Manufacturing features, structure, and properties of high-purity Mo-Re thin sheets

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Abstract. Manufacturing features, structure and properties of low-alloyed molybdenum sheets 0.5 mm thick made from the experimental Mo-3 wt.% Re single crystal are described and discussed in the present work. The developed technological scheme includes warm rolling of the initial ingot at a temperature of 1150 °C, with heating in the argon protective atmosphere, subsequent annealing at 850 °C for 2/3 h in a vacuum, no less than 1·10⁻³ mmHg, cold rolling at a temperature of 400 °C, and post-deformation annealing at 800 °C for 1/2 h. The results of microstructure analysis, physical and mechanical studies show that thin sheets are characterized by simultaneously high strength and plasticity, as well as the required temperature coefficient of linear expansion (TCLE), necessary for bonding with a glass by a thermo-compression welding. Obtained results reveal perspectives for the development of the application of thin Mo-3 wt.% Re sheets in vacuum engineering for the vacuum-tight metal-glass parts.

1. Introduction

Currently, for the manufacturing of various devices and items, used in electro-vacuum engineering, in particular in automation units, the TsM-2A-molybdenum alloy is one of the most commonly used alloy, that provides a unique combination of physical and chemical properties [1-5]. However, application of this alloy has some limitations. For example, bonding of a glass with the TsM-2A alloy requires using a soldering (at 1200 °C) instead of more economical thermo-compression (diffusion) welding (at 800 °C) [6-7]. In the previous studies, it was shown that high-purity Mo-Re alloys provide required functional characteristics and may be bonded with a glass by a thermo-compression welding, accordingly they have a high potential of being used instead of TsM-2A molybdenum alloy [8]. Therefore the aim of the study consist in the growing of molybdenum-rhenium (3 wt.% Re) single crystal, development of the technological regimes for manufacturing of thin sheets 0.5 mm thick and study of the microstructure, physical and mechanical properties of initial ingots and finished sheets, intended for application in vacuum engineering for the vacuum-tight metal-glass parts.

2. Materials and methods

The Mo-3.0 wt.% Re single crystal ingots were grown by the method of electron-beam zone melting from pure initial components: perfect molybdenum single crystals and pure Re wire. Melting was carried out with three zone steps, a velocity of 2 mm/min and a vacuum of 5·10⁻⁴-8·10⁻⁵ mmHg. After melting ingots were subjected to the homogenizing annealing at a vacuum of 1·10⁻³ mmHg at a temperature of 1600 °C for 3 h with the cooling in furnace at a rate of 10 C/min.
For the manufacturing of thin sheets with a thickness of 0.5 mm warm and cold rolling at the temperatures of 1150 °C and 400 °C on the duo and quarto rolling mills with a diameter of rolls 320 and 110/220 mm, respectively, were used. Microstructure was studied by NEOPHOT-2 optical light microscope. Before analyses, for the structure revealing, samples were electro-polished at a voltage of 30 V and a current of 3-5 A in the solution of concentrated acetic and sulfuric acids with the ratio of 7:1. The crystallographic orientation and subgrains disorientation of single crystals were determined by X-ray methods on the DRON-7 x-ray diffractometer. Analysis of oxygen and nitrogen content was carried out on a Leco TC-600 analyzer. The measurement technique includes reductive melting in a graphite crucible in a helium atmosphere. Oxygen content is defined by the detection of the amount of emitted CO₂ gas by an infrared absorption, nitrogen content defined by the detection of thermal conductivity. The thermal coefficient of linear expansion (TCLE) was determined by the high velocity quartz thermal dilatometer DL-1500 RH. The measurements were carried out at the temperature range of 20-800 °C on samples with the size of 4 mm², cut from the sheets in the longitudinal and transverse directions. Heating and cooling of the samples were performed with a rate of 20 K/min in a quartz cell in a furnace with infrared heaters. The mechanical properties were determined at a room temperature by the uniaxial tensile tests, using universal tensile machine INSTRON 3382 with a deformation velocity of 1 mm/min.

3. Results and discussion

3.1. Features of rolling procedure
The initial shape of melted ingots is irregular because of the features of electron-beam zone melting method, the diameter fluctuates from 24 mm to 20 mm. Therefore, before the deformation treatment, it is necessary to cut the side planes of the ingot for obtaining the regular shape and, consequently, eliminate the influence of deformation inhomogeneity along the height and width of the workpiece. During the rolling process of Mo-based alloys deformation homogeneity is critically important because of high probability of delamination tendency of finished sheets because of appearance of internal cracks after deformation of workpieces with irregular profile. After cutting of the side planes the size of samples before rolling equals 20×22×60 mm. According to the previous experience of obtaining thin sheets from Mo-based alloys [8], in order to exclude the possibility of delamination, that was observed in a certain number of finished sheets, deformation temperature was increased from 650 to 1150 °C, providing the possibility of corresponding increase of relative strain degree from 5-10 % up to 30-35 %. Avoiding of intensive oxidation, heating of samples before the deformation treatment, as well as intermediate heating, were carried out in an argon protective atmosphere. Rolling from the thickness of 20 mm to 2.1 mm was carried out in 7 passes with the decrease of relative strain degree from 30-35 % at the first three passes to the 15-25 % at the last four passes. For the decrease of properties anisotropy in the finished sheets, which is formed because of the monotonicity of deformation during the rolling process, samples were turned at a 90-degree along the longitudinal axis at the fifth pass. The billets obtained after rolling on the duo rolling mill were cut into several workpieces with the length of 50-70 mm and cleaned from a scale and a gas-saturated layer by electro-polishing in an acid solution: CH₃COOH+H₂SO₄ with the ratio of 7:1. After polishing, annealing in vacuum of 1·10⁻³ mm Hg at a temperature of 850 °C for 40 min with cooling at a rate of 10 °C/min was performed for removing of the deformation hardening before the subsequent rolling treatment. Workpieces 2.0 mm thick was processed by cold rolling on a quarto rolling mill to a final thickness of 0.5 mm at a temperature of 400 °C with a relative strain degree of 5-10 % for pass. Post-deformation annealing of finished sheets at a temperature of 800 °C for 0.5 h in a vacuum of 1·10⁻³ mmHg was performed to relieve the internal stress before implementation of sheets in the manufacturing process of the end items.

