SEGREGATION BEHAVIOUR OF NIOBIUM AND ITS INFLUENCE ON STRUCTURAL CHARACTERISTICS OF MOLYBDENUM SINGLE CRYSTALS PREPARED BY ELECTRON BEAM FLOATING ZONE MELTING

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SEGREGAČNÍ CHOVÁNÍ NIOBU A JEHO VLIV NA STRUKTURNÍ CHARAKTERISTIKY MONOKRYSTALŮ MOLYBDENU PŘIPRAVENÝCH ELEKTRONOVÝM ZONÁLNÍM TAVENÍM

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Abstrakt

Pro přípravu kvalitních monokrystalů nízkolegovaných slitin na bázi molybdenu i dalších vysokotavitelných kovů je nutné zkoumat vliv legujícího prvku na strukturní, mechanické a fyzikální vlastnosti monokrystalů a jeho chování během krystalizace za daných podmínek. Cílem experimentálních prací bylo posoudit vliv niobu na strukturní dokonalost monokrystalů molybdenu a jeho chování z hlediska segregačních charakteristik. Pro tento účel byly připraveny elektronovým zonálním tavením metodou floating zone monokrystaly nízkolegovaných slitin Mo-1.5 at.% Nb za různých podmínek krystalizace (1, 3, 5 mm/min), které byly podrobeny metalografické, chemické a rtg. analýze. Bylo zjištěno, že legování monokrystalů molybdenu niobem vedlo k drobení blokové struktury, tzn. zmenšení rozměrů subzrn a zvětšení úhlu desorientace jejich hranic. Současně se zvýšila i hustota dislokací. Z rtg. Laueogramů vyplývá, že monokrystaly těchto slitin byly připraveny s krystalografickou orientací osy růstu [110]. Provedená liniová chemická analýza vzorků prokázala vznik mikrosegregací niobu, tzv. růstových pásů, které se na koncentračních profilech projevily jako periodicky se střídající oblasti se zvýšenou a sníženou koncentrací niobu. Existence těchto chemických nehomogenit nasvědčuje tomu, že během zonálního tavení došlo k porušení stacionárních podmínek růstu krystalu, tj. došlo k fluktuacím mikroskopické rychlosti růstu v důsledku konvekce v tavenině. Z výsledků chemické analýzy pak byly stanoveny efektivní rozdělovací koeficienty niobu v molybdenu pro dané podmínky krystalizace, které se poměrně dobře shodují a blíží se vypočtené teoretické hodnotě rovnovážného rozdělovacího koeficientu.

Abstract

When preparing quality single crystals of low-alloyed alloys on the base of molybdenum as well as other high melting metals, it is necessary to investigate influence of alloying elements on the single crystal structural, mechanical and physical properties and their behaviour during crystallization under given conditions. The aim of the present work was to evaluate the influence of niobium on structural perfection of single crystals of molybdenum and its behaviour from the view of segregation characteristics. For this purpose single crystals of low-alloyed alloys Mo-1.5 at.% Nb were prepared by the electron beam floating zone melting

under various conditions of crystallization (1, 3, 5 mm/min). These single crystals were submitted to metallographical, chemical and X-ray analyses. It was found that alloying of molybdenum single crystals with niobium resulted in disintegration of block structure, i.e. reducing the sub-grain dimensions and increasing the angle of disorientation of their boundaries. Simultaneously, the density of dislocations increased. It can be concluded from X-ray Lauegrams that the single crystals of these alloys were prepared with crystallographical orientation of the growth axis [110]. The performed line chemical analysis of specimens proved creation of niobium micro-segregations, so called growth striations, which showed themselves on concentration profiles as periodically alternating areas with increased and decreased concentrations of niobium. 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. Effective distribution coefficients of niobium in molybdenum for individual conditions of crystallization were determined from the chemical analyses results. They agree relatively well and approach to the calculated theoretical value of the equilibrium distribution coefficient.

