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3D TECHNOLOGY OF GROWING LARGE TUNGSTEN CRYSTALS

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ABSTRACT

The evolution of liquid-phase methods for growing tungsten single crystals is analyzed. It is shown that methods of growing crystals with a single heating source cannot solve the problem of producing crystals of industrial sizes. Super large tungsten crystals of various configurations can be produced using 3D technologies and combined plasma-induction heating. This method has already been used for growing single crystal plates, billets for large-format single crystal rolling, single crystal ingots and crucibles. The next step will be the creation of a technology for growing bulk super large tungsten single crystals.

KEYWORDS: 3D additive technologies, tungsten, single crystal growth, plasma-induction zone melting, droplet transfer

INTRODUCTION

At present additive 3D technologies cover practically all the spheres of human activity: material production, medicine, science and art. A wide-scale application of 3D technologies is observed, particularly in mechanical engineering. Schweissen und Schneiden Fair held in September, 2023 in Essen, Germany can be a confirmation of this. Novel technologies are actively used in unit and small-scale production; they are introduced for manufacturing complex-shaped parts, for instance turbine blades, impellers, etc. Manufacturers note a high level of properties of the product metal, due to formation of a fine-grained structure, which can be assessed by grain size corresponding to numbers 6–10 [1].

Products are made from different metals and alloys: low- and high-alloyed and stainless steels, nickel alloys, aluminium-, copper-based alloys, etc., as well as plastics [2]. The 3D process uses initial materials in the form of wire or powder. Heating sources applied in metal product manufacturing are given in Table 1.

However, at application of 3D technologies in manufacture of parts from refractory metals and alloys (T_m > 2000 °C) problems arise because of the high temperature gradient, leading to internal stress formation. As regards refractory metals, known is a small number of works, reporting application of 3D technologies to manufacture products from molybdenum, tantalum, and tungsten [3, 4]. So, the publications give an example of application of additive wire surfacing technology (Figure 1).

Table 1. Heating sources, used in 3D technology

Type of power source	Number of real processes, %
Laser	~ 60
Electric arc	~30–35
Electron beam	~5–10

Further heat treatment of the ingot does not solve the problem of stress relieving, as the process of grain recrystallization and growth begins.

Tungsten ingots and products are not prone to recrystallization at heating, if they have a single crystal structure. Traditionally, tungsten single crystals are grown in the form of rods of up to 25 mm diameter. Considering the high melting temperature (W = 3690 K), high energy density sources of electric heating are used for tungsten single crystal growing, namely the electron beam or low-temperature plasma arc. Attempts to grow sound crystals of a larger diameter failed. The cause for it is the negative influence of the scale factor, which leads to high internal stresses.

Increase of linear dimensions of single crystals leads to two problems, namely containing the melt being deposited on the pool surface (tungsten has a very high density of 19.3 g/cm^3) and high thermomechanical stresses in the single crystal body (which is related to a high temperature gradient). High thermomechanical stresses promote generation of an additional number of dislocations (dislocation density may reach 10^7–10^8 cm^{-2}) and disorientation of sub-grains, which significantly impairs the single crystal structure quality.

A PWI development became an innovative solution, namely creation of plasma-induction 3D technology of growing super large single crystals of tungsten and molybdenum of different shape: plates, ingots and crucibles. Theoretically, this method does not have any limitations as to the size of the grown crystals. It can be implemented in practice through correct organization of preheating and creation of specified thermal conditions. Figure 2 presents a diagram of the unit for additive growth of refractory metal single crystals in the form of plates using the plasma-induction method.

