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> REFRACTORY, CERAMIC, AND COMPOSITE MATERIALS

# Experience in Improving the Manufacturing Properties of Semifinished Products and Quality of Thoriated Tungsten Products by the Deposition of Tungsten Coatings with WF<sub>6</sub> Hydrogen Reduction

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Abstract—Tungsten deposition from a gaseous mixture of its hexafluoride with hydrogen on the surface of a porous billet of thoriated tungsten makes it possible to fasten the particles of peripheral layers and its core between each other, as well as to form a more plastic shell on the surface capable of relaxing stresses appearing during rotary forging, thus preventing the destruction of semifinished products. This procedure makes it possible to perform the rotary forging of a pilot batch of insufficiently sintered billets of thoriated tungsten, which would be destroyed if treated uncoated. The improvement of manufacturing properties can be used when fabricating similar tungsten-based compositions (of  $W(La_2O_3)$  and  $W(Y_2O_3)$ ), as well as for other types of deformation. These results can be applicable for (i) lowering the sintering—welding temperature of bars (and rods) of dis-persion-strengthened tungsten-based compositions, thereby reducing power consumption and increasing the overhaul period of equipment; (ii) increasing the sizes of semifinished products using the existing equipment thereby increasing the production process productivity and expanding the range of output products; (iii) pro-ducing less environmentally hazardous thoriated tungsten products, multiply reducing the radiation exposure of operators; and (iv) using composite cathodes in arc xenon lamps, thereby increasing their service life by a factor of 2-3.

*Keywords:* tungsten, thorium oxide, tungsten hexafluoride, hydrogen reduction, deposition in pores, plastic sheath, rotary forging, composite cathode of gas-discharge lamps, service life, radioactivity reduction, ecology

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# INTRODUCTION

The presence of thorium dioxide  $(ThO_2)$  in tungsten provides an increase in the recrystallization temperature; retardation of the grain growth at elevated temperatures; and, consequently, higher strength material properties. In addition, the low electron work function, which is characteristic of thorium, is predetermined by use of thoriated tungsten as the emission active material [1, 2, 3, pp. 230, 231]. Tungsten rods with the ThO<sub>2</sub> additive are used to fabricate the most important constructions, as well as cathodes of arc xenon lamps for projector technique and cinematography.

The standard fabrication technology of rods of thoriated tungsten of the VT-50 grade foresees the pressing of bars or rods of the mixture of tungsten and thorium dioxide powders, preliminary sintering for ensuring the mechanical strength for compaction, and final sintering—"welding"—performed by directly passing the electric current through the corresponding billet, which is heated to 2800-3000°C [4]. Further, the sintered billet is subjected to rotary forging to a required diameter at  $t = 1500^{\circ}$ C [2, 5, 6]. When heating the bar by passing the current, the main heat removal is performed by radiation from its surface, which leads to the appearance of the temperature gradient over its section [3, p. 183; 4]. The aspiration to avoid overheating in the center of the sintered billet can lead to insufficient sintering its surface layers (especially in bar corners), which forms the conditions for crack formation and billet destruction during rotary forging. To prevent crack formation, it is necessary to fasten the surface particles of the billet with each other and with its central part by the deposition of the layer of dense and more plastic tungsten from the gas phase [7, pp. 7-60; 8, 9]. Stresses that appear during the for-mation will relax due to the plastic deformation of the tungsten coating in this case.

The goal of this study is to demonstrate the possibility of the gas-phase deposition of the tungsten coat-



Fig. 1. Reaction chamber for the deposition of the tungsten coating from the mixture of tungsten hexafluoride with hydrogen on bars and rods. (1) Case, (2) gas-distribution facility, (3) current lead, (4) bar (rod), and (5) gasket.

ing by means of reducing tungsten hexafluoride with hydrogen in order to increase the manufacturing properties of semifinished products made of thoriated tungsten and improve the quality of fabricated products.

