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PHASE COMPOSITION OF CATHODIC DEPOSITS SYNTHESIZED IN FLINAK-K_2TaF_7-KBF_4 MELT

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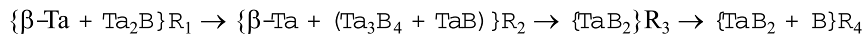
Abstract

The phase composition of cathodic deposits synthesized from FLINAK-K_2TaF_7-KBF_4 melt has been studied by the X-ray diffraction method. It is shown that boron content in the electrodeposit grows as the cathodic potential is increased from peak R_1 to peak R_4 in the voltammogram. The scheme of changes in the phase composition depending on the increasing current density is given as follows:



$$\{\beta\text{-Ta} + Ta_2B\}R_1 \rightarrow \{\beta\text{-Ta} + (Ta_3B_4 + TaB)\}R_2 \rightarrow \{TaB_2\}R_3 \rightarrow \{TaB_2 + B\}R_4$$

Keywords: **t**antalum borides, electrochemical synthesis, phase composition

1. Introduction

Refractory metal borides feature a number of useful properties such as high hardness, melting point and corrosion resistance, which explains the current interest in their production. One of the promising methods to synthesize borides is molten salt electrolysis.

In our earlier works [1, 2], we used linear voltammetry and reverse chronopotentiometry to study the electrochemical behavior of tantalum and boron in the oxygen-free *FLINAK-K_2TaF_7-KBF_4* melt. It was observed that at a molar ratio *B/Ta*=4 there are four

reduction waves in the cathodic part of voltammograms (Fig.1). This work presents the results of a more detailed study on the phase composition of cathodic deposits synthesized from *FLINAK*-K_2TaF_7-KBF_4 melt at the potentials of each of the four waves.

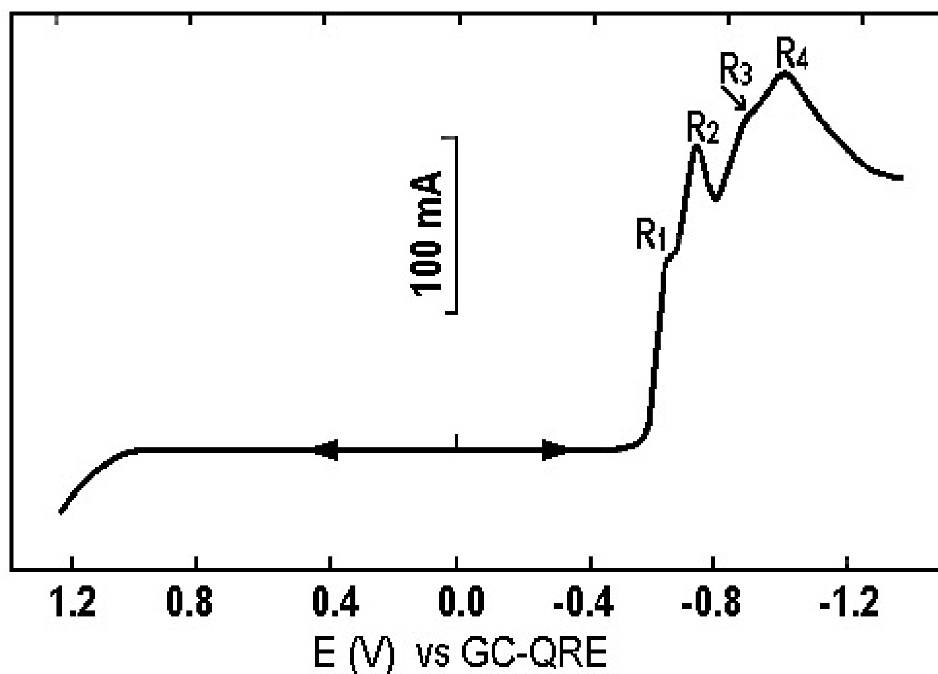


Figure 1. Voltammogram of FLINAK-K_2TaF_7-KBF4 melt with molar ratio B/Ta=4, T=710 ^{0}C, A_{Ag}=0.36 cm^2, scan rate V=0.25 $V{\cdot}s^{-1}$, K_2TaF_7 concentration - 0.222 mol. %.

2. Experimental

Phase analysis of the samples obtained electrochemically was conducted using a DRON-2.0 diffractometer (*Cu*-K_α radiation), and the international powder diffraction database JCPDS-ICDD.

