# STRUCTURAL CHANGES OF SINGLE CRYSTALS OF LOW-ALLOYED TUNGSTEN ALLOYS AT THERMAL CYCLING

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## Abstract

Parameters of sub-structure of single crystals of low-alloyed tungsten alloys from the system W-Nb and W-Mo were investigated after thermal cycling in argon protective atmosphere. The mode of thermal cycling of tungsten based single crystals consisted of heating to the temperature of 2500 °C and of cooling to the temperature of 500 °C with dwell of 3.5 s at those temperature. It was established with use of X-ray topography, OLM and SEM, that after 100 thermocycles dislocations were re-distributed, sub-boundaries of the 2$^{nd}$ order were "washed away" (disappeared), and the size of sub-grains of the 1$^{st}$ order and their angle disorientations increased – as a result of heat stresses. After 500 thermocycles formation of new boundaries was observed in the structure as a result of polygonisation, i.e. by ordering of dislocations of the same sign. Application of 2000 thermocycles led to an increase of size of new grains and that of their angle disorientations. All the tested samples preserved at the thermal cycling within the interval from 0 to 2000 thermocycles their single crystalline structure. Formation of oxides on the surface of single crystals is connected with residual content of oxygen in argon.

**Key words**: tungsten alloy; single crystals; thermal cycling; electron beam zone melting, X-ray topography

## INTRODUCTION

Single crystals of high-melting metals and their alloys find their application as perspective materials in lighting industry, electrical engineering, in electro-vacuum instruments or in nuclear technologies [1-10]. Many components of these instruments are during operation exposed to the effects of thermal cycling, which may lead to their destruction

as a result of irreversible structural changes. Processes, which take place during thermal cycling, were investigated in detail in the case of pure single crystals of tungsten and molybdenum. These processes comprise particularly typical change of sub-structure, i.e. disappearance of original grain boundaries and formation of new ones as a result of polygonisation, and change of physical-mechanical properties [1]. Alloying may accelerate these processes or prevent them. It may also initiate additional other phenomena in the course of thermal cycling, which are related to mutual physical-chemical interaction between alloying elements and base metal. Similarly influence of rhenium was investigated, as it efficiently influences the stability of single crystals structure during long-term thermal cycling [11-13]. Effects of alloying by other elements, such as Nb and Ta, or of mutual alloying of tungsten by molybdenum, or of molybdenum by tungsten, were investigated less intensively, namely in the area of lower concentrations.

Thermal cycling of single crystals with nominal composition of W-1.5 wt.% Nb and W-1.5 wt.% Mo in argon protective atmosphere in the interval from 0 to 2000 thermocycles was performed for the purposes of investigation of changes of structural parameters of single crystals and for evaluation of their resistance to thermal cyclic loads.

## 2. EXPERIMENT

Single crystals of low-alloyed alloys of tungsten with dimensions 5.5x2.75x60 mm were prepared for thermal cycling by electron beam zone melting (EBZM) in vacuum ($p = 10^{-2}$-$10^{-3}$ Pa) by the „floating zone“ method (FZ method) [1-5] at the Department of non-ferrous metals, refining and recycling of the Technical University of Mining and Metallurgy in Ostrava (VŠB-TU Ostrava), at the rate of movement of the molten zone of 3 mm/min. Thermal cycling was performed on the equipment PD-5, which was developed at the Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Moscow, Russia (IMET), and which after modifications is at present equipped with an efficient system for fixation of the sample in a water cooled working chamber of the equipment. Heating of samples in argon protective atmosphere at residual pressure of 0.5 atm was realised by passage of single current with simultaneous recording of the volt-ampere characteristics. The temperature was measured by optical pyrometer through the vitreous silica window of the recipient. Special programmable device controlled the selected modes of thermal cycling of single crystals of the above mentioned alloys, using the variants of 100, 500 and 2000 thermocycles: heating to 2500°C ± 150°C, dwell of 3.5 s, cooling to 1000°C, dwell of 3.5 s.