Keywords: tungsten, molybdenum, single crystal, electron beam floating zone melting, plasma metallurgy

1. Introduction

Single crystals of low-alloyed alloys on the base of high-melting metals represent new types of function materials for high temperature applications. Their unique and complex properties, especially higher plasticity, lower liberation of gases in work regimes, enhanced erosion and corrosion stability, elevated high-temperature creep resistance, higher stability at thermal cycling compared with adequate polycrystalline alloys allow to apply them successfully as a cladding material for fuel elements, components of nuclear reactors, thermal converters, electrodes of electric reaction engines, electric contacts, heating elements, collectors or emitters for electric-vacuum technology, etc. An important aspect of preparation of these function materials is a convenient crystallographic orientation of crystals, which has an essential influence on physical, chemical and mechanic properties owing to the anisotropy among orientations of crystals. Today's conventional technologies of preparation of single crystals of high-melting metals and their low-alloyed alloys include electron beam floating zone melting and plasma arc melting and/or combination of both these methods, which enables to achieve higher structural perfection of crystals and chemical purity [1].

2. Experiment

The aim of experimental work was to evaluate the influence of niobium on the structural perfection of single crystals of molybdenum and its segregation behaviour in dependence on various conditions of crystallization. For this purpose single crystals of low-alloyed alloys with the nominal chemical composition Mo-1.5 at.% Nb were prepared by the electron beam floating zone melting in vacuum with various rates of the molten zone pass at the Department of Non-Ferrous Metals, Refining and Recycling, VŠB- Technical University of Ostrava. As a starting material we used a polycrystalline rod of molybdenum, 3N purity and 6 mm diameter, in which a longitudinal slot 1 mm wide, 0.7 mm deep and about 20 cm long was milled. Little pieces of niobium sheet wound 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 by the speed 4 mm/min and then the rod gradually melted in given sections by the speeds 1, 3 and 5 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 obtained specimens we submitted to metallographical, chemical and X-ray analyses

2.1 Metallographical analysis

From all the single crystals of molybdenum alloys, specimens were taken by a crosscut and longitudinal cut and submitted to mechanical grinding and polishing. The microstructure of alloys was developed by chemical etching in the solution of 100 ml H_2O, 50 ml H_2SO_4, 50 ml HNO_3 and selected photographs taken by the Olympus GX51 microscope with the digital camera DP12 are documented in figures 1 to 3.

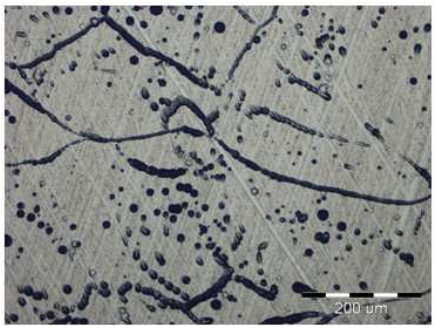

Fig.1 Dislocation substructure of Mo-Nb specimen (v = 1 mm/min); longitudal section

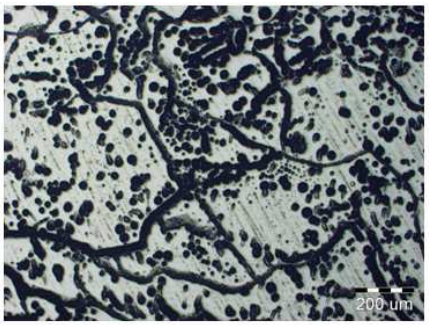

Fig.2 Dislocation substructure of Mo-Nb specimen (v = 5 mm/min); longitudal section

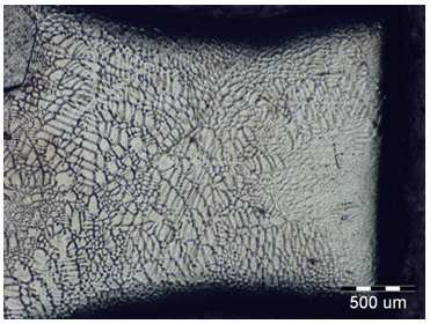

Fig.3 Microstructure of Mo-Nb specimen (v = 3 mm/min) - area of solidified zone; longitudal section

