INVESTIGATION OF THE MECHANISM OF ELECTROLYTIC POLISHING OF METALS

COMMUNICATION I. MECHANISM OF ELECTROLYTIC POLISHING OF DURALUMIN

A. Sh. Valeev

The mechanism of electrolytic polishing of metals has not been studied sufficiently up to the present time; consequently a number of problems relating to the choice of electrolyte and conditions of polishing are solved empirically.

The aim of the present paper is to make a contribution to the study of the mechanism of the polishing process by a study of the laws of the electrolytic polishing of duralumin.

EXPERIMENTAL

The specimens used for polishing were plates of D-16-T grade of duralumin, and the electrolyte was a mixture of equal parts by weight of phosphoric and sulfuric acids with an addition of 3% chromic acid, containing a certain amount of water.

Table 1 shows the specific gravities of this electrolyte with different water contents.

TABLE 1

Dependence of the Specific Gravity of the Electrolyte on its Water Content.

Electrolyte No.	Specific gravity	Concentration				
		°Be	H_2SO_4 (in %)	H_3PO_4 (in %)	H_2O (in %)	$H_2C_2O_4$ (in %)
1	1.712	60.1	43.0	43.0	11.0	3.0
2	1.685	58.7	41.5	41.5	14.0	
3	1.660	57.4	40.0	40.0	17.0	
4	1.635	56.0	38.5	38.5	20.0	
5	1.608	54.6	37.0	37.0	23.0	
6	1.587	53.4	35.5	35.5	26.0	

The investigation was carried out by electrochemical treatment of the specimens with simultaneous measurement of the electrode potentials, the voltage at the terminals of the electrolytic cell, and the current strength (or density); the quality of the treated surface was assessed visually, by changes in luster and by microscopic examination.

The treatment was carried out in a rectangular glass cell of 0.5 liter capacity. The potential of the specimen was measured against a standard calomel electrode. The luster was measured with the aid of a luster meter, consisting of a metallurgical microscope, selenium photocell, and mirror galvanometer, and was expressed as a percentage of the luster of a silver mirror. This method can be considered as an integral method [1]. With its aid it is possible to represent more correctly the microgeometry of the surface, rather than its luster in the psychophysical sense. The metallurgical microscope detects only the rays reflected from the surface perpendicular to the optical axis of the objective of the microscope, and therefore irregularities on the surface examined appear dark.

Before the anode treatment, the aluminum coating was removed from the specimen surface by coarse emery paper, followed by after-treatment with fine No. 00 emery. Thus, in all the experiments the texture of the surface was the same. A definite region of the surface was subjected to anode treatment. The remaining regions, and also the side edges, were isolated from the action of the electrolyte and the electric current by Bakelite lacquer. The cathode used in all the experiments was sheet lead, 0.5 dm^2 in size. The distance between the electrodes was 5 cm in all the experiments. The disposition of the lines of force of the electric field was constant in all the experiments.

Measurements of anode potential (with current flowing) and studies of the quality of the surface treatment were carried out in the current density range from 0 to 150 A/dm^2. The aim of these measurements was to determine the drop of voltage in overcoming the resistance of the film formed by the products of anodic dissolution, and therefore the tip of the liquid tap was not flush with the anode (the tip was cut off at a certain angle to its axis).

The duration of treatment was established in accordance with the amount of metal passing into solution, that is, with consideration of the current density and current efficiency; the periods of treatment were as follows:

Anode current density (in A/dm²)	5	10	20	30	40	60	80	100	150
Duration (in min)	20	10	5	4	3	2.5	2.0	1.5	1.0

The first experiment was carried out in order to determine the nature of the curves for the anode potentials, voltages, and quality of anode treatment in relation to the anode current density. The experiment was carried out in electrolyte No. 3 (Table 1). The working surface of the specimens was 5 cm².

The results of the experiments are shown in Figure 1 (b represents the first part of Diagram a on a layer scale), the points corresponding to polishing of the surface being shown by white circles on the curves. The voltage curve 2 is shifted a little to the right of the anode potential curve 1. This indicates that the main resistance to the electric current is concentrated in the layer of electrolyte adjoining the anode.

