Фізика аеродисперсних систем. – 2025. – № 63. – С.189-195

ФІЗИКА АЕРОЗОЛІВ

УДК 536.46

Orlovska S.G.

Odesa I.I. Mechnikov National University, Odesa, Ukraine
E-mail: svetor25@gmail.com
ORCID: https://orcid.org/0000-0003-1203-6978

Study of the patterns of growth of oxide structures on the surface of tungsten upon heating

The paper presents the results of studies of the features of the formation of oxide structures on the surface of tungsten wires heated by electric current in air. Stationary high-temperature oxidation modes of tungsten wires with diameters of 210 and 300 μm were studied by the electrothermographic method. It was established that at an average temperature of a tungsten wire of about 900 K, filamentous crystals appear on its surface, which grow rapidly and subsequently acquire a plate and branched shape. The dispersed composition, shape and surface density of the obtained tungsten trioxide microcrystals depend on the temperature and oxidation time. The growth rates of individual crystals in the longitudinal and transverse directions were determined. It was established that the crystals initially grow more actively in the longitudinal direction (in height), and then grow faster in width. Usually, the final size of the crystal in the transverse direction is larger than in the longitudinal direction. A linear law of growth of the maximum size of dendrites with time has been proved. Calculations of the fractal dimension of dendritic structures of tungsten oxide have been carried out. The obtained values of fractal dimension indicate that the growth mechanism is diffusion-limited aggregation (DLA) with the participation of the vapor phase WO_3. When tungsten is heated to high temperatures, the oxide partially turns into vapor and condenses on the surface in the form of dendrites.

Keywords: *Tungsten, tungsten oxide, filamentous crystals, dendritic structures, high-temperature oxidation, fractal dimension.*

Introduction. tungsten is widely used in high-temperature conditions, namely: nuclear power, electrovacuum systems, electric heaters, microelectronics and sensor systems. In an active gas environment, tungsten is oxidized. The presence of an oxide layer can significantly change the electrical conductivity, thermal conductivity, mechanical strength of the metal and other technical characteristics and, thus, worsen the quality of its use. On the other hand, tungsten oxides WO_3 and WO_2 are widely used in gas sensors, electrochromic devices, photocatalysts, plasma and optical elements. Understanding the physics of crystal growth directly on tungsten makes it possible to control the morphology (length, diameter, orientation of oxide structures) and create new high-quality functional materials.

Oxidation of tungsten is a complex process that includes successive stages of nucleation, the formation of primary oxide islands, their growth and the development of complex morphological structures - from compact films to needle-like, dendritic and filamentous WO_x crystals [1,2]. The conditions that affect the kinetics of this process are especially important: temperature, partial pressure of oxygen, tungsten surface structure, local temperature gradients and the presence of non-stationary factors, such

DOI: 10.18524/0367-1631.2025.63.347257

as current or plasma activation [3-7]. It has been shown in [4] that the growth rate of the oxide and the shape of the crystals significantly depend on the grain orientation. On polycrystalline tungsten, oxide crystals often grow unevenly: each grain has its own oxidation rate and its own crystallization direction. Dendritic structures arise under conditions of strong concentration and temperature gradients, which is characteristic of high-temperature oxidation and heating by current [1, 3, 5, 6]. Sublimation of WO_2 and WO_3 oxides is a key mechanism for the formation of long crystals and nanostructures. In contrast, reactive oxygen plasma allows the initiation of oxide growth at temperatures significantly lower than those required for thermal oxidation. Growth occurs uniformly over the surface, without sublimation processes. The oxide structure is finely crystalline, without needles and dendrites [7].

This work is devoted to the study of high-temperature oxidation of tungsten in air, elucidating the temperature regimes of oxide structure formation on the tungsten surface, and determining the geometric dimensions and growth rates of individual oxide crystals.