### **EXPERIMENTAL**

We used more that 200 bars with a section of  $11.5 \times 11.5$  mm and length of ~450 mm from those manufacturing batches of thoriated tungsten of the VT-50 grade which showed a negative result during manufacturing testing at first forging. Tungsten coatings were deposited on the surface of bars from the mixture of tungsten hexafluoride and hydrogen according to the reaction

$$WF_{6(gas)} + 3H_{2(gas)} = W_{(sol)} + 6HF_{(gas)}.$$
 (1)

The experiments were performed using a reaction chamber whose schematic is shown in Fig. 1 [10]. Bar 4 was fastened in current leads 3 along the axis of chamber 1, which is a vertically arranged cylinder with a diameter of 60 mm and length of 700 mm. The bar was heated to  $550-800^{\circ}$ C by passing an electric current through it. Chamber tightness was provided due to stuffing-box seals 5, in which the top and bottom current leads 3 were fastened. To compensate bar elongation during heating, the seal of the bottom current lead admitted its vertical motion.

The gaseous mixture of tungsten hexafluoride and hydrogen was supplied under atmospheric pressure into the reaction chamber from the top through gasdistribution facility 2, providing its uniform distribution over the chamber section, and was removed from the bottom through an identical device. The gas-mixture flow rate was ~8 mol/h. To measure the temperature, thermocouples were fastened to the bar at a distance of ~50 mm from the top and bottom bar ends; their readings were fixed before the process began and during the deposition of tungsten.

A convective gas flow (shown in Fig. 1 by arrows), which more intensely cools the bottom part of the heated bar, appears in the described reaction chamber due to the difference in temperature of the bar and chamber walls (~100°C). This results in the temperature being ~50°C lower than at the top bar part. The maximal temperature on the bar surface, in the presence of heat sink through current leads and described convection flow, was fixed at a distance of ~150 mm from its top end. It was 30-40°C higher than the temperature in the top thermocouple zone.

Fastening of surface particles will be efficient if its strong adhesion with the material of the coated surface is attained during the deposition of the tungsten coating. The authors of [7, p. 142; 11, 12], in order to acquire the strongly fastened coating on tungsten under atmospheric pressure, recommend a temperature higher than 700°C. In connection with this, to perform the experiments, we selected a temperature range of 710–720°C (in the bottom bar part), 760– 770°C (in the top bar part), and ~800°C (in the zone of the maximal temperature). To form dense tungsten coatings from the mixture of tungsten hexafluoride with hydrogen at  $t = 800^{\circ}$ C, it is necessary to hold the content of  $WF_6 \ge 50 \mod \%$  in it [7, Fig. 17]. The completeness of using  $WF_6$  cannot exceed 33% in this case. Therefore, a gas mixture with a content of  $WF_6 \ge$ 50 mol % was supplied after bar heating to the required temperature in order to deposit the first tungsten layer strongly fastened with the substrate. The current used for bar heating simultaneously decreased to the magnitude necessary to hold its temperature of 550°C, which led to a decrease in the bar temperature to  $550^{\circ}$ C for 5 min. The WF<sub>6</sub> content in the gas mixture decreased to  $\sim 25 \mod \% 4-5 \min$  after the process began, and the process further passed for 13-15 min with the stoichiometric ratio of components [8]. Approximately 140 g of  $WF_6$  was consumed during the process. The bar weight increased by 35–40 g after the tungsten deposition. The completeness of using  $WF_6$ was 43-45%.

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The bars were grouped initially by the section and then by the weight per the length unit (i.e., practically by the density) for the convenience and reduction of the preparation time of experiments. For each subgroup, 1–2 experiments were performed with measuring the temperature during the tungsten deposition, in the course of which the plot of varying the electric current force (*I*) was fixed depending on time ( $\tau$ ). In further processes, the temperature was not measured, but this plot  $I(\tau)$  was repeated.

