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# Single-crystal tungsten-based alloys with molybdenum and rhenium

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**Abstract:** Single crystals of ternary W-based alloys with 2% Re and less than 7% Mo have been grown for the first time at the Baikov Institute of Metallurgy and Materials Science RAS. Plasma arc melting allowed us to effectively purify the single crystals from a number of impurities. According to mass spectrometric analysis for 70 elements, the total content of impurities does not exceed 0.063%. It was found that, as the Mo content increases, the size of first-kind subgrains decreases and their mutual misorientation increases. In the W-based alloy with 2.3% Re and 6.7% Mo, no first-kind subgrains are observed, whereas second-kind subgrains are elongated along the growth direction. In this case, their total misorientation is well below that in the other low-alloy single crystals.

Single-crystal of binary tungsten-based alloys with rhenium were prepared by electron-beam zone melting (1% Re, mass fraction) and plasma arc melting (2%Re, 10%Re, 25%Re (mass fraction)). It was found that the low-alloyed (1%-2% Rh (mass fraction)) W-based alloys are characterized by a rather perfect single-crystal structure and misorientations of first- and second-kind subgrains of 20-50′ and 10-40′, respectively. Sections with the coarse-grained structure are observed in ingots of the alloy with 10% and 25% (mass fraction) Rh; in the alloy with 25% Rh, such structure is observed immediately from the seed.

A device for measuring the liquidus and solidus temperatures of refractory metallic alloys has been designed. The liquidus temperatures of ternary single crystals (W-Mo-Re) have been measured.

The studied single crystals, owing to their purity and high stability of the structure and properties, are widely used in electronics, electrical engineering, and analytical devices for various purposes.

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## 1 Introduction

Alloys of the W-Mo-Re and W-Re systems exhibit a unique combination of physical, chemical, and mechanical properties. These alloys are multifunctional materials that can operate under severe conditions [1]. The potentialities of the alloys can be widened by optimizing their chemical compositions and structures. The preparation of the alloys in the region of substitutional solid solutions in the form of single crystals al-

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lows one to increase their physical and mechanical properties and time-temperature stability.

Wide experience in single crystals of binary alloys of the W-Mo and W-Re systems with Re content more than 5wt% has been accumulated to date[2]. In this paper, we are the first to present experimental results on the preparation of W-Mo-Re and W-Re (in the range of low Re concentrations) single-crystalline alloys and their structure. The melting temperatures (liquidus temperatures) of the alloys were measured by a technique designed by us. It allows accurate determination of the solidus and liquidus temperatures. Based on the experimental data on the phase equilibria of the alloys and our previous data on the W-Mo-Re system alloys [3], we obtained reliable data on the equilibrium coefficients of distribution $K$ of molybdenum and rhenium in tungsten. The distribution coefficient $K$ is an important characteristic of solidification; it determines the effect of purification reached upon solidification and the uniformity of an alloy-component distribution. It is important to know the distribution coefficients for ternary and multicomponent systems. Calculation and experimental procedures for the determination of the parameters are now being developed[4].

## 2 Experimental

In this work, we prepared single crystals of W-based alloys of six compositions (%, mass fraction): < 0.05 Re and < 0.005 Mo, 2.0 Re and 0.03 Mo; 1.9 Re and 0.20 Mo; 2.0 Re and 1.04 Mo; 2.0 Re and 2.82 Mo, and 2.3 Re and 6.73 Mo (samples I, II, III, IV, V, and VI, respectively). The alloys are substitutional solid solutions. Single crystals of the binary W-Re system with low (1%, 2% (mass fraction)) and high (10%, 25% (mass fraction)) rhenium content also were prepared. The W-1%Re (mass fraction) single crystal was prepared along the growth direction [100] using electron-beam zone melting. The other crystals were prepared by plasma arc melting using a [110] seed. In all cases, the growth rate was equal to 1.5-2 mm/min. The prepared single crystals were 11-16 mm in diameter and 150-160 mm in length.

