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ELECTROCRYSTALLIZATION OF FIBROUS SILVER DEPOSITS FROM NITRATE MELTS - EXPERIMENTS AND MODELING

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Abstract

Fibrous silver deposits have been obtained in molten nitrates on a moving cathode. Cylindrical silver cathode was lifted from the melt $AgNO_3$-$NaNO_3$-KNO_3. It is found that the dimensions of the silver threads as well as their shape and thickness depend on the electrolysis parameters: the values of current and velocity of the cathode lifting. Systematic study of the silver dendrite structure has been performed on a scanning electron microscope. Geometric characteristics have been evaluated statistically and regression equations linking these constitutive properties of the deposits with the values of current and of lifting velocity have been obtained. A criterion for the description of dendrite shape under different conditions is proposed.

Keywords: silver, dendrite, lifting cathode, structure, criterion

1. Introduction

Electrodeposited crystalline silver exhibits good catalytic properties in a number of chemical reactions. For example, catalysts for the oxidation of ethylenglycol to glyoxal from electrodeposited silver dendrites are obtained [1,2]. The catalytic properties of

silver depend on the crystal structure as well as on the degree of crystal lattice perfection. Apparently, the latter in turn determines the quantity and the density of arrangement of the catalytically active sites. A good number of publications devoted to the description of the structure of silver dendrites obtained from nitrate melts is known [3-10]. Polyakov investigated in details silver deposits obtained from this type of electrolyte [3]. Gorbunova has shown [4] that silver dissolves in high-temperature zone which is the main factor that impacts the character of the cathodic deposit. Erdey-Gruz and Kardos [5] found optimal conditions for single-crystalline silver growth. Pure nitrate is the best electrolyte for that, while it is impossible to grow single-crystalline silver from chlorides. Barton and Bockris studied the dynamics of silver dendrite electrocrystallization from fused nitrate electrolytes under potential-controlled electrolysis conditions [6]. In spite of the significant scattering of experimental data, constant growth rate of dendrites has been found during the process. The growth rate increased significantly as the concentration of the melt and cathodic potential were increased. Authors concluded that there is an optimal dendrite tip radius at each value of potential, corresponding to the maximum possible rate of tip propagation to the bulk of the melt, which is not depleted in silver. Similar investigations have been performed in nitrate and chloride melts by Phylosofova and Baraboshkin [7-9]. It has been established that in the overpotential range of 5-60 mV the dendrite growth rate may be described by the dependence $v_T=k_TC^n$, where k_T is a quantity that rises as the concentration and temperature increase and n=1.34–1.50. The magnitude of the tip radius is 10^{-5} cm. Current density at dendrite tips reaches several hundred amperes per square centimeter. The main part of overpotential is the diffusion overpotential for dilute solutions and ohmic overpotential in individual melts. The structure of dendrites obtained from a number of solutions has been investigated by Wranglen [10], who noticed that the lateral branches of flat two-dimensional dendrites are inclined to the dendrite stalk at an angle of 60°. The flat dendrites of [110] orientation are single-crystals. The big diversity in silver dendrites shape is due to continuous changes in the conditions of their crystallization during galvanostatic electrolysis. The exchange current density of silver is very high, especially at high temperatures of the melt [11], and it may exceed 1000 A/cm^2 [12]. This leads to quick lengthening of dendrites and, accordingly, increase in the growth front area of crumbly deposit. As a consequence, the product of electrolysis consists of a mixture of different dendrite types crystallized in different conditions.

A method for electrodeposition of fibrous silver deposits under constant growth front area conditions is worked out at the Institute of High-Temperature Electrochemistry of the Ural Branch of the Russian Academy of Sciences [13]. Silver fibers, which are the bundle of long dendrite threads, have been produced. Their structure is determined by the parameters of electrolysis: current and lifting velocity of the cylindrical electrode from the melt. Revolving drum seems to be another variant for dendrite electrocrystallization. The trend in changes of the dendrite structure has been investigated as diffusion

limitations of the deposit growth front were removed step by step. Statistical description of the dependence of dendrite element dimensions on electrolysis parameters in the potassium-sodium nitrate eutectic containing 15 wt. % silver has been obtained [14]. A dynamic model for silver dendrite electrocrystallization under strict diffusion limitation conditions has been suggested. In this case, dendrites mainly have cylindrical shape [15]. The task of the present paper is to investigate the structural forms of silver fiber obtained from more concentrated melts as well as to develop general approach in description of the correlation between the quantitative characteristics of dendrite structural units and electrolysis parameters.

