THE EFFECT OF THE MELT COMPOSITION ON ELECTRODE PROCESSES AND STRUCTURE OF TANTALUM-BORIDE COATINGS

O.V. Makarova¹, L.P. Polyakova¹, E.G. Polyakov¹, A.A. Shevyryov¹, N.J. Bjerrum²

¹ -Institute of Chemistry KSC RAS, 14 Fersman Str., Apatity, 184200 Russia
² -Technical University of Denmark, Lyngby, DK-2800 Denmark

ABSTRACT

A comparative study of the mechanism of electrode processes and structure of cathodic deposits in FLINAK-K₂TaF₇-KBF₄ and FLINAK-K₃TaOF₆-Na₃B₃O₅F₆ melts was carried out in the temperature interval 700-750°C. The electrochemical behavior of boron and tantalum was studied by linear, cyclic and square-wave voltammetry. The products of interaction between the melt components were determined by the methods of X-ray diffraction, IR spectroscopy, chemical analysis and optical crystallography. Microprobe analysis, X-ray diffraction, SIMS, XPS, AES, optical scanning electron microscopy and STM were used for characterization of cathodic deposits. The governing role of oxygen in the process of interaction between tantalum and boron-containing components of the melt is shown. While not reacting with each other in the fluoride melt, they form complex species in the oxofluoride melt, with, probably, an oxygen bridge between tantalum and boron. Changing the melt structure results in a changed structure of the cathodic deposit. In fluoride melts multi-phase crystalline deposits are formed at the cathode. In oxofluoride electrolytes the cathode is plated with a laminated X-ray amorphous layer. Even fine techniques have not allowed to reveal the nature of individual microlayers of the deposit so far.

INTRODUCTION

Borides of refractory metals, tantalum borides in particular, feature high melting temperatures, hardness, electric characteristics, chemical resistance and therefore are regarded as advanced materials of the future (1). The electrolytic method of their production has always been considered as highly promising. The newly obtained results have shown that under certain condition microlayered coatings of tantalum boride are deposited at the cathode (2,3). This is particularly interesting in light of the data presented in the review (4). In this work it is inferred that 'such nanomultilayer structure results in significant increase of mechanical characteristics'. Depending on the nature of individual sublayers the microlaminarity may cause powerful anisotropy of physical properties of the entire coating. A more detailed study of properties of such materials may probably lead to new practical applications.
The aforementioned explains the interest the molten salt specialists have had to electrochemical synthesis of tantalum borides in the course of many years. However, owing to the complexity of the process many of its particulars are unknown so far and the available data are contradictory. So, it is still unclear how the melt composition affects the mechanism of electrode processes and the structure of the cathodic deposit.

In this paper we conducted a comparative study of the mechanism of electrode reactions in fluoride and oxofluoride melts. Moreover, we have traced the changes in the structure of cathodic deposits on transition from \( \text{FLINAK-K}_2\text{TaF}_7-\text{KBF}_4 \) melt to \( \text{FLINAK-K}_3\text{TaOF}_6-\text{Na}_3\text{B}_2\text{O}_3\text{F}_6 \) melt. An attempt was made to determine the chemical composition of individual sublayers of the cathodic deposit with the view to reveal the nature of lamination, clearly visible on sample cross sections.

EXPERIMENTAL

We used linear and cyclic voltammetry as the main method of electrochemical research. As a supplementary method square-wave voltammetry was employed. The experiments were conducted under the atmosphere of carefully purified argon in the temperature range 700-750°C. A silver rod served as an indicator electrode. A glassy-carbon can was used as a container for the electrolyte and a counter-electrode. The potentials were measured against a glassy-carbon quasi-reference electrode. The starting salts and electrolyte samples for XRD, IRS and optical crystallography (OC) were handled in a glove box.

RESULTS AND DISCUSSION

As we showed earlier, the number of cathodic peaks on the voltammogram of \( \text{FLINAK-K}_2\text{TaF}_7-\text{KBF}_4 \) melt depends on the ratio of tantalum and boron concentrations in the melt (5). At a molar ratio B/Ta=4 it attains four and all the cathodic peaks correspond to the solid product deposition. This accounts for the fact why at different current densities the deposits formed at the cathode have different phase compositions. The growth of current density results in the following changes of the cathodic deposit composition, which in a general way may be written as:

\[ \text{Ta}_{\text{cub}} \rightarrow \text{Ta}_{\text{tetragon}} \rightarrow \text{Solid Solution of B in Ta} \rightarrow \text{tantalum borides} \rightarrow \text{mixture of different tantalum borides} \rightarrow \text{tantalum borides} + \text{elemental boron} \].

