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3D TECHNOLOGY OF GROWING SINGLE-CRYSTAL INGOTS IN THE FORM OF HOLLOW TUNGSTEN CYLINDERS

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ABSTRACT

The paper presents the results of further development of the technology of growing superlarge single-crystals of refractory metals, developed at PWI of the NAS of Ukraine. Proceeding from the optimized technology and acquired experience, new generation equipment was manufactured, which allows growing single-crystals of refractory alloys in the form of a body of revolution. Experiments were performed on growing tungsten single-crystals in the form of a hollow cylinder, which can be used to manufacture such a product as a crucible. Technological parameters and energy modes were established, which allowed controlling the thickness of the wall being deposited. As a result of the experiments, an ingot with the deposited wall height of 68 mm, thickness of 20–22 mm and outer diameter of 85 mm was grown.

KEYWORDS: tungsten, single-crystal growing, hollow body of revolution, crucible, plasma-induction zone melting

INTRODUCTION

Today in Ukraine and abroad, there is a need for single-crystals of refractory compounds ($YAlO_3$, $Y_2Al_5O_3$, LiCaF, $YLiF_4$ etc.), alloyed with rare earth elements (Nd, Ce etc.) for the production of powerful solid state lasers and hypersensitive scintillators. The LED industry is developing rapidly, in particular, the production of ultraviolet LEDs, which requires an expansion of production of single-crystals of aluminium nitride. Most of the abovementioned crystals are grown from the liquid phase with the use of crucibles [1, 2], which minimize melt contamination, provide high operating temperatures, etc. Quartz, alundum, graphite, platinum, molybdenum, tantalum or tungsten are predominantly used for the manufacture of crucibles. Taking into account the set of physicochemical properties of the mentioned series of materials, tungsten most fully meets the requirements for high-temperature use when growing oxides and nitrides of certain metals with a melting point higher than 1800 °C. In addition, tungsten has the lowest coefficient of linear thermal expansion, which is very important when using crucibles in nonstationary thermal conditions [3, 4].

Traditionally, industrial production of crucibles from tungsten is associated with the technology of powder metallurgy. A significant disadvantage of such products is a low density of cermet tungsten (18.0–18.5 g/cm^3) compared to the density of tungsten in a remelted state (19.20–19.25 g/cm^3). The density of the crucible material determines its stability (amount of heat changes). Unlike density, more significant factor, affecting the stability of the crucible is its structure. During the technological process, in the polycrystalline structure of the walls of a tungsten crucible, as a result of cyclic processes of heating (cooling), recrystallization processes acquire a significant development, that cause the appearance and development of crevices, which leads to the destruction of the inner part of the crucible, especially on the boundary melt-atmosphere. An even greater problem in a sintered cermet tungsten is the penetration of melt into the crevices. A melt that gets to the powder metal crevices leads to the destruction of the inner surface of the crucible. This process has an uncontrolled avalanche nature, after the destruction of the first layer, a crack arises that propagates rapidly in the wall of the crucible. In addition to mechanical destruction, there is a chemical interaction of highly-reactive elements of the melt with the material of the crucible, which leads to the contamination of the melt and a rapid wear of the crucible.

Solving the problem of improving the stability of tungsten crucibles lies in the direction of creating a defect-free, dense and homogeneous structure.

It is known that at thermocyclic loads, single-crystalline tungsten has a high stability of the structure and is accompanied by a much smaller change in shape than polycrystalline one. Compared to polycrystalline specimens, in the single-crystal, the processes of high-temperature grain boundary diffusion of defects of crystalline structure are inhibited. The stability of the geometric shape of single-crystalline parts is associated with a more improved structure, high purity and density, which affects the stability of the thermal field and temperature gradient on the crystallization front of the melt.

Tungsten single-crystals produced by plasma-arc technology, are up to 40 mm in diameter in the intersection and have large inner stresses, which sometimes lead to the formation of crevices [5]. This makes it impossible to manufacture large-sized products from them, especially hollow cylinders.

