce dimeric complexes [1].

In the present work investigation results of the boron oxide effect on platinum-oxygen and tungsten electrodes in sodium tungstate melt electrochemical behavior. The interest to the carrying out of this investigation is determined by the following.

1. In the literature, the significant influence of boron oxide was noted onto the structure of cathodic deposits obtained from tungstate melts.
2. On the base of peculiarities of tungstate melts nature and structure it is possibly to wait the better solubility and less fugacity of boron oxide than was observed in halide melts.
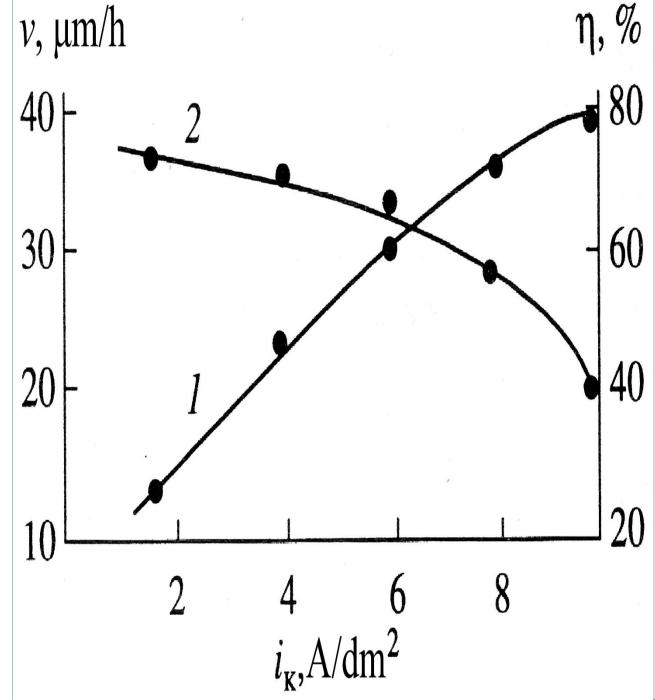3. Boron oxide as oxo-acid particle should affect on acid-base interactions in tungstate melts.
4. It is interesting to compare our results on studying of platinum and tungsten electrode electrochemical behavior in equilibrium conditions with the results of the present work.

In the present work we investigated the effect of boron oxide on electrochemical behavior of platinum-oxygen and tungsten electrodes in sodium tungstate melt.

Systems for the tungsten coatings electrochemical deposition were based on Na_2WO_4-B_2O_3 melt. As anode was used tungsten plates in alundum container or graphite crucibles, as cathodes – plates of metals for electrodeposition (10x20x1 mm).
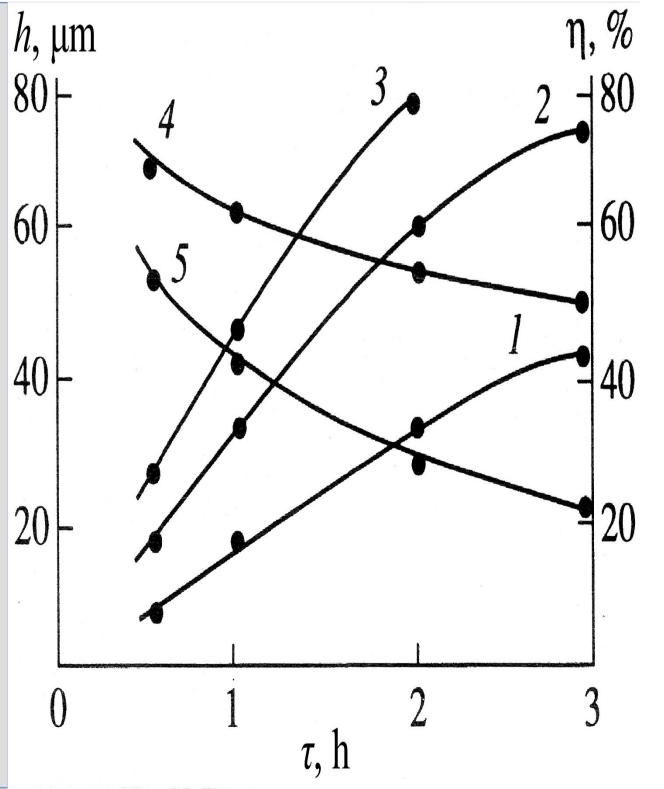
Results and Discussion