# EXPERIMENTAL RESULTS

We performed the deposition of coatings ~100  $\mu$ m thick on 202 bars from out-of-grade batches according to the described procedure. The sufficient deposition uniformity of tungsten was attained due to the effect of two factors:

-when supplying the initial gas mixture with the velocity lower than the convection flow velocity, it is diluted with the ascend gas flow mainly containing HF as the reaction product and is forced out into the descending branch of the convective flow. Relatively high WF<sub>6</sub> and H<sub>2</sub> concentrations in the upper part of the descending branch of the convective flow and their low concentrations in its ascending branch form the conditions for the diffusion of reacting components in the direction of the deposition surface, which has the maximal velocity at the top and is retarded upon the motion downward due to a decrease in the difference in concentrations of reacting components. The descending and ascending branches in the bottom chamber part have a close composition. Therefore, the diffusion supply rate of reagents to the deposition surface is close to zero. Here, the supply rate of reagents to the reaction surface is determined by the ascending branch of the convection flow. It decreases with the motion upward due to the consumption of reagents to the tungsten deposition. These two supply methods of reagents to the deposition surface, the intensity of which changes oppositely over the chamber height, ensure the relatively uniform tungsten deposition over the bar length [10].

—when heating the bar by passing the electric current through it, self-regulation of the tungsten deposition rate occurs. The segments on which a large tungsten thickness was formed have an increased section and smaller electrical resistance. A smaller amount of heat is released on these segments; the temperature decreases; and, consequently, the deposition rate of tungsten decreases. On the contrary, electrical resistance in segments of smaller section increases; the larger amount of heat is liberated; the temperature rises; and, by virtue of this fact, the deposition rate of tungsten increases [10].

The resulting thickness of the tungsten coating on bar faces varied from  $90-100 \,\mu\text{m}$  in the top part to  $70-80 \,\mu\text{m}$  in the bottom part, and it reached 110-120 and



**Fig. 2.** Deposition character of tungsten (fine hatching) in surface pores of various configurations. (a-c) With opening angle (a) >110°, (b) 90°, and (c) 60°; (d, e) with vertical walls; and (f) with a decreasing section towards the outer bar surface.

 $90-100 \ \mu m$ , respectively, at bar corners. The last fact is caused by the more intense supply of reacting substances due to the better surrounding of edges with the gas flow.

Structural studies showed that the surface of bars consisted of tungsten particles and pores differing in shape and sizes [13]. The deposition character of tungsten in them is schematically depicted in Fig. 2.

Pores with an opening angle towards the outer surface of more than  $110^{\circ}$  are completely filled with tungsten (Fig. 2a) [14, 15]. If their opening angle is  $90^{\circ}$  and  $60^{\circ}$  (Figs. 2b, 2c), then the unfilled narrow pore is observed, the extension of which decreases with an increase in the opening angle. Pores with vertical walls having a depth smaller by a factor of >2.5 than their diameter are filled completely (Fig. 2d). A pore with a shape close to triangular remains in similar pores of larger depth after the overlap of the outer orifice (Fig. 2e). Approximately the same pattern after the overlap of the outer orifice is characteristic of the pores, the diameter of which decreases in the direction of the outer bar surface (Fig. 2f).

In all cases, the first two outer layers and partially the third layer of the sintered billet are guaranteedly fastened between each other with deposited tungsten. When the outer pore orifice is not overlapped, reacting components have the possibility to penetrate into lowlying pores, also depositing fastening tungsten layers there. The smaller amount of reagents reaches the deeper billet layers, and thinner tungsten films are formed; however, we should take into account that they fasten the particles of layers, which are situated at a higher temperature during the preceding sintering. A dense layer of pure tungsten is deposited after overlap of pores; its thickness is determined by the duration of the process.

Fastening the particles of periphery layers of the sintered billet between each other and with its central

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part, as well as the formation of the shell of more plastic tungsten capable of relaxing stresses appearing during rotary forging on the billet surface allowed us to forge all bars treated by the described method to a diameter of 3 mm without any destruction. Our rods of thoriated tungsten had a tungsten coating ~15  $\mu$ m in thickness, which did not prevent their use as welding electrodes and cathodes of gas-discharge lamps. The presence of a more plastic coating on the rods also promotes their successful drawing when fabricating wire for filamentary cathodes. The surface layer can be removed by etching if necessary. The above-described effect will be attained with the similar treatment of tungsten bars with the La<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> additive.