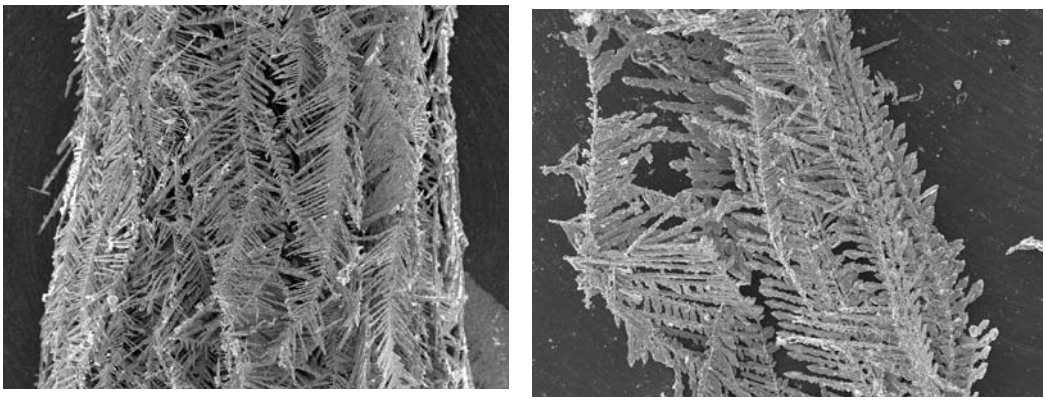
2. Experimental

The electrocrystallization of fibrous silver deposit was performed on the end face surface of a silver rod of 2-mm diameter in an open bath [13]. The potassium nitrate-sodium nitrate eutectic was used as the electrolyte. The experiments were carried out at temperatures from 250 °C (15 wt. % silver nitrate) to 280 °C (33 wt. % silver nitrate). The period of dendrite growth followed a short seeding period (1-2 min.) at low current densities to provide good adherence of the fiber to the substrate. The cathode was pulled up out of the melt at a constant velocity upon switching on the current, according to [14]. The obtained fibers of up to 15 cm long were washed with distilled water, dried, and photographed with the aid of a JSM 5900 LV scanning electron microscope. Pieces of the deposit were attached to the sample stage with conducting glue and then put into the vacuum chamber of the microscope. General view of the dendrite sample as well as the morphology and structure of dendrite elements were investigated. Fibrous bunches in the solidified melt were used for metallographic analysis. The cross-section in epoxy resin was treated with alcohol between polishing courses. The catalytic activity of silver dendrites was tested using catalysts prepared from the electrolytic fibers in the reaction of glyoxal production from ethylenglycol.

3. Results

The structure of the dendrite threads in the bunch changes depending on electrolysis parameters, viz. current, velocity of cathode lifting and melt composition (Fig. 1). The structure of the pattern shown in Fig.1 is the same along the height of the deposit and is independent of time (Fig. 2). Only orientation of the lateral branches regarding the dendrite stalk changes along the height of the bunch but dimensions of the elements stay practically the same.

The dendritic metal deposit appears to be a three-dimensional electrode with distributed rate of the electrochemical reaction along the electrode thickness (that is, along the height of dendrites) [16]. At high cathodic current densities the metal reduction is forced out to the surface of the deposit which is the growth front.



a) b)

Figure 1. Silver fibrous deposits of different structure: a) C_{Ag}=15 %, I=1 A, v=5 cm/min., magnification - 50 times; b) C_{Ag}=26 %, I=5 A, v=11 cm/min., magnification - 65 times.