3.2. Microstructure analyses
Results of crystallographic orientation study of the initial melted single crystal ingots of Mo-3 wt.% Re is shown in Figure 1.
According to the results of X-ray studies, the direction of the growth axis of obtained single-crystal ingots is [100]. Microstructure images of the initial ingots, obtained by optical light microscopy, are shown in Figure 2. Microstructure of the sheets, after warm rolling to 4.0 and 2.1 mm thick and cold rolling to the final 0.5 mm thick are shown in figures 3 and 4, respectively.

Figure 1. [100]-orientation and scattering of Mo-3 wt.% Re. Maximum radial and azimuthal angles of scattering are 4.5° and 7.5° respectively.

Figure 2. Microstructure of initial single crystal ingots in a transverse direction: x50 (a), x250 (b).

Figure 3. Microstructure of sheets 4.0 (a) and 2.0 mm (b, c) thick in longitudinal direction: x50 (b), x250 (a, c).
The study of the microstructure shows the process of structural transformation of the initial single-crystal structure, consisting of subgrains (Fig. 1), into a polycrystalline fibrous structure (Figure 3, 4) after warm and cold rolling. As the result of plastic deformation, the first order subgrains are shattered, stretched along the rolling direction and misoriented by torsion around same direction. The tortuous subgrain boundaries are straightened and located in accordance with the effective slip planes in the corresponding directions. At the same time, the subboundaries that do not correspond to these directions are gradually blurred and the internal stresses increase. Finally, the monocristalline structure transforms into a polycrystalline directional structure (texture).  

Comparative analysis of the impurities content in the initial single crystal ingots and finished sheets 0.5 mm thick reveals a high-purity of both ones, which indicates the absence of contamination in the process of sheets production by developed technological regimes because of chemical etching of the surface layer of the sheets after warm and cold rolling, as well as annealing in vacuum of at least $1 \times 10^{-3}$ mmHg. In the finished sheets the content of impurities remains on the almost the same value as compared with the initial ingot: the oxygen content, (wt.%) – 0.0006; the nitrogen content, (wt.%) – less than 0.001; the content of iron, silicon, manganese and chromium, measured by mass spectrometry, wt.% – 0.005, 0.002, 0.007 and 0.019, respectively.

3.3. TCLE

The results of dilatometric tests in the temperature range from 20 to 1000°C are shown in Figure 5.

Practically full agree of presented above temperature dependences $\Delta L/L_0$ evidences, that finished Mo-3 wt.% Re sheets characterized by required TCLE and are applicable for bonding with a glass by a thermo-compression welding.
3.4. Mechanical properties

Representative deformation diagrams of samples cut from Mo-3 wt.% Re sheet transversely and along the rolling direction are shown in Figures 6 and 7, respectively.

![Figure 6](image1.png)  ![Figure 7](image2.png)

**Figure 6.** Typical tensile diagrams of the sample, cut transversely the rolling direction  **Figure 7.** Typical tensile diagrams of the sample, cut along the rolling direction

Mechanical properties of the thin Mo-3 wt.% Re sheets 0.5 mm thick are shown in Table 1. Flat samples were cut along and transversely the rolling direction.

| No. | Rolling direction | $L_0$, mm | $F_0$, MM$^2$ | $\sigma_{0.2}$, MPa | $\sigma_{v}$, MPa | $\delta$, % |
|-----|-------------------|-----------|---------------|-------------------|-----------------|-------------|
| 1   | transverse        | 1.40      | 13.49         | 540               | 727             | 12          |
| 2   | transverse        | 1.40      | 13.48         | 433               | 709             | 15          |
| 3   | transverse        | 1.40      | 13.49         | 503               | 661             | 25          |
| 4   | transverse        | 1.47      | 13.53         | 691               | 691             | 18          |
| 5   | longitudinal      | 1.54      | 13.51         | 541               | 748             | 18          |
| 6   | longitudinal      | 1.55      | 13.51         | 774               | 774             | 26          |
| 7   | longitudinal      | 1.57      | 13.51         | 541               | 762             | 25          |
| 8   | longitudinal      | 1.54      | 13.51         | 444               | 761             | 19          |

Thus, alloying with Re in the amount of 3 wt.%, allows increase simultaneously both the strength and plasticity of the sheets, which can be explained by the so-called “rhenium effect” [9].

4. Summary

Thin sheets 0.5 mm thick were obtained from Mo-3 wt.% Re single crystal ingots by the technological scheme, included warm rolling of initial ingot at a temperature of 1150 °C, with heating in argon protective atmosphere, subsequent annealing at 850 °C, 2/3 h in vacuum, not lower than 1·10$^{-3}$ mm Hg, cold rolling at a temperature of 400 °C, and post-deformation annealing at 800 °C, 1/2 h. The results of microstructure analysis, physical and mechanical studies showed that thin sheets are characterized by simultaneously high strength and plasticity, as well as the TCLE, required for bonding with a glass by a thermo-compression welding. Obtained result reveals perspectives for development of the application of thin Mo-3 wt.% Re sheets in vacuum engineering for the vacuum-tight metal-glass parts.
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