INVESTIGATION OF THE MECHANISM OF ELECTROCHEMICAL POLISHING OF METALS

II. MICROSCOPIC OBSERVATION OF ANODE PROCESS DURING ELECTROLYTIC POLISHING OF ALUMINUM

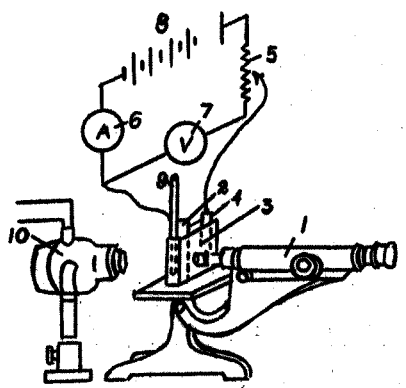
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As the result of a study of the processes occurring during anodic treatment of D-16T duraluminum over a broad interval of current densities in sulfur, phosphoric acid, chromic acid and water electrolytes in various concentrations, with and without stirring, and at various temperatures, we found, as reported in our first communication [1] that: (1) anode potential – current density curves, like those for the polishing of copper in phosphoric acid, showed two sharp rises and one flat and almost horizontal segment; (2) electrical polishing occurs only during the second rise and under conditions of formation of an anodic (viscous) film with resistance of 0.3-0.5 ohm/dm^2; (3) it does not occur along the flat segment of the curve even if the conditions of film formation and optimum resistance are met; (4) the optimum anodic potential for duraluminum polishing depends, all other conditions being equal, upon electrolyte temperature, and declines with decline therein. The conditions of temperature required for chemical polishing were determined on the basis of the relationship described above.

We have now subjected the process at the anode to microscopic study in order to determine why formation of the anode film with optimum resistance is accompanied by polishing along the second rise in the curve, and is not along the flat segment.

EXPERIMENTAL

The apparatus illustrated in the drawing was set up to permit these observations to be made.



Arrangement of the apparatus. 1) Microscope; 2) anode; 3) electrolyzer; 4) cathode; 5) rheostat; 6) amperemeter; 7) voltmeter; 8) source of constant current; 9) thermometer; 10) light source.

The microscope tube was set in horizontal position, and electrolysis was observed at a magnification of 56 diameters as it occurred at an anode in a glass electrolyzer, the electrolyte being 43% phosphoric acid, 43% sulfuric acid, 3% chromic acid and 11% water. The working surface of the anode – a duraluminum plate – was 1 cm^2. The rest of the plate was insulated with bakelite lacquer. The cathode was a lead plate, 10 cm^2 in area.

The following are the results of the observations, conducted in transmitted light at 60-80° C, with vertical anode position.

The metal dissolved and hydrogen was released without the electric power having to be turned on. After the current was on, and at current densities corresponding to the first steep rise in the curve of anode potential, liberation of hydrogen declined somewhat and ceased momentarily at the point of inflexion. At this moment, a cloudy liquid, differing in color from the main mass of electrolyte, formed over the entire surface of the anode. Very tiny bubbles of oxygen, few in number, appeared at the same time. Soon the thickness of liquid film became considerable, and it began to rise along the surface of the anode, along with the oxygen bubbles. As current density increased, the motion accelerated, the liberation of gas became stronger, the thickness of film decreased, and it became less cloudy and, finally, clear. The ascending movement of the film was accompanied by movement of the entire electrolyte: convection

currents appeared, moving up and down in circular fashion. These currents increased in force with the density of the electrical current and at d_a = 150 A/dm^2 they were so powerful that the thickness of the anodic film became insignificant, and the microscopic elevations on the surface were uncovered, or almost so.

