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METAL DESTRUCTION IN PROCESS OF MANUFACTURING PARTS FROM MOLYBDENUM AND NIOBIUM

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The effect of coatings with surface-active properties and aerothermoacoustic treatment on Mo and Nb stampability, mechanical properties, and microdistortions of the crystal lattice is considered. An improvement in the quality of products obtained by drawing using these technologies has been established due to an increase in plasticity and a decrease in microdistortions of the crystal lattice. Modification of the surface of the tool reduces distortion in the micro-regions of the crystal lattice, reducing the stresses of the 2nd and 3rd kind of deformed Nb and improving its formability and the quality of semi-finished products and finished products. Low formability of Mo and Nb is associated with the presence of brittle phases of lamellar and sharp-edged shape, which reduce ductility and toughness. For Nb, an additional negative factor is the presence of grains up to 40–50 μm in size.

Keywords: coatings; molybdenum; niobium; microstructure; aero thermoacoustic treatment; deformability

Introduction

A variety of products are made from refractory metals (molybdenum and niobium) - honeycomb panels of spacecraft, heat exchangers, shells of rockets and capsules, thermal and other screens, wing edge trim and stabilizers in supersonic aircraft, and much more. The shaping of semi-finished products from refractory metals and alloys is carried out, among other things, by cold stamping, for example, screens - hollow axisymmetric thin-walled parts with a flange or bottom, as well as without them. The screen material must have heat resistance, heat resistance, high electrical and thermal conductivity, high-temperature long-term strength. When operating at high temperatures, an important feature is the low thermal neutron capture cross section. Materials providing a complex of these properties - niobium and molybdenum [1].

To carry out cold plastic deformation (CPD) operations, for example, drawing, which is widely used for the production of a number of products, the workpiece material must have, in addition to the required strength values, the necessary plasticity characteristics.

Molybdenum is a valuable refractory metal with a melting point of about 2610°C [2]. The strength of the interatomic bond of molybdenum is so great that at room and high temperatures its strength is always high [3]. In addition, unlike other refractory metals such as Ta, Nb, Co, W, etc., molybdenum not only has a high melting point, excellent thermal conductivity, good electrical conductivity and corrosion resistance, has a low thermal expansion coefficient and high hardness [4]. However, its use as a structural material is limited by the increased brittleness that is known to occur due to intragranular fracture. Yoshinaka [5] believed that grain boundaries with sufficiently high energy are responsible for intragranular fracture in molybdenum. Meanwhile, Watanabe and Tsurekawa [6] investigated the relationship between intragranular fracture and grain boundary microstructure in 2D polycrystalline molybdenum and pointed out that increasing the resistance of polycrystalline molybdenum to intragranular fracture can be achieved by controlling the character of grain boundaries. Moreover, molybdenum and its alloys, due to their high melting point, high hardness [4], low-temperature brittleness [7], and poor ability for high-temperature oxidation resistance [8], could hardly be obtained by casting, forging and other mechanical processing, for except for the powder

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metallurgy method. However, the conventional processing of molybdenum by powder metallurgy requires long-term sintering at high temperature, which leads to excessive grain coarsening and subsequent deterioration of mechanical properties. Garg et al. [9] investigated the sintering mechanism of molybdenum powders and proposed an accurate model for calculating optimal molybdenum sintering cycles using the powder metallurgy method. On the other hand, molybdenum must be processed in a narrow range of high temperatures due to its significant resistance to deformation [10]. Microstructural analysis, mechanical behavior and testing of the properties of molybdenum and its alloys have been carried out by many researchers in recent years. For example, Laribi et al. [11] investigated the metallurgical and mechanical properties of molybdenum coating formed by flame spraying, studying its microstructure, hardness, and tribological resistance. In addition, Ciulik and Taleff [12], as well as Wang et al. [13] investigated the behavior of molybdenum sheet at temperatures from 1300 C to 1600°C, as well as its properties at elevated temperatures.

In industry, molybdenum strips of technical purity are used, obtained using the technology of cold plastic deformation (Specifications 11-90. Molybdenum strips). At the same time, blanks are obtained according to the scheme: annealing, cold rolling in two mutually perpendicular directions, which provides the required level of strength $\sigma_{temporary\ resistance}$ = 800-980 MPa, but at the same time the level of plasticity is low – δ = 1-2% (Specifications 48-19-272-83 Molybdenum bands), which makes it difficult or impossible to carry out cold plastic deformation (drawing). Plasticity can be increased during vacuum annealing of workpieces up to δ = 3%, but in this case the strength decreases to $\sigma_{temporary\ resistance}$ = 685 MPa. (Specifications 11-90).