Results and discussion. To study the kinetics of tungsten oxidation, an electrothermographic method was used, consisting of programmed heating of tungsten conductors with an electric current [5, 8]. The temperature of the tungsten conductor heated by the electric current was determined from the dependence of its resistivity on temperature. Considering that during the oxidation process, the conductor diameter decreases due to oxide formation, the following formula can be derived for determining the average conductor temperature:

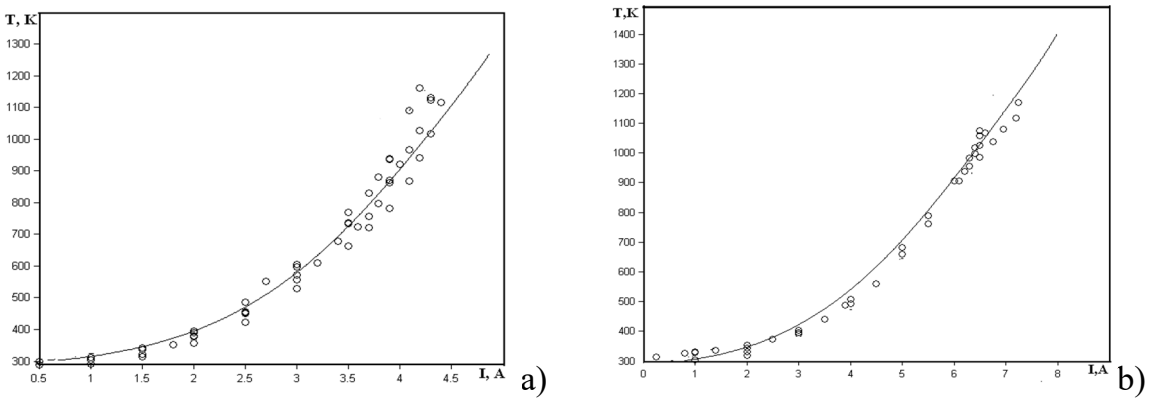
$$T = \left[\left(\frac{d}{d_b} \right)^2 \cdot \frac{L_b}{L} \cdot \frac{R}{R_k} - 1 \right] \left(\frac{1}{\gamma} - T_0 \right) + \left(\frac{d}{d_b} \right)^2 \cdot \frac{L_b}{L} \cdot \frac{R}{R_k} \cdot T_k , \qquad (1)$$

where d_b, L_b, d, L – the initial (with index b) and current (during the oxidation process) diameter and length of the conductor, respectively, m; R_k, R – the resistance of the conductor at room temperature (before the start of the experiment) and during the oxidation process, Ohm; T_k is the room temperature, K; T_0=273K; γ – the temperature coefficient of resistance, K^{-1}.

Let's analyze the research results. Crystal growth on the surface of tungsten conductors was studied under steady-state thermal conditions. These conditions are characterized by equal heat flows heating the conductor and dissipating heat to the surrounding space. As a result, steady-state temperatures are established on the conductor's surface, remaining unchanged for a relatively long period of time.

When an electric current flows through a conductor, heat is generated according to the Joule-Lenz law. Tungsten oxidizes readily in air, forming an oxide layer on the surface. At high temperatures, dendritic oxide structures develop on this layer. The oxidation reaction proceeds parabolically, releasing heat. Thus, Joule and chemical heat generation heat the conductor.

The mechanisms that remove heat from a conductor are convective-molecular heat exchange between the conductor's surface and air, radiative heat exchange according to the Stefan-Boltzmann law, and heat flow by conduction to the current-carrying contacts [5]. Equal heat input and heat removal are ensured by steady-state temperature



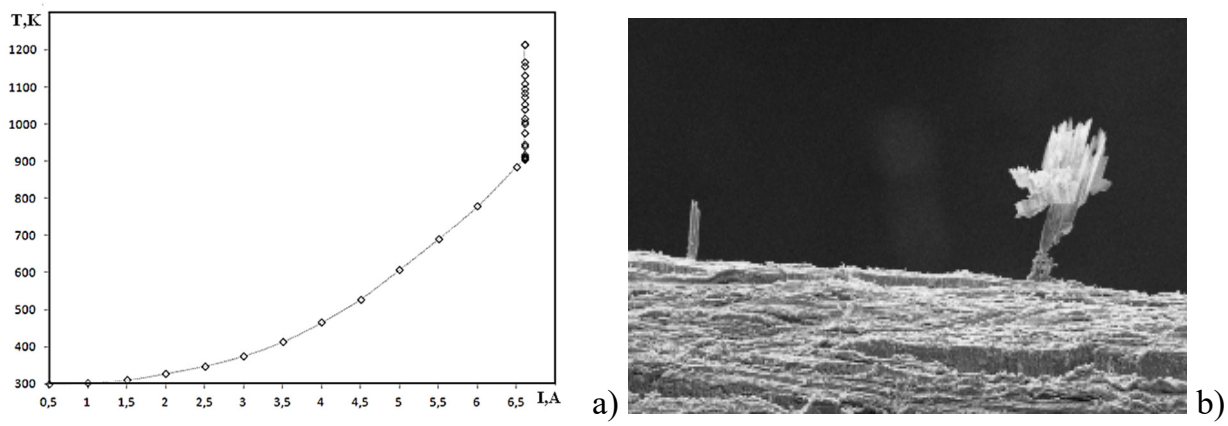
a) b)