3. Results and Discussion

The deposit to be formed at the first wave (R_1) potentials is β-Ta together with Ta_2B (Fig. 2, curve 1), which is the phase with the lowest boron content possible; it is thermodynamically stable only at temperatures above 2040 ^{0}C [3]. Being in the region of the first wave potentials, an increase in the current density does not lead to a qualitative

change of the composition of the cathodic deposit. Such an increase causes only change in the phase content ratio; i.e. the quantity of tantalum boride increases while the quantity of tantalum metal diminishes.

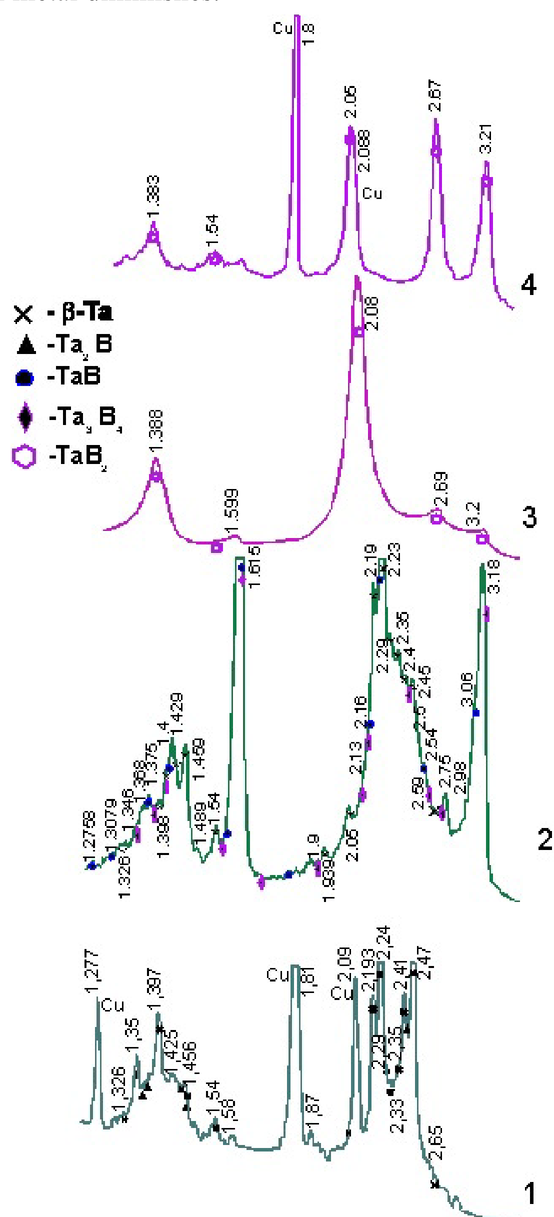


Figure 2. X-ray diffraction patterns of samples deposited onto a copper substrate in FLINAK-K_2TaF_7-KBF_4 melt with molar ratio B/Ta≥4, at T=710 ^{0}C and at the potentials R_1, R_2, R_3, and R_4 waves of Fig.1.

The crystal lattice of the β-Ta tetragonal phase (the structural type of β-U) is essentially different from the lattice of the normal α-Ta body-centered cubic phase (Fig. 3 and 4). As it is known from literature, the β-Ta phase can only be obtained under non-equilibrium conditions existing during electrolysis [4,5] and cathodic sputtering [6,7]. In the latter case, fine, 500 Å thick β-Ta films without traces of foreign elements were obtained in vacuum (10^{-8} Torr). Thus, it is not the obliging presence of boron in the system that causes the β-Ta phase to form under non-equilibrium conditions of the electrochemical synthesis, since this phase can be produced from an electrolyte containing not only boron but, according to [4,5], also from a boron-free electrolyte, consisting of no other elements but *Ta*. However, it cannot be ruled out that trace amounts of boron stabilize this phase. Authors in Ref. [4] have suggested that the reason for the appearance of tantalum with tetragonal structure (β-Ta) during the electrodeposition is the joint effect of high temperature, electric field and crystallization processes. The sinergy of the above factors creates conditions for realizing the electron transitions 4f $\rightarrow$ 5d and 6s $\rightarrow$ 5d, which stabilize the thermodynamically non-stable β-phase. The change in the tantalum crystal structure results in increased solubility limit of boron in β-Ta (up to 2 w/o as minimum [2] compared to 0.1 w/o in α-Ta [3]).