The structure of single crystals consists of sub-grains of orders I and II, elongated in the direction of growth, the disorientation angle of their boundaries being several minutes or degrees. On the specimen crosscuts the sub-grains have a polygonal shape. The boundaries of sub-grains were formed by dislocations and admixtures and the density of dislocations on these boundaries was by two orders higher than that in the sub-grain volume [1]. The influence of niobium on the molybdenum structure showed itself in all the cases, the block structure

disintegration happened compared to the pure molybdenum single crystal [2] and the angle of disorientation of boundaries increased. Simultaneously, the density of dislocations rose, which can be roughly estimated from the amount of etching patters formed in places where dislocations get on the specimen surface. Furthermore, the single crystal crystallographic orientation can be assessed from the etching pattern shape.

In the area of 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 niobium in central parts of cells is assumed.

It can be concluded from figs that the crystallization rate did not have a considerable influence on the micro-hardness of alloys. It was approximately same in all the cases and its maximum value was reached in the solidified zone where the niobium concentration was highest.

2.2 Chemical analysis

The line electron wave dispersion analysis was used for determination of concentration profiles of niobium in specimens of single crystals of molybdenum alloys in longitudinal direction, prepared under various crystallization conditions. The tests were performed in the company Vítkovice-Výzkum a vývoj s.r.o. Ostrava. The obtained concentration profile of niobium in molybdenum (v = 1 mm/min) is documented in fig. 4 as an example, the average values of niobium concentration from the beginning, middle and end of specimens are summed up in table 1.

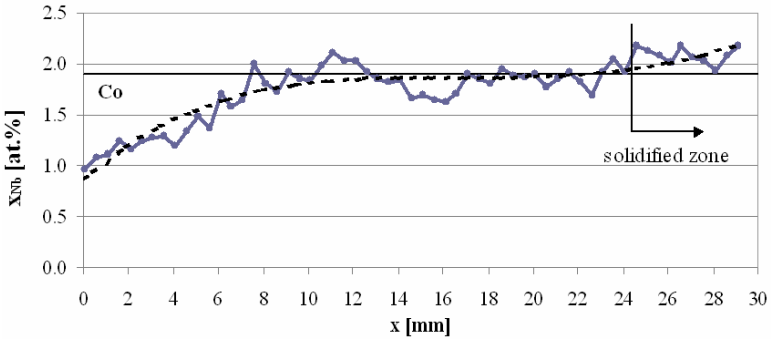

Fig.4 Concentration profile of niobium in molybdenum (v = 1 mm/min)

It is concluded from the chemical analysis results that the average concentration of niobium changed during the zone melting compared with the initial state. This phenomenon is probably connected with evaporation of molybdenum, less with evaporation of niobium, under high temperatures in vacuum and with the melt splashing caused by liberation of the gas contained in the material due to the powder material sintering at its production. In the specimen prepared with the crystallization speed 5 mm/min, the change of initial concentration was obviously also influenced by the rod inhomogeneous alloying since the used alloying material did not have constant dimensions.

All the determined concentration profiles of niobium in molybdenum showed irregular sinusoidal course. 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 of the growth striations formation is considered to be natural buoyancy convection inducing temperature fluctuations in the melt. If the molten zone length surpasses the critical value of the characteristic length of the melt column, the growth speed fluctuates, which results in inhomogeneous distribution of admixtures and consequently in formation of growth striations which basically reflect the real shape of crystallization interface. In addition, Marangoni convection, which is bound to the existence of the melt free surface, has essential influence on the occurrence of inhomogeneities in the melt. Formation of micro-segregations depends neither on the zone movement direction nor on the admixture content up to the critical concentration value. The growth striation formation is most influenced by temperature and concentration gradients as well as by the size of the critical length of the melt column [3].

Table 1 Average values of niobium concentration from the beginning, middle and end of specimens

v	c_{Nb} [at.%]			Co
[mm/min]	beginning	middle	zone	[at.%]
1	1,31	1,87	2,08	1,9
3	1,37	1,67	1,84	1,7
5	1,96	2,71	2,97	2,5

2.3 X-ray back reflection method by Laue

The X-ray back reflection method by Laue was used for determination of crystallographic orientation of single crystals of the molybdenum alloys. It was calculated from the Lauegrams (figure 5 to 6) that the prepared single crystals had the orientation of growth axis [110].

