Dependence of strength properties of electrolytic coatings on their substructure

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Abstract. The dependences of strength properties of iron coatings on the parameters of the microstructure of the metal during electrodeposition and heat treatment, characterized by dilatation, are established. The impact of high-temperature effects on the strength and structure of coatings is investigated. It is shown that dilatation can be used as a control parameter of the strength properties of iron.

Introduction

Soft and ductile electrolytic iron is not suitable for the restoration and hardening of machine parts. However, under ordinary electrolysis conditions, iron coatings are obtained in a plating bath, which are close in quality to hardened steel 45 and have a fine crystalline structure. Thus, electrolytic iron acquires high mechanical properties due to its saturation with structural defects. The most complete description of structural defects of electrodeposited metals in general and electrolytic iron is given in particular in the works of Yu. M. Polukarov, E.A. Mamontov, G.V. Guryanov and their students [1-4]. However, the general laws of structure formation have not yet been established. To select the main parameters of the fine structure, a criterion is needed to assess their contribution to the overall defectiveness of the metal. Such a criterion can be a change in the density and volume of the electrolytic iron - dilatation.

Therefore, the aim of this research was an attempt to consider the relationship of structural defects with metal dilatation based on an analysis of own studies of the influence of electrolysis parameters on the structure and properties of electrolytic iron and the authors’ works [5-7].

Research methodology

A detailed technology for obtaining composite electrochemical coatings (CEC) and coating samples was developed and described in works [7–10]. X-ray diffraction analysis was carried out on the DRON-3M device according to the procedure [11]. The block size of the mosaic (D) and microdistortion (ρ) was determined by the second-order moment method, the dislocation density (ρ) was estimated by the formula of P.B. Hirsch [12]. The morphology and microstructure of the substrate and coatings were studied using a MIM-8 microscope. The tensile strength of CEC was studied on samples in the form of rings [7]. Internal stresses were determined by the flexible cathode method.
The density of the coatings was determined by hydrostatic weighing [14]. Tests repeatability in the experiments ranged from 3 to 10. The experimental data were processed by methods of mathematical statistics. Regression analysis was used to make functional dependencies [15, 16].

Research results and their discussion
Starting to analyze the conditions of origin and formation of defects in the structure of electrolytic iron coatings in order to establish patterns of change in the mechanical properties of metal, it makes no sense to give a detailed description of all defects encountered in electrodeposited metals, which are described in detail in works [4, 17].

At the same time, to our mind to assess the overall defectiveness of materials, dilatation can be one of the parameters characterizing the structure of the coatings that can be operated when considering this problem.

The theoretical density of a metal ($\gamma_p$), having an ideal crystal lattice can be established quite accurately [4, 17]. All violations of the atomic arrangement in the lattice (structural defects) inevitably lead to a change in the density and volume of metals (dilatation). Accordingly, the contribution of a defect to a change in the specific volume or density of a metal can serve as an estimate of the significance of the contribution of this type of defect to a change in its submicrostructure.

For example, the equilibrium concentration of vacancies in metals ($C_v$) is defined as the ratio of the number of vacancies in the lattice ($n$) to the total number of nodes in the crystal ($N$). The concentration of vacancies depends on the heating temperature and reaches its maximum value at the melting point [17]:

$$C_v = A \cdot \exp\left(-\frac{\alpha_v}{\alpha_m \Theta}\right), \quad (1)$$

where $A$ is a constant depending on the type of lattice;

$\alpha_v$ is a vacancy energy;

$\alpha_m$ is a melting energy of a vacancy;

$\Theta$ is a similar temperature.

Thus, the maximum vacancy concentration determined using expression (1) for the electrolytic iron will be: $C_v = 10^{3}...10^{6}$ (at $\alpha_{v} = 0,019...0,04$, $\alpha_{m} =0,25$ [17]). Accordingly, the greatest dilatation (change in the volume and density) due to vacancies will be: $\delta_v = \Delta V/V = \Delta\gamma_{\text{фл}} n/N = 10^{3}$. The excess of vacancies frozen in the process of iron electrocrystallization flowing into loops, serves as a source of dislocations [4].

