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An Improvement of Liquid-Phase Methods for Growing of the Mo and W Single Crystals

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Single crystals of refractory metals with a given orientation are demanded in both the power-optics and high-power laser applications. The evolution of liquid-phase methods for growing such refractory metals as the molybdenum and tungsten single crystals is analysed. As shown, the methods for growing crystals with a single heating source cannot solve the problem of fabrication of industrial-sizes' crystals. The superlarge single crystals of various configurations, such as ingot and plates, can be grown using the combined plasma-induction method. The single-crystalline quality of the ingots and the preservation of the orientations of the selected crystallographic axes are confirmed by the x-ray method according to Laue images. The repeatability of physical and mechanical properties is shown by the indentation test.

Key words: tungsten, molybdenum, single crystal, plasma-induction zone melting.

Монокристали тяжкотопких металів із заданою кристалографічною орієнтацією є затребуваними в силовій оптиці та у потужних лазерах. Проаналізовано еволюцію рідкофазних методів вирощування монокристалів таких тяжкотопких металів, як молібден і вольфрам. Показано, що методи вирощування монокристалів з одним джерелом нагріву не можуть вирішити проблему одержання кристалів промислового розміру. За допомогою методу комбінованого плазмовоіндукційного витоплення можна вирощувати надвеликі монокристали різної конфіґурації. Монокристаліч-

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ність одержаних зразків і збереження кристалографічної орієнтації підтверджено рентґенівськими дослідженнями за методом Лауе; повторюваність фізико-механічних властивостей показано методом індентування.

Ключові слова: вольфрам, молібден, монокристал, плазмовоіндукційне зонне витоплення.

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1. INTRODUCTION

In the middle of the twentieth century, the following unique properties of single crystals of refractory metals were revealed: high plasticity, resistance to recrystallization and creeping at the plasma affection, alkali metal melt affection, radiation, thermal cyclic effect, and especial mechanical properties. The studies were carried out with single crystals of various purities, including high-purity and technical-purity crystals. However, the high expectations for the widespread usage of single crystals in industry, aerospace, and military technology have not yet been realized. The main reason is the small size of single crystals, typically in the form of rods up to 25 mm in diameter, making it difficult to manufacture large parts or structures. Due to the demands of novel tech, the application of the large-size molybdenum and tungsten single crystals is forecast in the following industries: x-ray technology as anticathode; in the electrical industry as contacts and wires; in laser technology as mirrors for optical and x-ray laser; nuclear and thermonuclear research installations as devices for particle channelling, *etc*. Therefore, improving well-known technologies of liquid-phase methods for obtaining high-purity single crystals in the form of ingots and plates (as billets for the large-size single-crystal rolled products) is an actual goal that can be achieved based on analytics of such methods' evolution.

2. TRADITIONAL LIQUID-PHASE METHODS FOR GROWING SINGLE CRYSTALS

The main liquid-phase method for growing single crystals of tungsten, molybdenum, rhenium, and tantalum is a crucible-free zone melting. An electron beam was originally used as a heating source [1, 2]. The molten zone (Fig. 1) is the main link in the process of converting a polycrystal into a single crystal. The method is unique for growing small-diameter single crystals. The crystals obtained by this method were used for research purposes and for manufacturing various parts of measuring instruments and scientific equipment. Attempts to increase significantly the diameter of single crystals failed. To increase the

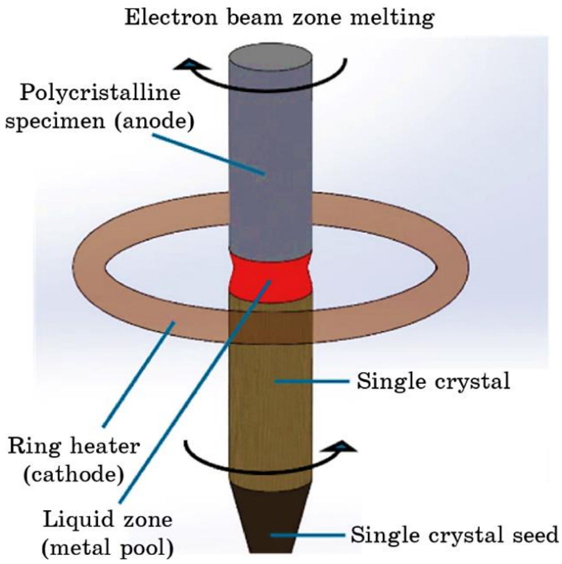

Fig. 1. Scheme of growing single crystals of refractory metals from the melt using a single heating source (electron-beam zone melting).

crystal diameter, it was necessary to increase the power of the electron beam gun. That led to an increased height of the molten zone and overheating of its surface layer, which resulted in a decreased viscosity of the melt and increased hydrostatic pressure in the lower part of the melt. The zone lost its stability, and the metal spilled.