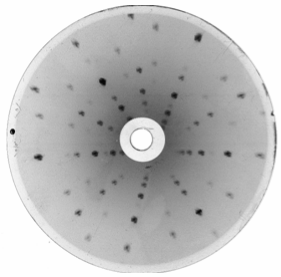

Fig.5 Lauegrams of Mo-Nb, prepared by crystallization rate 1 mm/min

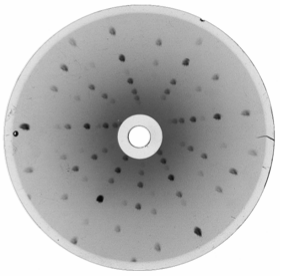

Fig.6 Lauegrams of Mo-Nb, prepared by crystallization rate 3 mm/min

3. Study of segregation characteristics of niobium in molybdenum – determination of effective distribution coefficient

Effective distribution coefficient describes the influence of transport processes taking place in the regions close to the phase interface at the speed of crystallization $v \neq 0$ and according to its value we can assess segregation abilities of elements in a basic material. Several methods based on experimental data of the zone melting can be utilized for its determination.

3.1 Burton – Prim – Slichter equation

Besides diffusion there are present convections in the molten zone, it means that there is a mixed transport of mass and the value of effective distribution coefficient k_{ef} lies between the values of the equilibrium distribution coefficient k_o and 1. For real numeration of k_{ef}, Burton, Prim and Slichter derived from the equation of continuity under convenient boundary conditions and taking into account the solidification rate v, the value of diffusion coefficient D_L and the simplifying assumption that the ratio of densities $\rho_S/\rho_L = 1$, the following relation between the equilibrium and effective distribution coefficients [3]:

$$k_{ef} = \frac{k_o}{ko + (1 - k_o)\exp\left(-\frac{v\delta}{D_L} \cdot \frac{\rho_S}{\rho_L}\right)} \tag{1}$$

The equilibrium distribution coefficient k_o is defined as an isothermal ratio of admixture element concentrations in the solid and liquid phases and is given by thermodynamic properties of both the basic component and admixture. The value used for our calculation was k_o = 0.88, which was determined on the basis of regression analysis of experimental input data from binary diagrams [4]. The value of the constant ratio δ/D was opted to be 100 s.cm^{-1}. The determined effective distribution coefficients of niobium in molybdenum for crystallization speeds 1, 3 and 5 mm/min are summarized in table 3. It is obvious from this table that with increasing crystallization speed also the value of k_{ef} increases and approaches to 1.

3.2 Determination of k_{ef} applying the method by Vigdorovič and Ivleva

The principle of this graphical-numerical method is finding an intersection of the hyperbolic function φ_1 and exponential function φ_2 for fictive opted values of distribution coefficient k for given input data – the width of zone b, the place of measuring the element concentration x, the concentration of admixture element $C(x)$ in the place x, the starting concentration C_o, the number of passes n.

The following holds for two and more passes of molten zone [3]:

$$\varphi_1 \approx \frac{1}{1-k}\left[1 - \sqrt[n]{\frac{C_{(x)}}{C_o}}\right] \qquad \varphi_2 = \exp\left(-\frac{kx}{b}\right) \tag{2}$$

The used input data for calculation and determined values of effective distribution coefficient of niobium in molybdenum for given conditions of crystallization are presented in table 2.

3.3 Method of solidified zone

This is a simple and relatively accurate method of determination of effective distribution coefficient at zone melting. Its principle is to compare the average concentration of admixture element in the zone $\bar{x}_{LB}$, which solidified with high speed at experiment, with the concentration of admixture $\bar{x}_{SB}$ in the place proximate to the solidified zone. The average concentrations of niobium used in calculations were presented in table 1. The obtained values of effective distribution coefficients of niobium in molybdenum for given speeds of crystallization are summarized in table 3.