In principle, the problem of growing large-sized tungsten single-crystals has been successfully solved at the PWI. A unique plasma-induction method of growing superlarge single-crystals of refractory metals (W, Mo) was offered. The latest technological equipment was developed and the technology of growing the largest in the world flat crystals of tungsten with the sizes 170x160x20 mm was optimized [6, 7].

Many years of experience became the basis for the creation of the latest 3D plasma-induction installation for growing tungsten single-crystals in the form of bodies of revolution (Figure 1) [8]. However, the technology of growing single-crystals in the form of bodies of revolution, especially hollow ones, has significant differences from the technology of growing profiled single-crystals in the form of plates. While growing single-crystal in the form of a plate, the inductor covers a single-crystal with a certain space and heats the surface of the single-crystal throughout the whole perimeter. In addition to heating, another important function of the inductor is maintaining a metal pool from leakage, i.e., providing its spatial stabilization. In the case with growing single-crystals in the form of hollow bodies, the inductor heats only the outer side surface of the crucible. The inner surface of the crucible is not heated by the inductor, and the metal pool is maintained by the surface tension forces. This imposes some complications in the technology development. Therefore, growing single-crystalline crucibles using 3D plasma-induction technology requires a comprehensive study.

In this sense, the aim of the work to create technological foundations for the production of single-crystals from tungsten is relevant.

TECHNOLOGICAL EQUIPMENT, MATERIALS AND PROCEDURE OF EXPERIMENTS

The equipment created at PWI is the next generation of equipment, which is distinguished by a computerized system for control of mechanisms, sensors of movement for stepper motors, and monitoring the process of single-crystal growth. During the design, the possibility of growing single-crystals in the form of bodies of revolution is provided: an ingot or a hollow cylinder with an outer diameter of up to 100 mm (4 inches). Regarding the development of technological fundamentals, optimizing the technology of growing tungsten single-crystals will occur for the crucibles of 85 mm diameter. On the one hand, in the thermophysical aspect, the technology almost

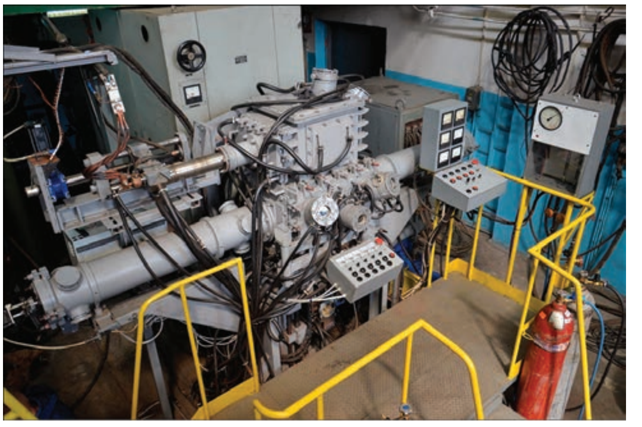

Figure 1. Equipment for growing tungsten single-crystals in the form of bodies of revolution

does not differ from the crucible with a diameter of 100 mm or more, and on the other hand, the resources in the form of consumables (tungsten, pure inert gases, etc.), power and time are saved.

In principle, 3D technology of growing hollow single-crystals in the form of bodies of revolution takes into account the basic technological approaches to the process of growing profiled single-crystals in the form of plates: layer-by-layer forming of a product on a single-crystalline embryonic crystal. The difference is the following. When growing single-crystalline plates, the layers are grown by a gradually movement of the plasmantron. The crystal is lowered down periodically after the formation of a layer is completed and in this case to form the next layer, the consumed rods are supplied alternately from each cassette. The difference in the work of the new installation while forming the crucible is the fact that the crucible rotates constantly around the vertical axis, the plasmatron is not moving, and the consumed rod is continuously supplied into the metal pool zone. In such a way, a gradual 3D surfacing by a local pool of layers on the embryonic crystal is carried out. Layer-by-layer forming of a single-crystal by moving the local pool has some advantages. The constant rate and direction of completion offsets the possible deviations of a set crystallographic axis of crystal growth, which is usually observed when growing axisymmetric crystals, when the pool is not local, but covers the whole horizontal section of the crystal. The cause of deviation of the axis of cylindrical crystals may be incomplete symmetry of the heat flux of the heating source and conditions of heat removal of the single-crystal surface.