According to mass-spectrometric analysis (performed for 70 elements), the total content of impurities (such as Na, Mg, Si, Al, Fe, K, Ca, P, Cu, Mn, V, and Co) is less than 0.063%; the content of each impurity mentioned above does not exceed 0.1-0.2 ppm. The technique and optimum conditions of crystal growth, as well as the starting metals, are discussed in our previous work[5].

All single crystals (samples I-VI) were grown at a rate of 1.5 mm/min using plasma arc melting [5] and single-crystalline seeds; the [100] crystallographic direction of the seeds coincided with the growth axis of the single crystals. Melting was performed in a plasma-forming gas atmosphere consisting of 85%Ar (vol. fraction) and 15%He (vol. fraction) at an excess pressure of 1.96 kPa.

Single crystals 10.5-12.5 mm in diameter and 150 mm in length were grown. The growth axis of the single crystals coincides with the [100] crystallographic direction.

The Mo and Re contents and the contents of associated impurities in the single crystals were determined by mass-spectrometric analysis on an EMAL-2 double-focusing mass spectrometer (PO Elektron, Sumy city). The metallographic study of W-Re single crystals was performed before and after the etching in a solution 10% NaOH + 10% $K_3Fe(CN)_6$ + 80% $H_2O$ using cross-sections cut from final portions of ingots.

To study the fine structure of the single crystals grown and to determine the size and subgrain misorientation, we used X-ray reflection-mode topography (a modified Berg-Barret technique) and $K_\alpha$ and $K_\beta$ radiation produced by a sharp-focus X-ray tube (the focus diameter is 40-50 $\mu$m). To determine the substructure parameters and orientation of the W-Re single crystals, we used an X-ray diffraction reversal-reflection

mode (Laue patterns). The feature of the mode consists on the use of a sharp-focus X-ray radiation source that allows one to obtain Laue reflections with a high degree of substructure resolution (Schulz reflection method). Along with the single-crystal orientation determination, we performed the qualitative and quantitative analyses of their substructure. We used "white" radiation produced by a BSV-7 sharp-focus type equipped with a copper anode.

To measure the melting temperature (liquidus temperature) of the single crystals under study, we designed a vacuum water-cooled chamber equipped with powerful current leads and a unit for the location, fixation, and alignment of samples within the working chamber between the current leads. The samples were heated with a direct current of 300-500 A produced by a power supply. The working chamber was filled with an inert gas (argon or helium) to an excess pressure of 49-59 kPa (0.5-0.6 kg/cm$^2$). Visual monitoring of the heated samples was performed using a window in the working chamber and an optical system (placed outside the chamber) that projects images on a screen. The temperature was measured using another (second) window of the working chamber that is placed at an angle of 90° with respect to the first window. The second window was located in front of a hole (made in a sample) that imitates blackbody upon measuring.

A VIMP-015M optical pyrometer was used as a measuring instrument.

When measuring the melting temperature by the optical pyrometer, we compare the color of heated sample and that of a filament. In this case, the errors related to the optical losses at the chamber windows (which can be soiled with evaporated metals), inadequacy of the blackbody model, etc., are inevitable. Because of this, the pyrometer readings were reduced to the true values of the melting temperature measured for standards, such as single-crystalline samples produced from the starting high-purity tungsten, rhenium, and molybdenum. This allowed us to refine the high-temperature (2500-3500 ℃) calibration of the pyrometer.

Samples as rods 25 mm in length and 2 @ 2 mm in section were spark-cut from the single crystals grown. A hole 1.8-1.9 mm in length and 0.4-0.5 mm in diameter was spark-cut at the center of one of the lateral faces of each sample. With this hole, the brightness of sample radiation upon heating is close to that of blackbody.

To refine the pyrometer calibration, along with the single crystals of tungsten and the tungsten-based alloys, we also used analogous (in size) samples of molybdenum ($T_m$ = 2620℃) and rhenium ($T_m$ = 3180℃) single crystals.

## 3 Results and discussion

The parameters of the single-crystalline substructure, such as the size of first- and second-kind subgrains and their mutual misorientation (Fig. 1), were determined using X-ray topography. Table 1 shows the data obtained.