Fig. 1. Dependence T(I) for tungsten conductors of length L = 0.1 m at air temperature T_g=293 K. a) d = 210 μm, b) d = 300 μm. Lines – calculation, circles – experiment.

regimes. However, at high temperatures, the rate of chemical reaction increases, leading to an increase in the conductor's temperature, and the process becomes non-stationary. At high temperatures, the conductor burns out. Figure 1 presents the results of experimental studies of the thermal oxidation regimes of tungsten conductors of different diameters in air as a function of the conductor surface temperature T versus the heating current I. The results of calculations using a physical and mathematical model are also presented [5].

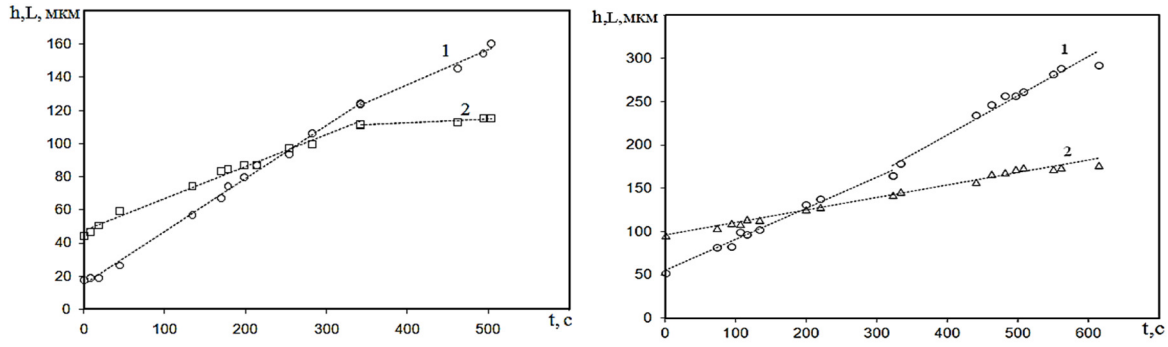
A good coincidence of calculated and experimental results is observed. The analysis of experimental data and calculated dependences showed that the stationary regimes T(I) in the temperature range 300K-800K are determined by the equality of Joule heating and heat losses by convection and heat conduction through the ends of the conductor. Radiation heat loss occurs above 800K. The chemical reaction on the surface of tungsten up to a temperature of 800 K is weakly expressed. In steady states in the temperature range of 760K - 800K, thin oxide films are formed: 5-10 microns [9]. However, at temperatures above 850K-900K, the chemical reaction of oxidation must be taken into account, since rather thick oxide coatings are formed on the conductor.

Simultaneously with the temperature measurement in the experiments, the surface of the sample was observed using an optical microscope and a digital camera. As soon as oxide crystals began to form on the surface of the conductor in the form of threads



a) b)

Fig. 2. Modes of oxidation of a tungsten conductor with a diameter of d = 300 μm and a length of L = 0.1 m (a); image of an oxidized conductor at the stage of crystal growth (b).



a) b)

Fig. 3. Dependence of the height (*h*) and width (*L*) of the tungsten oxide crystal on the oxidation time. 1 - *L*, 2 – *h*; a) crystal 1, b) crystal 2.

and branches (Fig. 2 b), the electric current stopped increasing. At the same time, the temperature of the conductor continued to rise due to heat release from the chemical oxidation reaction (Fig. 2a, vertical section of the T(I) dependence).

Investigation of the surface of tungsten conductors in stationary states made it possible to discover the following picture of the formation of an oxide layer. At temperatures T<900K, an oxide layer without features appears on tungsten, individual furrows and irregularities appear. At the same time, the primary oxide film is formed as follows: the initial stage of the reaction between metal and oxygen is gas adsorption on the metal surface. Adsorbed oxygen atoms are further arranged in the form of ordered structures. An important feature of the initial stage of oxide formation is that the metal surface is never clean. It already contains individual nuclei of the oxide, which are randomly distributed over the surface, possibly in those places where there are surface imperfections, impurity atoms, and mechanical deformations.