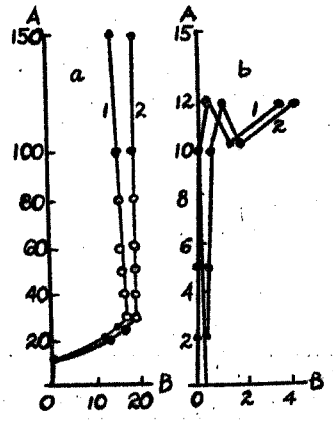


Fig. 1. Dependence of anode potentials and voltages on the current density for electrolyte No. 3 at 80°. A) Anode current density (in A/dm²), B) anode potential (in V).
1) Anode potential curve, 2) voltage curve.

Microphotographs (x 120) of the surfaces of the specimens treated at different current densities are shown in Figure 2. For equal times of electrolysis (from the amounts of metal passing into solution) each point on the anode potential curve corresponds to a definite type of treatment of the specimen surface. The curves show two ascents. The first ascent (Figure 1, b) represents etching of the metal with a black deposit, easily removed by rubbing (Figure 2, a)*. The first ascent is followed by a sudden decrease of current strength with simultaneous increase of anode potential and voltage. This is followed by a steady increase of current strength with a rapid increase of the anode potential (flat region). Here bright etching without a deposit occurs at first (Figure 2, b), which then passes into lustrous etching, or polishing without significant leveling of the surface (Figure 2, c and 2, d). The second ascent of the curve represents polishing (Figure 2, e), which at higher current densities passes into corrosion (Figure 2, f).

The second experiment was carried out to elucidate the effect of mechanical stirring of the electrolyte on the nature and the quality of the surface treatment (Table 2, Figure 3). The experiment was carried out in electrolyte No. 1 (Table 1). The working surface of the specimens was 5 cm².

A considerable difference is found in the course of the curves obtained with and without stirring. The curve obtained without stirring, at a current density $D_a < 22$ A/dm², lies considerably to the right of the curves obtained with stirring; at $D_a > 22$ A/dm² the first is already on the left of the second.

In practice, the following happens: without stirring, for example, at $D_a = 10$ A/dm², the voltage reaches 13 V (anode potential 12.47 V); if the stirrer is now put into action, the voltage falls to ~1 V. If the stirring is now stopped, it rises again to its initial level, that is, to 13 V. This can be done repeatedly. This indicates that the high anode potential is due to the accumulation of products of anodic dissolution, which can be dispersed by stirring the electrolyte, in the zone near the anode. The intensity of stirring is significant; if the stirring is not vigorous enough the voltage falls not to 1 V, but perhaps to 3 or 4 V and equilibrium sets in.

During electrolysis with stirring at current densities above 20 A/dm² the anode becomes coated with a thin oxide film ("temper color"). Thus, two processes occur during stirring, one of which, by aiding the diffusion of the products of anodic dissolution, lowers the anode potential, while the other, by causing the formation of a thin oxide film, raises it; at a definite current density (in the given case at ~22 A/dm²) the decrease of the anode potential by the first process is compensated by its increase by the second process, and therefore $\Delta e_a = e'_a - e''_a = 0$ (Table 2).

The high anode potential due to accumulation of the products of anodic dissolution indicates the high ohmic

* See plate page 831.

TABLE 2

Effect of Stirring on the Anode Potential and Anode Resistance in an Experiment with Electrolytic No. 1 (d = 1.712) at 80°.

With stirring			Without stirring		$e'_a - e''_a = \Delta e_a$ (in V)	$\frac{e'_a - e_0}{d_a} = r'$ (in Ω/dm²)	$\frac{e''_a - e_0}{d_a} = r''$	$r' - r'' = \Delta r$
D_a (in A/dm²)	V' (in V)	e'_a (in V)	V'' (V)	e''_a (in V)				
0	–	−0.19	–	−0.19	–	–	–	–
6.0	0.52	+0.08	0.48	+0.08	0	0.04	0.04	0
10.0	0.96	0.38	3.0-13.0	2.47-12.47	−12.09	0.06	1.26	−1.2
15.0	6.0	5.26	13.6	12.84	− 7.58	0.36	0.87	−0.51
20.0	13.6	12.58	14.2	13.2	− 0.62	0.64	0.67	−0.03
25.0	15.0	13.66	14.6	13.4	+0.26	0.55	0.54	+0.01
30.0	17.0	15.52	15.0	13.49	+2.03	0.52	0.46	+0.06
40.0	19.0	17.14	–	–	–	0.43	–	–
50.0	19.4	17.24	16.5	14.27	−2.97	0.34	0.29	+0.05
60.0	20.0	17.50	–	–	–	0.29	–	–
100.0	18.5	15.03	18.0	14.56	+0.47	0.15	0.14	+0.01
150.0	18.0	13.43	17.5	13.0	+0.43	0.09	0.09	0