Table 2 Input data for calculation and values of effective distribution coefficient of niobium in molybdenum determined by the Vigdorovič-Ivleva method

v = 1 mm/min			v = 3 mm/min			v = 5 mm/min		
C_o = 1.9 at.%			C_o = 1.7 at.%			C_o = 2.5 at.%		
b = 5.5 mm, n = 2								
x [mm]	c_{Nb} [at.%]	k_{ef}	x [mm]	c_{Nb} [at.%]	k_{ef}	x [mm]	c_{Nb} [at.%]	k_{ef}
0,1	0,96	0,71	0,6	1,28	0,86	1,1	1,72	0,8
1,1	1,11	0,73	1,6	1,29	0,84	2,6	1,79	0,78
3,1	1,27	0,73	2,6	1,30	0,82	3,1	1,76	0,75
7,1	1,64	0,8	6,6	1,42	0,78	6,1	2,12	0,81
8,6	1,73	0,83	8,1	1,42	0,75	7,6	2,23	0,83
17,6	1,85	0,83	11,6	1,53	0,75	9,6	2,27	0,81
19,6	1,87	0,85	18,1	1,63	0,76	15,6	2,40	0,80
21,1	1,85	0,80	19,6	1,65	0,78	23,6	2,47	0,81

Table 3 Comparison of determined effective distribution coefficients of niobium in molybdenum according to various methods for given conditions of crystallization

v [mm/min]	k_{efNb}^{Mo} VI	MZZ	BPS
1	0,791	0,900	0,897
3	0,796	0,906	0,924
5	0,799	0,913	0,944

VI-Vigdorovič and Ivleva method
MZZ-solidified zone method
BPS-Burton-Prim-Slichter theory

3.4 Discussion

When comparing the effective distribution coefficients of niobium in molybdenum shown in table 3, we can see that the values obtained by the method of solidified zone and from the Burton-Prim-Slichter equation agree very well and meet the condition that k_{ef} has to lie between the values k_o and 1. Effective distribution coefficients determined according to the method by Vigdorovič and Ivleva differ by about 13 %. This method is very sensitive to input data, especially to the determination of the starting average concentration C_o and the width of zone b, since the assumptions for b = const. cannot be exactly met for manifold zone melting and thus the errors grow with increasing number of passes. In addition, the greater the angle of intersection of both the functions is, the more accurate is this graphical determination of the value k_{ef}. Therefore this method is more suitable for $k < 1$ and less suitable for $k \approx 1$. Furthermore, it is obvious from the results that the solubility of niobium in the solid and liquid phases is approximately same, which means that the end part of ingot will not be markedly enriched with niobium and from this point of view niobium shows itself to be a convenient alloying element in molybdenum. The issue is creating of micro-segregations in the form of growth striations. If solidification proceeds very slowly, the concentration of admixture in the melt will be even and the concentration of admixture in the solidifying crystal is k_o 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 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 supercooling 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 [2]. To prepare chemically homogeneous crystals, it is necessary to opt a sufficiently low rate of crystallization or to ensure a convenient agitation of the melt so that the admixtures accumulated in front of the crystallization front may be efficiently transported from this interface into the melt volume.

4. Conclusion

This work deals with the influence of niobium on structural characteristics and its segregation behaviour is single crystals of molybdenum prepared by electron beam zone melting under various crystallization conditions. It was found that niobium causes reducing the sub-grain dimensions and increasing the angle of disorientation on their boundaries and simultaneous increase of the density of dislocations. It follows from the performed chemical analysis of specimens that micro-segregations in the form of growth striations created due to transport phenomena in the melt. They showed themselves as sinusoidal course of concentration profiles of niobium in molybdenum. From these experimentally measured concentration profiles of niobium along the rod melted gradually with the speeds 1, 3 and 5 mm/min, effective distribution coefficients of niobium in molybdenum, characterizing the segregation ability of niobium, were determined applying various methods. However, their application is burdened by certain errors with regard to the given conditions of experiments. It is obvious from the results that, considering the determined value of k_{efNb}^{Mo}, niobium is a convenient element for micro-alloying of molybdenum.

Acknowledgement

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