Niobium (Nb) is a metal with a melting point of 2468°C, a density of 8.57 g/cm^3, and a cubic crystal structure [14]. Niobium is used in the chemical, nuclear and electrical industries and in the production of superconducting wire [15, 16]. Niobium is able to interact with oxygen (O2), nitrogen (N2), water vapor (H2O), carbon monoxide (CO) and gases present in the environment. Because of these characteristics, niobium is produced and purified in an inert atmosphere or high vacuum.

There are three methods for producing products from Nb: powder metallurgy (PM), vacuum arc welding (VAW), and electron beam melting (EBM). The EBM process is more common and produces high purity metal, around 99.99%. During plastic deformation, the hardening process occurs due to the multiplication, interaction and distribution of dislocations, which is strongly influenced by the ESF (energy stacking fault). The evolution of the microstructure during plastic deformation is very important with respect to the deformation mechanism, mechanical properties and material formation. In addition, the deformation characteristics of the microstructure affect the behavior of the material during recrystallization [17, 18]. To conduct a qualitative microstructural analysis, niobium needs special preparation for metallography due to mechanical characteristics that can cause various surface disturbances. Niobium is supplied in the form of strips according to Specifications 48-19-264-84 in the annealed state.

However, it should be taken into account that Mo and Nb strips of the same batch according to specifications can differ significantly in deformability, which, when drawing followed by vacuum annealing, can lead to significant product defects.

One approach to improve ductility is microalloying molybdenum and niobium with aluminum, tantalum, magnesium, chromium, zirconium, or vanadium.

However, the anisotropy of plastic deformation can often lead to the destruction of the material [19, 20, 21].

In this regard, it is advisable to study the possibility of using technologies that improve the deformability of metals by increasing plasticity, not only by intermediate annealing. These technologies include: aero-thermoacoustic treatment - ATAT and the application of coatings with surface-active properties - surfactants, the use of which on steels and alloys has shown the possibility of increasing plasticity and deformability.

1 Materials and methods of research

The study of the effect of ATAT and surfactant coatings was carried out on sheets of Mo and Nb with a thickness of 0.15 mm. Mo was conditionally divided into 2 subgroups: Mo1 - with good deformability and Mo2 - with poor; the result of which are defects in the workpieces (scallops, cracks, poor-quality surface). The cause of the defect in the stamping of caps from an anisotropic strip is the texture of recrystallization, which results in a wavy edge - scalloped. Scallops are the result of different metal drawing in different directions with different wall thinning (Fig. 1b).

Aerothermoacoustic treatment (ATAT) was carried out on a facility created at Baltic State Technical University "Voenmeh" D.F. Ustinov according to the developed technology [1]. The surfactant FLUORO-surfactant coating was applied according to the developed scheme using ultrasonic cleaning. Mechanical properties were determined by static tensile testing on a Shimadzu AGX-100kN machine on flat standard specimens. The microstructure of the alloy was studied using a DSX 510 OLIMPUS optical microscope with software and a scanning electron microscope.

To determine the qualitative phase composition and microdistortions of the Nb crystal lattice in the initial state, with surface modification and subsequent drawing, a Rigaku Ultima IV multifunctional X-ray diffractometer was used. The diffractometer is equipped with a complex of control programs and a processing complex PDXL (X-ray Pow-der Diffraction Software). X-ray diffraction was carried out in focusing geometry according to the Bragg-Brentano scheme in filtered CuK□1 radiation. Microdistortion calculations (Δd/d) were carried out for all peaks using the Williamson-Hall method. The Nb sample without cold plastic deformation was used as a reference.

2 Results and discussion

The results of mechanical tests of Mo and Nb in the initial state, after acoustic treatment and application of pav-coating are presented in Table 1.