The central part, which was subjected to the required temperature, was cut out from all the samples by electro-spark machining. These samples were prepared by metallographical methods and then electrolytically polished (etched) in solutions of the following composition: single crystals of tungsten based alloys – 2% water solution of KOH at 12-14 V and 2-2.5 A. For development of micro-structure of the tungsten based alloys the etching agent Murakami of the following composition was used: 10 g NaOH + 10 g $K_3Fe(CN)_6$ + 80 g $H_2O$. Optical light microscope (OSM) equipped with digital camera and scanning electron microscope (SEM) were used for study of morphology and structural characteristics.

Method of X-ray topography with "scanning" performed by discrete rotation of investigated sample with his simultaneous exposure to characteristic irradiation by $CoK_{\alpha 1,2}$ within the given angle interval for back scatter of the types (310) and (200) on any planes was used for determination of parameters of sub-structure of tungsten alloys single crystals [14 and 16]. In this manner topograms of the central part of the samples were obtained for each single crystalline alloy before and after thermal cycling.

## 3. RESULTS AND DISCUSSION

Table 1 gives parameters of sub-structure of the samples in initial state and after thermal cycling, i.e. dimensions of sub-grains and angle of disorientation of their boundaries, which were calculated from the X-ray topograms (see Figs. 1 and 2). Savickij and Burchanov [1] classify the sub-grains of $1^{th}$ to $4^{th}$ order according to their dimensions. The sub-grains of $1^{th}$ order are formed due to the growth from the seed crystal, the subgrains of $2^{nd}$ and $3^{rd}$ order result of a polygonisation. It follows from this research, that character of changes of parameters of sub-structure of single crystals of all alloys during thermal cycling was practically similar. At first a disintegration of sub-structure was observed: in the tungsten based alloys – after 500 thermocycles. During subsequent thermal cycling sub-grains started to grow with simultaneous increase of the disorientation angle of their boundaries. After 2000 thermocycles all the samples if single crystals showed block structure with high disorientation angle of sub-grains' (blocks') boundaries.

Sub-structure of tungsten based single crystals before and after thermal cycling is documented in Figs. 3 and 4. In initial state the structure of single crystals consisted of sub-grains of the $1^{th}$ and $2^{nd}$ order with a disorientation angle of their boundaries of several minutes to degrees [1]. Boundaries of sub-grains are formed by dislocations and admixtures. During the first stages of thermal cycling of tungsten based single crystals (till 100 thermocycles) decrease in density of dislocations was observed, as well as "washing out"

(extinction) of the sub-grains of the 2nd order and of some parts of sub-boundaries of the 1st order (see Figs. 3b and 4b), which caused in the alloy W – 1.5 wt.% Nb an increase of dimensions of sub-grains of the 1st order. During subsequent thermal cycling (500 thermocycles) new sub-boundaries were formed as a result of ordering of dislocations of the same sign, i.e. polygonisation. These new sub-boundaries were observed particularly at the borders of the samples. At this stage of thermal cycling in central parts the old sub-boundaries were not completely "washed out", but new sub-boundaries were formed inside the old ones. Complete extinction of old sub-boundaries was determined during 500 to 2000 thermocycles (Fig. 3c,d and 4c,d). During subsequent thermal cycling newly created grains started to grow with simultaneous increase of disorientation angle of their boundaries. Newly formed structure did not differ significantly from the initial structure of single crystals, which was confirmed also by the X-ray topography. Fig. 5 shows the fine details of etch pits (inside): cones, hills, ribs and so on. This phenomenon is explained by different bound energy of atoms (Kossel-Stranskii theory), but no internal defects [1].

It was established from comparison of changes of structural characteristics of single crystals from the alloys based on tungsten and pure tungsten, which occurred during thermal cycling [1, 11-13], that alloying by the mentioned metals in concentrations up to 2 wt.% increases stability of the boundaries of the 1st order. In single crystals of pure tungsten the process of polygonisation was completed already after 300 thermocycles, while in the alloys of W-1.5 wt.% Nb and W-1.5 wt.% Mo the process of formation of new boundaries of new sub-grains inside the boundaries of original sub-grains only begins after 300 thermal cycles.