When using 3D technology, the crystal is formed in a controlled way. The temperature field in the area of forming the crystal in the plasma-induction method of growing is determined by the total action of heat fluxes from the plasmatron and high-frequency inductor. The pattern of the temperature field in the body of the crystal depends on the ratio of power parameters

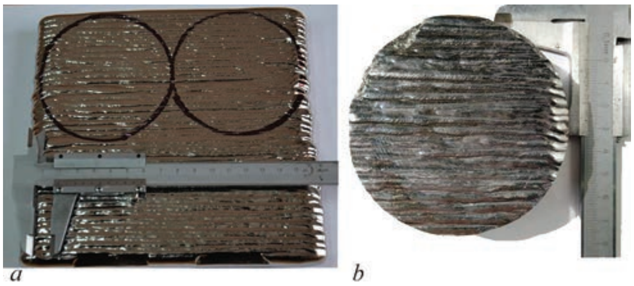

Figure 2. Tungsten single-crystal (*a*) and embryonic crystal that is cut out of it for growing crystals in the form of bodies of revolution with a diameter of 85 mm (*b*)

of heating sources and their spatial position relative to the grown single-crystal.

One of the determining factors in producing high-quality single-crystals without rough deviations from a set geometric shape is the invariance of liquid metal pool geometry in the process of growing. Based on these technological prerequisites, as a criterion that determines the ratio of capacities introduced by plasma-arc and induction sources of heating to the body of single-crystal, invariability of metal pool diameter was accepted.

As an embryonic crystal, a flat crystal with a set orientation of crystalline planes grown at PWI was used. From it discs were cut out (Figure 2). One of the discs was fixed on the bottom-plate and centered relative to the inductor with a certain space.

RESULTS OF EXPERIMENTS AND THEIR ANALYSIS

The first task when growing tungsten single-crystals in the form of hollow bodies of revolution was to establish the dependence of the influence of technological parameters on the diameter of the liquid pool, i.e., the wall thickness to be formed. While conducting experiments with the determination of the parameters of the plasmatron work, the effect of the current on the width of the pool was investigated, which had to form a wall of the crucible during a continuous rotation of the embryonic crystal (Figure 3).

Changing the power of the plasma-arc heating source, the diameter of the metal pool on the embryonic crystal was visually fixed, which continuously rotated in the horizontal plane. With the help of photographing, all stages of forming concentric circles were recorded. After a full revolution, the current was changed, which allowed a clear measurement of the pool width. The rate of revolution of the embryonic crystal was 30 deg/min, which was approximately the linear speed of the pool center of 14 mm/min. The power parameters of the experiment: current change from 300 to 600 A, arc voltage — 38–42 V, power of additional induction heating — 105–110 kW (anode power of the HF tube). As the experiments showed, the pool began to form at the plasmatron current of only 400 A. The displacement of the plasmatron from the axis of rotation of the embryonic crystal was 24 mm. The effect of the current on the width of the liquid pool on the embryonic crystal was investigated and, as a result, a dependence was obtained (Figure 4). However, at a further growing of the wall of the hollow cylinder and an increase in the height of the ingot, power parameters (arc current and induction heating) should rise. This is associated with an increase in the mass of the crystal to be maintained in a heated state and an increase in the radiation surface and heat losses.

