

MATHEMATICAL MODEL OF COMPOSITE MATERIALS FORMATION

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ABSTRACT

The aim of the present work is to develop, substantiate, and study a fundamentally new method of derivation of composite electrolytic films making it possible to control their composition and structure. We assume that, after the termination of the stirring-up of a bath containing the electrolyte-suspension with monodisperse spherical particles of the same density, a uniform sedimentation space is established. The upper boundary of this field will descend with a velocity depending on the dispersity and density of a powder, introduced into the electrolyte, and its viscosity. If one places, a horizontal cathode of area S in the bath at a certain depth simultaneously with the termination of stirring-up, all of the disperse phase situated in the electrolyte above the cathode will deposit on it. We substantiate the possibility of obtaining metal composite films with a prescribed composition by the method of cut-off of the sedimentation space over a horizontally located cathode. We present a calculation scheme and derive a formula which enables us to control the composition of the disperse phase in a composite electrolytic coating by the cut-off time. The results obtained open up new possibilities for forming the structure and, consequently, the properties of metal composite thin-film systems.

Keywords: metal, mathematical model, composite material, electrolytic coating

INTRODUCTION

According to modern concepts [1-5], the successful formation of composite electrolytic thin-film systems is related to the realization of three main stages: the arrival of particles of the disperse phase at the cathode surface, trapping (adhesion, sticking, and adsorption) of particles on this surface, and covering of particles by the electrolytically deposited metal. The realization of the first stage presents no substantial difficulties and can usually be provided with the help of various methods of stirring-up and mixing of the electrolyte-suspension (by agitators, bubbling, ultrasound, etc.) [6-12].

The second stage encounters much more complex problems. Adhesion, sticking, or adsorption are practically uncontrollable because a particle of the disperse phase can be washed away by the electrolyte flow, by other particles, or because of the Brownian motion. An important specific feature of the third phase consists of the fact that, in some cases, the ratio between the surface energies of disperse particles and the metal is far from optimum [13-17]. As a result, the particle is “pushed out” by the electrolytically

deposited metal. To overcome these difficulties, one usually applies a treatment of the reinforcing phase with various solutions.

According to the traditional technology, one carries out electrolytic deposition on a vertical cathode. But the concentration of the disperse phase of the coating is nonuniform across its thickness (due to gravity) and is uncontrollable [18-21]. The aim of the present work is to develop, substantiate, and study a fundamentally new method of derivation of composite electrolytic films making it possible to control their composition and structure.

MATERIALS AND METHODS

We assume that, after the termination of the stirring-up of a bath containing the electrolyte-suspension with monodisperse spherical particles of the same density, a uniform sedimentation space is established. The upper boundary of this field will descend with a velocity depending on the dispersity and density of a powder, introduced into the electrolyte, and its viscosity. If one places a horizontal cathode of area S in the bath at a certain depth H simultaneously with the termination of stirring-up, all of the disperse phase situated in the electrolyte above the cathode will deposit on it (Fig. 1a).

The number of deposited particles is $N = n_0 S H$, where n_0 is the concentration of particles of the disperse phase in the sedimentation space over the cathode. At the same time, if one places the cathode surface horizontally in the sedimentation space not immediately after the termination of stirring-up but after a time t_0 ("cut-off time"), the volume of the sedimentation space will decrease by $S h$ (Fig. 1b), where h is the depth of the descent of its upper boundary for the time t_0 . In this case, we have

$$N = n_0 S H - n_0 S h = n_0 S (H - h), \quad (1)$$

or, by taking $h = v t_0$ (where v is the velocity of sedimenting particles),

$$N = n_0 S (H - v t_0). \quad (2)$$

This implies that the number of particles N deposited in the course of sedimentation depends on the cut-off time t_0 , because all the remaining parameters (n_0 , S , H , v) are constant. The case where the particles form several layers is not interesting for our purposes because these layers, not cemented by the electrolytically deposited metal (due to the low deposition velocity of the metal u as compared with v), do not form a strong composite coating. Furthermore, upon multilayer screening of the cathode surface by particles of the disperse phase, electrolysis is greatly hampered or is terminated entirely. Therefore, in what follows, we consider the case where the particles deposited on the surface of the horizontal cathode after the cut-off form a discontinuous monolayer.