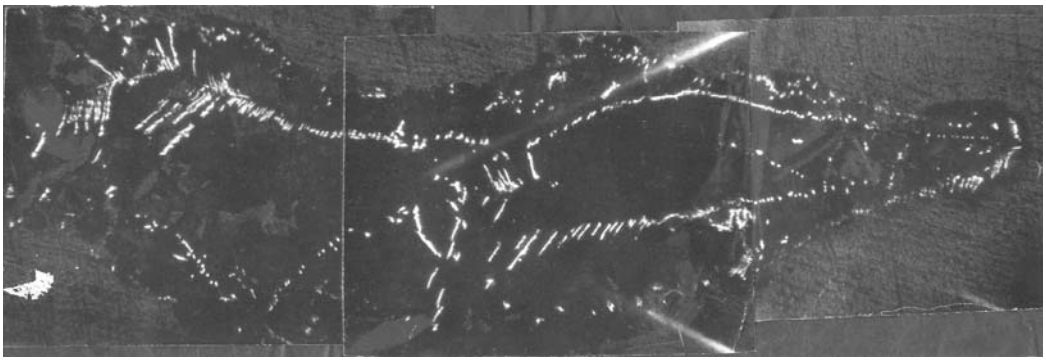


Figure 2. A longitudinal section of the fibrous deposit. The lower end of the bunch, magnification - 112 times.

Let us consider N dendrite tips with radius of curvature, r_T and surface area, $2\pi r_T^2$ is being developed on the unit area of the growth front. Under galvanostatic electrolysis conditions, dendrites growing on the face surface of a cylindrical electrode with radius r_0 form growth front in the form of a hemisphere of radius r_0+y [15], where y is the length of a dendrite. At current I the cathodic process is localized on dendrite tips, so the current density on them, i_T, is $I/(2\pi(r_0+y)^2 N \cdot 2\pi r_T^2)$.

The Faraday law in differential form

$$\frac{dy}{dt} = \frac{V}{zF} \cdot i_T \qquad (1)$$

allows to obtain the correlation between the dendrite length y and time t:

$$r_0^2 y + r_0 y^2 + \frac{1}{3} y^3 = \frac{V}{zF} \cdot \frac{I}{4\pi^2 r_T^2 N} \cdot t \qquad (2)$$

where V is the molar volume of metal, F - Faraday constant, N - density of distribution of the growing dendrite tips on the unit area of the deposit growth front. In accordance with equation (2), the slope of tangent to the $r(t)$ dependence decreases in time. Thus, if one is lifting the cathode at any time of the electrolysis with a velocity of dy/dt, the electrolysis conditions will not be changed and, as a consequence, the dendrite structure will be stable.

The statistical description of the correlation between dendrite characteristics and electrolysis conditions for the deposition from the electrolyte with 15 % of silver was done by the method of regression analysis [14]. The length of dendrite lateral branches, their thickness as well as the thickness of a dendrite stalk were chosen as structural parameters. The values of current, I, and of cathode lifting velocity, v, were used as independent variables. The measurement of the dimensions of the dendrite elements mentioned above was performed with the help of the SEM images. Only those dendrites in the images that occurred in the plane parallel to the sample stage of the microscope were used. A sample of 20-40 measurements was obtained for each specimen. The average values for each experiment were normalized by the value of mean-square approximation and then the regression coefficients were calculated for the normalized values of the variables. The effects of reciprocal action of the electrolysis parameters were taken into account by the introduction of extra variables into the linear regression equation. Analysis of the multiple correlation coefficients R obtained during the statistical modeling procedure showed that the effects of second order must be taken into account so that the value of R is above 0.55.

The comparison of the regression equations obtained shows that in both cases lifting velocity of the cathode from the melt is the main factor influencing dendrite dimensions (see Table 1). The lateral branches shorten as the cathode lifting velocity is increased. The effects of parameters interaction are rather appreciable in both cases. In spite of the difference in signs before the first two coefficients, the common character of the correlation between the length of lateral branches and electrolysis parameters do not practically change as the silver content of the melt is increased (Fig.3). At the same time, one may observe that in the more concentrated melt the relative dendrite length change is less pronounced in all the range of variation of current, as well as velocity of the cathode lifting. The creation of statistical models becomes especially difficult when analyzing dendrites deposited from concentrated melts. The reason is that in diluted melts the crystallization process is controlled by the diffusion transport of metal ions to dendrite tips. It is confirmed by almost cylindrical form of lateral dendrite branches [14].

