Фізика аеродисперсних систем. – 2018. – № 55. – С. 54-58

UDC 536.46

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The oxide structures formation on the surface of tungsten

The temperature regimes and the kinetics of the formation of tungsten oxide crystals on the surface of a tungsten conductor heated by an electric current in air were studied, as well as the fractal dimension of branched oxide formations. It was shown that at the temperature higher than 1100 K, separate formations were observed on the surface of the conductor. These were nuclei of tungsten oxide crystals, which over time grew into branchy formations. The fractal dimension of the structures obtained at different stages of growth was calculated using the principle of object coverage. It was determined that at the initial stage, the growth of crystals proceeds according to the mechanism of the Brownian motion "cluster-cluster", then along the Brownian motion "particle-cluster".

The use of tungsten oxides in the chemical industry as catalysts (dehydration of alcohols, cracking of hydrocarbons) determines the relevance of studies of temperature regimes and patterns of their formation. Branched nano- and microcrystalline oxides, in addition to catalytic properties, have unique qualities and high reactivity.

The aim of this work is to study the temperature regimes and kinetics of the formation of tungsten oxide crystals on the surface of a tungsten conductor heated by an electric current in the air, and to study the fractal dimension of branched oxide formations.

To study high-temperature oxidation, an experimental stand was used [1], the scheme of which is shown in Fig. 1. The study was carried out by the "hot filament" method on tungsten conductors of the IA brand which have a diameter d = 200 μm and a length L = 10.2 cm. Conductors were heated by an electric current in the air.

The stationary temperature regime was set by changing the amperage, which was gradually increased at an interval of 2 minutes. The temperature of the tungsten filament during the oxidation was determined by the electrothermographic method, and at the stage of the conductor glowing (at high heating currents), the temperature was simultaneously measured with a brightness pyrometer (EOP type) at a fixed point of the sample. The optical prefix made it possible to determine the appearance of oxide crystalline formations on the surface. After it, with a fixed current strength, the growth of individual oxide crystals on the surface of the conductor was observed.

The temperature of an electrically heated metal conductor is determined by the dependence of the specific resistivity on temperature.

$$\rho = \rho_0 \left[1 + \gamma (T - T_0)\right]. \quad (1)$$

Here ρ_0 – specific resistance at temperature T_0 = 273 K, Ω·m; γ -temperature coefficient of resistance, K^{-1}.

For the conductor temperature at any time, we have:

 DOI: http://dx.doi.org/10.18524/0367-1631.2018.55.149896

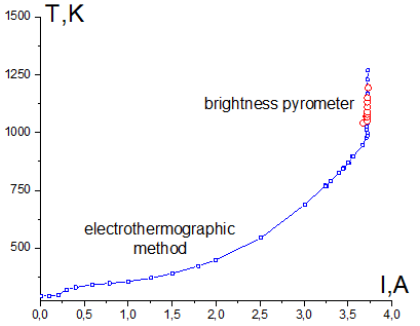

Fig. 2. Tungsten conductor temperature dependence of the current strength

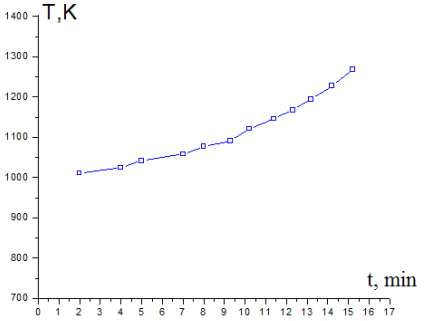

Fig. 3. Temperature regime of growth of tungsten oxide crystals

$$T = \left(\frac{R}{R_k} - 1\right)\left(\frac{1}{\gamma} - T_0\right) + \frac{R}{R_k} T_k . \qquad (2)$$

Where T_k – ambient temperature, K, R_k – resistance at temperature T_k, Ω.

The accuracy in determining the temperature by the electrothermographic method is: for a low-temperature range of values of 2%, and for a high-temperature range it does not exceed 5%.

In the high-temperature range, when the conductor glowed, the non-contact method of brightness pyrometer was used to measure the temperature.