The surface morphology of the single crystals after thermal cycling is presented in Fig. 6 and 7. Growth bands (Fig. 6a and 7a), which were formed as a result of variation of the crystallisation rate, became visible after electrolytic etching of the surface of the sample in the initial state. The width of grow bands increased with the increasing number of thermocycles as a result of increasing density of dislocations and their redistribution during thermal cycling. The pores and their accumulation, which were formed as a result of a combination of the oxidation and evaporation processes during thermal cycling, were observed on the surface of W-Nb specimens. The surface morphology was changed after 100 thermocycles. In the case of W-Mo specimens, the surface morphology was changed slightly up to after 500 thermocycles in comparison with W-Nb specimens. After 2000 thermocycles morphology of the surface was completely changed (Fig. 6d, 7d), and sub-grains boundaries were visible on it.

## 4. CONCLUSIONS

The presented work investigated influence of conditions of high-temperature cycling under argon protective atmosphere on changes of structural parameters of single crystals form low-alloyed tungsten alloys. It follows from the realised experiments, that all investigated single crystals of low-alloyed tungsten based alloys preserved under the given conditions of thermal cycling their single crystalline structure. In the course of thermal load the original structure of single crystals was reshaped, while new boundaries of sub-grains were created as a result of polygonisation. For application of single crystals of high-melting metals in the form of various components, such as electro-vacuum instruments and equipment it is necessary to use high-purity input materials, as well as protective atmosphere or high vacuum in order to prevent possible oxidation and contamination of their surface.

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Table 1 Parameters of sub-structure of the samples in initial state and after thermal cycling calculated from the X-ray topograms

| Sample | **Before thermocycling** | | **100 thermocycles** | | **500 thermocycles** | | **2000 thermocycles** | |
|---|---|---|---|---|---|---|---|---|
| | Sub-grain size (mm) | Disorientation angle | Sub-grain size (mm) | Disorientation angle | Sub-grain size (mm) | Disorientation angle | Sub-grain size (mm) | Disorientation angle |
| **W–Nb** | 0.2-1.0 | 10-15’ | 1-3 | 0.5°(1$^{st}$ order) 10-15 (2$^{nd}$ order) | 0.05 | 15-20’ | 0.2-1.0 | 0.5-1.5° |
| **W–Mo** | 0.1-0.5 | 15-20’ | 0.1-0.5 | 0.5°(1$^{st}$ order) 10-15’ (2$^{nd}$ order) | 0.05-0.2 | 20’ (1$^{st}$ order) 10’ (2$^{nd}$ order) | 0.2-0.7 | 1-2° |

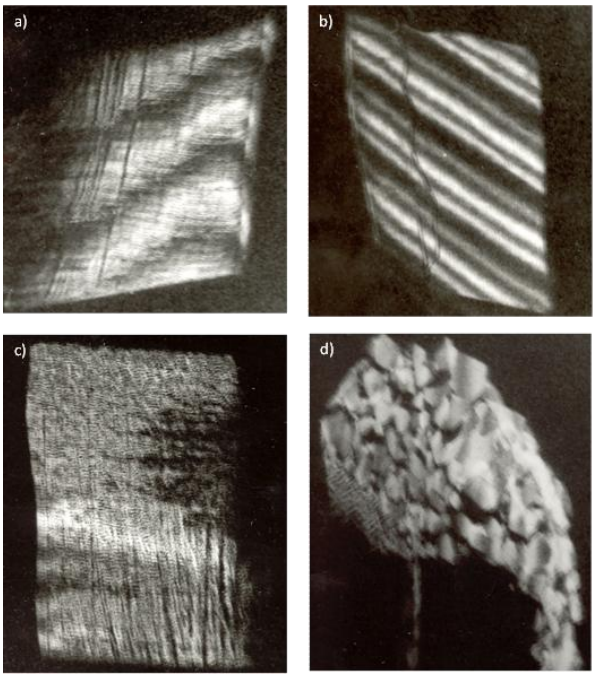


Fig. 1 X-ray topograms of W-Nb specimens (longitudial section): a) initial state; b) after 100 thermocycles; c) after 500 thermocycles; d) after 2000 thermocycles