The system for the tungsten coatings electrochemical deposition based on Na_2WO_4-B_2O_3 melt was studies. The influence of boron oxide concentration, temperature, cathode current density, and duration of electrolysis on cathode deposits composition and structure was investigated; optimal parameters of reversive tungsten deposition from Na_2WO_4-B_2O_3 melts were selected. Tungsten is deposited if the boron oxide concentration does not exceed 10 mol %; with higher boron oxide concentrations, tungsten oxides and bronzes are showing at XRD patterns. Continuous coatings were obtained at 1073-1323 K and current density up to 50 A/dm^2. The higher is the electrolysis temperature, the coarser are the deposit grains.

Well adhered, uniform, continuous, non-porous coatings were obtained at 1173 K with current density 1-10 A/dm^2. In the initial deposition period, the deposit grains size was decreased with the current density increase. With current density higher than 10 A/dm^2, grains size was increased significantly, the roughness amplitude increased from 1 up to 2-3 µm, and the progressive growth of individual protrusions turned into dendritic formation preventing the further coating deposition. Below 1 A/dm^2, substrate corrosion rate exceeds tungsten deposition rate, causing poor coatings adhesion. Tungsten deposition rate within studied current density range are 15-40 µm/h, and tungsten current yield – about 85%. (Fig. 1).

Fig. 1. The dependence of the tungsten coating deposition rate (1) and of its current yield (2) at the St3 samples on the current density.

With the electrolysis duration increase, the current yield decreases (Fig. 2).

With coating thickening, its surface structure changes from fine-crystalline with uniform grains to coarse-crystalline. To obtain fine-crystalline coatings, a reversive electrolysis mode was used. The cathodic-to-anodic-phase ratio was within 20-40 range; the anodic phase duration was 0.5-2.0 s, and the anode current density was 15-50 A/dm^2. To obtain a good coating, the following electrolysis parameters are optimal: cathodic phase duration – 20 s, anodic phase duration – 0.5-1.0 s, cathode current density – 8-10 A/dm^2, anode current density – 15-30 A/dm^2. Electrolysis carrying out in this mode makes it possible to halve the coating roughness with an increase of its thickness up to 200 microns.

Continuous, well-adhered to the substrate, tungsten coatings were deposited onto graphite, nickel, copper, molybdenum, tungsten, machine-building structural steels, heat-resistant and tool hard alloys, nitrided and nickel-plated titanium. The coatings microhardness is 4.3-4.5 GPa.

The substrate layers adjacent to the coatings are noticeably hardened, which indicates the mutual diffusion of the coating and the substrate elements. A diffusion zone 10-15 microns thick is found by X-ray microprobe analysis of the cross-section of steel 3 (St3) sample coated with tungsten [2]. Due to the coating, the wear resistance increased by 3-5 times and was only slightly lower then the resistance of the samples borated from the gas phase.

Fig. 2. The dependence of the tungsten coating thickness (1-3) and of its current yield (4-5) at the St3 samples on the electrolysis duration. Current density, A/dm^2: 1, 4 – 4; 2, 5 – 6; 3 – 8.

Conclusions

To increase the surface hardness of metals, their wear and corrosion resistance, tungsten coatings obtained by electrolysis of tungstate-borate melts can be recommended.

References

1. Malyshev V.V., Kushkov H.B., and Shapoval V.I., High-Temperature Electrochemical Synthesis of Carbides, Silicides and Borides of VI-A group metals in ionic melts, J. Applied Electrochemistry, 2002, V. 32, No. 5, P. 573-579.
2. Lee M., X-Ray Diffraction for Materials Research: From Fundamentals to Applications, 2021, Apple Academic Press, 302 p., ISBN 9781774635933.