When analyzing the β-Ta structure (space group P-42_1m, a=10.211 Å, c=5.306 Å, number of *Ta* atoms in the elementary cell Z=30, Fig.4) we tried to assess the maximal quantity of boron that can be dissolved in this phase, in the following way. The β-Ta structure can be represented as consisting of a combination of 164 distorted Ta_4 tetrahedra which, being joined by common vertexes, ribs and faces, totally fill the space. The average distance from the center to the vertex in each of the tetrahedrons is approximately 1.9 Å, which does not contradict the possibility for B atoms to locate in each of them. The tetrahedra centers occupy two twofold, eight fourfold and sixteen eightfold structural positions. The distances between the centers of either rib- or face-adjacent tetrahedra vary from 0.6 to ~2 Å, which allows to ignore the simultaneous filling of them with B atoms. Centers of the Ta_4 tetrahedra having only a common vertex depart from each other to a distance of 3.12-4.1 Å, therefore, they can be considered as positions for *B* atoms location. The analysis of various combinations of such Ta_4 tetrahedra has yielded several variants of combinations for the structural positions of possible location of *B* atoms in the β-Ta structure. It turned out that the maximum number of simultaneously filled non-adjacent Ta_4 tetrahedra is 14 per elementary cell, which corresponds to 2.7 w/o *B*. It can be suggested that the formation of the Ta_2B compound containing 2.9 w/o *B* is caused by the filling of adjacent Ta_4 tetrahedra in the β-Ta structure, which destroys its structure due to the appearance of short B-B bonds. The stabilizing role of *B* for the β-Ta structure can be explained by increased concentration of valent electrons per each of *Ta* atoms forming this structural type, which normally is characteristic of binary intermetallic compounds with valent electron concentrations of 6-7 electrons per atom [4]. The presence of *B* atoms raises this value from 5 in the pure β-Ta phase to 6.4 at 2.7 w/o *B*.

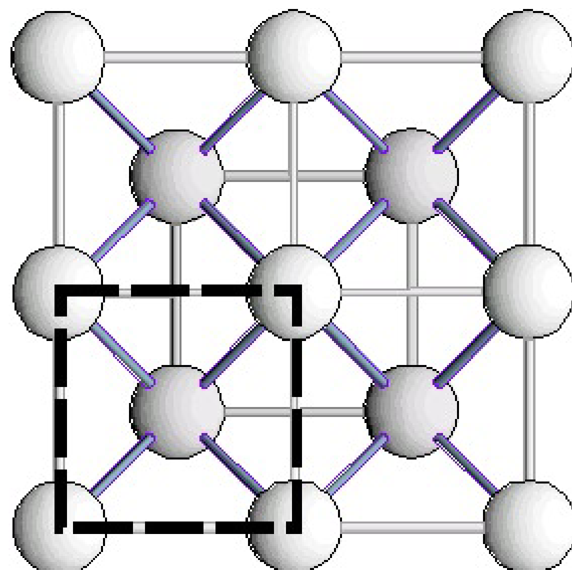


Figure 3. The structure of α-Ta (Im3m a=0.3058 Å): projection to z-axis. The dotted line highlights the elementary cell [9].

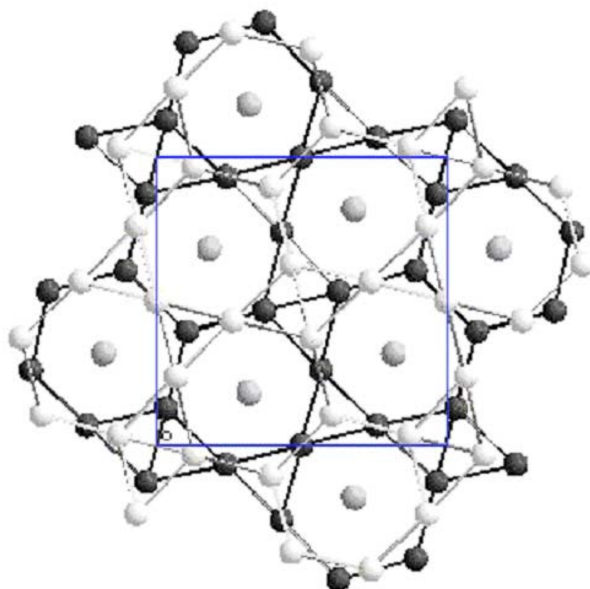


Figure 4. The structure of ß-Ta (P 42_1 m a=10.211 Å, c=5.3064 Å). Projection along the fourth-order axis. Two identical hexagon-triangular atom layers (the white and black circles) are located at two levels (z=0.75 and 0.25, respec tively) along the 4th axis. The atoms of the square-triangular atom layer (the gray circles) are located at z=0 and 0.5 align the hexagonal channels of the structure. The square marks an elementary cell [4].

