

## FEATURE OF CRYSTAL FORMATION DURING ELECTROCHEMICAL SYNTHESIS

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Morphology of the potassium - sodium oxide tungsten bronze single crystals with a tetragonal structure growing during the electrolysis in the melt at 700°C under potentiostatic conditions has been studied. It was supposed that the process of self-organization takes place.

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### Introduction

In our previous work [1] it was expressed a proposal that the process of self-organization takes place in hexagonal crystals. This conclusion was made on the base of study of the growth rate anisotropy and the morphology of tungsten bronze single crystals during the electrolysis in the melt. The mechanism of such self-organization exists to be the selection of single parts of crystal according to their electrical conductivity.

It is the interest in detailed study of crystal growth of another structure which will allow us to make a general conclusion in respect with the possibility of self-organization of tungsten bronzes in growth process.

### Experimental procedure

The bronze was obtained by electrolysis of the  $0.325 \text{ K}_2\text{WO}_4 - 0.325 \text{ Na}_2\text{WO}_4 - 0.35 \text{ WO}_3$  melt. According to our studies this bronze is isostructured to tetragonal bronze  $\text{K}_x\text{WO}_3$ .

During the electrolysis the temperature of 700°C was kept. The wires (a copper and platinum) were used as a cathode. They were previously vacuum sealed by melting into refractory glass and then the ends of the electrodes obtained were polished until all the scratches were disappeared. A tungsten wire covered with bronze layer of the same composition as electrodepositing one on cathode was used as an anode and as a reference electrode.

The structure of bronzes and crystal faces were determined by using the "DRON-3" model diffractometer. Sometimes optical researches were used for faces definition.

The morphology of faces was investigated with the "Camebax" installation.

In the experiments of bronze single crystal growth a two - pulse method was used. At first a pulse of a constant magnitude (140mV) and duration (1 s) was applied to the cell. At those pulse parameters a bronze single crystal was nucleated on the cathode. Then the second overpotential pulse was applied which supported the crystal growth. The second pulse magnitude was varied in the course of the experiments from 0 to 110 mV with a step of 5-10 mV.

### Results and discussion

Fig.1 shows the scheme of crystal habitus changes in the overpotential range from 30 to 90 mV. The detail description of crystal refaceting was made in our work [2]. In this work some peculiarities of crystal growth of K-Na oxide tungsten bronzes with a tetragonal structure were studied. In particular, the decreasing of the crystal growth rate in the  $\langle 001 \rangle$  direction during increasing of the overpotential from 40 to 50 mV was found. It was established that these effects are connected with refaceting of the crystal apexes.

Simultaneously with determination of crystal faces its morphology was investigated with the purpose to find out of their growth mechanism.  $\{051\}$  faces have a rough surface that promotes fast growth, but  $\{001\}$  face, which appears after overgrowing of  $\{051\}$  faces, is smooth. The growth of such face goes by the layer mechanism. It remains smooth up to 45 mV then the forms in a kind of "snails" appear on it. Further increasing of potential up to 50 mV results to the growth of these forms. Simultaneously with occurrence

of "snails" the faces  $\{031\}$  appear. During increasing of overpotential the share of these faces is increased, but they always remain porous. According to our investigation only faces  $\{031\}$  and  $\{110\}$  exist in the monocrystal in the overpotential interval 50 - 90 mV. It should be noted that irrespective of

overpotential the faces  $\{110\}$  have an identical morphology. On photos we see the growth layers extending in  $\langle 001 \rangle$  direction. Overpotential rise up to 90 mV results to overgrowing of  $\{110\}$  faces and transformation into bipyramid.

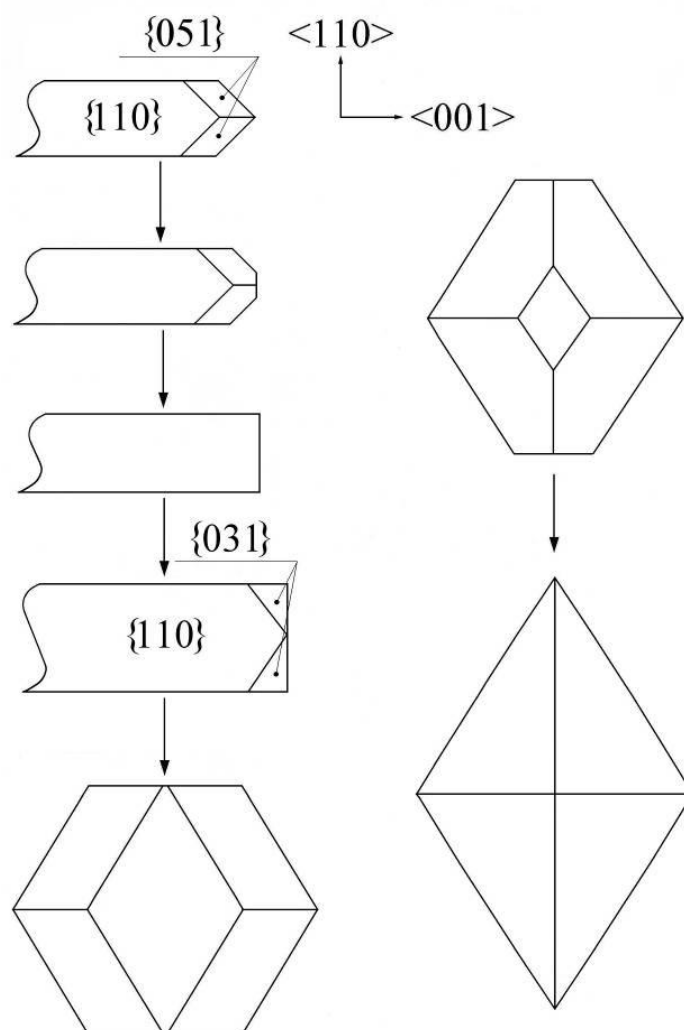


Figure 1. Scheme of crystal habitus changes in the overpotential range from 30 to 90 mV.