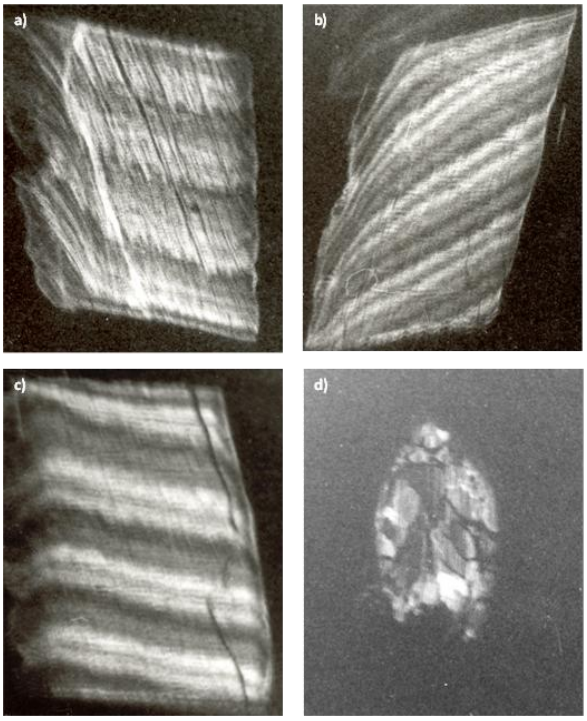


Fig. 2 X-ray topograms of W-Mo specimens (longitudial section): a) initial state; b) after 100 thermocycles; c) after 500 thermocycles; d) after 2000 thermocycles (cross section)

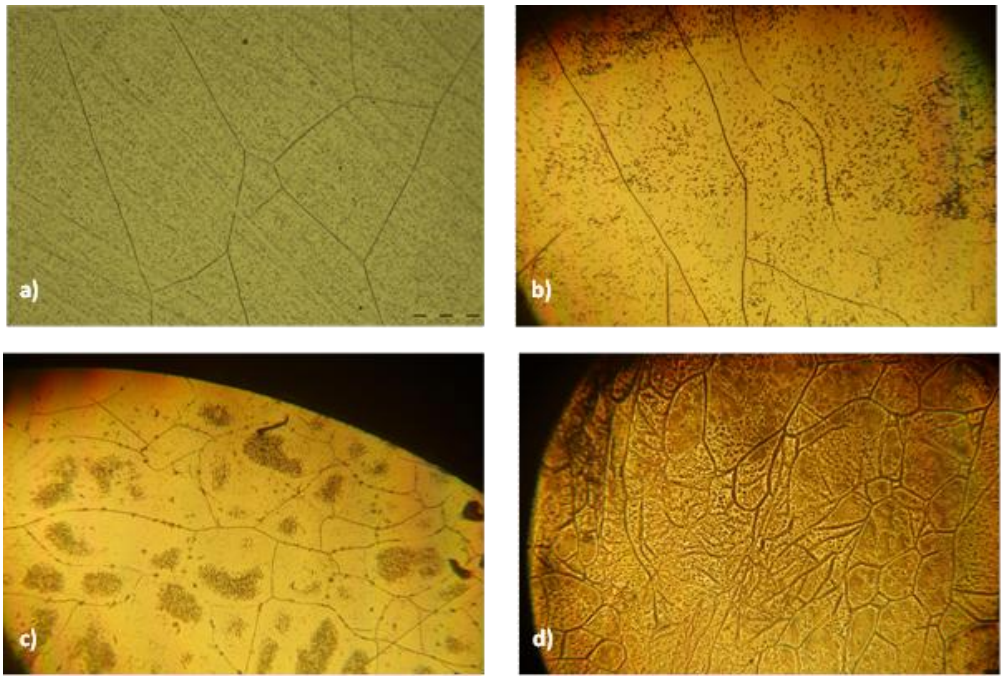


Fig. 3 Microstructure of W-Nb single crystals before a) and b) after 100 thermocycles (mag. 200x); c) after 500 thermocycles (mag. 200x); d) after 2000 thermocycles (mag. 100x)