The limiting radius of a single crystal can be estimated from the conditions of equality of the additional pressure, which creates surface tension forces at a point of a cylindrical surface that limits the liquid (pressure p_1 is calculated by the Laplace formula $p_1 = \sigma/R$), and hydrostatic pressure of liquid metal $p_2 = \rho g h$.

The main condition for the stability of the pool: $p_1 \geq p_2$, $\sigma/R \geq \rho g h$, or $R \leq \sigma/(\rho g h)$, where R is the radius of the single crystal [m], σ is the coefficient of surface tension depending on temperature [J/m^2], ρ is the density of liquid metal [kg/m^3], g is the acceleration of gravity [m/s^2], h is the zone height [m].

Various methods of zone melting using electron beam heating have been developed: zone compression melting and peripheral zone melting. The practice of growing cylindrical single crystals of molybdenum has shown that it is impossible to grow crystals of large diameters (more than 30 mm) using these methods [3]. The development of plasma-arc heating sources made it possible to create a new method for growing tungsten and molybdenum single crystals, which was similar to the Verneuil method (Fig. 2) [4]. A characteristic feature of this method is that with an increase in the diameter of a single crystal, it is

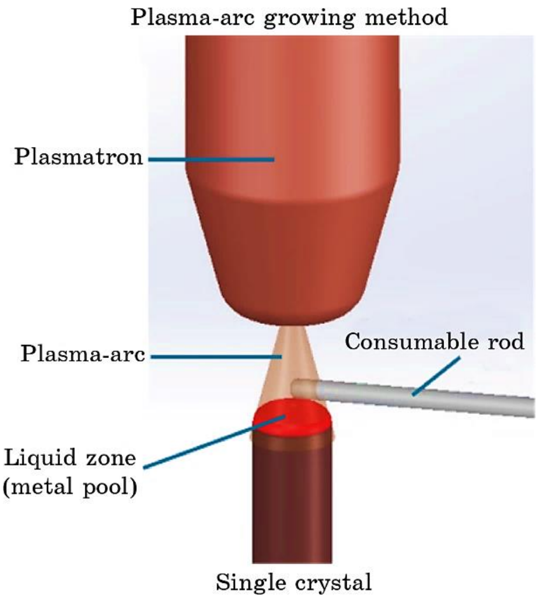

Fig. 2. Scheme of growing single crystals of refractory metals from the melt using a single heating source (plasma-arc growing method).

necessary to increase significantly the current of the plasmatron, which results in overheating of the pool surface. At the same time, the pool completely covers the end face of the single crystal and with a slight instability of the process; it is very difficult to keep it from spills. Analysis of these methods shows that the use of a single heat source does not allow for solving the main problem—the problem of growing large single crystals. With an increase in the size of the crystal, problems arise associated with overheating of the metal pool, keeping the pool from spills, and high thermal stresses in the single crystal [5].

3. PLASMA-INDUCTION METHOD FOR GROWING SINGLE CRYSTALS

The plasma-arc technology of growing single crystals was further developed with the creation of a combined plasma-induction method with a droplet transfer of liquid metal into a pool [6]. Integration of two independent heating sources made it possible to obtain a new effect: grow not only large but also profiled single crystals, for example, in the form of plates. The method has several fundamentally different characteristics compared to the methods described above: the flexible control of the thermal state of a single crystal is provided by equipment with a high-frequency heating source (Fig. 3). As a result, the level of

Fig. 3. Equipment for plasma-induction growing of single crystals.

stresses in the crystal decreases and number of dislocations decreases. The use of a high-frequency heating source makes it possible not only to heat the crystal but also to keep the pool from spills due to levitation forces; the crystal is formed by moving the local metal pool (Fig. 4). When the pool moves under the influence of a plasma arc, a consumable polycrystalline rod is remelted. Thus, crystal formation occurs layer by layer. The metal in the form of drops enters the local metal pool with the diameter of 20–25 mm and the depth of 2.0–2.5 mm. With an increase in the diameter of the consumable polycrystalline rod, the mass of the droplets as well as the range of changes in the depth and diameter of the pool increases.