Experiments show that bipyramid is steady in a comparatively narrow overpotential interval 90 - 110 mV. It was found that the overpotential rise above 110 mV results in the loss of stability of the plane growth front of the  $\{031\}$  faces. The formation of many ledges on these faces occurs (Fig. 2), then during the growth process the ledges

transform to tetragonal needles elongated in the  $\langle 001 \rangle$  direction. Their side faces are the  $\{110\}$  planes and the upper base is the  $\{001\}$  plane. These needles have no azimuth disorientation and due to it they intergrow to form a regular crystal (Fig. 3). Upper base  $\{001\}$  of this crystal becomes comparatively smooth (Fig. 4).

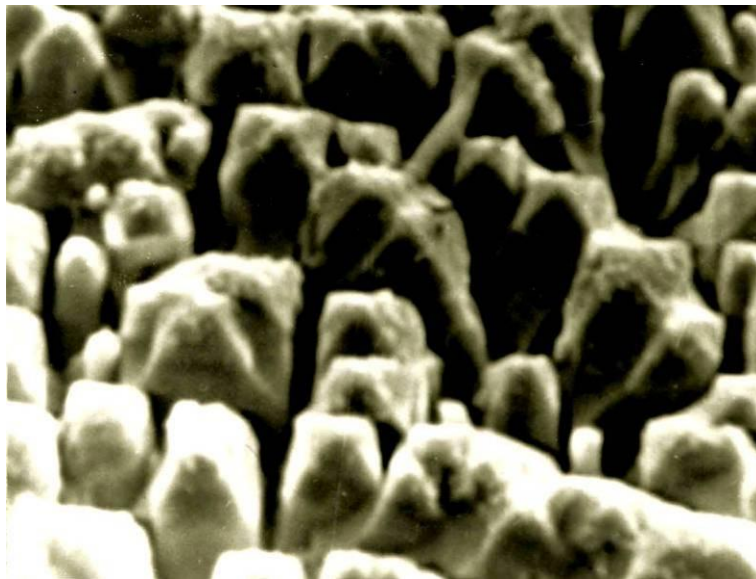
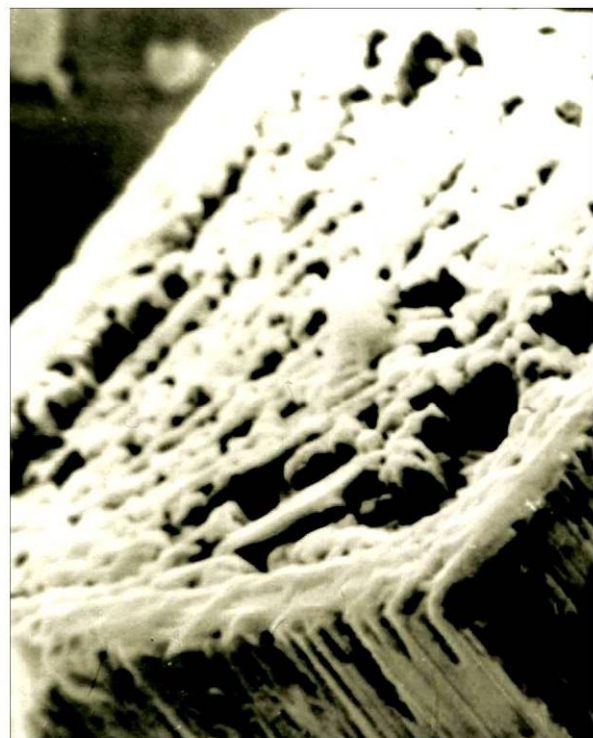


Figure 2. Morphology of the bipyramid  $\{031\}$  face at the moment of the loss of stability in the plane growth front (x4000).



a



б

Figure 3. Regular crystal obtained from the bipyramid at 110 mV (a - x100, b- x800)



Figure 4. Morphology of the prism  $\{001\}$  face formed by intergrowth of separate needles (x6000).

#### Conclusion

In the present work the morphology of monocrystals of oxide tungsten bronzes with tetragonal structure growing by electrolysis of molten salts has been studied. It was established, that morphology of crystals depends on overvoltage.

The process of formation of many needles on the crystal surface is similar to the process in hexagonal crystals. Moreover all

of this appears only at definite overpotential values and so we can conclude that the process of self-organization takes place in tetragonal crystals too.

#### References

1. S.V. Vakarin, A.N. Baraboshkin, K.A. Kaliev, V.G. Zyrianov, J. Crystal Growth 151(1995)121.
2. A.N. Baraboshkin, S.V. Vakarin, K.A. Kaliev, Kristallografiya 34(1989)1583.