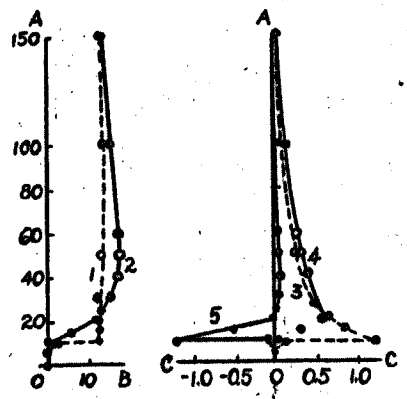


Fig. 3. Dependence of the anode potentials and resistances on current density for electrolyte No. 1 at 80°. A) Density of anode current (in A/dm²), B) anode potential (in V), C) anode resistance (in Ω/dm²). Anode potential curves: 1) without stirring of the electrolyte, 2) with stirring; anode resistance curves: 3) without stirring (r'), 4) with stirring (r''), 5) the difference curve $r' - r'' = \Delta r$.

resistance of the latter. In order to calculate the specific resistance it is necessary to know, among other things, the thickness of the layer of these products; but as this is not known exactly, we will limit ourselves to calculating the resistance due to the products of anodic dissolution, per unit area of the anode. In these conditions Ohm's law takes the form:

$$\frac{e_a - e_0}{D_a} = r,$$

where e_0 is the static potential; $e_a - e_0$ is the potential difference expended in overcoming the resistance of the products of anodic dissolution (polarization resistance); r is the resistance per 1 dm² of the surface.

If the specific resistance of the anode products is taken as constant, the value of r in each separate case will give an indication of the thickness of this layer. The resistance of the anode products (anodic resistances) calculated with the aid of this Formula are shown in Table 2 and given graphically in Figure 3.

It is seen from the curves that the maximum resistance, equal to 1.26 Ω/dm² (maximum thickness of the anode film) is found at D_a = 10 A/dm² without stirring; with stirring at this current density the resistance is only 0.06 Ω/dm² while the maximum anode resistance with stirring, equal to 0.64 Ω/dm², is obtained at 20 A/dm². Electropolishing commences at an anode resistance of 0.3 − 0.5 Ω/dm², both with and without stirring. Further increase of the current density leads to decrease of the anodic resistance and to deterioration of the surface − etching.

The curves in Figure 4 show the results of experiments on the effect of temperature, with and without stirring of the electrolyte, on the nature of the curves and the quality of the surface treatment. The experiments were carried out with electrolyte No. 1 (Table 1), and the specimens in this case had a working surface of 1 cm². The curves are supplemented by data on luster measurements.

Fig. 5, a shows sets of curves for the anode potentials at different temperatures with and without stirring in electrolyte No. 5 (Table 1), and Figure 5, b shows the corresponding curves for the anode resistances.