The dislocation density in the electrolytic iron can be extremely high and can reach $10^{12}...10^{13}$ cm$^{-2}$ [1-4]. At the same time, there is an upper limit to the possible dislocation density, limited by the permissible distance between dislocations $L=2r$, where $r = (2...3) b$ is the radius of the dislocation core; $b$ is the shortest distance in the lattice. When only nuclei remain, there will be no lattice - it is impossible to separate individual dislocations in a substance [17]. Therefore, dislocations exist only at their density $\rho \leq 10^{13}...10^{14}$ cm$^{-2}$. According to the estimates of $\delta_d = 1,5\rho b^2$ [11], the dilatation due to the dislocations for the electrolytic iron with a limiting dislocation density of the order of $\rho_{\text{фл}} = (6 b)^2 = 4,52 \cdot 10^{13}$ cm$^{-2}$ will be $\delta_d = 5,56 \cdot 10^{3}$. Despite the approximation of the calculations, this value coincides quite well with the relative change in the volume of iron and most other “pure” metals when the thermodynamic temperature changes from zero to the melting point $\Delta V/V = 6 \cdot 10^{2}$ [17]. The comparison of $\delta_d$ and $\delta_v$ allows one to single out the dislocation density among the main parameters of the iron submicrostructure, which are responsible for the dilation (changes in density and volume).

X-ray structural studies of the electrolytic iron showed that linear defects are concentrated inside the boundaries separating individual fragments, the volume of which is metal sections with a fairly perfect structure. Tightening of the electrolysis modes (increase of overvoltage during the metal evolution) leads to a decrease in fragments and an increase in the misorientation angle between them.
It should be noted that the sizes of coherent X-ray scattering areas (mosaic blocks - D), taken in many works as the main characteristic of the fine structure of electrolytic coatings, are directly related to the density of dislocations concentrated in the subgrain boundaries, for example, by the dependence [11]:

$$\rho = 3 D^2.$$  \hspace{1cm} (2)

To derive the dependences linking the density of dislocations and the size of mosaic blocks with the dilatation of electrolytic iron, we use the literature relation to determine the density of dislocations concentrated within the boundaries of subgrains [12]:

$$\rho = K_\delta (D b)^{-1},$$  \hspace{1cm} (3)

where $K_\delta$ is a coefficient depending on the shape of the grains. Replacing in the equation (3) $\rho$ by the value of the blocks according to formula (2), we obtain a relation that directly relates the dilatation and the size of the mosaic blocks:

$$D = K_\delta b \delta^{-1},$$  \hspace{1cm} (4)

and to relate the density of dislocations to dilatation (the density of the electrolytic iron) from equations (2) and (3) we can obtain the expression:

$$\rho = 3 K_\delta b^2 \delta^2.$$  \hspace{1cm} (5)

For a preliminary estimate of the coefficient $K_\delta$, we use the Hirsch equation, which is widely used for the experimental analysis of the dislocation structure of electrolytic iron [12]:

$$\rho = \beta (3 D B)^{-1},$$  \hspace{1cm} (6)

where $\beta$ is the misorientation angle determined experimentally. Taking into account that the relative elongation of the sample $\varepsilon = \beta$ [17] and $\varepsilon = \delta/3$, making the corresponding replacements in (6), we obtain:

$$\rho = \delta (9 D b)^{-1}.$$  \hspace{1cm} (7)

A comparison of (2) and (6) allows to pre-set the value of $K_\delta = 1/9$ and the boundary conditions:

$$\begin{align*}
\text{at } \delta \to 0, & & D \to \infty, & & \rho \to 0; \\
\text{at } \delta \to \infty, & & D \to 0, & & \rho \to \infty.
\end{align*}$$  \hspace{1cm} (8, 9)

