Soviet-era science, translated into English

# Physical Chemistry

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1960

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## Abstract

## Full Text

# Physical Chemistry

**G. S. Vozdvizhenskii, G. A. Gorbachuk, and G. P. Dezider' ev**

# The Mechanism of Electrolytic Polishing of Metals in the Light of Electron-Microscopic Studies of the Surface at Various Stages of Treatment

*(Presented by Academician A. N. Frumkin, January 28, 1960)*

In most published works, electron-microscopic studies during electrolytic polishing are used only to characterize surface cleanliness, to assess the possibilities and limits of smoothing microroughnesses ([1]). At the same time, the electron microscope is also finding application in solving electrochemical questions ([2]), in particular the mechanism of electrolytic polishing of metals ([3]).

In our work ([4]) it was clearly shown that, both in the initial stages of the process of anodic dissolution and in the stages corresponding to the external effect of electropolishing, structural etching invariably takes place; its scale differs depending on the degree of electrochemical inhomogeneity of the surface. The electron-microscopic photographs we obtained do not indicate any suppression of structural etching throughout the entire electropolishing process. There is only a regular decrease in the scale of etching, associated with a decrease in the electrochemical inhomogeneity of the surface.

In our subsequent investigations we sought to obtain experimental material linking the process of anodic dissolution with the structure of the metal. To this end, we studied the process of electrolytic polishing on specimens of rolled and annealed copper and brass.

The objects selected for study were sheet copper (cold-rolled) of grade M1 and sheet brass (cold-rolled) of grade L59. Electrolytic polishing was carried out in an 11.35 M solution of orthophosphoric acid containing, respectively, 4.8 and 2.9 g/l of copper. Special experiments established that the optimum current density (limiting) in electropolishing is 14.5 mA/cm$^2$ for copper specimens and 19 mA/cm$^2$ for brass specimens.

Specimens etched to reveal a distinct microstructure (copper for 4 min at 20° in a 10% solution of ammonium persulfate; brass for 2–3 min at 20° in a mixture of aqueous ammonia solution and hydrogen peroxide), after metallographic inspection, were suspended in the electropolishing bath. After the prescribed time had elapsed, the specimen was removed from the bath, washed, dried, and again subjected to metallographic inspection. Then a lacquer replica was taken from it, which was shadowed at a small angle (7-18°) with chromium and submitted for electron-microscopic examination.

Metallographic (200×) and electron-microscopic (23,000×) photographs of the surface of rolled copper specimens treated under the indicated conditions are shown in Fig. 1, and those of brass specimens in Fig. 2*. The numbers indicate the treatment time in minutes.

* In Figs. 1-4, the upper rows of photographs are optical micrographs, and the lower rows are electron micrographs.

Another series of experiments was carried out with specimens annealed in vacuum (copper at 700° for 1½ hours, and brass at 600° for 2 hours, with cooling together with the furnace). The optimum current density for electropolishing the copper specimens was 21 ma/cm$^2$, and for the brass specimens 16 ma/cm$^2$. Metallographic (200×) and electron-microscopic (23,000×) photographs of annealed copper specimens treated under the conditions indicated above (etched and electropolished for various lengths of time) are shown in Fig. 3, and those of annealed brass specimens in Fig. 4.

The initial surface of all the specimens investigated is, of course, heterogeneous in electrochemical respect. Therefore chemical etching in a solution of ammonium persulfate for the copper specimens and in a mixture of aqueous ammonia solution and hydrogen peroxide for the brass specimens reveals a distinct structure (in Figs. 1-4).

Anodic dissolution of the specimen takes place with the participation of an acceptor contained in the electrolyte—apparently phosphoric acid. At the beginning of treatment, access of the acceptor is provided practically to all parts of the surface, and therefore there are no restrictions on the development of anodic-dissolution figures. They should develop on all scales, in accordance with the dimensions of the electrochemical inhomogeneity. In the subsequent stages of dissolution, access of the acceptor into the depth of the etch pit that has formed becomes more difficult; this should lead to a delay in their development in depth, and the dissolution process should pass over to new areas, spreading over the surface.

As optical microphotographs (200×) show for rolled material, the external effect of chemical etching in the corresponding solutions corresponds to the orientation of the crystals in the rolling direction (texture). In this case, for brass L59, as for a more heterogeneous material and consequently one possessing greater electrochemical inhomogeneity, the orientation of the crystallites in the rolling direction is observed to a considerably lesser degree than for copper.

Electrolytic polishing not only does not obscure the effect of chemical etching —the distinctly revealed microstructure with the corresponding orientation of the crystallites—but, on the contrary, reveals it still more sharply. The treated (bright, especially on copper) areas of the surface are elongated in the direction of rolling.

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Fig. 1.

Figure 1: Fig. 1.

Fig. 2.

Figure 2: Fig. 2.

In the electron-microscopic photographs the effect of chemical etching of the initial surface likewise corresponds to the orientation of the crystallites—etching here reveals numerous oriented displacements within the crystallites. This is especially clearly manifested on the copper specimens. The clear picture of these areas also is not obscured by electrolytic polishing. In the subsequent stages they are revealed even more distinctly, but do not deepen; instead, they broaden, owing to the restriction of access of the acceptor into the depth of the etch pits. Consequently, in electropolishing there is no so-called suppression of structural etching, but only a change in the scale of anodic dissolution in accordance with the change in the scale of electrochemical inhomogeneity.

A comparison of the optical microphotograph of a rolled copper specimen treated for 11 min. with the electron-microscopic photograph is especially illustrative. In the first, bright areas elongated in the rolling direction are observed; in the second, they also appear, but in the form of anodic-dissolution figures covered with a finer pattern. The linear dimensions of the bright areas in the first photograph approximately correspond to the elongated figures in the second, as follows from a comparison of the magnifications (23,000 : 200   100). The relatively large electrochemical inhomogeneity of the brass specimens is additionally manifested in the fact that, in the electron-microscopic photographs, junctions of differently oriented crystallites are more readily detected. For the copper specimens this phenomenon is rare.

On the annealed material (both for copper and for brass), in principle, the same picture of chemical and electrochemical dissolution is observed,

than on the rolled one, but this picture already corresponds to the structure formed during annealing. In these cases as well, active destruction of the crystal surface takes place. Large crystals are covered with the finest etching pits, which gradually expand. Since in the annealed material the crystallites are larger than in the rolled material, the traces of their attack become noticeable even at low magnification (200×). Annealing disorients the arrangement of crystallites, and therefore the anodically treated surface elements show no orientation either in optical or in electron-microscopic photographs.

Fig. 3.

Figure 3: Fig. 3.

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Fig. 4.

Figure 4: Fig. 4.

If, on the rolled material, a substantial difference was observed in the results of anodic treatment of copper and brass specimens, caused by a substantial difference in their electrochemical heterogeneity, then on annealed specimens this difference is already smoothed out, owing to the fact that upon annealing both materials became more or less equally disoriented. The relatively greater electrochemical heterogeneity of the brass specimens is manifested only in the easier detection, in electron-microscopic images, of junctions between differently oriented crystallites.

Thus, the choice we made of specimens for the experimental investigation of the mechanism of electrolytic polishing of metals with the aid of an electron microscope has proved well justified. It made it possible to illustrate clearly the leading role of the metal structure in this mechanism. Structural etching of an electrochemically heterogeneous surface is the basis of the mechanism of electropolishing and occurs at all its stages. Diffusion limitations with respect to the acceptor play an important role, ensuring a gradual decrease, in depth, of the scale of structural etching.

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Received
28 I 1960

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*Note: Figure translations are in progress. See original paper for figures.*

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