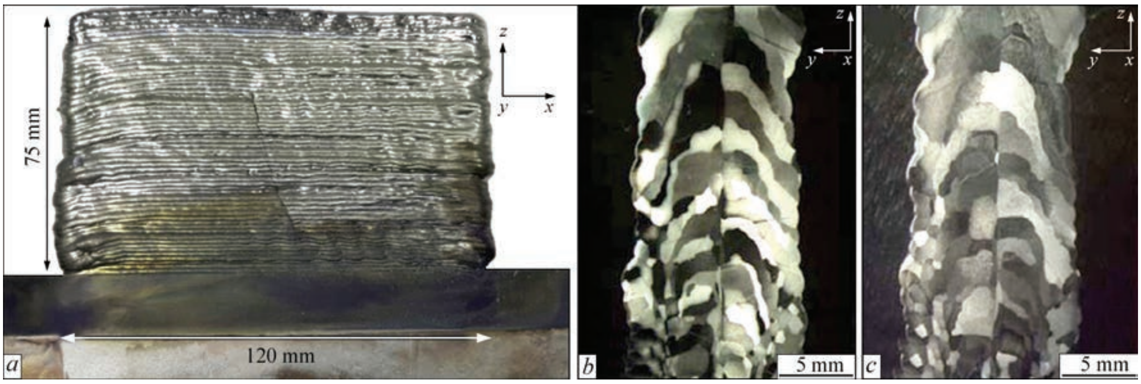

Figure 1. Formation of coarse-grained polycrystalline structure and cracks from internal thermal stresses in a tungsten ingot, produced at wire and indirect arc surfacing (*a*), microstructure of the cross-section (*b*) and after heat treatment (*c*)

EQUIPMENT AND MATERIALS

To solve the problem of growing large and high-quality tungsten single crystals, the objective of development of the appropriate technology was set. The idea of simultaneous application of two different sources of electric heating, namely plasma and induction sources was proposed by PWI specialists for the first time. Each of the above heating sources has its functions: plasma-arc one creates a moving local metal pool on the face of the crystal being built-up, remelts the consumable rods, fed into the melting zone, and forms the single crystal body of the specified configuration; induction source contains the local metal pool from spilling and creates the specified temperature field in the crystal body.

Additional heating of the crystal significantly reduces the radial and axial temperature gradients, which promotes lowering of the dislocation density and internal stresses and formation of a more perfect structure. In this case, despite the use of a local pool, which forms the single crystal while moving, no stresses develop in the crystal, which would promote crack initiation and increase of the number of dislocations. At such temperatures the dislocations annihilate and at evaluation of the single crystal quality their number does not exceed $1 \cdot 10^6$ mm^{-2}. The technology completely eliminates cracking or fracture of the crystals, either in the process of growing or during part manufacturing.

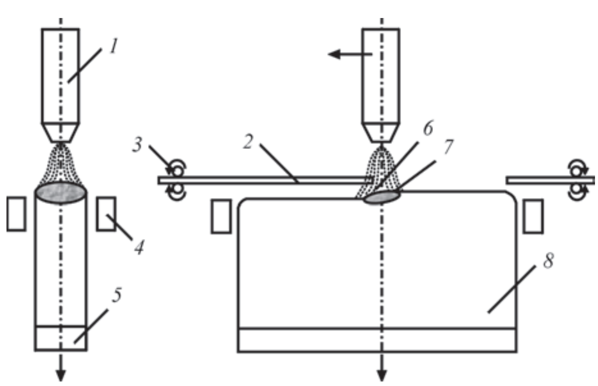

Figure 2. Schematic of the unit for additive growing of refractory metal single crystals using plasma-induction method: *1* — plasmatron; *2* — consumable rod; *3* — rod feed mechanism; *4* — inductor; *5* — seed crystal; *6* — plasma arc; *7* — local pool; *8* — single crystal

The essence of the method consists in that plasmatron, while performing a reciprocating movement, displaces the metal pool, which, while being replenished through rod remelting, forms the crystal layer by layer, being essentially similar to additive arc surfacing. After each plasmatron pass the single crystal is lowered to the height of the deposited layer, thus ensuring stable conditions for the growing process.

This method was used to develop equipment (Figure 3) and technology of growing profiled single crystals of refractory metals (tungsten and molybdenum) in the form of plates (Figure 4).

The crystal forms under the conditions of heating by an inductor high-frequency field to temperatures, characteristic for hot deformation range. It is known that at these temperatures dislocation movement takes place under a simultaneous impact of external stresses and temperature. Dislocations turn out to be not rigidly attached to "their" slip plane, and they can move from one plane into another one, choosing the easiest path. This is regarded as an additional degree of freedom of dislocations. At such an unregulated movement of dislocations the probability of their collision becomes higher, and thus, the number of their annihilation cas-

Figure 3. Unit for growing refractory metal single crystals in the form of plates

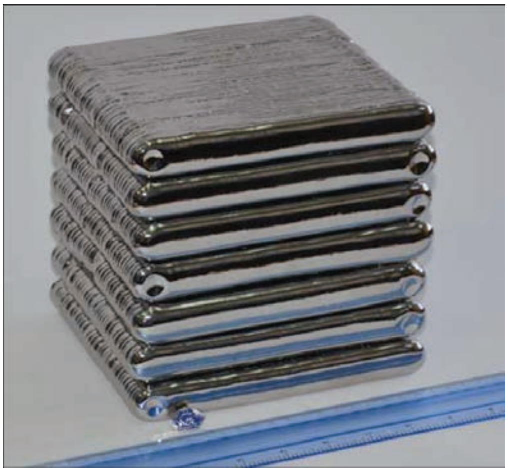

Figure 4. Appearance of flat tungsten single crystals of 170×160×20 mm dimensions