RESULTS AND DISCUSSION

We can characterize the discontinuity of such a monolayer of deposited particles on the cathode after the cut-off by the continuity factor $0 \leq k \leq 1$ describing the cathode surface covered by a monolayer of particles. Consequently, we can characterize a composite electrolytic film with a certain content of disperse particles by the factor k

depending on the cut-off time t_0 . We can determine this time proceeding from the following considerations. If σ is the averaged cross-section area of the disperse particles ($\sigma = \pi R^2$ if the particle is a sphere of radius R), we have

$$N\sigma = k S, \quad (3)$$

where N is the number of particles deposited on the surface of the horizontal cathode after the cut-off in the time t_0 . Using Eq. (1), we can write

$$n_0 \sigma S (H - v t_0) = k S, \quad (4)$$

whence

$$t_0 = \frac{n_0 \sigma H - k}{n_0 \sigma v}. \quad (5)$$

Hence, to obtain a zero concentration of particles $k = 0$, we must make the cut-off after a time

$$t_m = \frac{H}{v}. \quad (6)$$

In this case, only the deposition of metal occurs on the cathode. Each metal is characterized by a certain velocity of electrolytic deposition u depending on the conditions of electrolysis. One can take these data from reference books or determine them experimentally. In order to obtain a high-quality composite electrolytic film, the next layer of disperse particles must deposit on the previous one, which is overgrown by metal. Otherwise, the coating will not be strong because only the metal can bind particles of the disperse phase into a single composition.

Starting from the velocity of electrolytic deposition of the metal u and the mean diameter of particles of the disperse phase $d = \sqrt{4\pi/\sigma}$ (for the sake of simplicity, we assume that they are spherical), we can determine the time necessary for overgrowing a deposited monolayer of particles:

$$t_1 = \frac{d}{u}. \quad (7)$$

To obtain a composite electrolytic film with a statistically uniform distribution of particles across its thickness (Fig. 2a), we must take the overgrowth time t_1 to be equal to the period of stirring-up of the suspension T minus the stirring-up time t_2 , i.e., $t_1 = T - t_2$. Hence, we obtain