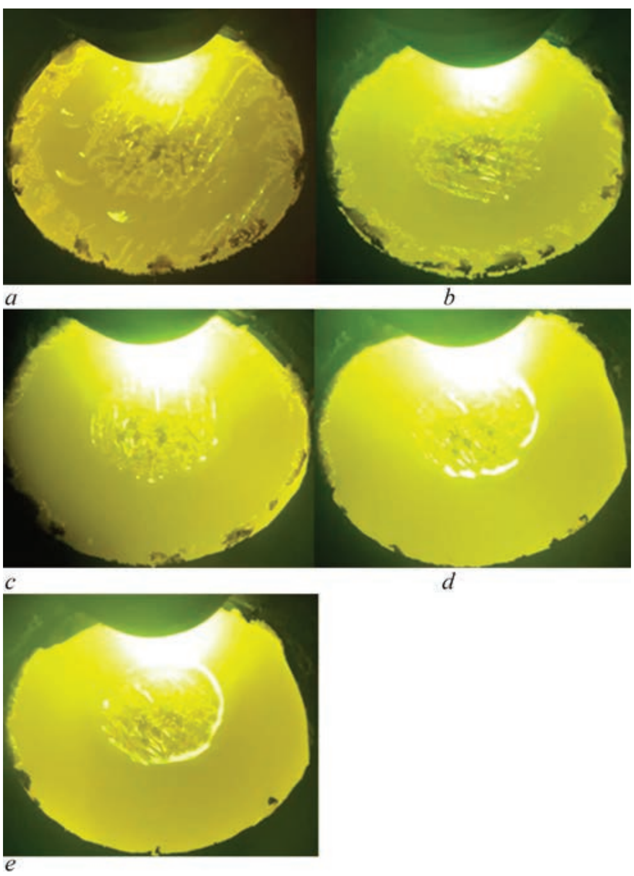

Figure 3. General appearance of the liquid tungsten pool, depending on current, A: *a* — 400; *b* — 450; *c* — 500; *d* — 550; *e* — 575

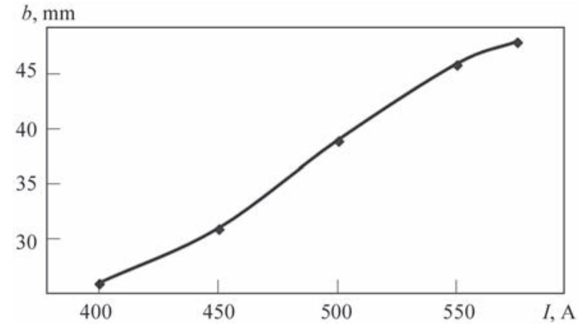

Figure 4. Effect of plasmatron current on the width of a metal pool

The final appearance of the surface of the embryonic crystal after the experiments and melting of the central part to align the entire upper part is shown in Figure 5.

Based on the experience of growing flat and cylindrical tungsten single-crystals, the diameter of the local pool was maintained at 22 mm. The formation of a single-crystalline crucible was carried out as a result of scanning by a local pool along the concentric trajectories in the plane of growing with an average radius of 30–31 mm. Calibrated tungsten rods with a diameter of 8 and 800 mm long (about 650 mm is remelted), with the purity of 99.95 wt.% were used to power the pool (Table 1). Previous studies have shown that refining and contamination of tungsten during plasma-induction zonal melting does not occur. Melting modes were optimized on the condition of stability of the ratio of the linear speed of the local pool and the rate of rod feed.

The process of growing ingots in the form of hollow cylinders was performed for the first time, so its study was divided into three stages. At each stage, a set quantity of single-crystal layers were grown. After completing the task of the stage, the process was stopped, the crystal was investigated and then mounted on the bottom-plate and growing of the following layers was continued. This approach made it possible to study in detail the processes of forming individual layers, to optimize the technology of positioning ingot and plasmatron during stops, to investigate the heredity of the crystalline structure and defect arising. The crystal was removed between the melts, etching by chemical reagents of the upper, outer and inner surfaces was performed.

Figure 5. Outer surface of the embryonic crystal before the experiments on growing the walls of the hollow single-crystalline cylinder

After the first tests, two consumable rods were remelted, which made approximately six cylindrical layers. As a result, when optimizimg the process of growing a hollow cylinder, a wall of 20–22 mm thick was produced and approximately 13–15 mm high. The technological scheme and the process of drop transfer of the melt is shown in Figure 6.