Electrolysis at the second wave potential yields a hardly identifiable coating consisting of β-Ta and a texture containing presumably a mixture of *TaB* and Ta_3B_4 (Fig. 2, curve 2). Increasing the current density within the second wave causes the blurring of peaks in the β-Ta X-ray patterns. The reflections of boride crystallographic planes also undergo changes. This is evident in increasing intensities of reflections from the planes with interplane distances of 3.2, 1.6 and 1.06 Å, as well as in degeneration of the remaining reflections. On the face of it, the above interplane distances seem to be dissimilar-order reflections from the same plane system, but this is not exactly correct. The *TaB* and Ta_3B_4 borides belong to the rhombic syngony and have highly close *a* and *c* parameters of the elementary cells (Table 1), therefore some of their reflections are superimposed.

Table 1. Parameters of elementary cells of tantalum borides [8]

TaB *a*=3.28 *b*=8.67 *c*=3.15 Å			Ta_3B_4 *a*=3.29 *b*=14.0 *c*=3.13 Å		
d, Å	I/I_1	hkl	*d*, Å	I/I_1	hkl
3.066	50	110	3.21	90	110
1.6397	14	200	1.64	90	200
1.0658	2	062	1.06	15	330

Analysis of Table 1 shows that tantalum monoboride reflections taken into consideration belong to different planes, and none of the bands is among the strongest. The interplane distances (3.21 and 1.06 Å) of the phase Ta_3B_4 characterize one and the same family of planes parallel to {110}, whereas the (200) plane with *d*=1.64 Å does not belong to this family but coincides at these reflection angles with a similar plane of tantalum monoboride due to the equality of *a* parameter for both borides. This is probably why the peak at *d*=1.64 Å corresponding to the sum of one of the most intensive reflections – Ta_3B_4 and a medium-strong monoboride reflection is for the most part the strongest and the narrowest. The location, shape and width of the superpositional reflection 110 depend on the ratio of tantalum borides in the coating, which is due to a significant difference in their *b* parameters. The simplified scheme of the relationship between the X-ray pattern and TaB/Ta_3B_4 ratio in the cathodic deposit is as follows:

$TaB>Ta_3B_4$**:** superimposition of reflections from 200 planes of both tantalum borides gives rise to the strongest peak. The unseparated maximum corresponding to the superimposition of reflections from 110 planes of both borides is shifted to the position of the monoboride plane with *d*=3.066 Å.

$TaB=Ta_3B_4$: the strongest peak, caused by two tantalum borides, still corresponds to

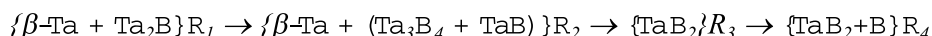
the reflection of their planes 200. The superimposition of the strong reflections 100 of *TaB* and Ta_3B_4 gives rise to a wide band with two maxima approaching respectively *d*=3.066 and 3.21 Å.

$TaB<Ta_3B_4$: the heights of the first two bands are approximately equal since the tantalum monoboride contribution to the reflection from plane 200 diminishes, whereas the relative intensity of the reflection 110 of Ta_3B_4 with I/I_1=90 increases; for the same reason the position of the second band approaches *d*=3.21 Å.

Electrolysis at the potentials of the third wave yields tantalum diboride, while at the potentials of R_4 – a mixture of TaB_2 with elemental boron, which deposits at the cathode as a black powder (Fig. 2, curves 3 and 4).

Conclusions

Identification and analysis of X-ray patterns of the cathodic deposits obtained by electrolysis at potentials corresponding to waves R_1-R_4 demonstrate trends in the composition change. The resulting scheme of the change with increasing current density during the electrolysis of *FLINAK*-K_2TaF_7-KBF_4 melt is as follows:



$$\{\beta\text{-Ta} + Ta_2B\}R_1 \rightarrow \{\beta\text{-Ta} + (Ta_3B_4 + TaB)\}R_2 \rightarrow \{TaB_2\}R_3 \rightarrow \{TaB_2 + B\}R_4$$

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