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TÍTULO: Influencia de las condiciones de crecimiento de monocristales de molibdeno en la perfección de su estructura

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RESUMEN: Se considera el método de obtención de monocristales a partir de metales refractarios por el método de fusión por zona con el uso de calentamiento por haz de electrones. Se determinan los principales factores que afectan el número de dislocaciones en monocristales crecidos, utilizando el ejemplo de monocristales de Mo, y se establecieron las condiciones óptimas para el crecimiento de monocristales con densidad de dislocación reducida.

PALABRAS CLAVES: fusión de zonas, monocristales de molibdeno, dislocaciones.

TITLE: The influence of Molybdenic Monocrystal Growing Conditions on the perfection of their structure.

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ABSTRACT: The method of monocrystal obtaining from refractory metals by the method of zone melting with the use of electron beam heating is considered. The main factors affecting the number of dislocations in grown monocrystals are determined. Using the example of Mo monocrystals, the optimal conditions for the growth of monocrystals with a reduced dislocation density were established.

KEY WORDS: zone melting, monocrystals of molybdenum, dislocations.

INTRODUCTION.

Molybdenum (Mo) is one of the metals widely used in industry and scientific research. It has a number of unique properties, such as high-temperature strength and high refractoriness. Besides, molybdenum has a high thermal stability, it has a small cross section for the capture of thermal neutrons. These properties of molybdenum made it possible to use it widely to fabricate the shell of missile and aircraft heads, the refractory metals and the alloys based on them serve as thermal shields. Besides, refractory metals and their alloys serve as the main structural material. Heat shields, wing lining and stabilizers in supersonic aircraft are manufactured from Mo. Some parts of straight-flow rocket and turbojet engines (turbine blades, rocket engine nozzles) operate in very difficult conditions.

For some areas of technology, high-purity oriented monocrystals of molybdenum are needed. For example, the use of such monocrystals in atomic beam detectors has significantly increased the actual signal-to-noise ratio in atomic-beam tubes (ALTs). The monocrystals of molybdenum are used effectively as the emitters in atomic beam detectors and in ion sources of mass spectrometers. Pure monocrystalline molybdenum is used to produce the mirrors for powerful gas-dynamic lasers. The monocrystals of refractory metals with a high degree of purification are the most promising basis for the creation of new instruments in radio electronic industry and X-ray equipment for the production of various parts of electronic tubes, X-ray tubes and other vacuum devices (Lyakishev, Burkhanov, 2002).

DEVELOPMENT.

Main part.

Monocrystals have a number of unique physical properties that are absent in the metals and alloys of a polycrystalline state with technical purity. The quality of molybdenum single crystals largely determines the characteristics of this metal, which are important criteria during the evaluation of its use prospects in high technologies. In order to solve a number of practical problems it is necessary to obtain pure and perfect monocrystals of metals with large free paths of electrons at low temperatures. These properties of metals depend not only on the amount of impurities in monocrystals, but also on the perfection of their structure considerably. Dislocations are the main type of imperfections in monocrystals. Therefore, it is important to establish the dependence of dislocation density in monocrystals under various growing conditions and to determine the optimal conditions.

A necessary condition for perfect molybdenum monocrystal obtaining is the combination of high vacuum and high temperatures. Electron-beam zone melting in vacuum is the most complete one for these requirements. Monocrystals and polycrystalline ingots of high purity molybdenum are obtained by this method most often. The method of zone purification is often used to produce the monocrystals of refractory metals.

The essence of the method consists in the melting of a small section (a zone) of a solid rod and in a slow movement of this molten zone along the road. Heating for the creation of a molten zone is produced in various ways: either by high-frequency currents, or by electron-beam method, which is widely used nowadays.

The workpiece serving as the anode is strengthened in the cooled clamps so that it can change its dimensions freely during heating without stresses. An annular cathode made of tungsten wire is fixed in the holders. When the cathode is heated, a flow of electrons arises as the result of thermionic emission. The electron flux is focused by the use of molybdenum plates.