Observations with the electrodes in horizontal position (the anode underneath) showed the film on the anode to develop at the same current densities as in the vertical position, but the later processes differed somewhat from those in vertical arrangement. After appearance of the film there was a period of calm upward diffusion thereof, oxygen bubbles also rising. When anodic current density reached approximately 15 A/dm^2, the boundary between the film and the electrolyte became sharply marked, liberated oxygen bubbles rising straight and fast until they struck this boundary, at which point they began to combine and increase in dimensions. Upon attainment of a given size they broke through the surface and rose upward. At the point of breakthrough there appeared an upward-pointing tongue of anode products, and the anode liquid flowed toward this point, carrying oxygen bubbles from adjacent points. Further rise in current density brought an intensification of this phenomenon, and the boundary between film and electrolyte took on the appearance of a raging sea. The result is a difference in the thickness of the anodic film at various points. This is apparently the explanation for the inability to obtain satisfactory polishing in horizontal anode position at considerable current densities. The electrolyte becomes clearer at the points of anode liquid breakthrough, which is evidence of the lack of color of the anode products. If the current be turned off, the liquid film gradually disappears and, after cessation of convection in the electrolyte, the remnants of the film descend a little, the electrolyte being clearer at these points. This leads to the conclusion that the specific gravity of the anodic products is somewhat greater than that of the electrolyte, while their rate of dissolution in the electrolyte is insignificant. The ascending motion of the anodic products during electrolysis is entirely a result of the Joule effect, large amounts of heat being liberated in this manner, the anodic film, because of its low conductance, being the site of this phenomenon.

The microscope studies showed that the anodic film, existing in the interval 0.3-0.5 ohm/dm^2, differs in thickness and nature as between the flat segment of the curve on the one hand, and the second rise, on the other. Along the flat segment the thickness of the film is considerable, and it is cloudy in appearance, while along the second rise it is fine and transparent. Consequently, the concentration of anodic products in the film is considerably lower along the flat segment of the curve than it is along the rise. This is why a high concentration of the products of anode solution in the portion of the electrolyte immediately adjacent to the anode is a condition of electrolytic polishing in our experiments. The low concentration thereof at medium current densities results in oxidation of the surface of the metal.

The foregoing experimental data is not capable of explanation in terms of the existing theories of electrical polishing.

If we accept the theory of Jacquet, electrical polishing should have occurred in our experiments along both the flat and rising segments of the curve, given identical thicknesses of anodic film or identical anodic resistance, as occurs when copper is polished in phosphoric acid. But the fact is that polishing takes place only along the second ascent, i.e., when the concentration of anodic products in the anodic zone is high, considerable current densities being required for this.

Jacquet's theory also falls in face of the fact that while a film may form at the anode when copper is processed in metaphosphoric acid, the surface of the metal is not polished when this occurs.

These factors compel us to seek other explanations for the mechanism of electrolytic metal polishing.

A Contribution to the Theory of the Electrical Decrystallization of Metals

Vozdvizhensky [2] has expressed belief in the need for development of a new brahch of theoretical electrochemistry, which he would name the science of the electrical decrystallization of metals. And he has himself presented fundamental theoretical postulates in this direction.

Vozdivizhensky and his associates have shown [3-8] that textured metal surfaces give the best results in electrolytic polishing. He has also shown that the quality of the oxide film obtained by electrochemical oxidation of a textured surface, is considerably higher than otherwise. Consequently, the preparation of a surface for electrolytic polishing and electrochemical oxidation must consist of providing it with texture [9].

This practical conclusion flowing from the theory of electrical decrystallization makes it possible to predict the outcome of the electrolytic polishing process and that of electrochemical oxidation in terms of the thoroughness with which the metal surface has acquired a texture.

The theory of electrical decrystallization holds that when a metal undergoes electrolytic polishing, the first portions of the surface to dissolve are those which are most active in terms of electrochemistry. They include areas formed by angles, ridges and incomplete or destroyed components of the crystal lattice of the metal. The difference between the static potentials of various crystal edges has been experimentally determined, and is of the order of a few millivolts [10], while the dynamic potentials of various crystal edges may, under conditions of electrolytic polishing, differ by 50 to 100 millivolts, and this apparently is the basic reason for the selective anodic solution of the metal surface. This shows the electrolyte and the procedure followed in electrolytic polishing to be of major importance, and thus poses a further group of questions in the theory of electrical decrystallization.

