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THE EFFECT OF CRYSTALLIZATION CONDITIONS ON TANTALUM DISTRIBUTION IN MOLYBDENUM AND TUNGSTEN DURING ELECTRON BEAM ZONE MELTING

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The distribution of tantalum in molybdenum and tungsten single crystals during electron beam floating zone melting under different crystallization conditions was investigated. The performed line chemical analysis of specimens proved creation of tantalum micro segregation, so-called growth striations, which showed themselves on concentration proﬁles as periodically alternating areas with increased and decreased concentrations of tantalum. The existence of these chemical inhomogeneities suggests that stationary conditions of the crystal growth were disturbed during the zone melting, i.e. fluctuations of microscopic rate of growth occurred due to convection in the melt. The determined effective distribution coefficients of tantalum in molybdenum and tungsten approach to calculated theoretical values of the equilibrium distribution coefficient.

Key words: zone melting, tantalum, molybdenum, tungsten, inhomogeneities.

INTRODUCTION

The high purity, chemical homogeneity and structural perfection have an essential influence on properties of single crystals of refractory metals and their low-alloyed alloys. Thanks to a complex of physical, mechanical and chemical properties, they represent prospective materials for contemporary, modern technology, especially as high-temperature structural components [1, 2]. Basic attributes of single crystals, compared to adequate polycrystalline materials, include much more stable structure, lower creep speeds, high strength, good plasticity, the high Young's modulus, wear resistance and high radiation resistance. A negative property of pure single crystals of refractory metals, especially tungsten, is their low plasticity, which limits their processing technology. The plasticity can be improved, to a certain extent, by alloying these metals with other refractory metals, such as Re, Ta, Mo, or Nb, in the amount up to 5 wt.%. However, when preparing single crystals of tungsten and molybdenum-based alloys by the electron beam zone melting technology [1-7], heterogeneous distribution of alloying elements often occurs, which results in structural heterogeneity and the structure sensitive properties [1, 7]. This paper deals with the effect of crystallization conditions on the tantalum distribution in molybdenum and tungsten single crystals during their preparation by electron beam floating zone melting. Effective distribution coefficients of tantalum in molybdenum and tungsten for individual conditions of crystallization and structural characteristics prepared single crystalline alloys are also studied.

EXPERIMENTAL

Single crystals of tungsten and molybdenum-based alloys with the nominal chemical composition of Mo-1,5 at.% Ta and W-1,5 at.% Ta were grown from the melt using the electron beam floating zone melting in a vacuum applying two different zone pass rates - 1 and 3 mm/min. in RMSTC of the VŠB-Technical University of Ostrava. A polycrystalline rod of molybdenum, of 3N purity and 6 mm in diameter, was used as the starting material, in which a longitudinal slot 1 mm wide, 0,7 mm deep and approx. 20 cm long was milled. Little pieces of tantalum sheet enwound with the basic metal wire were inserted into the slot. The rod prepared in this way was placed in the electron beam zone furnace where the alloying itself was performed applying two passes of the molten zone along the whole length of the rod at the speed of 4 mm/min. and then the rod was gradually melted in the given sections at speeds of 1 and 3 mm/min. At the end of each section a molten zone was solidified by a high speed with the objective to prevent diffusion processes and to preserve the admixture concentration in the zone corresponding to the liquid phase. The concentration profiles of tantalum in molybdenum and tungsten on longitudinal sections were obtained using the scanning electron microscope JCXA 733 equipped with EDAX EDAM 3 probe. The X-ray reflection-mode topography (a modified Berg-Barret technique) and Ka and Kb radiation produced by the sharp-focus X-ray tube (the focus diameter

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is 40 - 50 µm) was applied for determination of the angular disorientations of sub-grains in given single crystals [4]. The back-reflection Laue method (X-ray beam perpendicular to the face-end section) was used for determination of their crystallographic orientation. The microstructure study was carried out using the light optical microscope Olympus GX-51 connected with digital camera DP12 and the high resolution field emission gun-scanning electron microscope QUANTA 450 FEG.

RESULTS AND DISCUSSION

Metallographic analysis

Single crystals of refractory metals with bcc-lattice prepared using the EBFZM are characterized by a specific dislocation substructure with the size of sub-grains, which can be divided into three orders of magnitude [1]. The sub-grains of the 1st order are formed due to the growth from the seed crystal, the sub-grains of the 2nd and 3rd orders result from a polygonisation. The microstructure of W-Ta single crystals prepared by the zone pass rate of 3 mm/min is shown in Figure 1 as an example, where the existence of sub-grains of the shape of polygons in cross section and long columnar sub-grains elongated in the direction of growth formed at crystallization is visible.