The brightness temperature T_b of a non-black body with a monochromatic coefficient of radiation $\varepsilon_{\lambda T}$ having a true temperature T is numerically equal to the temperature of the black body at which the monochromatic brightness $E^0_{\lambda T_b}$ of the black body is equal to the monochromatic brightness $E'_{\lambda T}$ of this non-black body

$$E^0{}_{\lambda T_b} = E'_{\lambda T} \qquad (3)$$

$$e^{-\frac{C_2}{\lambda T_b}} = \varepsilon_{\lambda T}\, e^{-\frac{C_2}{\lambda T}},$$

from which, after logarithm and transformations, we finally obtain the relationship between T_b and T

$$T = \left(\frac{1}{T_b} - \frac{\lambda}{C_2} \ln \varepsilon_{\lambda T}\right)^{-1}. \qquad (4)$$

It follows from equation (4) that the brightness temperature T_b is always lower than the real temperature. For small values $\varepsilon_{\lambda T}$ and high temperatures, the difference $T–T_b$ can reach several hundred degrees.

Fig. 2 shows the experimental dependence of the conductor temperature on the heating current in stationary states.

The analysis of the T (I) dependence shows that, the stationary states of the conductor untill reaching the temperature of 700K were determined by the equality of the

Joule heat release and the convective heat flow to the surrounding gas and to the terminals in which the conductor was fixed. At temperatures above this point, oxidation begins from releasing heat and forming an oxide layer on the conductor surface. At temperatures exeeding 1000 K, a glow of the wire appears, radiation heat loss increases. The release of heat due to the chemical oxidation reaction leads to increase of the temperature and the thickness of the oxide layer of the sample surface. The vertical section of the curve corresponds to the temperature regimes of the crystals appearance and growth [2].

Fig. 3 it shows the time-extended temperature regime of crystal growth on the surface of the primary oxide film. During this period, the temperature of the conductor increased by almost 300K in 15 minutes. This is a consequence of the chemical reactions flow on the conductor surface that lead to thickening of the basic oxide layer.

Having studied under the microscope the conductor at various stages of oxidation, it was established, that with a gradual increase in temperature, at first a continuous oxide layer is formed on the surface of the tungsten, then, due to various mechanical stresses in the metal and oxide film, it cracks, causing longitudinal grooves and ditches. At temperatures above 1000 K, individual filamentary crystals begin to appear on the oxide layer surface, which subsequently transform into branched oxide structures.

The axial growth rate of whiskers is described by the equation [3]:

$$\frac{dL}{dt} = I + \frac{4I\lambda_s}{d} th\left(\frac{L}{\lambda_s}\right), \tag{5}$$

$$I = \frac{m}{\rho}(A - A_o).$$

Where λ_s – average length of the diffusion path of an atom before re-evaporation, m – is the mass of an atom, ρ – density of a substance, A, A_0 – the number of collisions of particles with a surface in a gas and a saturated vapor, respectively.

This formula consists of two terms: the first part describes the axial growth rate, due to the direct condensation of steam on top, the second - the other part, due to the deposition of particles on the side faces, followed by diffusion to the top. The second term depends on the diameter of the whisker crystal, as well as on time (through L). With increasing the oxidation time, oxide structures amount on the surface and the geometric dimensions raise.

Fig. 4 shows various samples of tungsten oxide crystals. They are formed on the shores of cracks in the oxide film, each of them have a thin base foot, and can reach 200 μm. Depending on the temperature and the holding time in a non-aggressive non-stationary mode, two forms of crystals can be distinguished. The first one is in the form of two-petals - which obtained by heating the conductor to 1470 K in 10 minutes. Strongly branched structures - bushes - are formed in 15-20 minutes at the temperature 2100K.

