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Abstract

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INVESTIGATION OF THE PROCESS OF POLISHING ALUMINUM BY THE METHOD OF RADIOACTIVE TRACERS

Despite the wide use and practical importance of metal polishing, the mechanism of this process has still not been sufficiently studied. The work of I. V. Grebenshchikov ([1]) established that chemical reactions play an essential role in the polishing process. The oxide layer present on the metal surface is gradually removed during polishing owing to chemical interaction with the polishing material, which contains, in particular, stearic acid. The latter, according to Grebenshchikov ([1]), is vigorously adsorbed by the oxidized surface of the metal and can be removed from polished specimens by the action of organic solvents. The cleaned metal surface is capable of again forming an oxide film, which interacts with the polishing components.

In work ([2]) it was assumed that, when steel is polished, iron tristearate is formed on its surface as a result of the reactions indicated. However, no confirming experimental evidence was obtained on this question.

In the present investigation the task was set, using the polishing of aluminum as an example, to clarify in greater detail the behavior of stearic acid, a preparation of which was labeled with C-14 in the carboxyl group. The work was carried out on sheet clad duralumin of grade D16-ATV, 1 mm thick. The specimens were polished with a paste based on chromium oxide and labeled stearic acid with a specific activity of the long-lived isotope C^{14} of 7 mCi/g, which corresponds to an activity
$a = 7 \cdot 10^{-3} \cdot 3.7 \cdot 10^{10} \cdot 60 = 1.55 \cdot 10^{10}$
disintegrations per minute.

Polishing was performed with flannel cloths until a bright mirror surface was obtained. The polished specimens were subjected to radiometric control on a "Volna" type apparatus with an MST-17 counter. After this, the polished specimens were extracted with benzine in a Soxhlet apparatus under severe conditions (75°, 5 hours), and the activity was determined again.

The activity of the six specimens studied before extraction with solvent fluctuated within fairly wide limits (350–440 imp/min), which is explained by the unequal amount of stearic acid remaining on the aluminum surface. As a result

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

of extraction with benzine, the activity of the surface decreases by approximately a factor of 2.5 and becomes completely identical for the different specimens studied (Fig. 1). It is important to note that extraction with an organic solvent does not remove all the stearic acid from the surface of the polished aluminum. In the process of polishing, part of the acid is irreversibly bound to its surface. It apparently represents chemisorbed acid that has entered into chemical interaction with aluminum and has formed salt-like surface compounds not washed off by solvents. These compounds may be, for example, aluminum monostearate, in which one valence of the aluminum atom is expended on chemical

* With the participation of R. V. Artamonova.

bond with the fatty-acid residue, and two others—to bonding with the substrate of aluminum oxide or of the metal itself. The formation of a surface distearate, in which bonding with the substrate is effected by one of the three valences of the aluminum atom, is less probable.

The decrease in the activity of the specimens after extraction should be attributed to a reduction in the total thickness of the organic film as a result of removal from the surface, under the action of the solvent, of adsorbed molecules of stearic acid and of the stearates formed, which are held on the surface by forces of physical adsorption. The degree of chemical modification of the surface of the polished aluminum specimens studied proved to be surprisingly constant (Fig. 1). This may be connected with the formation, during polishing, of a saturated monomolecular chemisorbed layer of stearic acid.

Fig. 1. Activity of aluminum specimens polished with a paste based on stearic acid containing C^{14} in the carboxyl group. 1—before extraction with benzine; 2—after extraction with benzine

Fig. 2. Change in the activity of polished aluminum specimens as a function of the duration of extraction and hydrolysis. 1—extraction with benzine; 2—hydrolysis at 100°

Investigation of the kinetics of extraction of the polished specimens showed (Fig. 2) that the main part of the soluble organic film is removed from the metal surface during the first hour. This process is completely completed in three hours of Soxhlet extraction. Further prolonged extraction no longer changes the surface activity. After 9-hour extraction with benzine, the polished specimens were subjected to additional successive extraction with carbon tetrachloride, absolute ethyl alcohol, benzene, and acetone. However, the listed solvents, according to

the activity measurements, are not capable of removing the stearic acid firmly fixed on the surface.

At the same time, the hydrolytic stability of the surface compounds formed on the metal was studied. For this purpose, the polished and extracted specimens were kept in boiling distilled water for various periods of time. Their radioactivity was then measured.

From the data obtained (Fig. 2) it is seen that a sharp decrease in activity on the polished aluminum surface is observed in the first 15 min of hydrolysis. Further residence of the specimens in boiling water has almost no effect on the surface activity. Some part of the chemisorbed stearic acid (about 28%) does not undergo hydrolysis even under conditions in which the specimens are boiled in water for nine hours.

