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Preparation of tungsten crucibles starting from tungsten fluoride

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The study results are presented on technology development for forming of cylindrical tungsten crucibles starting from tungsten fluoride by reduction WF_6 with hydrogen in horizontal flow-type reactor under reduced pressure. It has been shown, that one way to nonporous with smooth outer surface, high surface purity and high strength consists in the deposition process realization in diffusion area at 550°C and the partial pressures ratio in the gas mixture $P_{H_2}/P_{WF_6} = 10/1$.

Приведены результаты исследований по отработке технологии формирования тиглей цилиндрической формы из фторидного вольфрама методом водородного восстановления WF_6 в горизонтальном проточном реакторе при пониженном давлении. Показано, что одним из режимов получения плотных непористых тиглей с гладкой наружной поверхностью, высокой чистотой поверхности материала и высокой прочностью является осуществление процесса осаждения в диффузионной области при температуре 550°C и отношении парциальных давлений в смеси газов $P_{H_2}/P_{WF_6} = 10{:}1$.

Tungsten crucibles for crystal growing have a series of advantages as compared to similar equipment made of other materials, e.g., molybdenum. For example, the priority of tungsten are due to its heat resistance inertness against chemical reactions with the other substances. The preparation of such crucibles using usual metallurgy methods is difficult because the tungsten infusibility, problems with attainment of high purity level and inconvenience of the technological equipment. The gas-phase method using, for instance, tungsten fluoride, is of much better promise. The tungsten fluoride deposition has been studied long ago (see, e.g., [1, 2]). The homogeneous and heterogeneous stages of the process have been explored completely enough. The originality of this work consists in what follows. The construction approaches to the experiments themselves are rather original and simple. Those include the arrangement and design of the components involved (the substrate geometry and arrangement, direction and flow rate of the gas mixture, etc.), as well as the process conditions (the concentration ratio of the gas mixture, pressure in the working chamber, the substrate temperature, etc.). The realization modes of the efficient deposition process are simple and original, too. So, for instance, to provide the uniform thickness of the crucible walls and to suppress the point effects under the deposition, cylindrical substrate was made with rounded edge between its side and butt surfaces. Many others technological solutions described below were realized. The deposition modes were elaborated

in detail and optimized. As a result of this work, the technology for preparation of workpieces with guaranteed high quality characteristics (the structure homogeneity, optimum microhardness, continuity, etc.).

One more moment is to noted defining the advantage of the gas-phase methods to manufacture the above workpieces. At present, there is the trend to grow ever larger crystals for electronic engineering. To that end, ever larger crucibles are necessary. So, while in 1990 sapphire crystal were grown in 100 mm diameter crucibles and in 2000, in those of 150 mm, at present, the crucibles of 350 mm and more in diameter are required [3]. Traditional technologies of cutting or pressing are expensive and require cumbrous equipment. The cost and compactness of the equipment using gas-phase methods depend weakly on the crucibles size.

For manufacturing of crucible with the wall thickness exceeding 0.5 mm, it is reasonable to use tungsten hexafluoride reduction with hydrogen due to high reduction rate and relatively low process temperature.

In this work, the study results on use of the gas-phase method to manufacture cylindrical crucibles in horizontal flow-type reactor under reduced pressure. The experiments were done in the setup for material preparation from gas phase described in [4]. The reactor of 200 mm diameter provided to get the crucibles of up to 120 mm diameter and 150 mm height. A cylindrical substrate made of AG-1500 grade graphite was mounted on a "rod" within the reaction chamber in the active zone of an inductive HF generator. The substrate dimensions, shape, and the outer surface finish grade conform to required characteristics of the crucible inner surface.

At the sharp edge between cylindrical wall and flat butt end of the substrate, the deposition rate was higher than that at other areas due to strong heating of the edge by induction fields, as well as electrostatic "edge" effects. The difference in the deposition rates causes a bulged wall of the product at that edge (Fig. 1a); thus, the substrate was made with rounded edge. At the rounding radius of 10 % of the internal crucible diameter, a workpiece is formed with the same wall thickness in all geometric directions (Fig. 1b).