As the molybdenum content in the W-based single crystals with~2% Re increases, the mutual misorientation of the first-kind subgrains increases monotonically and the subgrain size decreases. In this case, the amount of the second-kind subgrains increases and their misorientation decreases only slightly. The subgrains are elongated along the growth axis. The dislocation density increases from $5\times10^6$cm$^{-2}$ to $8\times10^7$ cm$^{-2}$.

**Table 1 Characteristics of the substructure of the W and W-Mo-Re single crystals**

| Sample | Subgrain size, mm | | | | Subgrain misorientation deg | | | |
|---|---|---|---|---|---|---|---|---|
| | Longitudinal section | | Transverse section | | Longitudinal section | | Transverse section | |
| | 1st-kind | 2nd-kind | 1st-kind | 2nd-kind | 1st-kind | 2nd-kind | 1st-kind | 2nd-kind |
| I | 1−1.5 | 0.3−0.4 | 1−3 | 0.13−1.5 | 0.3−0.6 | 0.03 | 0.1−0.25 | 0.1 |
| II | 0.7−1.2 | 0.3−0.4 | 1−3 | 0.1−0.5 | 0.6−1.5 | 0.04 | 0.15−0.4 | 0.1−0.5 |
| III | 1−2 | 0.15−0.3 | 1−3 | 0.1−0.5 | 1−3 | 0.04 | 0.15−0.4 | 0.1−0.15 |
| IV | 0.8−1.5 | 1.15−0.3 | 0.5−1 | 0.1−0.3 | ~1.5 | 0.04 | 1.5−1 | 0.1−0.15 |
| V | 0.3−1 | 0.1−0.3 | 0.5−1 | 0.1−0.3 | 1−2.5 | 0.04 | 0.5 | 0.2 |
| VI | − | 0.1−0.3 | − | 0.1−0.3 | − | 0.5−1 | − | 0.25 |

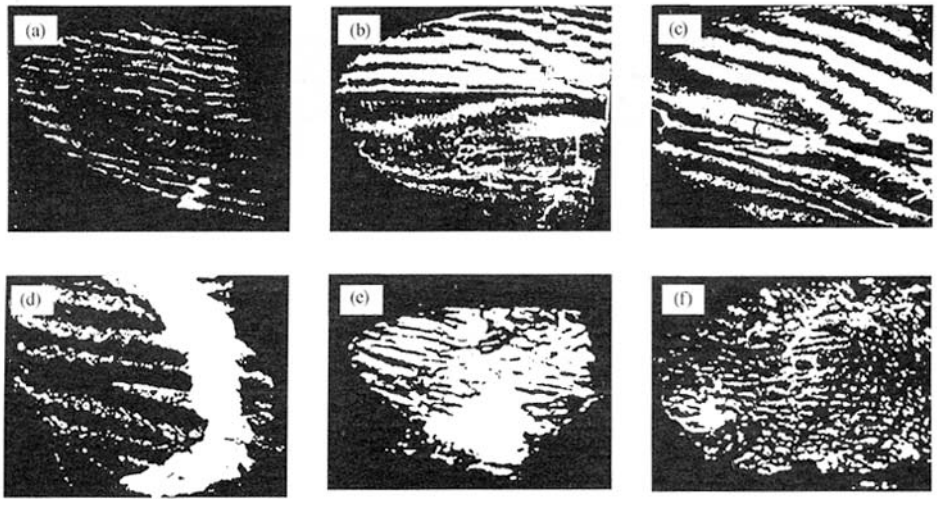


**Fig. 1** X-ray topographs of samples I-VI of the W-Mo-Re single crystals taken in the [200] reflection. The (100) plane is perpendicular to the growth direction

According X-ray diffraction and metallography data, the W+1% Re (mass fraction) single crystal produced by electron-beam zone melting is characterized by relatively perfect single-crystal structure (Fig. 2). The average misorientation of first- and second-kind subgrains is 20-40′and 5-10′, respectively. The perfection of the substructure of the W+2% Re (mass fraction) produced by plasma-arc melting is slightly worse than that of W+1%Re(mass fraction), i.e., the average misorientation of first- and second-kind subgrains is 30-50′and 10-20′, respectively. The density of etching pitches for both single crystals is virtually the same and equal to $1\times10^{6}$ $cm^{-2}$. The W-Re single crystals with the high rhenium content are substantially worse than the low-alloyed single crystals. The W+10% Re (mass fraction) has a developed substructure, i.e., the misorientation of first-kind