Figure 5. New unit with computer control for growing refractory metal single crystals in the form of bodies of rotation

es rises (their density is decreased) on the one hand, and on the other hand — their proneness to formation of regular dislocation structures characterized by dislocation coalescence into low-angle boundaries, is increased. Conditions, as which the single crystal forms, ensure a higher quality of the single crystal structure, than with the methods, where no additional heating is used (electron beam and plasma-arc).

Crystals grown with application of the above method have not as smooth side surface, but it does not prevent their use without any additional machining as billets for wide-format rolling.

The developed additive technology of 3D growing large commercial purity single crystals of refractory metals is based on the conducted long-term thorough investigations, which allowed establishing and studying the following:

- thermal field distribution in the single crystal using mathematical models and experimental data;
- working ranges of the change of technological parameters of crystal growth process;
- structural characteristics and regularities of structure formation in the grown single crystals.

Calibrated tungsten rods of 8 mm dia, 800 mm length and $W \geq 99.97$ wt.% purity were used as consumable materials for replenishing the pool (Table 2).

EXPERIMENTAL STUDIES AND DISCUSSION OF THE RESULTS

Further study of the process enabled development of a new unit for 3D growing of super large tungsten single crystals in the form of bodies of rotation, based on the same principles (Figure 5).

Developed equipment is a qualitatively new generation of equipment, featuring a completely computerized system of controlling the actuators, sensors of displacement and control of single crystal growth process. The design envisages the possibility of growing single crystals in the form of bodies of rotation (cylinder or hollow cylinder) of up to 100 mm outer diameter. At present a thermal unit has been developed, and optimization of the technology of growing tungsten single crystals of 85 mm diameter is going on.

The developed technology is fundamentally based on the technology of growing flat single crystals. However, in the new unit the crystal is continuously rotating around a vertical axis. A cylindrical billet made from a flat single crystal of a set orientation is used as a seed crystal. Figure 6 shows a photo of the process of single crystal growing, where arrows mark the direction of feeding the consumable rod into the plasma arc meting zone and the direction of single crystal rotation.

Building up takes place layer-by-layer due to movement of the local pool and the plasmatron from the central to the peripheral parts so that the liquid pool covers the entire surface and the previous deposited layer. After layer deposition on the entire upper surface of the crystal, it is lowered down. Equipment allows feeding the rods from both sides, both in the ingot center, and with radial displacement relative to the center. Figure 7 shows a tungsten crystal of 85 mm diameter with 90 mm of built-up layers [5].

At this stage after technology optimization preliminary evaluation of single crystallinity of the produced ingot was performed using chemical etching of the surface in a mixture of equal volume fractions of hydrofluoric and nitric acids. The ingot surface etched in such a way had alternating longitudinal (vertical) matte and shiny stripes characteristic for single crystals. The pattern of

Table 2. Chemical composition of 8 mm tungsten rods

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

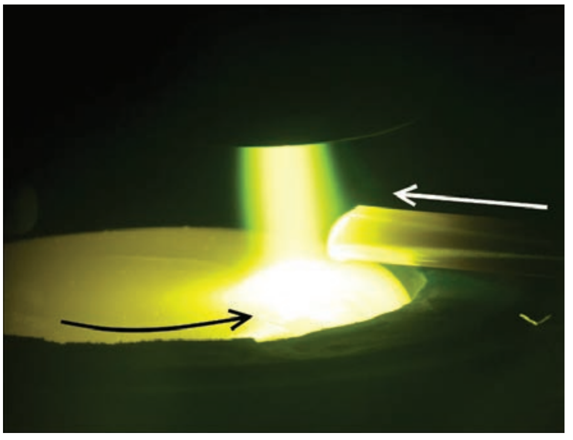

Figure 6. Process of growing a tungsten single crystal in the form of the body of rotation