When the heating element is moved, the molten zone is shifted in the direction of uncrystallized substance. The metal melts at the leading edge of the molten zone, and the solidification of the melt and controlled crystallization in the seed conditioned direction takes place. An additional purification of the crystal material is also observed in the process of crystallization. Zone cleaning provides the reduction of impurity content in the metal due to their different solubilities in the liquid and the solid phase, as well as the evaporation of low-melting impurities and the impurities with high vapor pressure.

The redistribution of impurities along the length of a sample occurs in the process of zone melting. The impurities that increase the melting point of molybdenum: tantalum, tungsten and rhenium, and therefore having a distribution coefficient greater than one, are collected by vertical zone melting in the top part of the sample. The impurities with the melting point lower than molybdenum: aluminum, iron, nickel, cobalt, manganese, copper, vanadium, etc. with the distribution coefficients less than one are accumulated in zone melting at the bottom of the billet. The efficiency of the purification process for different elements is different and depends on the distribution coefficient value (Glebovsky, Shtinov, Sidorov, 2011).

The monocrystals obtained by zone melting usually have a cylindrical shape. If during the production of semiconductor materials, it was possible to solve the problem of monocrystal obtaining with controlled impurity distribution and containing a minimum number of structure defects, then the problem of crystal obtaining with a given structure remains unresolved for metals. The problem of obtaining perfect single crystals for metals turned out to be much more difficult than for semiconductor materials. This is explained by the fact that the energy of the formation of dislocations in metals is much less than for semiconductors. And structural defects in metals appear much easier under the same conditions. This is especially evident when the single crystals of refractory metals are grown. Therefore, in order to obtain perfect metallic monocrystals with a certain structure and distribution of impurities, it is necessary to use the methods that allow to control and to regulate heat fluxes, impurity content and other factors affecting the perfection of crystal structure.

An electronic crucible-free zone melting is the best method to obtain the monocrystals of refractory metals. A loop cathode and a reliable stabilization provide a satisfactory symmetry of an electron beam, which guarantees a stable picture of the temperature field in a molten zone. The orientations of obtained monocrystals were close to each other in all cases. Dislocations appeared on the planes (110) almost always. Both the orientation of crystals, and the identification of planes, on which the dislocations were studied, were performed by X-ray diffraction method.

The main factors affecting the number of dislocations:

1. The amount of impurities in a metal;
2. The number of dislocations in an initial layer on which a monocrystal is developed;
3. The temperature field in a developed monocrystal.

Polycrystalline purity samples of 99.9% were used as the starting material. The observations were performed on the cylindrical surface obtained after the growth, which was not subjected to mechanical action. Monocrystals were subjected only to chemical treatment, in order to avoid the appearance of new dislocations not conditioned by the growing conditions of monocrystals. Monocrystals were first subjected to electronic polishing, and then to chemical etching. The method of selective etching was widely used in the study of dislocations. The method is based on the fact that the binding energy of atoms near the dislocations is much less than in a non-deformed lattice.

Therefore, the places of dislocation output to a crystal surface interact with a specially selected reagent more quickly than the surface surrounding the dislocation.

The result of such etching is the etch pits appearance on crystal surface. Their calculation allows to determine one of the most important crystal characteristics - the dislocation density, expressed by the number of etching pits per square centimeter. Flares appeared on the surface of the sample after etching, which were the collection of etching pits. These flares were observed only in the initial and the final part of the samples. The main (middle) part of the samples looked polished, which indicated a low density of etching pits.

The dislocation density in the "seed layer" was approximately the same and not less than 10^8 cm^{-2} for all grown crystals. The distribution of dislocation density along grown single crystals was determined in the work with different number of zones passes and at different velocities of a molten zone motion. The obtained results are shown in Fig. 1-4. It can be seen from the graphs (Fig. 1 and 3) that the highest dislocation density is observed at the beginning and at the end of the sample. It is much smaller in the middle part and varies insignificantly.