The homogeneity of the heat field at the cylindrical substrate surfaces was provided by a specially designed inductor, special substrate arrangement geometry within the

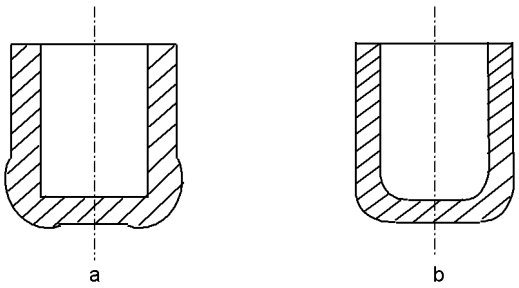
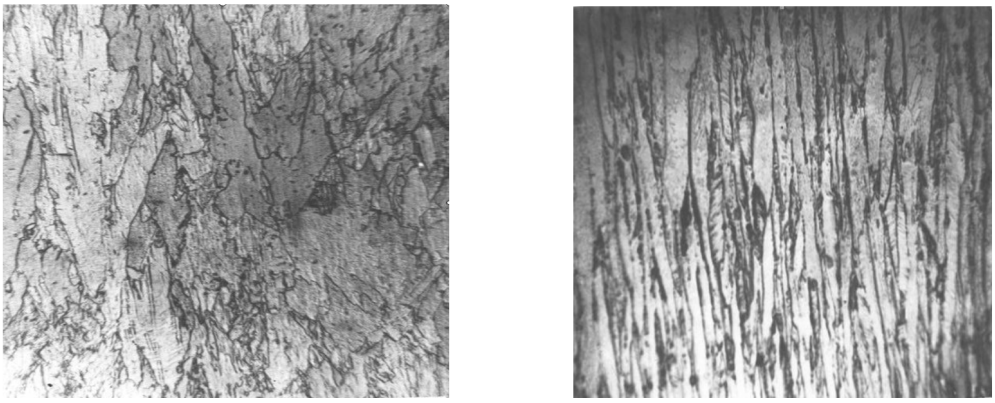


Fig. 1. Effect of rounded substrate edge the crucible configuration: (a), unrounded edge, the crucible with locally thickened wall; (b) substrate with rounded edge, the crucible with uniform wall thickness.

reaction chamber and its rotation about longitudinal axis during the deposition process. The uniform temperature distribution and thus the same deposition rate at different areas was provided also by the substrate massiveness, its high thermal capacity and thermal conductivity. The maximum temperature difference between different substrate surface points amounted 10°C at its average temperature of 550°C.

The crucible manufacturing procedure was as follows. Hydrogen was fed into the reaction chamber evacuated previously to 10^{-2} Torr. The pump-out rate was adjusted to maintain the pressure in the chamber at 30 Torr. To degas the substrate and to purify additionally its surface, it was annealed first at a temperature exceeding the deposition one by 150–200°C. After reduction of the substrate temperature, tungsten hexafluoride was fed into the chamber in required amount and the deposition process was run till the necessary crucible wall thickness was attained. After the deposition process was over, the graphite core of the workpiece was removed by drilling.

The crucible obtained was examined considering the presence of mechanical defects (pores, holes, cracks, exfoliations, etc.); physico-mechanical characteristics of the crucible material defining its working performance were studied also. The material density was determined by hydrostatic weighing. The crucible material microstructure was studied on transverse sections in the as-made and annealed condition and its microhardness was measured. The material purity and quantitative content of the impurities were determined by chemical analysis. The concentration of typical impurity (fluorine) was measured also using nuclear physics method [5]. The fracture character



a b

Fig. 2. Microstructure of fluoride-originated tungsten (×200) obtained at T_s = 450°C, P_{H_2}/P_{WF_6} = 50:1 (a) and at T_s = 550°C, P_{H_2}/P_{WF_6} = 10:1 (b).

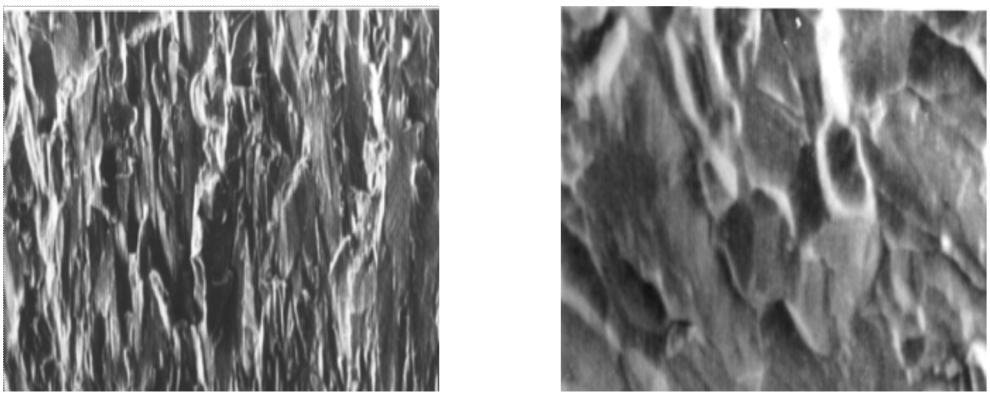


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Fig. 3. Fracture structure fluoride-originated tungsten deposited at different conditions: T_s = 450°C, P_{H_2}/P_{WF_6} = 50:1 (a, ×800) and at T_s = 550°C, P_{H_2}/P_{WF_6} = 10:1 (b, ×1200).

was studied using a REMMA-200 raster electron microscope.