The polarization of the anode differs in various electrolytes. Consequently, the difference in the anodic potentials of the more and less active segments of the surface will also differ. Thus it is obvious that the electrolyte used and the procedure followed in electrolytic metal polishing must be such as to facilitate the appearance of the greatest possible difference between the anodic potentials of the more and less active portions of the surface of the metal being polished.

In order to make this rule concrete it is necessary to clarify the reason for the formation of the given difference in dynamic potentials during electrolytic polishing.

It is necessary in the first place to note that the electrolytes used in electrolytic polishing are, for the most part, concentrated and viscous. The result is that, as anodic dissolution proceeds, marked changes in concentration occur in that portion of the electrolyte adjacent to the anode, as a result of accumulation of products of anodic solution. Sometimes these variations in concentration are so obvious that low magnification makes it possible to see the boundary between the products of anodic solution and the electrolyte per se (specifically, when polishing is in phosphoric acid or mixtures in which it is present). This fact served Jacquet [11] as the basis for his familiar theory of the viscous film in electrical polishing. However, the fact is that these changes in concentration (the viscous film) play a different role than that ascribed to them by Jacquet.

The surface forming the boundary between two phases is known to possess free surface energy which tends to reduce. . It is capable of spontaneous reduction either by change in geometric form (where bodies of liquid are concerned) or by adsorption of ions, atoms or molecules from the surrounding medium (where liquid or solid bodies are involved). Adsorption is greater along those segments of surface which possess greater superficial energy, i.e., along the more active segments (where crystalline bodies are concerned, the portions of surface formed by angles, ridges, incomplete or destroyed components of the crystals). This results in a considerable equalization of surface energy over the entire surface, so that experiments fail to reveal any large difference in the static potentials of the various borders of metal crystals or in the surface potentials of metals with different degree of texturing.

If it were possible to prevent adsorption and to measure the potentials of pure metallic surface in solutions, considerable differences in the static potentials of the different edges of crystals would be revealed. However, this is something we are incapable of doing under static conditions, as the surface of the metal inevitably becomes covered with an adsorption layer, no matter what the medium used. However, that which is unattainable under static conditions, to all appearances, is possible under dynamic conditions, or, in other words, the process of anodic solution may be employed to create conditions in which adsorption is reduced. On the basis of these considerations it becomes possible to give greater concreteness to the rule stated above. The electrolyte and the procedure selected for electrolytic metal polishing must be such as to assure that polishing will be accompanied by maximum reduction in adsorption on the surface being polished.

In accordance with the Gibbs Equation:

$$G = -\frac{c}{RT}\frac{d\sigma}{dc},$$

it is possible to attain a reduction in the amount of substance adsorbed, G, by diminishing the concentration, c, of adsorbent substance, raising the temperature, T, and reducing the surface activity $\left(-\frac{d\sigma}{dc}\right)$ of the substance being adsorbed.

It has been shown in practice that, in the majority of cases, elevation of temperature leads to an increase in the polishing capacity of the electrolyte, i.e., it corresponds completely to the mechanism of electrolytic polishing postulated above. The question as to the effect of concentration and surface activity is much more complex. The question at issue is reduction in the concentration of substances with high surface activity in the space near

the anode during anodic solution, and the substitution for them of substances having lower surface activity relative to the given metal.

Adequate experimental data to prove the foregoing is unfortunately lacking as yet, but it is possible to draw certain conclusions from the practice of electrical polishing.

It is known that metal will not polish in solutions of highly soluble true salts (i.e., copper in copper sulfate), nor will it polish in dilute acid solutions, even of phosphoric acid. From this we may conclude that it is dissociated products that are surface-active relative to metals.