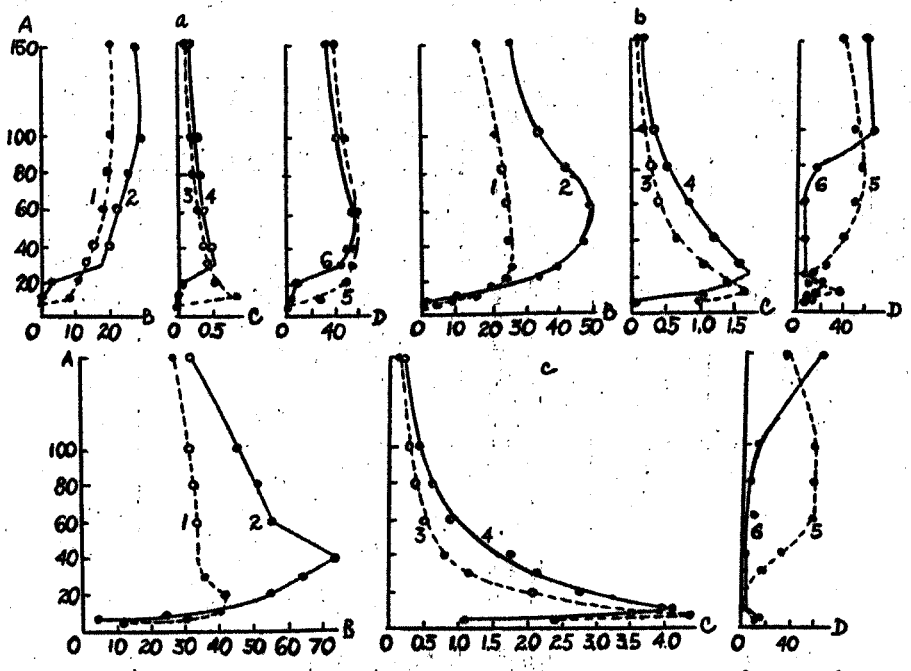


Fig. 4. Dependence of the anode potential, resistance, and luster of the surface on the current density, for electrolyte No. 1 at temperatures: 80°C (a), 55°C (b) and 40°C (c).
A) Anode current density (in A/dm²), B) anode potential (in V), C) anode resistance (in Ω/dm²),, D) luster (in %).
Anode potential curves: 1) without stirring of the electrolyte, 2) with stirring; anode resistance curves: 3) without stirring, 4) with stirring; luster curves: 5) without stirring, 6) with stirring.

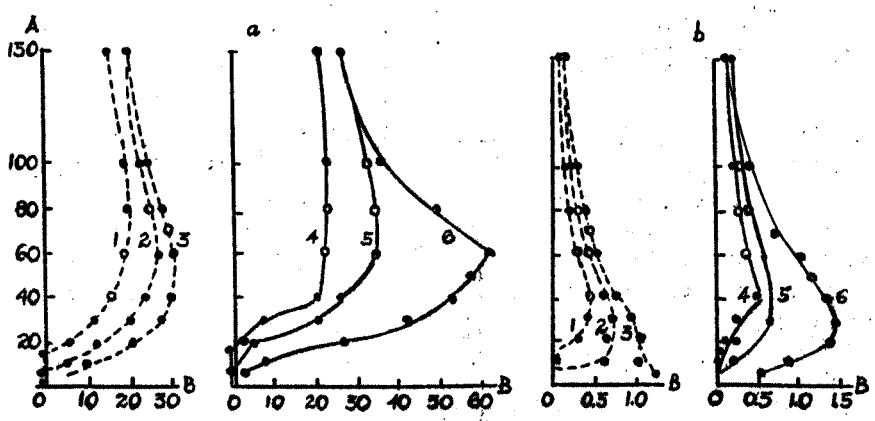


Fig. 5. Dependence of the anode potentials (a) and resistance (b) on the current density for electrolyte No. 5 at different temperatures.
a: A) Anode current density (in A/dm²), B) potential (in V). Without stirring: 1) at 80°C, 2) at 65°C, 3) at 48°C; with stirring: 4) at 80°C, 5) at 65°C, 6) at 48°C.
b: A) Anode current density (in A/dm²), B) anode resistance (in Ω/dm²). Without stirring: 1) at 80°C, 2) at 65°C, 3) at 48°C; with stirring: 4) at 80°C, 5) at 65°C, 6) at 48°C.

The optimum conditions of polishing are compiled from all the tables and graphs in Table 3. This table was used as a basis for the diagram for the dependence of the anode potential on the electrolyte temperature (Figure 6). As this figure shows, the optimum anode potential increases with decrease of temperature.

In the diagram the points for the experiments with stirring are shown by circles, and without stirring, by triangles.

TABLE 3

Selection of Optimum Conditions of Polishing from the Results of All Experiments.

Specific gravity of electrolyte	Temperature (in °C)	D_a (in A/dm²)	Anode potential (in V)	e (in V)	r (in Ω/dm²)
a) From experiments with stirring					
1.71	80	40	21.0	19.7	0.50
	80	60	24.0	22.4	0.41
	70	100	31.0	28.8	0.29
	55	100	36.5	34.1	0.34
	48	100	36.0	32.4	0.32
	40	150	38.0	32.1	0.21
1.60	80	60	23.0	22.0	0.37
	80	80	24.5	23.3	0.29
	65	60	36.0	34.3	0.43
	65	80	33.5	31.7	0.32
	48	100	38.0	34.7	0.35
b) From experiments without stirring					
1.71	80	30	14.2	13.2	0.45
	80	40	17.1	15.8	0.40
	70	60	26.0	24.4	0.47
	70	80	24.0	22.1	0.32
	55	60	27.5	25.6	0.44
	55	80	26.0	23.7	0.30
	48	60	36.0	33.3	0.55
	48	70	34.0	31.1	0.44
	40	60	37.5	33.9	0.55
	40	80	37.0	33.0	0.41
	40	100	36.0	31.6	0.31
1.6	80	40	18.0	17.0	0.44
	80	60	20.5	19.5	0.32
	65	80	26.7	25.2	0.32
	48	60	34.0	31.3	0.53
	48	70	33.0	30.0	0.43

The points obtained may be arranged in bands which show an approximately linear relationship between the optimum anode potential and the temperature. It is noteworthy that the points corresponding to experiments without stirring lie to the left of the points corresponding to experiments with stirring of the electrolyte.