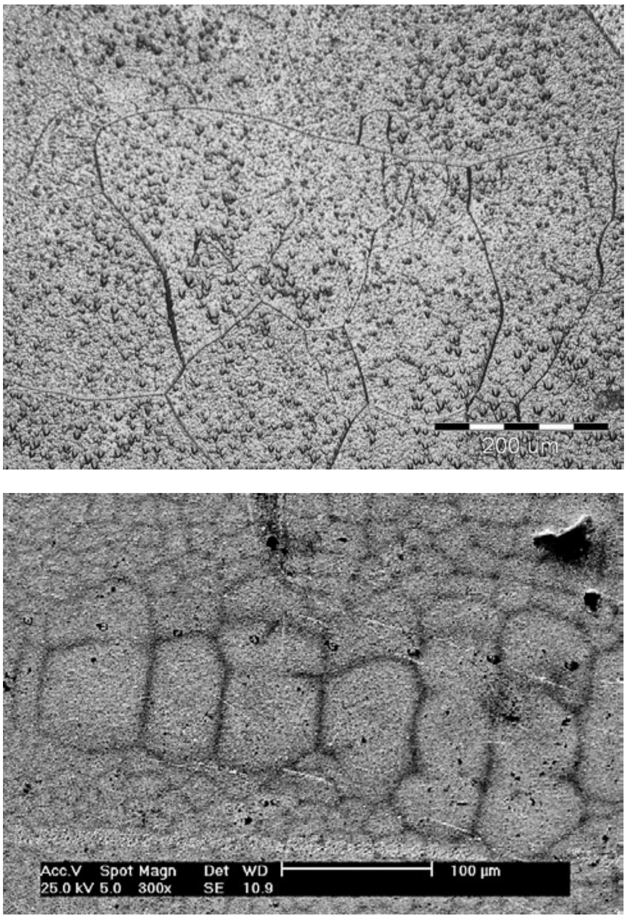

Figure 1 Microstructure of W-Ta single crystals prepared by the zone pass rate of 3 mm/min: a) sub-grains in central part of crystal; b) SEM-BSE image of rapid solidified zone

The crystallographic orientation of all single crystals was 16 - 20° from [100]. According to these investigations the alloying of molybdenum and tungsten by tantalum and increasing zone pass rate resulted in increasing of the etched pits density. It may be identified as the dislocation density at the grain body because it is necessary to count some more dislocations at the 1st sub-grain boundaries, but it is impossible. The dislocation density of these single crystals was about 10^5 to 106 cm^{-2}. The results of the study of crystal structure by X-ray topography are summarized in Table 1. An evident tendency exists of increased angular disorientation of sub-grains with the increasing zone pass rate and the fragmentation of a substructure, where Mo-Ta single crystals are characterized by a more perfect structure, in comparison with W-Ta single crystals. In the area of a solidified zone, a polycrystalline structure with traces of dendritic formations was observed, as well as creation of a cellular-fibrous structure in the places where an increased concentration of tantalum in W-Ta alloys at cell boundaries or increased concentration of tantalum in the case of Mo-Ta alloys in central parts of cells is assumed.

Table 1 Structure parameters of single crystals of tungsten- and molybdenum-based alloys

Sample	Zone pass rate	Disorientation of sub-grains	
		1st order	2nd order
	mm/min	(′)	(′)
W-Ta	1	15-20	~ 5
W-Ta	3	20-25	~ 5
Mo-Ta	1	10-15	~ 5
Mo-Ta	3	15-20	~ 5

Chemical analysis

All the determined concentration profiles of tantalum in molybdenum and tungsten for the given zone pass rates showed an irregular sinusoidal course – see Figure 2. This concentration scatter indicates that stationary conditions of the crystal growth were disturbed during the zone melting, i.e. the microscopic rate of growth fluctuated due to convection in the melt, which is manifested by the growth striations formation and/or growth nuclei – periodically alternating regions with a decreased and increased concentration of an alloying element.

