Low-alloyed molybdenum single crystals: preparation, structure and properties

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Abstract. Investigation concerns the method of preparation of low-alloyed molybdenum single crystals directly from molybdenum rods and wire, rod or foil containing the appropriate alloying metal, excluding the stage of pre-fusion of the components in an arc furnace, which is more economical than traditional method. In this way Mo-W, Mo-Ta (1.5 wt.% alloying elements of each) and Mo-Re (2 and 3 wt.%) single crystals were prepared by electron-beam zone melting. Authors discuss in more detail the structure and structural parameters of prepared single crystals. Some structural features of Mo-2 wt.% Re and Mo-3 wt.% Re single crystals are explained. Moreover the coefficient thermal linear expansion (CTLE) was measured for Mo-Re single crystals. As shown the proposed method ensures the preparation of single crystal even in single stage melt. The structural imperfections may be removed by following re-melting.

1. Introduction

High purity and structure perfection made the metallic single crystals the indispensable object of basic research. Single crystal of refractory metals became the real materials of modern engineering thanks to their unique complex of physical-mechanical and chemical properties [1-3]. Their plasticity, low gas evolution, increased resistance during thermal cycling, exposure to radiation, resistance to effects of plasma, vapour and molten alkali metals allows their use in devices of lighting, electrical, electro-vacuum industries and in nuclear power engineering. Anisotropy and alloying of metallic single crystals offers ample scope for control of their properties [1]. Refractory metals of VA and VIA group, rhenium are characterized by the existence of broad region of solid solution between them [3], that is why the alloying offers large opportunities for obtaining of the alloys single crystals with optimal properties. It is established that alloy single crystals with high content of alloying elements are characterized by high strength but low ductility, and this fact results in problems in commercial use. However mutual alloying of molybdenum by tungsten and tungsten by molybdenum in range of concentration smaller than 1-1.5 wt.% harden the metallic matrix, while the ductility remains at sufficient level [1, 2]. Moreover in accordance to “Re-effect” [1] rhenium increases as strength as the plasticity of alloys. So it is extend the range of application for the low-alloyed molybdenum and other refractory metals single crystals. At present, all the traditional technologies for production of single crystals include the pre-manufacturing production of alloy ingots. This method is not only prolonged, but also associated with the introduction of a mixture of alcohol and glycerol and with the contamination of prepared alloy by carbon. The aim of this work is to obtain and to investigate the low-alloyed molybdenum single crystals: Mo-W, Mo-Ta (up to 1.5 wt.%) and Mo-Re (2 and 3 wt.%), using a more economical and energy-efficient method, i.e. directly from molybdenum bars and
alloying metal in form of wire, rod or foil. So the traditional production of starting ingots for melting is excluded.

2. Experiment

Molybdenum rods after second re-melting (99.99%) with diameter of 9 mm, Ta- and W-wire (Ø 1 mm), Re-rod (Ø 5 mm) and (Mo-47 wt.% Re) alloy (foil, $h = 0.5$ mm) were used as starting materials. High pure and perfect [100] Mo single crystal were used as a seed crystal. For preparation of single crystals the molybdenum rods were turned to a diameter of 8 mm. Further the special recess of $1 \times 1$ mm was grooved with milling cutter along the entire length of the rod. In accordance to composition of preparing alloy the alloying metal (tantalum-, tungsten -wire, rhenium rods or (Mo-47 wt.% Re) alloy — foil) was put into this groove and the groove was pressed with a molybdenum wire. Such bars were melted using the electron - beam zone installation YUB2-3B (Japan). Parameters of melting are the next: voltage 10 kV-12 kV, electron beam current 250-350 mA, vacuum $>8 \times 10^{-4}$ Pa, velocity 2 mm/min. [110] Mo-1.5 wt.% Ta, [110] Mo-1.5 wt.% W, [100] Mo-2 wt.% Re and [100] Mo-3 wt.% Re single crystals were prepared by above explained technology. Composition of impurities in single crystals was determined by method of quantitative spectral analysis, and the content of alloying elements was determined by chemical method. Macrostructure of the surface was revealed by etching of ingot surface in mixture of concentrated acetic and sulphuric acids in ratio of 7:1. Etching parameters are 30 V and 3-5 A. The cylinders were cut perpendicularly to the growth axis from all the grown single crystals by electro-erosion cutting. These samples were subjected to mechanical polish and electro-polish in solution of above composition. The electro-polish was necessary to remove the work-hardened surface layer deformed during the cutting and grinding of samples. Optical light microscope (OLM) was equipped with digital camera. Substructure of single crystals was revealed by electro-polishing in a mixture of sulphuric and acetic acids (1:7 by volume) at low current densities. The crystallographic orientation and disorientation sub-grains of single crystals were determined by x-ray methods (Laue, Berg-Barrett and X-ray diffraction by DRON-7). CTLE was determined by high-velocity quartz thermal dilatometer DL-1500 RH.