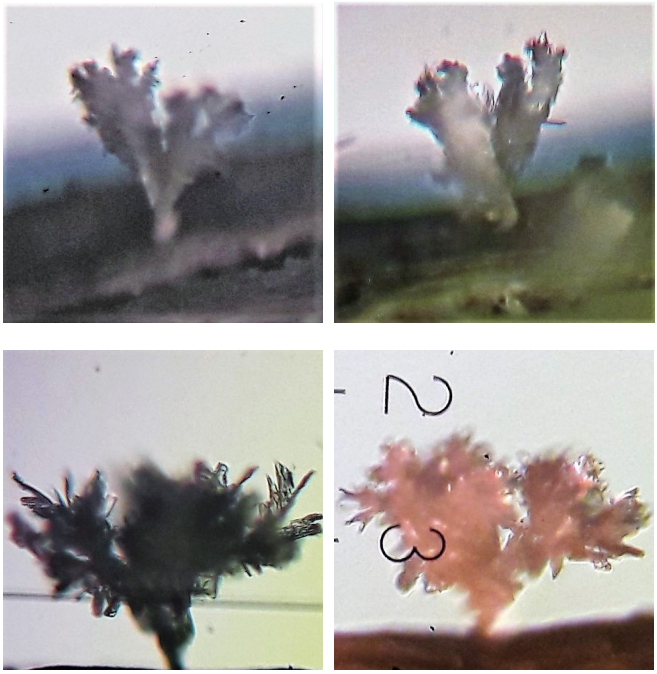

Fig. 4 Tungsten oxide crystals on the conductor surface

In order to determine the mechanisms of crystal growth at different stages, their fractal dimension (D) was calculated. There are a lot of approaches to the estimation of fractal dimension [4], the most commonly used method is cell cover. At the moment there are several works devoted to correlating the fractal dimension and cluster formation mechanism. Fractal clusters, or fractal aggregates, it is customary to call structures that are formed when solid aerosols are combined in a gas in the case of diffusional character of their motion. The fractal cluster has a characteristic branched structure. As a result of using the works of Smirnov [5], it was determined that the fractal dimension D = 1.4 corresponds to the Brownian motion and the formation of the structure by the cluster-cluster principle, and D = 1.6 is the Brownian motion of the particle-cluster.

Conclusions: The temperature regime and the kinetics of the appearance and growth of tungsten oxide crystals on the main oxide film surface are determined. It is shown that the formation of crystals does not occur at temperatures below 1000K. It is established, that in the process of quasistationary oxidation plate or bush-like oxide structures are formed, which is due to the temperature regime of tungsten oxidation. It is obtained that at the beginning stage the growth of crystals occurs according to the principle of Brownian cluster-cluster motion, and the growth into branched structures - according to the mechanism of Brownian particle-cluster motion.

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Орловская С.Г., Лисянская М.В.

Образование оксидных структур на поверхности вольфрама.

В работе изучаются температурные режимы и кинетика образования кристаллов оксида вольфрама на поверхности вольфрамового проводника, нагреваемого электрическим током в воздухе, а также проводятся исследования фрактальной размерности разветвленных оксидных образований. Показано, что при температуре больше 1100К на поверхности проводника наблюдалось появление отдельных образований – зародышей кристаллов оксида вольфрама, которые с течением времени разрастались в ветвистые образования. Проведен расчет фрактальной размерности полученных структур на различных этапах роста по принципу покрытия объекта. Определено, что на начальном этапе рост кристаллов идет по механизму броуновского движения «кластер-кластер», затем по механизму «частица-кластер».

Орловська С.Г., Лисянська М.В.

Утворення оксидних структур на поверхні вольфраму.

В роботі вивчаються температурні режими і кінетика утворення кристалів оксиду вольфраму на поверхні вольфрамового дротика, що нагрівається електричним струмом в повітрі, а також дослідження фрактальної розмірності розгалужених оксидних утворень. Показано, що при температурі більше 1100К на поверхні провідника спостерігалася поява окремих утворень - зародків кристалів оксиду вольфраму, які з плином часу розростались в гіллясті структури. Проведено розрахунок фрактальної розмірності отриманих структур на різних етапах росту за принципом покриття об'єкта. Визначено, що на початковому етапі зростання кристалів йде за механізмом броунівського руху «кластер-кластер», потім за механізмом «частинка-кластер».