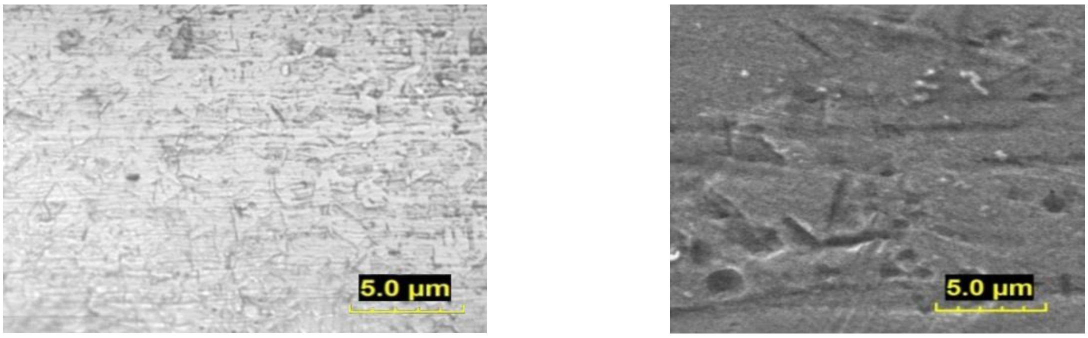
Table 1. Mechanical properties of Mo and Nb in the initial state and after ATAT.

No. mode	Type of initial processing	Additional processing, processing time	Mechanical properties		
			$\sigma_{0,2}$	$\sigma_{temporary\ resistance}$	δ
				MPa	%
Mo					
1	annealing, cold rolling (as delivered)	-	949	986	1.5
2	annealing, cold rolling	The impact of air flow and acoustic field with a sound pressure level of 140-160 dB. within 10 min.	830	960	2.8
3	annealing, cold rolling	The impact of air flow and acoustic field with a sound pressure level of 140-160 dB. within 20 min.	935	1115	3.3
4	annealing, cold rolling	-	-	900-980	1-2*
5	annealing, cold rolling	Annealing for 30-40 min.	-	685	2,0; 3,0**
Nb					
1	delivery condition - annealed	-	151	230	8,2
2	delivery condition - annealed	The impact of air flow and acoustic field with a sound pressure level of 140-160 dB. within 15 min.	122	250	27
3	delivery condition – annealed	-	-	200	15

Mo: 4.5 – Mode ТУ 11-90, Specifications 48 -19 -273-91, *Nb- Mode 3 Specifications 48-4-317-74

From the above results of testing the mechanical properties of Mo samples that have undergone acoustic treatment (ATAT) according to the optimal mode No. 3, it can be seen that both σw (slightly) and δ% increase simultaneously, which makes it possible to avoid the appearance of defects in the product when using cold plastic deformation technology, such as scalloping and cracks.

According to the test results of Nb samples that have undergone acoustic treatment (ATAT) according to the optimal mode No. 2, it can be seen that the strength (σtemporary resistance) practically does not change, but significantly, more than 3 times, δ% increases compared to the initial value. This allows both to use a large degree of deformation in the production of products, to reduce processing time, and to reduce the loss of expensive materials due to defects. The study of the Mo microstructure of both subgroups showed that in the Mo1 structure with good deformability, slip lines and bands, fault bands (slip line curvature) are fixed, which indicates that during the deformation process, dislocation slip in two or more systems of planes and reactions at their intersection, which corresponds to the stage of multiple slip (Fig. 1). In this case, slip bands are formed, which are a pack of slip lines. At the stage of multiple slip, the structure of the metal becomes more complicated (Fig. 1.a), the dislocation density increases significantly.

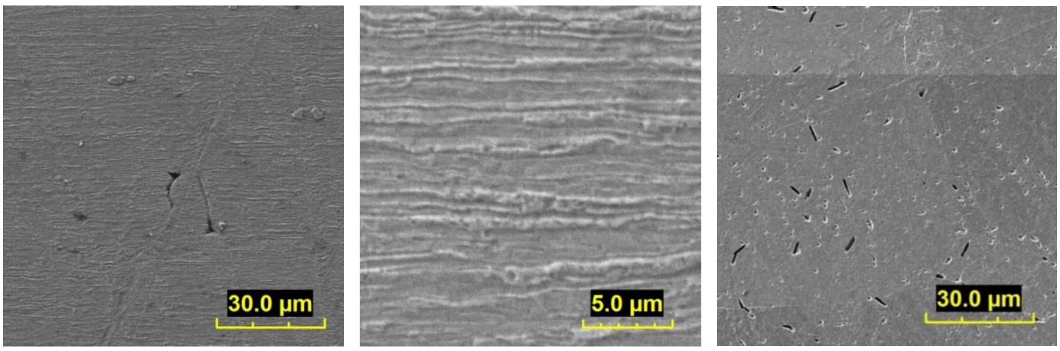


a) b)