Extrapolation of the bands to their intersection with the ordinate axis gives the condition for polishing at $e_a = 0$, or without current (chemical polishing); according to the diagrams the temperature here should be 110-125°C. A special experiment showed that in fact chemical polishing of the specimens takes place at a temperature of 115°C. It must, however, be noted that the quality of the polishing is rather inferior to electropolishing and the composition of the electrolyte in these conditions quickly changes due to the rapid decomposition of chromic anhydride, and therefore it is difficult to determine the optimum condition for chemical polishing. This does not mean, however, that it is not possible to find an electrolyte for chemical polishing which does not undergo a great change in its chemical composition.

DISCUSSION

Analysis of the curves obtained establishes the following facts.

1) As the current density increases to a definite value, which depends on the temperature and concentration of the electrolyte, there is an approximately linear relationship between the current density and anode potential, and this region of the curve corresponds to a mat dissolution of the surface of the specimen with a dark tarnish.

When the upper limit is reached there is an abrupt break in the straight line, which corresponds to a decrease of the current density with simultaneous sharp increase of the anode potential (Figure 1, b). The nature of the

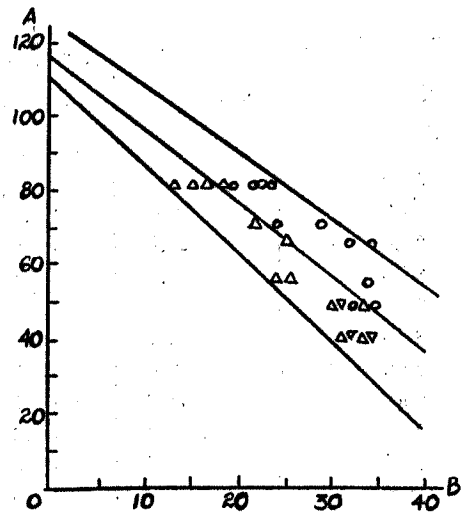


Fig. 6. Dependence of the optimum anode potential on the temperature.
A) Temperature (in °C), B) anode potential (in V).

dissolution of the anode also changes here: the black deposit vanishes and bright etching begins. This corresponds to the instant when the whole anode surface is covered by a layer (very slight at first) of the products of anodic dissolution, which differs greatly in composition and properties from the electrolyte.

Further, depending on the temperature and concentration of the electrolyte, there is a flat or nearly horizontal portion of the curve. Here a small increase of current density corresponds to a considerable increase of the anode potential, which is greater as the temperature is lower and the concentration of the electrolyte is higher. The quality of the anode surface gradually changes over this region. At first the surface is polished, and attains a certain luster while remaining uneven. The structure of the surface hardly changes with time during the process. Each consecutive point in this region corresponds to a surface finish on the anode which differs slightly from the previous point by greater smoothness and polish in polishing at high temperatures (for example at 80°C) or by greater tendency to oxidation at low temperatures. The upper limit of this region depends both on the temperature, and on stirring of the electrolyte. The limiting value of the potential is higher at lower temperatures; thus, while at 80°C (without stirring) it is equal to ~10 V (Figure 4, a), at 40°C it is ~40 V (4, b). While at high temperatures this potential is due only to the accumulation of liquid products of anodic dissolution in the anode zone (as is indicated by the absence of any noticeable oxide film on the treated specimen), at low temperatures it is also associated with the formation of an oxide film. Stirring of the electrolyte leads to still greater oxidation, and as a result to increase of the potential (anode resistance).

When the extreme limit of this region is reached, the curve ascends again, the transition to the new ascent being gradual at high temperatures and abrupt at low, and the curve turns sharply in the direction of low potentials. At high temperatures electropolishing commences at the beginning and in the middle of this region (with corrosion at the end), and at low temperatures in the middle and at the end.