Nor have any indications been obtained as to the interaction between \( \text{K}_2\text{TaF}_7 \) and \( \text{KBF}_4 \) in molten fluoride eutectic (5). Thus, a bond between boron and tantalum is only formed in the process of electrodeposition. This is witnessed by significant depolarization observed during the boron deposition at the electrode, whereby at more positive potentials tantalum nuclei have already been formed. The cathodic deposits obtained in fluoride electrolytes, independently of the experimental conditions, were crystalline.
On the contrary, cathodic deposits from oxofluoride melts were X-ray amorphous. The shape of X-ray patterns characterized by two haloes (Fig. 1) indicates to their amorphous or microcrystalline structure. The structure of this type of coatings in the images obtained by optical and scanning electron microscopy represents an alternation of layers of differing intensity. Increasing the resolution makes visible finer layers and reveals the microlaminarity of the coatings.

Voltammograms with a greater number of cathodic and anodic peaks observed in fluoride electrolytes containing tantalum and boron are essentially simplified if oxide ions are added to it. Fig.2 illustrates these changes by the example of FLINAK-K$_2$TaF$_7$-KBF$_4$-Na$_2$O melt. As is clearly seen in the figure, one of the cathodic and one anodic peak commence to dominate on the cyclic voltammograms as the molar ratio O/(Ta+B) grows. When the above ratio reaches unity, the voltammograms are characterized by single cathodic and single anodic peaks. Believing the resolution of linear voltammetry insufficient in the case of complicated curves like these, we applied a finer method - square wave voltammetry. However, the SW voltammograms as well feature only one cathodic peak (Fig. 3). This is a corroboration of the process of tantalum and boron reduction in an oxofluoride melt being one-stage.

Changes observed on the voltammograms are caused by significant changes in the melt structure when oxygen is added to it. The mixtures of K$_3$TaOF$_6$ and Na$_3$B$_3$O$_5$F$_5$ were melted under inert atmosphere, cooled and analyzed by XRD, IRS and OC. The data obtained by all the...
methods coincide. In the region of molar ratios B/Ta from 1/2 to 2/1 the intensity of responses characteristic of \( \text{K}_3\text{TaOF}_6 \) decreases. While the boron concentration in molten samples increases, the concentration of NaF as a product of thermal decomposition of \( \text{Na}_3\text{B}_3\text{O}_3\text{F}_6 \) increases. Alongside with this, a new phase appears in the samples in growing quantities. It is characterized by refractive indexes \( N'p=1.629; N''g=1.780; \) a wide band in the IR spectrum in the region 650-670 cm\(^{-1}\) and a doublet 523 and 535 cm\(^{-1}\) and a wide set of peaks in the X-ray pattern in the region of interplanar distances of 1.4 to 4.3 Å. At B/Ta=2 the above changes attain their maximum values whereas in the X-ray pattern a new intensive peak 11.3-11.5 Å appears.

Further increasing of the B/Ta ratio from 2/1 to 6/1 causes the response intensity of the new phase to decrease slightly as well as the NaF concentration to grow monotonously and a new tantalum-bearing phase - \( \text{K}_4\text{Ta}_6\text{O}_{17} \) to appear.

The data of this series of experiments have allowed us to suppose that in contrast to oxygenless melts, tantalum and boron in oxofluoride melts interact with each other. Apparently, they form heteronuclear complexes with a bridge oxygen bond in the nucleus. It is these complexes that give the single cathodic peak on cyclic and square-wave voltammograms (Fig. 2,3).

An attempt was made to reveal the nature of laminated X-ray amorphous tantalum boride coatings formed at the cathode in oxofluoride melts. Reasoning that individual layers differ by the component concentration, we studied their distribution at a cross section of the samples while a probe was moving from the outer surface to the substrate. As is it had been anticipated, microprobe analysis proved to be too crude a method to determine the composition of individual thin sublayers. Therefore for confirmation of regular changes of the composition on moving the probe across the section we used methods with a resolution of hundreds and tens of angstrom - SIMS, XPS and AES. As is evident from Fig. 4, the whole length of XPS profile, with the exception of the edge effect, represents smooth, almost straight lines. No periodic fluctuations of concentration pointing to different chemical composition of individual layers of the deposit were observed. The same is characteristic of the method with the highest resolution ability used, i.e. AES.

Fig.3. Cyclic (a) and square wave (b) voltammograms of FLINAK-K\(_3\)TaOF\(_6\) -Na\(_3\)B\(_3\)O\(_3\)F\(_6\) melt at 700°C. B/Ta molar ratio=2/1. 1-differential, 2-back, 3-forward, \( \Delta E=5 \text{ mV}, E_{sw}=25 \text{ mV} \)
### CONCLUSIONS

1. Oxygen in the melt exerts a decisive effect on the mechanism of electrode processes in fluoride melts containing K$_2$TaF$_7$ and KBF$_4$.
2. In the absence of oxygen the process of cathodic deposition of the components consists of several stages. The growth of oxygen concentration results in a one-stage cathode process.
3. In oxygenless melts crystalline multiphase deposits are formed at the cathode. In the melts with oxygen the cathodic deposits are X-ray amorphous and feature a microlaminated structure.
4. The nature of individual fine layers has not found a satisfactory explanation yet.

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