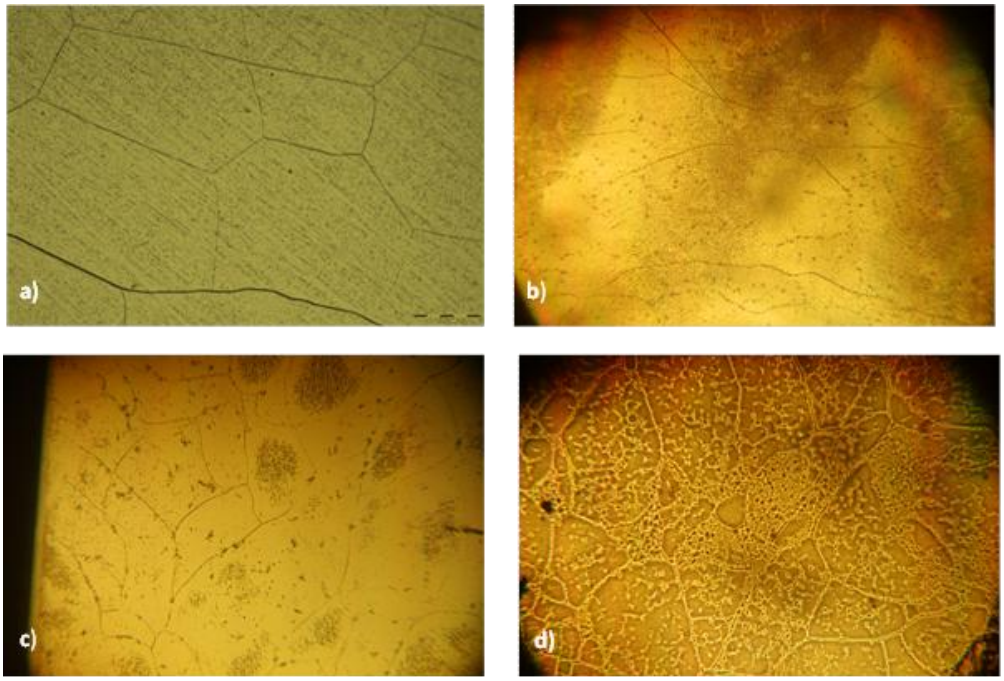


Fig. 4 Microstructure of W-Mo single crystals before a) and b) after 100 thermocycles (mag. 200x); c) after 500 thermocycles (mag. 200x); d) after 2000 thermocycles (mag. 100x)