Table 1. Normalized regression coefficients for the length of lateral branches depending on the silver content of the melt

Silver content, %	Absolute term	x1 (current)	x2 (velocity)	x1.x2	Multiple correlation coefficient
15	-0.35	0.198	-0.757	-0.668	0.993
26	0.122	-0.255	-0.462	-0.313	0.56

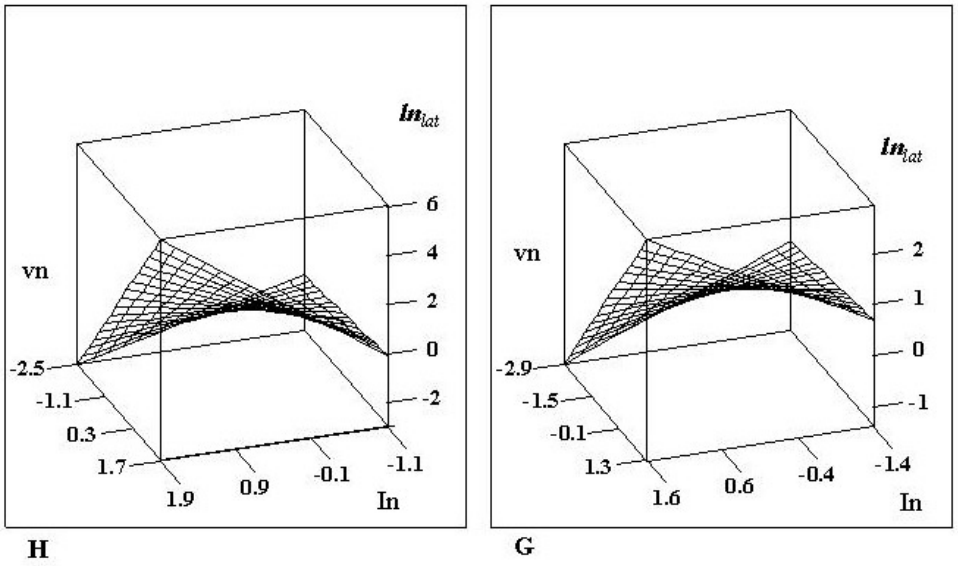
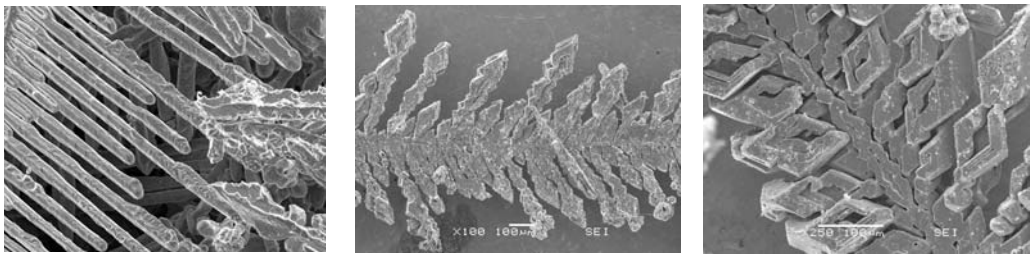


Figure 3. Dependence of the length of dendrite branches on current and cathode lifting velocity in melts with different silver concentration. A 3-dimensh ional representation of regression equations. Silver content, wt. %: H-15, G-26. All the variables are normalized.