As a result, approximately at the temperature T ≈ 900K averaged along the length of the conductor, individual oxide crystals begin to appear on the surface in the form of threads and bushes. It was established by the optical-digital method [5] that the temperature of the surface of the conductor in the place where the crystals are actively growing exceeds 1100K. As the temperature and oxidation time increase, the crystal sizes and their density on the tungsten surface increase.

To study the kinetics of the growth of oxides formed on the surface of the conductor, individual crystals were selected and observed during their oxidation using optical digital imaging. The processing of digital images made it possible to determine the change in the geometrical dimensions of the crystals in the longitudinal and transverse directions, as well as to calculate the rate of their growth. In fig. 2 presents the growth dynamics of the geometric dimensions of two tungsten oxide crystals in the longitudinal (h) and transverse (L) directions.

An analysis of the time dependences of the longitudinal and transverse dimensions of the crystals indicates a linear growth law. It is also evident that, at the initial stage of growth, the longitudinal size of the crystals is larger than the transverse size. Subsequently, due to the predominant growth rate in the transverse direction, the width of the crystals exceeds their height. The crystals branch and merge with neighboring crystals. The observation time of the crystals was limited to the moment of their overlap due to the increase in their geometric dimensions in the transverse direction. The height

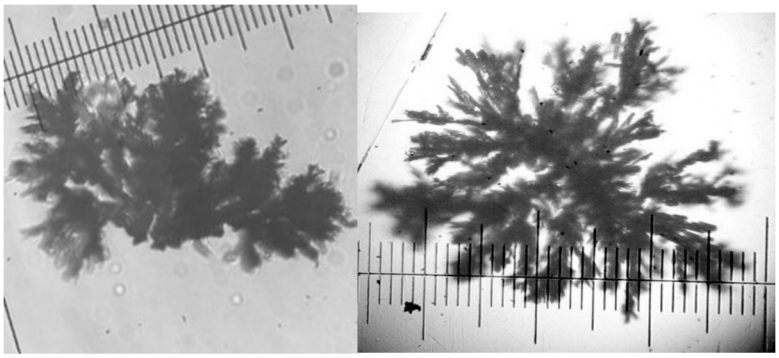


Fig. 4. Typical dendritic structures formed on the surface of tungsten wires heated to temperatures of 1750-1950 K.

of the branched structures ranges from 100 to 150 μm. The second crystal was quite large when it was observed on the surface of the tungsten conductor (Fig. 2b). By the end of its "lifetime," its height had increased by 1.5 times, and its width by 6 times. The obtained dependences made it possible to determine the growth rates of tungsten oxide crystals in the longitudinal and transverse directions. In the longitudinal direction, the crystal grew at a rate of 0.11-0.14 μm/s (maximum 0.2 μm/s), in the transverse direction - 0.35-0.45 μm/s. It was also noted that some crystals, having reached a certain size, began to evaporate intensively and disappeared from the surface of the main oxide.

Crystals formed on the surface of the conductor were studied individually to determine their fractal dimension. The value of fractal dimension is often directly related to the process that created the structure.

The calculations showed that for the high-temperature region, the values of the fractal dimension of dendritic crystals lie within the range D = 1.65–1.8 (in 2D projection). The fractal dimension of simpler crystals (thickened filaments, plates) lies within the range D=1.1–1.2.

For high temperatures, the general morphology of the dendritic structure is observed: a thick stem or branches in several directions, to which thin branched branches are attached. The resulting fractal dimension may indicate that the WO_3 dendritic structures were formed in a diffusion-limited regime – i.e., the rate of delivery of reagents (O_2 molecules or oxide vapor) to the growth front was lower than the instantaneous rate of attachment. The growth of the crystals occurred through vapor-condensation processes, i.e., the formation of gaseous WO_3 and its condensation on the crystal surface. The low mobility of adsorbed atoms and molecules on the surface (low surface displacement) also contributes to the uneven thin branches.

Conclusions. Thus, the temperature regimes at which dendritic oxide structures formed and grew on the surface of tungsten conductors heated by electric current were studied. It was proved that the activation of oxidation processes occurs at temperatures above 900K, which subsequently leads to a transition to a non-stationary oxidation regime. It was established that in the presence of chemical (oxidation) and phase (sublimation and evaporation of oxide) transformations, branched crystal structures of WO_3 are formed on the surface of an oxidized tungsten conductor. The average temperatures of the conductor and local surface temperatures at which crystals form and grow have

been determined. The growth rates of the geometric dimensions of crystals in the longitudinal and transverse directions have been found. The linear dependence of the sizes of growing crystals on time has been proven. Calculations of the fractal dimension of crystals have been performed. The obtained values indicate that dendritic structures of tungsten oxide were formed under conditions of limited diffusion of reagents with the participation of the vapor phase WO_3. When tungsten is heated to high temperatures, WO_3 oxide partially vaporizes and condenses on the surface in the form of dendrites.