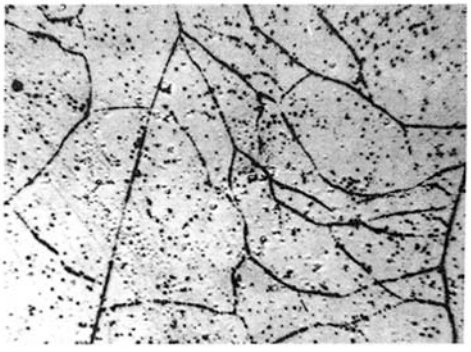

**Fig. 2** Substruct(x500), optical microscopy of the W-2%(mass fraction) Re single crystal

subgrains is several degrees; we failed to determine the misorientation of second-kind subgrains. The W+25% Re (mass fraction) is characterized by the presence of sections with the polycrystalline structure (the grain size is 0.05-0.5 mm).

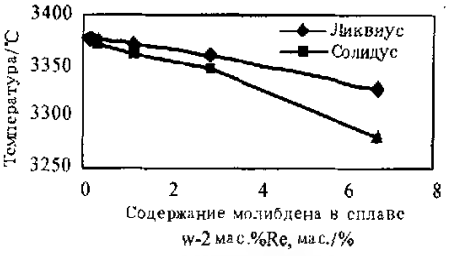


**Fig. 3** Liquidus and solidus (tentative) of the W-Mo-Re alloys with 2% Re

Figure 3 shows the melting temperature (or the liquidus temperature $T_L$) of the single-crystalline W-Mo-Re alloys with 2 % Re. It is seen that the liquidus temperature $T_L$ decreases slightly as the Mo content increases to~7%: the liquidus temperatures $T_L$ of samples I, II, III, IV, V, and VI are equal to 3380, 3380, 3377, 3374, 3362, and 3328℃, respectively.

The solidus temperature ($T_S$) was only determined for alloy VI ($T_L$= 3328℃); it is equal to 3280℃. Thus, the difference between the $T_L$ and $T_S$ temperatures of the alloy is 50℃. Because of the inadequate sensitivity of the optical technique used for the measuring temperature, we failed to determine the solidus temperatures of the other single-crystalline alloys. The W-based alloys containing less than 7% Mo are characterized by very narrow $T_L$-$T_S$ temperature ranges.

## 4 Conclusions

(1) Single crystals of ternary W-based alloys with 2% Re and less than 7% Mo have been grown for the first time. Plasma arc melting allowed us to effectively purify the single crystals from a number of impurities. According to mass spectrometric analysis for 70 elements, the total content of impurities does not exceed 0.063 %.

(2) It was found that, as the Mo content increases, the size of first-kind subgrains decreases and their mutual misorientation increases. In this case, the dislocation density increases from $5\times10^6$ to $8\times10^7$ $cm^{-2}$. In the W-based alloy with 2.3% Re and 6.7% Mo, no first-kind subgrains are observed, whereas second-kind subgrains are elongated along the growth direction. In this case, their total misorientation is well below that in the other low-alloyed single crystals.

(3) The W-based single crystal with the low (1% and 2%, mass fraction) and high (10% and 25%, mass fraction) rhenium contents were produced by electron-beam zone and plasma arc melting, respectively. The low-alloyed single crystals are characterized by highly perfect structure, i.e., the misorientation of first- and second-kind subgrains is 20-50′ and 5-20′, respectively.

(4) A device for measuring the liquidus and solidus temperatures of refractory metallic alloys has been designed. The liquidus temperatures of all grown single crystals and the solidus temperature ($T_S$= 3280℃) of the alloy with the maximum contents (2.3% Re and 6.7% Mo) of alloying elements have been measured. The difference between the liquidus and solidus temperatures of the alloy is rather low and equal to 50℃. The method of automated measurement of temperature with a photosensor (developing now) and the improved device for measuring the melting temperature will allow us to obtain the exact values of the solidus and liquidus temperatures.

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