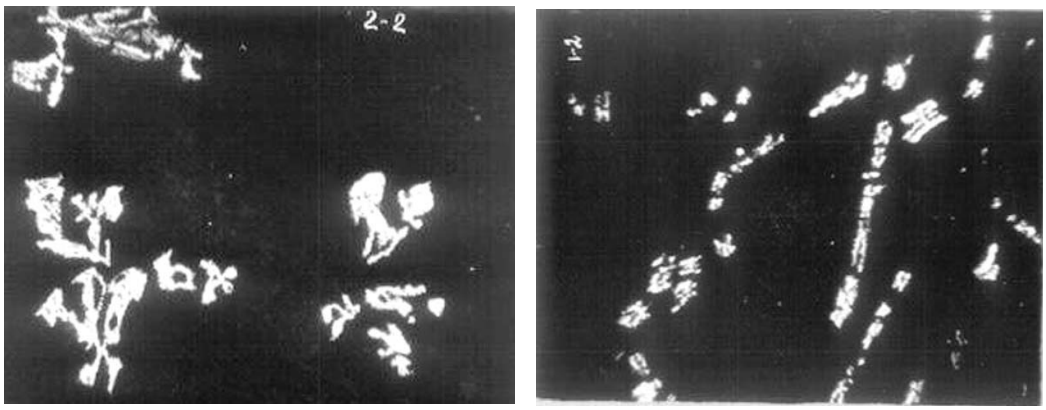
Besides, the results of calculations made on the basis of diffusion-controlled model of the process are in a good agreement with experimental data concerning the length and thickness of lateral dendrite branches [15]. However, in more concentrated melts both the dimensions of dendrite elements and their shape change. Close to cylindrical *n*-faced form of the lateral branches turns into flat rhombic one (Fig.4).

Moreover, in more concentrated melts the flat lateral branches become hollow. It may be seen in the photos of the metallographic cross section of the dendrite bunch (Fig.5). At the same time, in the melt containing 33 wt.% silver the lateral branches are arranged



a) b) c)

Figure 4. Different shapes of lateral branches and of their tops. Nitrate melts with different silver concentration. Silver content, wt. %: a-15, b-26, c-33. Magnification: a-600, b-100, c-250.



a) b)

Figure 5. A cross section of the fiber bunch. Silver content, wt. %: a-33, b-26.

in different planes at different angles between them and the stalk which is a five-times-twinned crystal. However, in the more diluted electrolyte the lateral branches are in one plane. It is clear that such a drastic change in the crystal shape makes it impossible to calculate, for example, the lateral branch width because this branch consists of a sequence of rhombic hollow plates.

4. Discussion

The experimental data presented indicate that it is impossible to describe different dendrite forms by statistical equations only. The change of the lateral branch shape from

cylindrical to flat tells about substitution of the limiting stage of the process. Indeed, it is difficult to talk about dominating diffusion limitations when dealing with melts containing 26 or 33 wt. % silver. At the same time, the unfilled rhombus-like elements of the lateral branches make us conclude that the transport rate of the metal ad-atoms to growth sites is insufficient. In the course of electrolysis at all regimes the end of the fiber bunch of the same length stays immersed in the electrolyte. It permits to evaluate by Eq.(1) the current density on the dendrite tips because the lifting velocity of the cathode is practically equal to dendrite growth rate. When the lifting velocity exceeds the dendrite growth rate the fiber bundle brakes. On the contrary, too low lifting velocity leads to a short circuit between the fiber cathode and the anode being on the bottom of the bath. The variation of cathode lifting velocity from 0.5 to 12 cm/min means the rise in current density i_T from 473.5 to 1420 A/cm^2. The metal discharge on the dendrite tips occurs, as a rule, under mixed control of the process [16]. In this case, the exchange current density should essentially exceed 1000 A/cm^2. If one assumes current density to be diffusion-limited and determined by spherical diffusion, then dendrite tip radii ($9.9\cdot10^{-4}$–$1.8\cdot10^{-5}$ cm) must be much less than those measured experimentally. It means that there should be another limiting stage during this process. For example, it is known that transport rate in concentrated electrolytes may be determined by electroconductivity of the melt [9], the value of the latter being the complex function of composition and temperature for the ternary system $AgNO_3$-KNO_3-$NaNO_3$.