Physico-mechanical characteristics fluoride-originated tungsten are defined by the condensate deposition conditions, including the substrate temperature and tungsten hexafluoride concentration in the gas phase.

Several modes of the gas-phase deposition were studied. The substrate temperature and relative partial pressures in the gas mixture were varied as follows: T_s = 400–650°C, P_{H_2}/P_{WF_6} = 50/1–10/1, respectively. At low-temperature deposition, i.e., T_s 400 to 450 C and rather low WF_6 content (the partial pressure ratio P_{H_2}/P_{WF_6} = 50:1), the crucibles obtained had insufficient inner surface finish, corresponding to that of the substrate surface, an admissible impurity content, as well as smooth outer surface free of mechanical defects. The crucible material density amounted 19.1 g/cm^3. The layer growth rate at the specified conditions was of 25 to 30 μm/h. Under such conditions, the deposition process to obtain a crucible with wall thickness of 3 mm lasted 100 h. The metallographic studies have shown that in those conditions, a small-columnar non-equilibrium structure is formed characterized by irregular boundaries and presence of separate shrubs (Fig. 2a). Such a structure is thermally unstable and recrystallizes itself well. So, after annealing at 2000°C for 2 h, the primary recrystallization was completely terminated, the microhardness decreased herewith from 4500 MPa in the as-deposited state to 3800 MPa after the anneal.

The formation of the thermal unstable structure is due to presence of a considerable amounts of the impurities. The measurements have shown that in fluoride-originated tungsten obtained in the above conditions, the total impurity content is about $4 \cdot 10^{-2}$ mass%. Among the main impurities,

the highest is the molybdenum concentration (~$5.8 \cdot 10^{-3}$ mass %); in smaller amounts iron (~$4.2 \cdot 10^{-3}$ mass %), copper (~$3.9 \cdot 10^{-3}$ % mass) and aluminum (~$3.7 \cdot 10^{-3}$ mass %) are present. Oxygen, nitrogen and silicon are present in about the same concentration of $3 \cdot 10^{-3}$ mass %; the content of other elements does not exceed 10^{-3} mass %.

Under low temperature and low WF_6 concentrations, the fluorine presence in condensates of fluoride-originated tungsten is due mainly to binding of lower fluorides. As a rule, the fluorine content in the deposits is maximum in this case. The nuclear-physical measurements have shown that the fluorine concentration in the deposited crucible material is significant and amounts ~$7.5 \cdot 10^{-3}$ mass %.

The mentioned impurities, including fluorine, are interstitial ones; their content exceeds the solubility limit in tungsten. The impurities are arranges predominantly along the grain boundaries, they are weakly bound with the matrix and weaken considerably the grain cohesion in the material. The grain boundaries become the most fragile structure element, defining the general brittleness of the workpiece. This fact is confirmed by Fig. 3a showing the fracture microphoto where the predominant inter-crystalline fracture character is seen.

Increasing substrate temperature at the same contents WF_6 in the gas phase (P_{H_2}:P_{WF_6} = 50:1) results in a significant increased deposition rate. Fig. 4 shows the temperature dependences of the process rate for this case (curve *1*).

It is seen in Fig. 4 that in the studied temperature range, the deposition rate increases continuously and exceeds 100 μm/h at T_s > 550°C. However, a deterioration of the material quality occurs in this case. Already at T_s≈500°C, the surface "globulization" starts to occur and the microstructure non-equilibrium increases; the latter becomes shrubby, its microhardness increases. As T_s increases further, the dendritic growth character becomes predominating, the structure loses compactness, the condensate density decreases considerably.

Depending on the tungsten deposition mode from hexafluoride (the operating pressure, concentration ratio in the gas mixture, the substrate temperature, etc.), the process may run in both kinetic and diffusion regions, which, in turn, are differentiated into smaller stages, characterized by their own particularities [6]. At low temperature and hexafluoride concentrations, the process in kinetic region is limited by molecular adsorption, but at high values of the parameters, by the desorption phase. At intermediate temperatures and high hexafluoride concentrations, the transport of the operating gas to the substrate is defined by diffusion. In the diffusion stage, the deposition results in a higher quality structure of the condensate material. The morphology of the growth surfaces in diffusion region is characterized by a high ordering of separate crystals without essential distortion of growing pyramid faces, as well as by a weak dependence of the structure growth rate on the substrate temperature.