The first condition (8) crystallographically corresponds to the ideal material without any defects (with an ideal crystal lattice). The second condition (9) cannot be satisfied, since the parameters of the substructure and dilatation of the metal are limited by the limiting values $D_{\text{min}}$, $\rho_{\text{max}}$ and $\delta_{\text{max}}$, corresponding to the maximum strain at which the metal loses its crystalline structure (in the first approximation it is an amorphous (liquid) metal). Therefore, the lower boundary condition (9) of the equations (3) - (5) should be clarified by taking the melting point as the limit state of the metal. We will try to do this for the iron, taking the minimum block size equal to the lattice constant. If according to the works [17, 18], one accepts a change in the sediment volume $\Delta V = 3 \alpha T_{\text{mel}}$, iron melting point $T_{\text{mel}} = 1806 \pm 5$, K, thermal expansion coefficient $\alpha = (1,02 \ldots 1,43) \cdot 10^{-5} \text{K}^{-1}$, density of the liquid metal $\gamma_{\text{liq}} = 7,0 \ldots 7,13$ g/cm$^3$, then $D_{\text{min}} = b = 2,48 \cdot 10^{-8}$ cm; $K_\delta = \delta_{\text{max}} = (\gamma_{\text{liq}} - \gamma_{\text{sol}}) / \gamma_{\text{sol}} = 0,064 \ldots 0,113$, $\rho_{\text{max}} = (1,08 \ldots 2,16) \cdot 10^{13}$ cm$^{-2}$. It should be noted that the value of $K_\delta$ is close in magnitude to the theoretically established $K_\delta = 1/9$, and the dislocation densities of iron $\rho_{\text{max}}$ with $\rho_{\text{pp}}$ are the same in order. The dependences of the dislocations density ($\rho \times 10^{15}$ cm$^{-2}$) and block sizes ($D$, A) on dilatation will take the form (figure 1):
It is interesting to trace how the fine structure and density of coatings change under different electrolysis conditions. Since electrolytic iron is characterized by a high degree of chemical purity, a change in density can only be associated with the process of sediment deformation during electrodeposition, its saturation with structural defects, and also due to microcracking of sediments, especially those obtained from cold chloride electrolytes.

Experimental studies to determine the influence of electrolysis conditions on the parameters of the submicrostructure of sediments showed that toughening the electrolysis conditions leads to an increase in the density of dislocations and grinding of mosaic blocks to limiting values (at $\delta=0.06...0.07$), followed by the formation of stable submicrocracks in them. The most wear-resistant coatings corresponded to the transition from monolithic sediments to fractured ones. Thus, hardening of the material was observed, due to the process of plastic deformation of the sediment during electrolysis, similar to submicrostructural hardening during plastic deformation. Although under “hard” electrolysis conditions, sediments were penetrated by a dense network of submicrocracks, their shear strength increased. It is possible that cracks additionally resisted the movement of dislocations, due to which the microhardness of the coatings increased, but the wear resistance decreased [4, 6, 8].

The analysis of the experimental data made it possible to establish the dependence $D=f(\delta)$ (figure 2):

$$D = 17.45 \delta^4.$$  

(12)

The dependence $\rho=f(\delta)$ can be divided into two sections (figure 3). In section I at $\delta \leq 0.055...0.065$, the function had the form:

$$\rho = 14.5 \delta^6.$$  

(13)

Equations (13) and (14) make it possible to relate the strength parameters of materials to their dilatation when their submicrostructure changes under various electrolysis conditions. At the same time, considering the mechanisms of plastic deformation of real metals, it should be borne in mind that the parameters of the submicrostructure can characterize the properties to a certain limit - ultimate hardening, corresponding to $\delta=0.06...0.07$, after which a new type of defects - submicrocracks - appear in the structure of the material.
In section II (at $\delta > 0.06 \ldots 0.07$), the dependence $\rho = f(\delta)$ underwent a kink and changed its character. When processing the experimental data, a linear dependence $\rho = f(\delta)$ was established:

$$\rho = 1.16 + 3.52\delta.$$  \hspace{1cm} (14)

The experimental dependence $H_{\mu} = f(\delta^{1/2})$ also had a linear character with a kink in the area of $\delta = 0.06 \ldots 0.07$ ($D = 250 \ldots 350$ A). The section of the curve before the inflection is characterized by the process of plastic deformation during electrolysis, grinding of mosaic blocks, and increase in the density of dislocations, due to which sediments are hardened to the limit state. In the area of fractured sediments (beyond the inflection of the curve), the influence of cracks leads to the inflection of the function $H_{\mu} = f(\delta^{1/2})$. Since cracks impede the movement of dislocations, they thereby strengthen the material; however, the pattern of their action differs from substructural hardening of monolithic sediments.