On the basis of the experimental data obtained, the number of molecules of chemisorbed stearic acid, N_1, corresponding

per 1 cm^2 of the surface of polished aluminum. The calculation was made according to the formula

$$N_1 = \frac{b \cdot N}{a \cdot M}, \tag{1}$$

where a is the activity of 1 g of the labeled stearic acid used ($1.55 \cdot 10^{10}$ decays $\cdot$ min^{-1}), b is the number of β-radiation pulses recorded per 1 min from 1 cm^2 of the surface of polished aluminum, N is Avogadro' s number, and M is the molecular weight of stearic acid. The specific activity of the specimens after extraction was 42 pulses/min $\cdot$ cm^2, which, at a counting efficiency of 0.0165, gave the total activity value

$$b = 42 : 0.0165 = 2545 \text{ pulses/min} \cdot \text{cm}^2.$$

Substituting the corresponding numerical data into equation (1), we obtain

$$N_1 = \frac{2.545 \cdot 10^3 \cdot 6.03 \cdot 10^{23}}{1.55 \cdot 10^{10} \cdot 284.5} = 3.5 \cdot 10^{14}.$$

Thus, on 1 cm^2 of the surface of a polished and extracted aluminum specimen there are $3.5 \cdot 10^{14}$ grafted molecules of stearic acid. If, according to the data of ([3]), the area occupied by one molecule of stearic acid during adsorption is taken to be 21 $Å^2$, then the chemisorbed molecules will occupy a surface of $3.5 \cdot 10^{14} \cdot 21 = 0.74 \cdot 10^{16}$ $Å^2$, or 0.74 cm^2. Consequently, the degree of filling of the aluminum surface after extraction is approximately 3/4. Taking the calculated value of the area occupied by one aluminum atom to be, on average, $7 \cdot 1$ $Å^2$, we find that one molecule of chemisorbed stearic acid on the surface

corresponds approximately to four aluminum atoms. Apparently, the strongest bond of aluminum with the residues of stearic acid is not formed uniformly over the entire surface, but predominantly at certain points associated with lattice defects or dislocations in the metal.

An electron diffraction pattern of a polished aluminum specimen after its extraction with benzene reveals a significant amorphous film and the structure of metallic aluminum.* As a result of hydrolysis the picture changes. In the electron diffraction pattern, through the thin amorphous film, the structure of the gamma modification of aluminum hydroxide of composition $Al_2O_3 \cdot H_2O$ is clearly visible; in our experiments (Table 1) it is characterized by interplanar spacings close to those reported in the literature.

Table 1

Interplanar spacings of the hydroxide film on duralumin after its polishing, extraction, and hydrolysis

Intensity	3	5	2	2	1	3	1
d for the specimens studied, Å	2.38	1.88	1.67	1.44	–	1.31	1.14
d for the gamma modification $Al_2O_3 \cdot H_2O$ ([3]), Å	2.34	1.85	1.67	1.44	1.42	1.31	1.13

The results of the radiometric measurements are in agreement with data from studies of the wettability of the surface of polished specimens by water. After polishing, duralumin acquires stable hydrophobic properties, which are not eliminated by extraction of the specimens with benzene under the indicated severe conditions. The contact angle of wetting of polished aluminum by water proved to be 99°, whereas thoroughly cleaned initial specimens are well wetted by water (θ about 0°). After extraction with solvent, the wetting angle of polished aluminum changes insignificantly ($\theta = 87°$). A control unpolished duralumin specimen, after extraction under the same conditions and drying, continues to be wetted by water rather well ($\theta = 15°$).

* The electron-diffraction study was carried out by N. A. Shishakov.

Thus, the use of stearic acid labeled with carbon in the carboxyl group made it possible to establish that, in the polishing process, acyl radicals are grafted onto the surface of aluminum. The resulting surface compounds impart hydrophobic properties to the polished specimens even after their extraction with organic solvents. It may be considered beyond doubt that such organochemical modification of the aluminum surface promotes the polishing process itself, since the surface compounds formed protect the metal surface from oxidation. At the same time, these compounds are apparently an important factor determining the increased corrosion resistance and mechanical strength of polished specimens in comparison with unpolished ones.

The considerations developed here are consistent with data obtained in studies of the adsorption of stearic acid from solutions in organic solvents or from melts on copper, iron, and aluminum ([5–7]). In the cited works, the phenomenon of chemisorption of the acid on the indicated metals with the formation of salt-like bonds was established. The formation of such organic films was confirmed by the fact that they are not removed upon heating in vacuum or after exposing the specimens to organic solvents.

In the case of polishing considered by us, the indicated chemical interactions between stearic acid and the oxide film or the metal itself are greatly facilitated by the formation of a fresh aluminum surface during the polishing process under the dispersing action of the abrasive.

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