The use of two sources of heating made it possible to influence actively the shape of the interface between the solid and liquid phases. The pool with the plasma-induction method has a flatter shape than with the plasma-arc method. If phantom grains are formed in the sur-

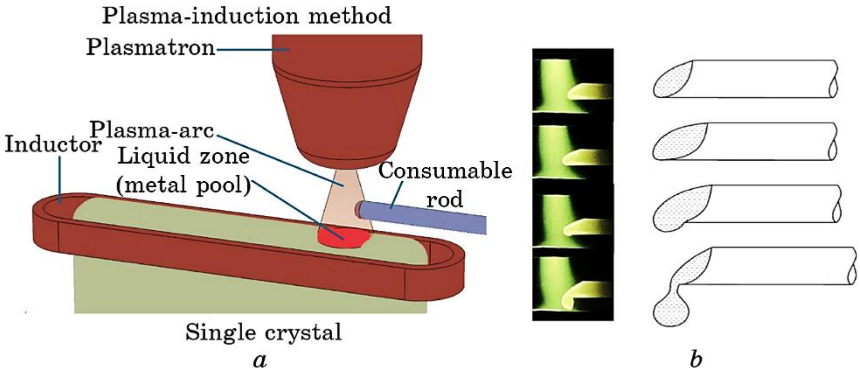

Fig. 4. Schemes of plasma-induction method for growing single crystals (*a*) and liquid-metal droplet transfer from a consumable rod (*b*).

Fig. 5. Appearance of tungsten single crystals (plasma-induction floating zone melting): profiled single crystal 20×160×170 mm; cylindrical crystal ∅ 85 mm; hollow cylinder ∅ 85 mm, 68 mm height of the deposited wall, thickness 20–22 mm.

face layer, they do not grow inward, and they are pushed out onto the crystal surface. A small local pool, whose trajectory of movement can be controlled, in combination with two heating sources, allows growing tungsten single crystals of theoretically unlimited sizes and shapes (Fig. 5): flat ingots for large-format single-crystal rolled products, pipes, crucibles, rods of large diameters, *etc*.

Of greatest interest is the $3D$ plasma induction technology for growing large single crystals of molybdenum and tungsten which has already been implemented for growing plates with a size of 160×170×20 mm (Fig. 6). Such an approach solves the main problem: increasing the size of single crystals up to industrial.

The results of the study of monocrystalline plates grown from technically pure molybdenum and tungsten are interesting. Metal refining in the process of growing single crystals is insignificant (Table 1). In-

a *b*

Fig. 6. Products made of single crystals: anticathode of an x-ray photographic lamp (*a*), welded tungsten monohedral tubes for thermionic converters (nuclear power plants for powering space objects) (*b*).

TABLE 1. Chemical composition of the Mo and W single crystals.

Material		Non-metallic impurities, $\times 10^{-4}$, wt.%				Metallic impurities, $\times 10^{-4}$, wt.%						
		O	N	H	C	Al	Fe	Ni	Si	Mo	W	Ca
W	Source material	20	–	–	40	30	30	–	30	300	Base	40
	Single crystal	14	20	4	30	25	20	30	27	300		30
Mo	Source material	20	–	–	40	20	30	20	30	Base	300	30
	Single crystal	10	20	2	30	18	25	20	30		300	25

gots have a slight deviation from the shape that does not exceed 2 mm from the parallelism of the largest edges.

Volumetric single-crystallinity in the layers of the tungsten and the molybdenum ingots were confirmed by research with such analytical criteria: the misorientation angle of the subgrain structure is less than 2°; the deviations in growth directions specified by the primary single-crystal base (seed) not exceeding 0.053° according to reflection Laue, and the volumetric repeatability of physical and mechanical properties by indentation test.

Using the x-ray method of Laue images makes it possible to evaluate the single crystallinity of a small sample with an area of up to 5 cm^2. The area of the large plate being evaluated is at least 100 times larger than the capabilities of the equipment used. Such an ingot can be considered as a solid monocrystalline body in the case when during a multipoint x-ray examination, for example, of the lateral surface having the largest area, the disorientation of the subgrain structure does not exceed the allowable limits equal 5 angular degrees or 0.087 radians. To determine the single crystallinity of the ingot, on its lateral surface along its length and height, epigrams were taken at points located at intervals of 10–15 mm (20–30 points). The identity of the epigrams (indices of the plane and directions in it) served as a confirmation that the ingot was a monocrystalline body. An additional check consisted of repeating such a procedure while rotating the sample through an angle of 3.14 rad. These epigrams were also 'identical'. At the same time, the spread of deviations from the direction of growth did not practically exceed 0.055 rad [7, 8]. The fully-grown crystal adopts the orientation of the seed crystal. By comparing the x-ray images and Laue reflexes of the 'as-grown' crystal (without subsequent heat treatment) and the seed crystal, it was determined that they are practically identical (Fig. 7). The x-ray diffraction patterns for each face showed nearly identical features, confirming that the in-got is a single crystal body without significant crystal structure defects.