The main reason for the formation of growth striations is considered to be the natural buoyancy convection inducing temperature fluctuations in the melt. In addition, the Marangoni convection, which is bound to the existence of the melt free surface, has essential influence on the occurrence of inhomogeneities in the melt. If solidification proceeds very slowly, the concentration of an admixture in the melt will be even and the concentration of an admixture in the solidifying crystal is the equilibrium distribution coefficient k_o [6] multiple of the concentration in the melt ($c_S = k_o c_L$). If the rate of solidification increases, the moving front of solidification will displace the admixture faster than it can diffuse

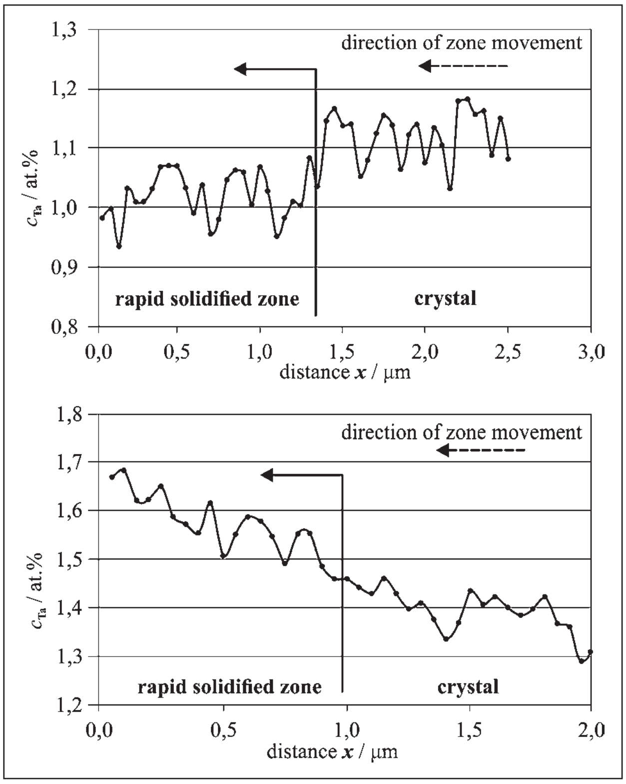

Figure 2 Concentration profile of tantalum in molybdenum (a) and tungsten (b) single crystal prepared by the zone pass rate of 3 mm/min.

into the main melt volume and an enriched layer creates on the interface. The accumulation of admixtures in front of the crystallization front and enhancement of concentration super-cooling may invoke a considerable rise of the rate of the crystallization front shift. After occupying a certain portion of admixtures on the interface, their concentration in the melt decreases or returns to the initial value and the process repeats [1].

Furthermore, it is obvious from the results that the solubility of tantalum in the solid and liquid phases is approximately the same, which means that the end part of the ingot was not markedly enriched (W-Ta system) or impoverished (Mo-Ta system) with tantalum and from this point of view tantalum shows itself to be a convenient alloying element in molybdenum and tungsten. The effective distribution coefficients k_{eff} of tantalum in molybdenum and tungsten, which describes the influence of transport processes taking place in the regions close to the phase interface at the speed of crystallization $v \neq 0$, were calculated using the method of a rapidly solidified zone. The principle of this method consists in the comparison of the mean concentration of admixture element x_{LB} in a quenched zone (no diffusion processes could proceed) to the mean concentration x_{SB} in the place just in front of the solidified zone when the stationary state of crystallization was achieved. The mean concentrations of tantalum used in calculations and obtained values of k_{eff} for given speeds of crystallization are presented in Table 2.

It is evident from the results that values keff of tantalum in molybdenum and tungsten converges to 1 with the increasing zone pass rate, which corresponds with the Burton, Prim and Slichter theory [6].

Table 2 **Mean concentrations of tantalum in Mo and W and obtained values of k_{eff} for given zone pass rates**

Sample	Zone pass rate	x_{SB}	x_{LB}	k_{eff}	k_o
	mm/min	at.%	at.%		
Mo-Ta	1	1,55	1,35	1,14	1,32
Mo-Ta	3	1,12	1,02	1,10	
W-Ta	1	1,53	1,81	0,84	0,79
W-Ta	3	1,38	1,58	0,87	

CONCLUSIONS

It was found that the angle of disorientation of grain boundaries in molybdenum and tungsten-based single crystals increases with the increasing zone pass rate, and the simultaneous increased density of dislocations. Irregular concentration changes in the alloying elements contents, along the axis of the crystal under the given conditions of the crystallization, were identified in individual samples using the SEM-EDX micro-probe. These micro-segregations of alloying elements in the form of periodically alternating growth bands, with the reduced and increased concentration of these elements, are connected with the existence of the natural buoyancy convection in the melt due to temperature fluctuations [1, 6]. From these experimentally measured concentration profiles of tantalum along the rod melted gradually at the speeds of 1 and 3 mm/min, the effective distribution coefficients of tantalum in molybdenum and tungsten were determined using the method of a rapidly solidified zone.

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Note: The responsible translator for English language is
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