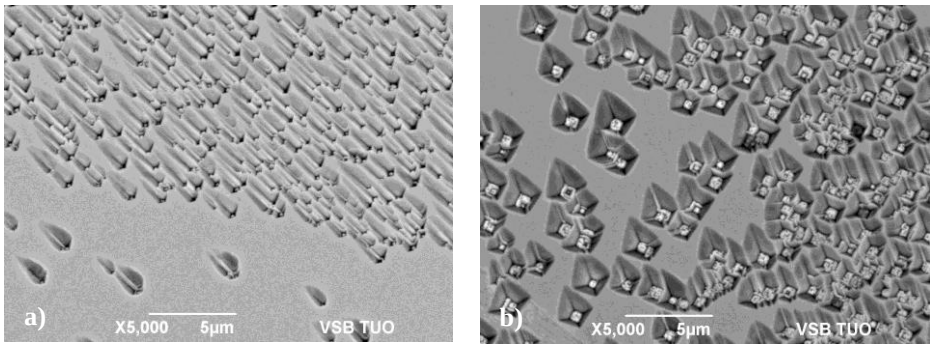


Fig. 5 SEM images of the fine details of etch pits

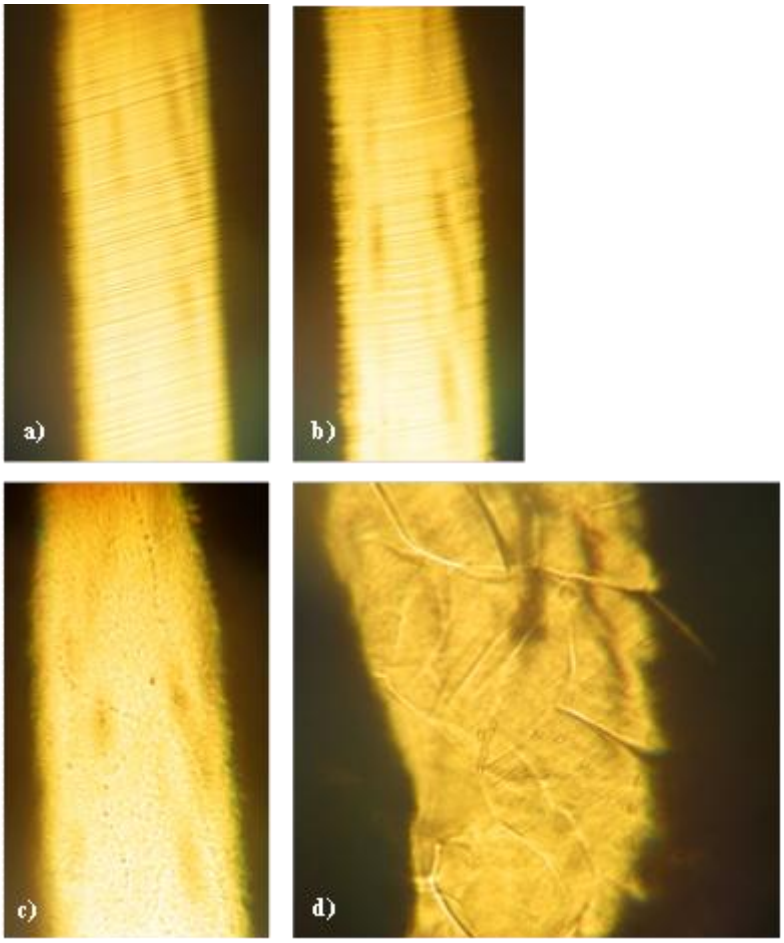


Fig. 6 Surface morphology of W-Mo specimens in the initial state (a) and after 100 thermocycles (b), 500 thermo cycles (c) (mag. 100x) and 2000 thermocycles (d) (mag. 250x)

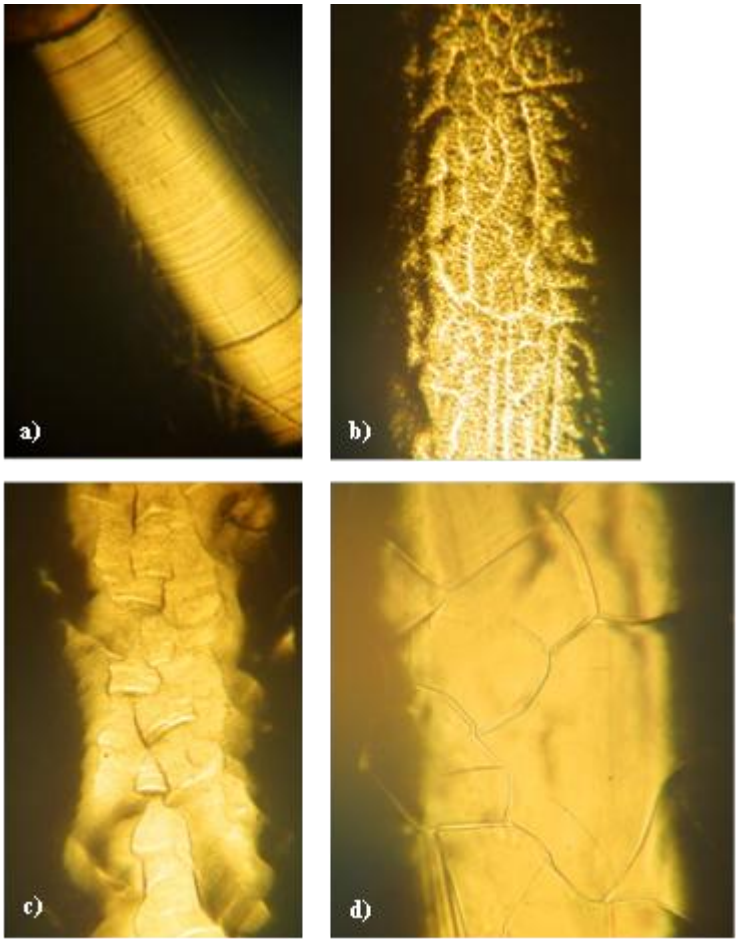


Fig. 7 Surface morphology of W-Nb specimens in the initial state (a) and after 100 thermocycles (b), 500 thermocycles (c) (mag. 100x) and 2000 thermocycles (d) (mag. 250x)