It is necessary to pay attention to the following fact: the quotient I/v is measured in coulomb/m. If one takes into account the surface area of the growth front $S_{G.F.}$ with units of m^2, then the quotient $I/(S_{G.F.}\cdot v)$ will have units of coulomb/m^3. It denotes the quantity of electricity flowed through the unit area of the growth front of dendrite deposit during one second of the cathode lifting. Taking into account the Faraday law, it is easy to obtain the dimensionless criterion Cr characterizing electrolysis conditions:

$$Cr = \frac{C_m S_{G.F.} vzF}{I} \tag{3}$$

where C_m is the concentration of electroactive substance in the melt (mol per volume unit), $S_{G.F.}$ - area of the growth front, F - Faraday constant. Criterion Cr is the quotient of quantity of substance being in the unit volume of electrolyte to the quantity taken away through the unit area of the growth front at the deposit/electrolyte interface. It is certain that this relationship has significant influence on the regime of crystal formation. Criterion Cr includes the value $S_{G.F.}$, which is very difficult to determine experimentally. However, in the first approximation it may be taken as independent of time. In this case, one may obtain the following expression for the criterion Cr^* having units of cm^{-2}:

$$Cr^* = \frac{C_m vF}{I} \tag{4}$$

where silver concentration in the melt is measured in mol/cm^3 and cathode lifting velocity has units of cm/s.

Experimental data for the melts of three different concentrations are presented in Fig. 6. As it can be seen in the figure, the length of the lateral branch decreases as the criterion is increased. At the same time, in concentrated electrolytes the lateral branches are longer than in diluted ones. The experimental points are scattered around the trend lines, which show power dependencies. The largest deviations are observed in more concentrated melts. A possible reason for the significant scattering of the experimental data is that the presumed condition $S_{G.F.}$=const is not always satisfied. The growth front area forms at the beginning of cathode lifting. Upon switching on the current, the dendrite needles begin to grow fast in the hemisphere space in the direction normal to the cathode with seed. Cathode movement makes the needles fold up in the horizontal plane to pack into a bunch. It is very likely that depending on the electrolysis regime (current, lifting velocity, silver content of the melt) the form and area of the growth front may vary. Some extra experimental work is needed to answer this question.

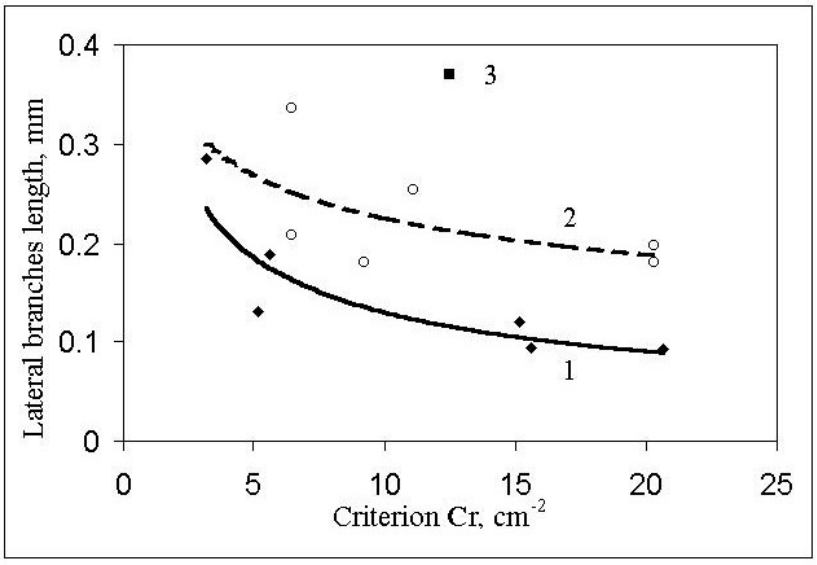


Figure 6. Dependence of the length of lateral branches on the value of the criterion Cr in melts with different silver concentration. Silver content, wt. %: 1-15, 2-26, 3-33.

5. Conclusions

Fibrous silver deposits consisting of dendrite threads have been produced. The dendrite structure is determined by melt composition and electrolysis parameters: current and velocity of the cathode lifting from the melt.

In the region of preferable diffusion control, the dimensions of dendrite elements (length of the lateral branches, their width) are satisfactorily described by regression equations.

A general approach for the estimation of dendrite structural characteristics has been proposed. The experimental data show that the dimensions of dendrite elements (the length and width of lateral branches) decrease as the dimensionless criterion is increased.

As the value of the criterion diminishes, the shape of dendrite branches varies from almost cylindrical to flat rhombic, which is due to the change in the nature of the limiting stage of the process.

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