A large number of dislocations at the beginning of the sample is explained by the germination of seeds in a monocrystal and the accumulation of impurities at the beginning of the sample with the distribution coefficient $k>1$. The increase of dislocation density at the end of the sample arises from the accumulation of impurities in this region at $k<1$ and the thermal shock at the end of the passage zone. It can be seen from the graphs (Figure 1 and 2) that the dislocation density decreases as the number of zones passes increases. The reduction of dislocation density is most effective in the first passages of the zone. A further increase of zone passage number does not lead to a significant decrease of dislocation density, which can be explained by purification degree decrease. From this it can be concluded that more than four or five zone passes is impractical.

With the growth of crystals, the dislocation density is determined mainly by the temperature field in a grown monocrystal. During the growing of refractory metal monocrystals, the main heat removal is explained by radiation. The temperature, as the coordinate function along a sample, in the case of a cubicle free zone melting with zone heating by electron bombardment is set by the expression (Buchade, 2016).

$T(x) = (\alpha x + T_{ПЛ}^{-3/2})^{-2/3}$; $\alpha = 10^{-5}\varepsilon/kr$, где k - where k is the metal thermal conductivity ratio; ε is its emissivity; r is the radius of the melted rod. The calculations show that the temperature gradient for the samples of molybdenum with the diameter of 3 mm makes approximately 150 deg/mm, which gives the dislocation density of $2.5 \cdot 10^5$ cm^{-2} (Indenbom, 1957; Ameen, Ahmed, and Abd Hafez, 2018; Gil, González. 2018) according to theoretical estimates. This agrees well with the values observed in our samples.

CONCLUSIONS.

The density of dislocations depends on the cooling rate of a crystal, which is mainly determined by the molten zone velocity. At high zone velocities, the temperature gradient increases. This leads to the dislocation density increase. Figures 3 and 4 show the dislocation density distributions along the sample at various zone velocities and the dependence of the dislocation density on zone velocity. The speed of zone movement varied from 0.3 to 1 mm/min. It can be seen from the graphs that the dislocation density increases with zone velocity increase. But with the increase of zone movement speed 3 times, the density of dislocations increases only by 30%. This can be explained by the fact that the main heat removal is performed by the emission from the molten zone and the temperature gradient is slightly dependent on zone velocity.

The quality of grown monocrystals is significantly influenced by a sharp change of crystallization front velocity during one zone pass. Such a change can occur with the variations in the power of electron bombardment. The places of power variation have a local change in the density of dislocations and in some cases, the structure of a monocrystal is disturbed (the appearance of blockiness). The studies of a structure perfection dependence on the growth conditions of molybdenum monocrystals showed that it is optimal to grow monocrystals with 3 - 4 zone passes. At that the speed of the last pass must be small.

BIBLIOGRAPHIC REFERENCES.

1. Ameen, A. M., Ahmed, M. F., and Abd Hafez, M. A. (2018). The Impact of Management Accounting and How It Can Be Implemented into the Organizational Culture. Dutch Journal of Finance and Management, 2(1), 02. https://doi.org/10.20897/djfm/91582
2. Buchade, P. B. (2016). Comparative Study of Energy Saving in Theme Based Area by Luminary Replacement Strategy. International Journal of Engineering, Science and Mathematics, 5(1), 210-218.
3. Gil, Eduardo González. (2018). "Modelo institucional de gestión universitaria: Universidad Santo Tomás de Colombia." Opción34.86: 259-285.
4. Glebovsky V.G., Shtinov E.D., Sidorov N.S. (2011). Research of the processes of high-purity molybdenum obtaining process. Perspective materials. №11 pp. 51-53
5. Indenbom V.L. (1957). Crystallography, 2, 5.
6. Lyakishev N. P., Burkhanov G.S. (2002). Metallic monocrystals. - Moscow: ELIZ. - 312 p.

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