The peculiarity of the latest technology is the fact that when growing the outer side of the crucible, which is formed from a liquid state in the field of high-frequency electromagnetic field, is subjected to a strong effect of the field that maintains the metal pool and forms, practically, a perfect cylindrical shape.

Table 1. Chemical composition of tungsten rods of 8 mm diameter, wt.%

Si	Mg	Sn	Ni	Al	Mo	N	C
<0.001	<0.0001	<0.0001	0.0002	0.0002	0.017	0.002	0.001
As	Sb	Pb	Fe	Bi	Ca	P	O
<0.0001	<0.0001	<0.0001	0.0013	<0.0001	<0.001	<0.001	0.0046

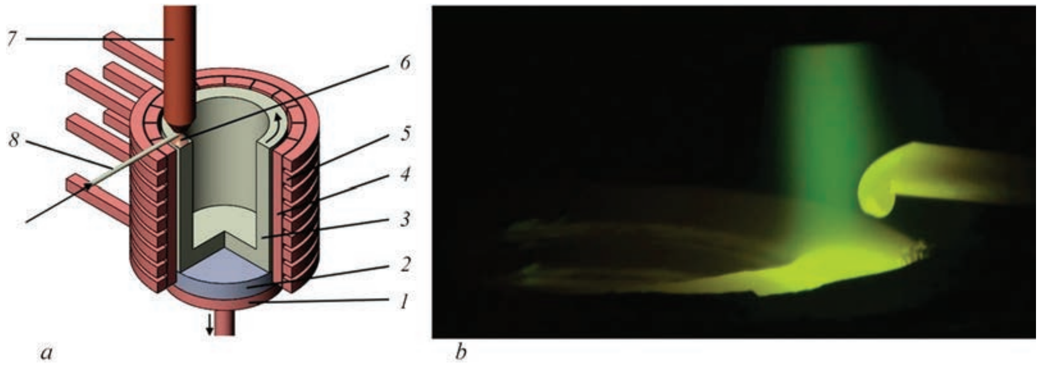

Figure 6. Scheme (*a*) and the process of remelting the consumed rod (*b*) during growing the ingot in the form of a hollow cylinder: *1* — bottom-plate; *2* — support; *3* — single-crystal; *4* — sectional wall; *5* — inductor; *6* — heat flux from plasmatron; *7* — consumed rod; *8* — plasmatron

Figure 7. Tungsten single-crystal: *a* — after the first stage of deposition of 6 layers and surface etching; *b* — after the second stage of growing, the height of the wall is 35–37 mm

The metal pool on the inner side of the crucible is not maintained by the electromagnetic field, which can lead to a leakage of the melt. Therefore, when growing a crystal in the form of a hollow cylinder, a layer formation scheme is used when the plasma heating source is shifted from the middle of the pool closer to the inductor. The pool acquires a rather complicated front of crystallization, which is formed by certain factors — absence of heating of the inner side of the wall of the crucible with a significant overheating of the outer one. As a result, slightly different conditions of crystal growth in the vertical plane arise that passes through the axis and radius. Due to this feature of thermal field, the inner surface of the crucible will be colder with relative to the outer one. This will create different conditions of solidification tungsten and the formation of dislocations in different parts of the crucible. In our opinion, in such circumstances, on the inner surface of the crucible, subboundaries, subgrains and exits of the edges of the crystal lattice will be more noticeable.

After melting, the sample of the crystal was etched with a chemical solution H_2SO_4:HNO_3:H_2O in a ratio of 2:2:4, which allowed identifying the boundaries of subgrains and the features of the structure formation and its orientation. Depending on the orientation of the crystal lattice, the rate of etching metal is different, so it is possible to monitor the formation and heredity of the single-crystalline structure. As a result of etching, the sample acquires a matt tint (Figure 7, *a*).