2) Parallel experiments with and without stirring of the electrolyte showed that up to a certain current density, which depends on the temperature, the products of anodic dissolution which accumulate in the anode zone can be removed by stirring; the potential then falls considerably (for example, from 13 to 1 V in Figure 3). Above a certain current density, which depends on the temperature, it is not possible to remove completely the products of anodic dissolution and to expose the anode surface; a certain layer of film remains on the anode, and this film is increasingly dense with higher current density. This is apparantly associated with the dielectric properties of the anode products.

The following was established from calculations of the anode resistance. In the absence of external influences, such as mechanical stirring of the electrolyte, the formation of the anode film is completed at $D_a \cong 10$ A/dm^2 (Figure 4, curves 3), and above this the resistance falls rapidly with increase of current density. This is caused, firstly, by evolution of gas, which increases with increasing current density; secondly, by convection currents due to the temperature difference between the layer of the electrolyte near the anode and its general mass. The effect of stirring by convection currents should be proportional to the heat evolved, or proportional to the product $e_a \cdot D_a$. Polishing takes place not at the maximum value of the anode resistance, but at a value of 0.3-0.5 Ω/dm^2, independently of the concentration, temperature, and stirring of the electrolyte. This anode resistance can be reached both in the flat region of the anode potential curve, and in its second ascent. However, electropolishing occurs only in the second ascent. In the flat region, at this anode film resistance, only lustrous etching occurs without appreciable leveling of the surface (at high temperatures) or oxidation (at low temperatures).

3) Experiments at different temperatures show that stirring of the electrolyte increasingly intensifies the oxidation effect as the temperature decreases (Figure 4); the maximum effect occurs at medium current densities (~50 A/dm^2). The lower the temperature, the wider is the range of current densities where oxidation occurs (see the luster curves). The absence of oxidation at very high current densities with stirring, even at low temperatures,

is apparently explained by the fact that the effect of mechanical agitation with a stirrer becomes insignificant in comparison with the effect of stirring by the evolved oxygen, which, although considerable, does not lead to the removal of the anode products. It is found experimentally that, with stirring, polishing occurs at higher current densities than without stirring; while at current densities at which polishing takes place without stirring of the electrolyte, oxidation takes place on stirring. Further increase of the current density in experiments with stirring should lead to a still greater decrease of the film thickness than in experiments without stirring, and to corrosion of the surface. The fact that, nevertheless, a film with maximum resistance is formed in these conditions and polishing occurs, is apparently explained by the fact that mechanical stirring of the electrolyte favors decrease of the temperature of the anode film (the temperature of the anode film is considerably higher than the temperature of the electrolyte) by accelerated heat exchange with the main mass of electrolyte. This leads to a decrease of the convection currents, and consequently to a decrease of their attenuating affect on the anode film. Therefore, with stirring, a film with optimum resistance is formed at higher current densities than without stirring.

Thus, mechanical stirring has different functions according to the current density: at low current densities it favors removal of the anode film and leads to corrosion of the surface; at medium current densities it produces oxidation, and at high current densities, it results in polishing.

4) At a lower concentration of electrolyte (Figure 5) the above laws apply with the only difference that both the polishing and the oxidizing action of the electrolyte are less pronounced than in a more highly concentrated electrolyte.

5) Both the anode potential curves and the anode resistance curves for specimens differing only in size, with other conditions the same, are somewhat different (Figures 3 and 4); accordingly, there are some differences in the optimum conditions (potential, current density) for polishing, due to differences in electrolyte convection and diffusion of the anode products.

6) The formation of a film with the optimum resistance of 0.3-0.5 Ω/dm^2 is displaced in the direction of lower current densities and lower anode potentials with increase of electrolyte temperature. Extrapolation of this relationship to zero potential gives the temperature condition for chemical polishing, which, of course is possibly only on the condition that the given metal dissolves chemically in the given electrolyte at that temperature.

SUMMARY

1. Study of the behavior of Duralumin D-16-T during anodic treatment in a mixture of phosphoric, sulfuric, and chromic acids under different conditions showed that electropolishing occurs in the second ascent of the anode potential – current density curves, at a definite resistance of the anode film, equal to 0.3-0.5 $\Omega\ dm^2$.

2. A regular relationship exists between the optimum anode potential and the electrolyte temperature in electropolishing; temperature conditions for the chemical polishing of Duralumin have been established on this basis.

LITERATURE CITED

[1] G. Schmaltz, Surface Quality, Translated from German, edited by Prof. P. A. Boguslavsky.

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