3. Results and discussion

The composition of impurities in law-alloyed molybdenum single crystals is on average the following ($10^{-3}$ wt.%): 0.1 C, 0.01 O, 80 W, 5.0 Fe, 2.0 Si, 7.0 Mn, 19 Cr. In prepared single crystals a clear tendency is evident of efficient removal of carbon (by 2 order of magnitude), and of other elements (by several times), which is consistent with our previous studies [4]. An inhomogeneous distribution (locally) of alloying elements was found in the central part of crystals and on the periphery. It may be eliminated by subsequent re-melting.

At investigation of macrostructure after etching of single crystal surface the alternating light and dark strips were observed as a result of various etching of edges. Moreover some sub-grains off the first order were also observed visually without additional magnification.

The results of investigation of W- and Ta-containing single crystals by X-ray topography and optical light microscopy are shown in Table 1 and figure 1, 2. The single crystals are characterized by minor disorientation of sub-grain boundaries of the furst order and large-block structure of ingots.

The Mo-2 wt.% Re and Mo-3 wt.% Re alloy single crystals contain the alloy element about by twice as many as W- and Ta-containing molybdenum single crystals and are characterized by enough perfection, but Mo-2 wt.% Re single crystal is more perfect (figure 3).

The substructure of this single crystals (figure 4) is identical to substructure of Ta- and W-alloyed single crystals (figure 2) and is characterized by minor disorientation of sub-grain boundaries of the first order and large-block structure of ingots.

However the substructure defects in prepared single crystals are different. In Ta- and W-alloyed single crystals pores were observed (locally) (figure 2c), in Re-alloyed of that inclusions were revealed on near-surface layer (figure 4c, d). The Mo-2 wt.% Re ingot contains inclusion twice as large and
twice as many as a Mo-3 wt.% Re of that. Probably the method of placing of alloying metal in process of the forming of starting bar before the melting is responsible for origin of inclusions.

**Table 1.** Structure parameters of low-alloyed molybdenum single crystals

| Composition          | Angle of disorientation of sub-grains, deg. | Size of sub-grains, mm, | Crystallographic orientation of the grown axis, (according to Laue pattern) |
|----------------------|---------------------------------------------|--------------------------|--------------------------------------------------------------------------------|
| Mo-1,5 wt.% W        | 0,4                                         | 0,2-0,3                  | 3° from [110]                                                                  |
| Mo-1,5 wt.% Ta       | 0,4                                         | 0,2-0,3                  | 7,5° from [110]                                                                |

**Figure 1.** X-ray topograms of Mo-1,5 wt.% Ta single crystal with the growth axis orientation [110] at the beginning (a) and at the end (b) of the ingot.

**Figure 2.** Substructure of Mo-1,5 wt. %Ta single crystal at the beginning of ingot: a — area of large block in the centre of the sample; b — fine sub-grain on the periphery; c — pores.
Figure 3. [100]-orientation and scattering of Mo-2 wt.% Re (a, plane of cut is 25° relative to [100]) and Mo-3 wt.% Re-single crystals (b, plane of cut is 14° relative to [100]). Maximum radial and azimuthal angles of scattering are no excess 3° for (a) and 4.5° and 7.5° accordantly for (b).

Figure 4. Substructure of (Mo-2 wt.% Re) single crystal at the beginning of ingot: a — area of large block in the centre of the sample; b — fine sub-grain on the periphery; c — large and small inclusions on the near surface layer. d — Inclusions on the near surface layer of Mo-3 wt.% Re single crystal.

The coefficient thermal linear expansion (CLTE) were measured for Mo-Ta and Mo-Re single crystals. It was be determined that only Re-alloyed single crystals is characterized by CTLE which is identical to CTLE of glass (figure 5) and can be used as construction material for welding with glass in electronic industry.
4. Conclusion
More economical with comparison of traditional method and energy saving technology was designed for preparation of low-alloyed molybdenum single crystals directly from molybdenum bars and alloying material in form of wire, rod or foil containing the corresponding alloy element; the stage of pre-fusion in an arc furnace is excluded. To understand the appearance mechanism of inclusions in Re-alloyed molybdenum single crystals and to avoid their formation it is necessary to carry out additional experiments.

Acknowledgements
The work was carried out according to the state task No. 075-00746-19-00.

5. References
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Figure 5. Curves of $\Delta L/l_0$ for Mo-3 wt.% Re alloy single crystal with curve of glass (green).