References:

1. *Kumao, A., Fujita, Y., and Endoh, H.* Growth of dendritic and needle tungsten oxide crystals studied by high-resolution electron microscopy // Ultramicroscopy. – 1994.- Volume 54, Issues 2-4, P. 201-206.
2. *Polleux, J., Pinna, N., Antonietti, M., and Niederberger, M.* Template-free synthesis and assembly of single-crystalline tungsten oxide nanowires and their gas-sensing properties // Angewandte Chemie International Edition. – 2005, Volume 45, Issue 2. – Pages 261-265.
3. *Gu G., Zheng B., Han W. Q., Roth S., and Liu J.* Tungsten Oxide Nanowires on Tungsten Substrates // Nano Letters. - 2002. – Volume 2, Issue 8. – P. 849–851.
4. *Schlueter K., Balden, M.* Dependence of oxidation on the surface orientation of tungsten grains // International Journal of Refractory Metals and Hard Materials. – 2019. – Volume 79. – P. 102–107.
5. *Orlovska S.G., Shkoropado M.S., Karimova F.F.* Investigation of temperature regimes of oxidation of tungsten and molybdenum wires in air// Physics and chemistry of solids. – 2012. – Vol. 13, No. 4. – P. 790-794.
6. *Baek Y., Yong K.* Controlled Growth and Characterization of Tungsten Oxide Nanowires Using Thermal Evaporation of WO_3 Powder // The Journal of Physical Chemistry C. – 2007. – Vol 111, Issue 3. – P 1213-1218.
7. *Romanyuk A., Melnik V., Oelhafen P.* Oxidation of tungsten surface with reactive oxygen plasma //Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms . – 2005, Volume 232, Issues 1–4, P. 358-361.
8. *Orlovskaya S.G., Shkoropado M.S., Karimova F.F.* High Temperature Oxidation and Destruction of Metal Filaments in Air //Ukrainian Journal of Physics. - 2011. - V.56, №12. –P.1312-1315.
9. *Orlovska S.G., Shkoropado M.S., Shevchenko Yu.A., Odnostalko A.O.* Investigation of high-temperature heat and mass transfer and oxidation of refractory metal samples in air// Physics and chemistry of solids. – 2014. Vol. 15, No. 2. – P. 384-387.

Фізика аеродисперсних систем. – 2025. – № 63. – С. 189-195

Орловська С.Г.

Вивчення закономірностей росту оксидних структур на поверхні вольфраму при нагріванні

АНОТАЦІЯ

В роботі представлено результати досліджень особливостей утворення оксидних структур на поверхні вольфрамових дротиків, що нагріваються електричним струмом в повітрі. Вивчено стаціонарні високотемпературні режими окислення вольфрамових дротиків діаметрами 210 і 300 мкм електротермографічним методом. Встановлено, що при середній температурі вольфрамового дротика близько 900 К на його поверхні з'являються ниткоподібні кристали, які швидко зростають, і надалі набувають пластинчатої і гіллястої форми. Дисперсний склад, форма і поверхнева густина отримуванних мікрокристалів триоксиду вольфраму залежать від температури і часу окислення. Визначено швидкості росту розмірів окремих кристалів в повздовжньому та поперечному напрямках. Встановлено, що кристали спочатку активніше зростають в повздовжньому напрямку (в висоту), а потім швидше ростуть в ширину. Зазвичай кінцевий розмір кристала в поперечному напрямі більший ніж в повздовжньому. Доведено лінійний закон зростання максимальних розмірів дендритів від часу. Проведено розрахунки фрактальної розмірності дендритних структур оксиду вольфраму. Отримані значення фрактальної розмірності вказують на те, що механізмом росту є дифузійно обмежена агрегація (DLA) при участі парової фази WO_3. При нагріванні вольфраму до високих температур оксид частково переходить в пару й конденсується на поверхні у формі дендритів.

Ключові слова: *Вольфрам, оксид вольфраму, ниткоподібні кристали , дендритні структури, високотемпературне окислення, фрактальна розмірність.*