## POSSIBLE VARIANTS OF PRACTICAL USE

## Lowering the Sintering–Welding Temperature of a Billet

The final sintering-welding of the bars and rod billets made of thoriated tungsten can be performed at 2600-2700°C, and then insufficiently sintered peripheral billet layers can be fastened by the deposition of a thin layer of dense and pure tungsten from the gas phase. This technical solution makes it possible to decrease the probability of extremely undesirable overheating and catastrophic growth of tungsten grains in the central billet part (especially when fabricating billets with a large section), as well as decreases the power consumption of the most power-consuming operation by ~20%. A decrease in the sintering-welding temperature prolongs the service life of high-temperature equipment units, increasing its overhaul period, and lowers evaporation of WO<sub>2</sub> forming according to the reaction

$$W + 2H_2O = WO_2 + 2H_2,$$
 (2)

when using insufficiently dried hydrogen. The latter is a consequence of a decrease in evaporation intensity of WO<sub>2</sub> and equilibrium shift in reaction (2) towards the formation of tungsten [3, pp. 184, 185].

#### An Increase in the Formed Billet Section

The temperature difference between the center and a surface of the sintered billet under its heating by the direct passage of the electric current increases with an increase in its section. A decrease in the admissible temperature of the outer billet surface during sintering expands the range of temperatures and makes it possible to increase the section of a billet subjected to sintering, thereby increasing the productivity of the slowest stage of the process chain. Larger billets of thoriated tungsten can be fabricated in this way using the existent equipment by just replacing the facilities at the compaction operation.

## Formation of Environmentally Purer Products

Currently produced rods (electrodes) of thoriated tungsten are packed into the transport tare and delivered to a consumer. The radioactive dust is formed during the transportation because of the attrition of the contacting rod, which can pour from the unsealed tare. An operator working with such a product is subjected to radioactive irradiation coming from the rods and from the dust, which can enter his lungs. The deposition of a gas-phase coating (0.25-0.3 mm thick) on the surface of the sintered billet of thoriated tungsten with the subsequent rotary forging makes it possible to form electrodes for welding with an outer coating of pure tungsten  $\geq 50 \ \mu m$  in thickness. The transportation of such rods excludes the formation of radioactive dust, while the operator will not be subjected to danger. The coating of pure tungsten protects the operator against  $\alpha$ -radiation and  $\beta$ -radiation almost completely, and protects against  $\gamma$ -radiation by more than 80%.

Sources of radioactive radiation are only the rod ends and a sharpened cone of the electrode. The sizes of the emitting surface decrease by a factor of  $\sim 100$ .

## Combined Electrodes of Arc Xenon Lamps

When developing high-power xenon lamps  $(\geq 5 \text{ kW})$ , cathodes of thoriated tungsten of such diameter, which could not be provided by fabrication from above-considered rods, were required. The stated problem can be solved as follows. The tungsten coating 3-5 mm in thickness was deposited according to the above-described procedure on the preliminarily forged dense rod of thoriated tungsten by reducing WF<sub>6</sub> with hydrogen. Formed roads 14-18 mm in diameter were subjected to rotary forging to the required diameter. Combined cathodes, the inner part of which consisted of thoriated tungsten and the outer part consisted of pure tungsten, were fabricated from them. Such cathodes fulfilled all necessary functions to hold the electric arc in lamps. The outer coating of pure tungsten considerably retarded the evaporation of various impurities from the central cathode part and transparency loss of a quartz envelope. This resulted in an increase in the service life of lamps by a factor of 2-3.

# **CONCLUSIONS**

Fastening the particles arranged on the surface of a porous billet of thoriated tungsten by the deposition of a tungsten coating from a gaseous mixture of  $WF_6$  and hydrogen prevents the crack nucleation and destruction of semifinished products under impact loads appearing during rotary forging.

Using this technical solution makes the following possible:

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(i) decrease power consumption by  $\sim 20\%$  due to a decrease in temperature at the sintering–welding stage of billets;

(ii) increase the service life of thermally stressed equipment units;

(iii) increase the sizes of billets and increase the productivity of the equipment;

(iv) fabricate products with a lower radioactive emission intensity;

(v) develop composite materials with improved operational characteristics.

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