Fig.1. Mo1 microstructure with good deformability, a – slip lines are continuous stripes, a high value of Mo plasticity is noted, b – slip lines are strongly fragmented, a slight decrease in the value of Mo plasticity is noted

The structure of Mo indicates a relatively uniform distribution of dislocations. Dislocations bypass barriers (fields of elastic stresses, inclusions of different sizes) that arise during their movement due to the transverse slip of screw dislocations. The presence of blocked dislocations leads to fragmentation of slip bands (Fig. 1.b). The metal under consideration is characterized by a rather fine-grained structure with a grain size range of 3-15 μm n, and the largest number of grains has sizes in the range of 4-10 μm, which allows having sufficient plasticity with the required strength.

The microstructure of a material with poor deformability - Mo2 is shown in Fig.2. It is characterized by a significant decrease, in comparison with Mo1, in the length of slip lines in slip bands. The reason may be the “jamming” of possible slip planes inside the sample by various barriers, such as inclusions, including sharp-edged ones (Fig. 2. a).



a) b) c)

Fig.2. The microstructure of the material with poor deformability - Mo2, a - there are sharp-edged inclusions in the slip planes, the plasticity of Mo is slightly reduced, b - a cellular streaky structure is formed, where light subgrains are cells with a smaller number of dislocations, dark stripes are zones with a high density of dislocations , there is a more noticeable decrease in Mo plasticity, c - there are lamellar inclusions up to ~5-8 μm in size, which significantly reduce Mo plasticity.

In metals with a bcc lattice (Mo, Fe, Nb), during plastic deformation, the processes of formation of dislocation tangles develop in the local volumes of crystals, where they intersect, i.e. a cellular dislocation structure is formed. Due to the unevenness of the sizes of grains and cells, a cellular streaky structure is formed (Fig. 2. b). Light subgrains are cells in which there are fewer dislocations, dark stripes are zones in which the density of dislocations is high. When the content in Mo of more than 0.1% of interstitial impurities may be the segregation of impurities along the grain boundaries, which leads to delamination of the metal in the process of plastic deformation. Stratification is a manifestation of the anisotropy of mechanical properties and the segregation of impurities. Stratification also occurs when the banded structure remains after recrystallization, which is present in Mo2, and can determine its reduced plasticity (Fig. 2. b).

In the structure of Mo2 with especially degraded deformability (Fig. 2. c), there are lamellar inclusions (or cavities formed after brittle inclusions are chipped) up to ~ 5-8 μm in size, as well as small inclusions, obviously reducing the plasticity of Mo. The structure of Nb in the initial state is shown in Fig.3.

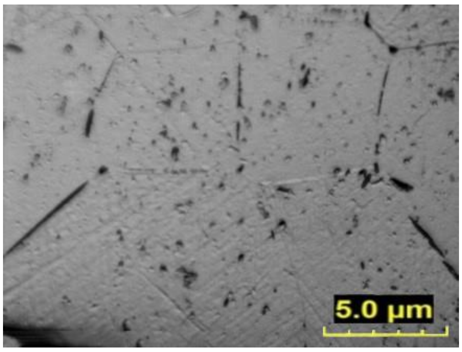


Fig.3. Microstructure of Nb, with phases of different sizes, separated along the grain boundaries and along the grain and causing a certain decrease in the plasticity of Nb.

The Nb grain size is in the range of 5–50 μm. The largest number of grains have a size of 15-40 μm. The metal is characterized by a significant uneven grain size. According to specifications, the Nb grade (Hb-1) contains 0.01% of each of the impurities (nitrogen, oxygen, carbon). In Fig. 3, one can see the presence of phases of different sizes, separated along the grain boundaries and along the grain. The grain size significantly affects the plasticity and deformability of Nb. The embrittlement of Nb with coarse grains is determined by the higher concentration of oxygen and other impurities along the grain boundaries, which is associated with its shorter length. This results in a reduced plasticity of Nb and the presence of defects, which are also characteristic of Mo. In the Nb static tension diagram (in the neck region), the deformation proceeds according to a mixed mechanism: zones of ductile and brittle fracture alternate with a large zone of brittle fracture.