$$T_0 = t_2 + t_1 = t_2 - \frac{d}{u}. \quad (8)$$

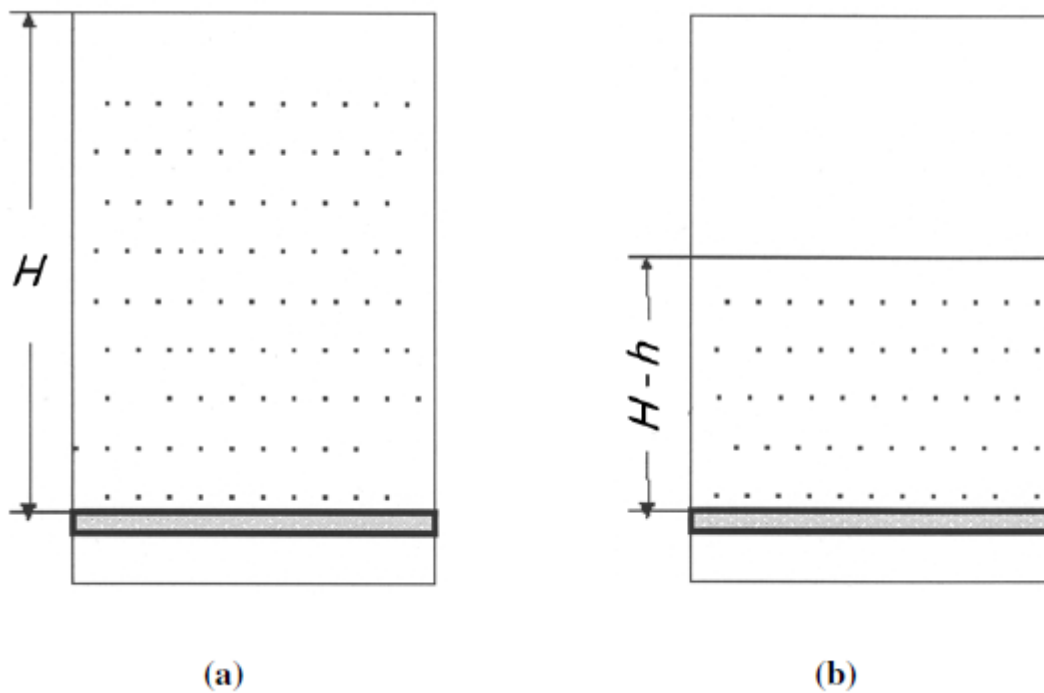


Fig. 1. Diagram illustrating a cut-off of the sedimentation space over the cathode simultaneously with the termination of stirring-up (a) and after a certain time t_0 (b).

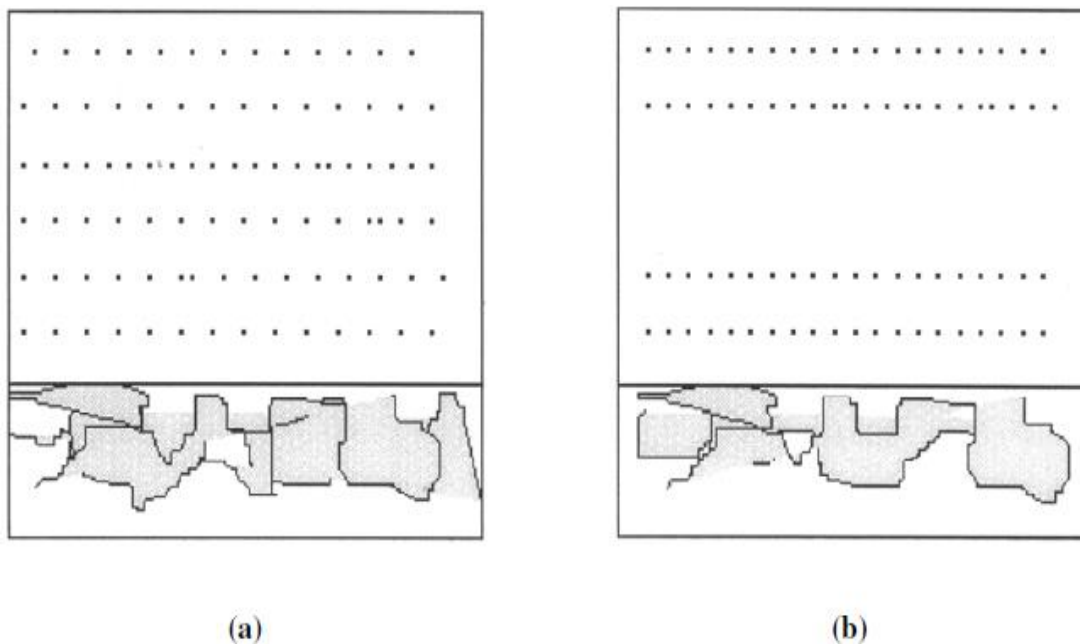


Fig. 2. Scheme of variants of a quasiuniform distribution of disperse particles in a composite electrolytic film: (a) quasiuniformly over the whole volume of a composite electrolytic film, (b) layerwise

This formula enables us to calculate the minimal admissible value of the stirring-up period for the given particle sizes and velocity u . If $T > t_2 + t_1$, the composite electrolytic film will be layered (Fig. 2b). In this case, it is possible to change the distance between layers according to the experimenter's wish.