Figure 7. Appearance of a tungsten crystal of 85 mm diameter

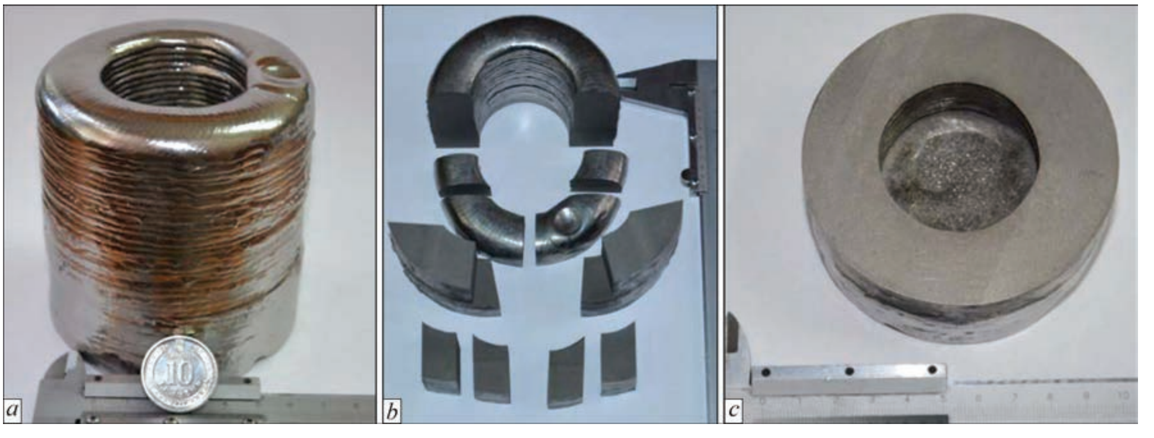

Figure 8. General view of a tungsten single crystal in the form of a hollow body of rotation of 85 mm diameter (*a*); view of the upper part (*b*) and bottom part with the seed crystal (*c*) after cutting up the ingot

stripe distribution was indicative of the provided by the seed crystal heredity of the single crystal structure and absence of sub-blocks of another crystallographic orientation on the ingot side surface.

The next step in development of the technologies of growing super large tungsten single crystals was an attempt to grow a crystal in the form of a hollow cylinder, as a billet for manufacturing crucibles and pipes. It resulted in growing by the novel 3D technology a tungsten crystal in the form of a hollow cylinder on a continuous seed single crystal of 85 mm diameter for the first time in the world. The grown crystal has a built-up wall of 68 mm height and 20–22 mm thickness (Figure 8). Surface examination after ingot etching by chemical reagents showed the heredity of the structure from the seed single crystal and all the signs of structure single crystallinity in the entire crystal.

Microstructural studies yielded the average value of 4150 MPa for the vertical plane, and 3840 MPa for the horizontal plane. A pronounced difference in microhardness in different planes points to anisotropy of properties, characteristic for the single crystal structure. Variations of microhardness values within 10 % in one plane is attributable to structural inhomogeneity of metal single crystals, consisting of sub-blocks and subgrains with low misorientation angles of up to 3°.

CONCLUSIONS

A unique additive 3D technology of growing refractory metal single crystals in the form of 170–160–20 mm plates and bodies of rotation (cylinder and hollow cylinder) of 85 mm diameter was developed at PWI. The next step was optimization of the technology of growing tungsten single crystals in the form of hollow bodies of rotation. An ingot of 85 mm diameter, 20–22 mm wall thickness (for hollow ingots) and 68 mm height was grown. Such a shape will allow using tungsten as tubular billets, for manufacturing elements of a complex curvature or crucibles.

REFERENCES

1. ISO 643:2019: *Steels — Micrographic determination of the apparent grain size*. https://www.iso.org/standard/72193.html
2. Mukherjee, T., Elmer, J.W., Wei, H.L. et al. (2023) Control of grain structure, phases, and defects in additive manufacturing of high-performance metallic components. *Progress in Materials Sci.*, **138**, 101153. DOI: https://doi.org/10.1016/j.pmatsci.2023.101153
3. Marinelli, G., Martina, F., Lewtas, H. et al (2019) Microstructure and thermal properties of unalloyed tungsten deposited by Wire +

Arc additive manufacture. *J. of Nuclear Materials*, **522**, 45–53. DOI: https://doi.org/10.1016/j.jnucmat.2019.04.049

4. Marinelli, G., Martina, F. Ganguly, S., Williams, S. (2020) Grain refinement in an unalloyed tantalum structure by combining Wire + Arc additive manufacturing and vertical cold rolling. *Additive Manufacturing*, **32**, 101009. DOI: https://doi.org/10.1016/j.addma.2019.101009
5. Shapovalov, V.O., Nikitenko, Yu.O., Yakusha, V.V. et al. (2020) Manufacture of super large tungsten single crystals in the form of rotation bodies. *PAST*, 125(**1**), 60–63. DOI: https://doi.org/10.46813/2020-125-060

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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