An increase in the plasticity of Mo and Nb during ATAT (Table 1) is associated both with the refinement of phases, grains and their fragmentation, and with a decrease in internal stresses. deformation also proceeds through a viscous mechanism with minimal fracture.

To determine the microdistortions of the crystal lattice, X-ray diffraction analysis of 6 samples of niobium was carried out after various stretching. X-ray diffraction qualitative phase analysis of the samples revealed the following: the main phase in all samples is Nb. There is no texture in the first sample (the ratio of the peak intensities corresponds to the tabular data of the powder state (textureless). In all other samples, some redistribution of the reflection intensities is observed, probably caused by the previous plastic deformation. Surfactant was applied to samples 3, 5, 6 before deformation. Results of microdistortion calculations crystal lattice are given in Table 2.

Defects, manifestations in the process of shaping of tissues from Nb coating with a decrease in plasticity, which in turn may be associated with damage in microregions - stresses of the second kind, i.e. accumulation of imperfections in the crystal structure. Data on the damage of the crystal lattice ($\Delta d/d$) allow us to judge the amount of elastic deformation, which is a material. The width of the diffractive paints (in terms of the magnitude of the values of $\Delta d/d$) can be produced with the growth of lattice defects. The role of growth in the reduction of plasticity in the process of plastic deformation is determined by the fact that elastically damaged microregions under external load become decomposition concentrators and turn into crack nuclei.

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Table 2. Calculations of microdistortions of the crystal lattice

Calculations of microdistortions of the crystal lattice	Δd/d, 10^{-3}	(110) – (220)		
		$\cos(\theta_1)/\cos(\theta_2)$	β_2/β_1	$tg(\theta_2)/tg(\theta_1)$
1 source disk	-	1.26	1.22	2.51
2 tubule with a diameter of ~ 3 mm,	1.9	1.26	2.28	2.51
3 ------- « + surface-active substance	1.7	1.26	2.31	2.51
4 glass with a diameter of ~ 8 mm, min h=4mm	1.5	1.26	2.33	2.51
5 glass with a diameter of ~ 8 mm ,min h=8mm + surface-active substance	2.5	1.26	2.27	2.51
6 glass with a diameter of ~ 12 mm + surface-active substance	2.1	1.26	2.30	2.52

From the dislocation point of view, elastically distorted microregions are clusters of edge dislocations if they are located in such a way that the stress fields reinforce each other. This contributes to the appearance of microcracks and a decrease in ductility and toughness.

As is known, in the presence of lattice distortions in metal microregions, the width of the lines is proportional to the tangent of the reflection angle, and in the case of small crystals, to the secant of the same angle. An analysis of the values of microdistortions (Δd/d) in samples 2–6 Nb showed that the found ratios of the true linewidth at large and small reflection angles β2/β1 were closer to tg(θ2)/tg(θ1) than to ces(θ2)/ces(θ1). Therefore, distortions occur mainly due to the growth of distortions in the microregions of the crystal lattice.

The distortion in the microregions of the crystal lattice of sample 3 with surfactant is somewhat less than that of sample 2 without coating at the same degree of deformation. Consequently, the surfactant ensures greater plasticity of Nb during deformation and better product quality. With a decrease in the degree of deformation of sample 4 with respect to samples 2 and 3, the distortion of the crystal lattice decreases. In the presence of surfactants on samples 5 and 6, an increase in the degree of deformation to 30% makes it possible to obtain a sample without defects.

Conclusion

1. Low formability of Mo and Nb is associated with the presence of brittle phases of lamellar and sharp-edged shape, which reduce ductility and toughness. For Nb, an additional negative factor is the presence of grains up to 40–50 μm in size.
2. Acoustic treatment of Mo and Nb improves ductility and toughness without compromising strength, improving formability.
3. Modification of the surface of the tool reduces distortion in the micro-regions of the crystal lattice, reducing the stresses of the 2nd and 3rd kind of deformed Nb and improving its formability and the quality of semi-finished products and finished products.
4. In the technological process of obtaining products according to the Mo and Nb drawing-annealing scheme, annealing can be replaced by ATAE, which will reduce the duration and cost of the process, while improving the quality of products.

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