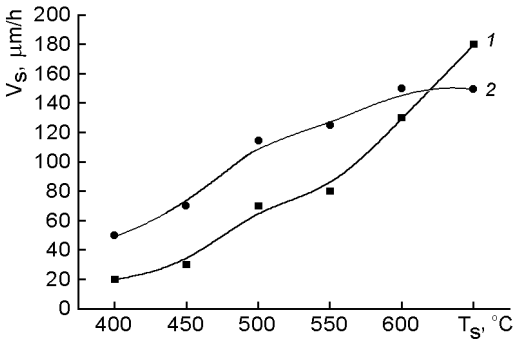

Fig. 4. Dependences of the tungsten layer growth rate on the deposition temperature at different WF_6 content in gas phase: P_{H_2}/P_{WF_6} = 50:1 (1), P_{H_2}/P_{WF_6} = 10:1 (2).

In experiments at increased WF_6 content up to P_{H_2}/P_{WF_6} = 10:1 in the interval T_s range of 450 to 650°C, a dense nonporous material is formed with smooth outer surface. The workpieces are similar in appearance to the crucibles got at lower concentration of hexafluoride and low substrate temperature (i.e. in the mode described above), but differ considerably in the material characteristics. The temperature dependence of the deposition rate for this case is shown in Fig. 4, curve *2*. The slope decrease of the curve *2* at temperature T_s above 530°C evidences the process running in diffusion region. The crucibles got at such WF_6 concentrations exhibit a high material density of 19.2 g/cm^3 close to theoretical one, that evidences the absence of micropores. The microstructure is columnar, the column size increases with elevating temperature from 20×200 μm to 30×250 μm. The material structure is close to equilibrium one, thermally stable, does not recrystallize under annealing at T = 2000°C for 2 h. The microstructure type of the fluoride-originated

Table. Microhardness of fluoride-originated tungsten condensates obtained at gas component ratio P_{H_2}/P_{WF_6} = 10:1 in as-deposited state and after annealing for 2 h at 2000°C

T_s (°C)	450	500	550	600	650
As-deposited	3975	4045	3990	4150	4080
Annealed	3880	3850	3930	3945	3925

tungsten obtained at T_s = 550°C and P_{H_2}/P_{WF_6} = 10:1 is shown in Fig. 2b. Thermal stability of the structure is evidenced also by the condensate microhardness values presented in the Table. Microhardness in the as-grown state is independent of the deposition temperature and changes within 3950–4150 MPa, but decreases down to 3850–3950 MPa after annealing.

The purity degree of the crucibles material obtained in such conditions exceeds considerably that attained at deposition from gas mixture with lower tungsten hexafluoride content and amounts 99.99 % to similar characteristic of the substrate surfaces; the total impurity content does not exceed 10^{-2} mass %. The Mo ($1.5 \cdot 10^{-3}$%), Fe ($1.1 \cdot 10^{-3}$ %), Cu ($1.0 \cdot 10^{-3}$ %), Al ($0.9 \cdot 10^{-3}$ %), O_2 ($1.7 \cdot 10^{-3}$ %), and N_2 ($0.6 \cdot 10^{-3}$ mass %) concentrations are much lower. The fluorine concentration drops to 10^{-3} %. The reduction of the total impurity amount promotes the formation of nearly equilibrium condensate structure and hardening of the grain boundaries. The latter is confirmed by fracture photo shown in Fig. 3b, which evidences the fact that the trans-crystalline fracture fraction is higher than in the fluoride-originated tungsten obtained at the lower WF_6 content.

A crucible obtained at T_s = 550°C, P_{H_2}/P_{WF_6} = 10:1, is shown in Fig. 5.

Technological tests on sapphire crystal growing in crucibles made by gas-phase recovering of tungsten from hexafluoride by hydrogen were realized at STC "Institute for Single Crystals" in a "Crystal 606" HF unit. The crystals obtained had admissible low impurity contents, including carbides, and the crucibles had a sufficient life time.

Thus, during the studies, technology was improved to obtain high-quality crucibles satisfying the operational requirements from fluoride-originated tungsten. Among the modes providing high-quality workpieces by gas-phase method, is the following: T_s = 550°C, P_{H_2}/P_{WF_6} = 10:1. The deposition rate in such conditions is about 125 μm/h and hexafluoride fraction reacted at each act pumping through the reaction chamber amounts 70 %. The unevenness of the crucible wall thickness ataverage thickness of 4 mm does not exceed 0.2 mm. The use of the gas-phase methods for manufacturing of large diameter crucibles seems to be of good promise.

Fig. 5. A crucible made of fluoride-originated tungsten.

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Одержання тиглей зі фторидного вольфраму

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Представлено результати дослідів з відпрацювання технології формування тиглей циліндричної форми зі фторидного вольфраму методом відновлення WF_6 воднем у горизонтальному проточному реакторі при зниженому тиску. Показано, що одним із режимів одержання щільних непористих тиглей з гладкою зовнішньою поверхнею, високою чистотою поверхні матеріалу та високою міцністю є здійснення процесу осадження у дифузійній області при температурі 550°С та відношенні парціальних тисків у суміші газів $P_{H_2}/P_{WF_6} = 10{:}1$.