The volumetric similarity of layers of Mo and W single crystals by

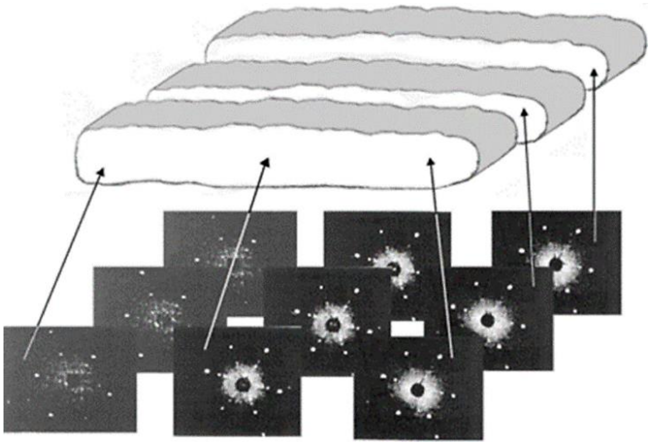

Fig. 7. X-ray Laue method for determination of structure orientation in three sections of the flat tungsten single crystal (direction <100>).

the distribution of such physical-mechanical properties as H and E was the second criterion for assessing the single-crystallinity ingots of Mo and W. Mechanical testing was carried by Oliver and Pharr method according to ISO/FDIS 14577-1 (metallic materials, instrumented indentation test for hardness and materials parameters, part 1, test method, 2015). The test was carried out with 40 g, 100 g, and 200 g of load on the indenter. The high density and ordered crystal structures are confirmed by the repeatability of the indentation diagrams in all layers of the ingots (Fig. 8). The indentation test showed the middle values at 200 g uploading on the indenter for molybdenum $H = 3$ GPa, $E = 165$ GPa and for tungsten $H = 6.5$ GPa, $E = 250$ GPa, what characterize tungsten as an ultra-hard metal.

Therefore, the results of the study of single crystals suggest that the plasma-induction technology as one of the liquid-phase methods is the most effective one for growing large crystals of refractory ultra-hard metals Mo and W. Specialized equipment to obtain significantly increased size of single crystals makes it possible. Research is currently underway to intensify the process of growing flat single crystals to reduce their cost.

4. CONCLUSIONS

Obtaining large ingots of refractory metals with a single-crystal structure is still a difficult technical task. Analysis of the development of methods for growing single crystals has shown that it is impossible to grow large single crystals of molybdenum and tungsten using a single source of high-temperature heating and a large metal pool. The problem is solved by the use of at least two heating sources and the use of a

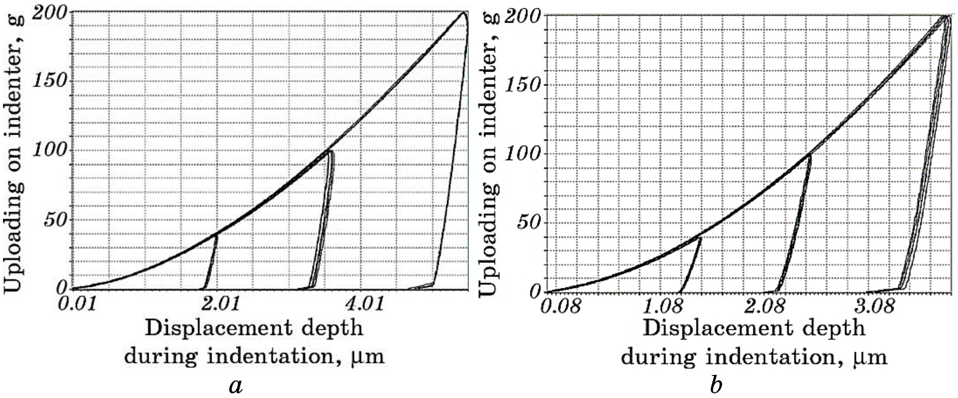

Fig. 8. Indentation diagrams at various loading on indenter: Mo (*a*) and W (*b*).

local movable metal pool: the transformation as additive 3*D* technology. When replacing the plasma-arc heating source in the plasma-induction method of growing with an electron-beam source, it will be possible to create a shallow flat pool equal in area to the cross-section of a single crystal. At the same time, the perfection of the crystal structure, the efficiency of the process can be increased, and the cost can be reduced. With the development and refinement of the plasma-induction method of growth, new opportunities are emerging for expanding the production and application of single crystals of refractory metals. Volumetric single-crystallinity in the layers of the molybdenum and tungsten ingot is confirmed by research with such analytical criteria as the misorientation angle of the subgrain structure is less than 2°, the deviations in growth directions specified by the primary single-crystal base (seed) not exceeding 0,053° according to reflection Laue, and the volumetric repeatability of physical and mechanical properties.

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