If the given thickness of a metal layer is equal to L , the time of its production is

$$t = L / u. \quad (9)$$

Using different ratios between the stirring-up periods, we can obtain various alternations of compositions. For example, in the case of double alternation

$$T = \frac{d}{u} + t_2, \quad T = \frac{d}{u} + t_2 + \frac{L}{u}, \quad (10)$$

we can create a composition consisting of two layers of the disperse phase divided by a metal layer of thickness L (Fig. 2b). If necessary, we can deposit a composite electrolytic film with a variable concentration of the disperse phase across its thickness, e.g., with an increase or, vice versa, a decrease in the content of disperse particles while approaching the coating surface (Fig. 3a, b). We see from (2) that, to obtain such coatings, it is necessary to calculate the cut-off time for the required particle distribution in the composite electrolytic film

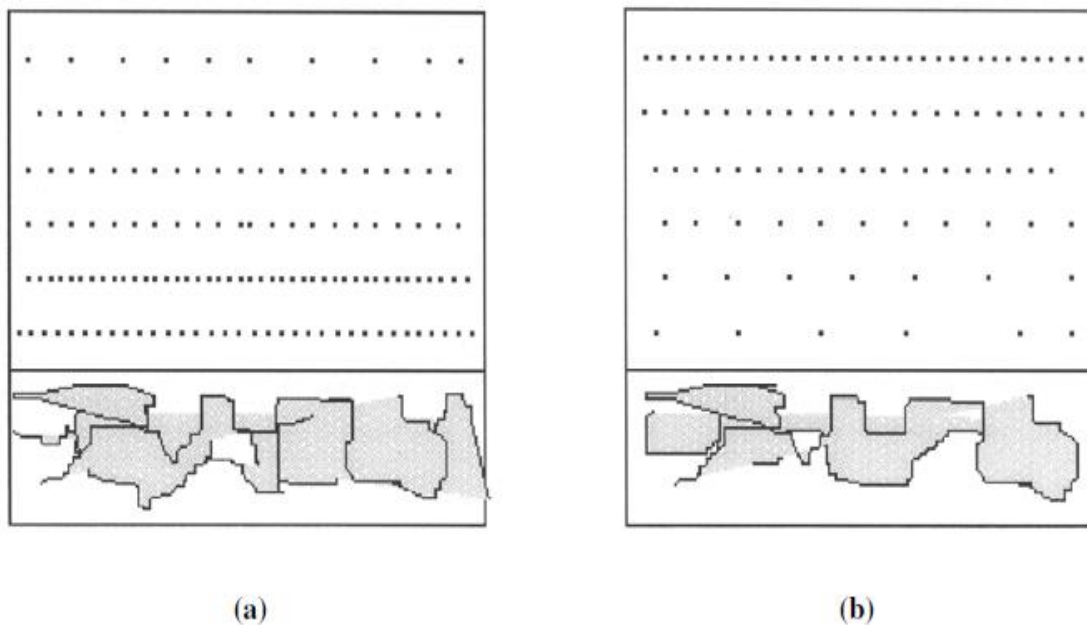


Fig. 3. Scheme of variants of the distribution of the disperse phase across the thickness of a composite electrolytic film with an increasing (a) and a decreasing (b) particle concentration.

CONCLUSIONS

The developed mathematical model makes possible to obtain given distribution of disperse phase in electrolytic coating. Thus, we can by method of “cutting off” the sedimentation space above horizontal cathode regulate coating structure, and, consequently, functional properties.

To obtain special functional properties, a subsequent thermal exposure is recommended. High temperature will promote formation of layers with a heterogeneous structure. The alternation of structured and pure metal layers provides possibility of wide range functional properties obtaining.

Thus, it is easy to predict the deposition of a composite electrolytic film by the method of cut-off of the sedimentation space over the cathode by means of simple calculations. They enable one to obtain a wide variety of compositions only in the case of a quasiuniform distribution of disperse particles over the whole volume with electrolytic deposition or over the layer along the surface under deposition.

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