Before the appearance of stable microcracks in the iron structure, the dependence of the microhardness ($H_{\mu}$, GPa) of electrolytic iron on dilatation had the form (figure 4):

$$H_{\mu} = 0.15 + 20.48\delta^{1/2},$$  \hspace{1cm} (15)

and in the area of fractured sediments:

$$H_{\mu} = 5.22 + 0.16\delta^{1/2},$$  \hspace{1cm} (16)

Considering the physical nature of microhardness and the relation $\sigma_m \approx \frac{1}{3}H_{\mu}$ \hspace{0.6cm} [20], we obtain expressions for the yield strengths of iron coatings ($\sigma_m$, GPa) before and after the formation of submicrocracks, respectively:

\begin{align*}
\text{Figure 2.} & \text{ Relationship between the size of dislocation blocks and dilatation of the electrolytic iron.} \\
\text{Figure 3.} & \text{Relationship between dislocation density and electrolytic dilatation of iron: I – sediment area without cracks; II - area of fractured sediments.}
\end{align*}
\[ \sigma_t = 0.05 + 6.83 \cdot \delta^{1/2}, \]  
\[ \sigma_t = 1.74 + 5.33 \cdot 10^{-2} \cdot \delta^{1/2}. \]  

Figure 4. Relationship between microhardness and electrolytic dilatation of iron before (1) and after (2) the formation of submicrocracks.

Thus, the low strength of sediments of electrolytic iron is explained by the features of the formation of the coating on the cathode, by the initial structure, and defects in the crystal structure. Indeed, if we construct the dependence of tensile strength of electrolytic iron \( \sigma_t \) on the dilatation and size of mosaic blocks, we can establish that these values are very closely interconnected with each other (figure 5, a and b). Moreover, the dependences \( \sigma_t = f(\delta) \) and \( \sigma_t = f(D^{1/2}) \), constructed according to experimental studies, reveal three characteristic areas: I - an increase in \( \sigma_t \) associated with an increase in dilatation, due to the refinement of the mosaic blocks and increase in the density of dislocations up to the transition of the structure to an “extremely” deformed state, until submicrocracks appear; II - a linear decrease in \( \sigma_t \) with an increase in dilatation due to the formation and increase in the density of new defects (submicrocracks) developing in the sediment when the electrolysis conditions are tightened; III - the area of an almost vertical drop in strength before the destruction of sediments (with an increase in the size of submicrocracks penetrating the sediment completely). Thus, when the dilatation reaches \( 0.06 \ldots 0.07 \), the coating ceases to resist tensile loads. Such sediments are extremely fragile and does not disperse from the surface of the part due to its high adhesion to the base and a sufficiently good shear within the size of subgrains.

Figure 5. Dependence of tensile strength on dilatation (a) and dimensions of mosaic blocks (b) of electrolytic iron.

Thus, the revealed dependence of the strength of “pure” electrolytic coatings on dilatation has shown that the area of their hardening due to the substructural changes is limited to \( \delta_{\text{max}} \leq \delta \leq \delta_T \) (area II, figure 6). Area III (\( \delta > \delta_T \)) corresponds to the transition of the metal structure to an “extremely” deformed state, with the appearance of submicrocracks and a drop in strength properties. Such sediment can be strengthened by post-electrolysis processing techniques aimed at “healing” submicrocracks, for example, by subsequent heat treatment. In the area I at \( \delta \leq \delta_{\text{min}} \) an increase in strength is possible due to the formation of coatings and other materials with a minimum concentration...
of defects, which requires the development of new technological methods for producing sediment and materials in general.

![Figure 6. Relationship between strength and dilatation of the electrolytic iron.](image)

Since the performance of the coating process requires toughening the conditions of electrolysis, but at the same time the sediment requires higher strength and wear resistance, it is necessary to apply any technological methods in the post-electrolysis period aimed at “healing” of submicrocracks. Such methods include obtaining composite electrochemical coatings (CEC) based on iron with the inclusion of solid dispersed particles, such as boron carbide, and heating parts with coatings, for example, by high-frequency current, laser, or other methods [1,4].

**Conclusions**

The dependence of the strength properties of electrodeposited metals on dilatation as an integral parameter of the submicrostructure is established. The possibility of increasing the strength of electrochemical coatings by introducing filler into them with subsequent heat treatment to form strong interfacial bonds is shown. The choice of filler and modes of post-electrolysis heat treatment of coatings as technological methods for their hardening should be carried out with strict regard to the influence of thermodynamic processes of phase interaction on the magnitude and sign of the high voltage of the material.

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