Anode potential attains 1.5-2.0 V when copper is polished in phosphoric acid, while the potential of aluminum polished in mixtures of sulfuric, phosphoric and chromic acids is 10-15 V. This high potential is necessary to overcome the resistance of products of anodic solution forming a liquid film around the anode, the thickness of which is $\sim 50\,\mu$ when copper is polished in phosphoric acid. If so negligible a layer of anodic products shows marked electrical resistance, there can be no doubt that these products are weakly dissociated. If we consider the fact that polishing takes place only when such a film of products of anodic solution is present around the anode, it becomes clear that one of the conditions of electrical polishing is the filling of the zone around the anode with weakly-dissociated products. And this leads to the same conclusion, to wit, that weakly-dissociated products show low surface activity in relation to metals.

The more concentrated a given electrical polishing electrolyte (i.e., orthophosphoric acid), the lower the current density at which polishing of a given metal will begin [12] (horizontal portion of polarization curve) and the more universal the electrolyte will be, i.e., the higher its capacity to polish various metals. This testifies to the fact that one of the conditions of electrolytic polishing is absence or a low concentration of water from the area around the anode. This permits the conclusion that water is also surface-active relative to metals, apparently due to the high polarity of the water molecules.

No single electrolyte is capable of polarizing all the metals. For example, copper and its alloys polish well in orthophosphoric acid, but iron and steel do not, i.e., different salts of the same acid show different surface activities relative to specific metals.

If a given metal does polish in a given electrolyte, the polishing properties increase with the operation of a given bath, a phenomenon explainable in terms of the steady accumulation of anodic solution products showing low surface activity. It is known that, the more dilute the electrolyte, i.e., the greater its surface activity, the longer it must be operated before good results can be obtained.

The universal electrolyte [13] consisting of 88% orthophosphoric acid and 12% chromium anhydride (water content of electrolyte lacking or negligible) requires no preliminary operation.

Allowance for adsorption makes it possible to explain the phenomena occurring in our experiments during anodic processing of duraluminum. As already stated above, electrical polishing takes place only along the second rise in the curve, when the anodic film becomes concentrated and dense. This results in the creation of conditions for the desorption of surface-active substances (anions, water molecules and other active particles) for the selective appearance of the excess energy of more active portions of the surface relative to the less active, and for selective solution of the former, i.e., for electrical polishing.

The polishing of copper in phosphoric acid is also possible along the flat segment of the curve of anode potentials only because this results in the formation of a dense film of anodic solution products, due to absence of gas liberation.

Allowance for adsorption makes possible, along with other factors, explanation of the oxidation of the sample at moderate current densities, and polishing at higher densities. The reason lies in the fact that rise in current density increases the oxidizing action of the electrolyte upon the anode, thanks to adsorption. However, parallel therewith, elevation of current densities brings an increase in the rate of solution of the anode, and this results in the formation of an ever denser film of anodic solution products, a reduction in electrolyte and water concentration in the zone immediately adjacent to the anode, and a reduced probability of adsorption.

In this conflict between two opposing forces, related to the rise in current density, the first force — the oxidizing action of the electrolyte — triumphs at moderate current densities, and the second — its polishing action — rules at higher densities.

The above conditions for the formation of a film on the anode with specific electrical resistance, at which the polishing of the surface of the anode occurs, are at the same time the conditions for reduction of adsorption, and this is clear evidence of the interdependence of the two phenomena – adsorption and polishing. This is testified to by the reduction as temperature increases, in optimum current density and anodic potential required for polishing, and by the fact that chemical polishing may be performed if temperature is high enough.

SUMMARY

1. Microscopic study of the dissolution of a duraluminum anode in a mixture of sulfuric, phosphoric and chromic acids, and water has shown that the condition required for electrolytic polishing is the formation in the zone adjacent to the anode of a dense, concentrated film of weakly-dissociated products of anodic solution.

2. A condition of electrolytic polishing is minimal adsorption by the polishing surface of surface-active materials.

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