Figure 8. Aappearance of tungsten single-crystal in the form of a hollow body of revolution of 85 mm diameter

At the second stage, further studies of the process of remelting and forming were carried out when growing tungsten single-crystal in the form of a hollow body of revolution. While setting the same modes as in the first experiment, nine horizontal layers were deposited. The experiment showed that the process is stable, the thickness of the wall does not change, no leakages from the outside and inner sides occur. On the outer side, the solidified layers formed some waves, which is associated with the hydrodynamics of the liquid metal pool in the electromagnetic field of a high-frequency inductor. However, it did not lead to a large leakage of metal, also there were no electrical short-circuits. The total height of the welded wall was approximately 35–37 mm, the weight of the sample was 5.23 kg (Figure 7, *b*).

The third stage confirmed the stability and regularities of selected parameters for growing a crystal in the form of a 3D object. The overall height of the wall of the deposited crystal was approximately 68 mm, the weight was 7.635 kg with an outer diameter of 85 mm and the wall thickness of 20–22 mm (Figure 8). The final mode of growing crystal: plasma arc current is 415–550 A, the total power of a high-frequency generator is 170 kW, the dependence is shown in Figure 9. Taking into account the efficiency of the generator, the design of the thermal unit, the load of

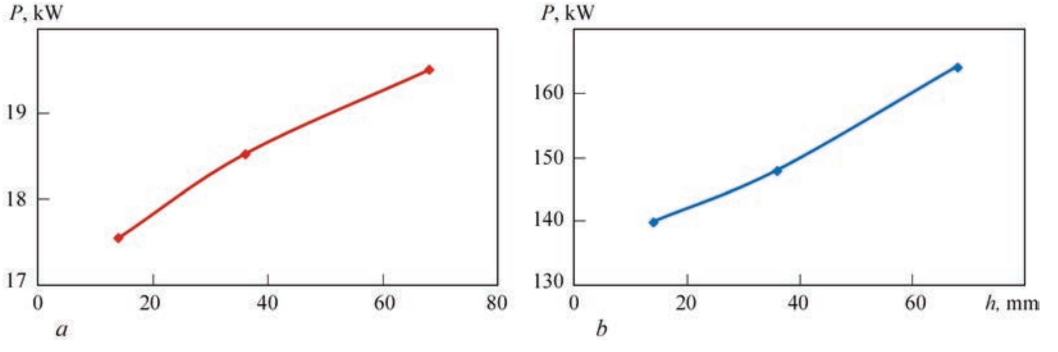

Figure 9. Dependences of change in power parameters on an increase in height while growing a hollow tungsten single-crystal of 85 mm diameter: *a* — change of power of the plasma arc; *b* — change of total power of high-frequency generator

the inductor with a crystal, the efficient power transmitted by the crystal may be 60–70 % [9]. At the speed of movement of the pool within 15–16 mm/min, the mass of drops that are formed and moved to the local pool, ranges from 1.3 to 1.4 g. The mass rate of growing is 14–15 g/min. The surface of the single-crystal is characterized by a slight ribbing, which is associated with a layer-by-layer formation. The thickness of the grown single layer is 2.3–2.4 mm.

During visual inspection on the surface of the ingot, it is possible to see vertical bands, which differ in the reflective capacity of light. These bands correspond to the structure of the elementary crystalline lattice (BCC) of tungsten, which is hereditary distributed throughout the whole ingot, forming a single-crystalline structure. In the adjacent bands, the reflective capacity changes, which corresponds to the planes or faces of the crystalline lattice, which indicates the heredity of the single-crystalline structure throughout the whole volume. In addition, these bands correspond to a part of the embryonic crystal that was subjected to melting.

CONCLUSIONS

For the first time in the world based on the latest technology developed at PWI of the NAS of Ukraine, a tungsten ingot in the form of a hollow cylinder on a solid single-crystalline embryonic crystaly with a diameter of 85 mm was grown. The grown crystal has 68 mm of the deposited wall with a thickness of 20–22 mm. The surface inspection after etching of the ingot by chemical reagents showed the heredity of the structure from the single-crystalline embryonic crystal and all the signs of the monocrystalline structure throughout the crystal.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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