ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 10, pp. 1835−1839. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © V. Burokas, A. Martushene, G. Bikul'chyus, A. Ruchinskene, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 10, pp. 1683−1687.

INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Aluminum Alloy Etching in Phosphoric Acid Solutions

V. Burokas, A. Martushene, G. Bikul'chyus, and A. Ruchinskene

Institute of Chemistry, Vilnius, Lithuania

Received August 13, 2008

Abstract—The rate of dissolution of aluminum and qualitative properties (gloss and uniformity) of its surface were examined as influenced by the concentration of H_3PO_4 and fluorine-containing compounds and their nature, as well as by the temperature, pH, and various additions (acids, surfactants, inhibitors).

DOI: 10.1134/S1070427209100176

An essential aspect in extensively applied powder painting technologies is thorough pretreatment of the metal surface. The adhesion and the total corrosion resistance of the metal surface are increased by phosphating after degreasing. For improving the quality of phosphate coatings it is recommended to deoxidize the aluminum surface before phosphating.

Aluminum is typically etched in a hot sodium hydroxide solution which is followed by brightening in a dilute nitric acid solution [1]. In the case of silicon-containing aluminum alloys, fluoride ions are added to the brightener solution [2]. In this procedure the aluminum ions are accumulated in the alkali solution, thereby making the latter unsuitable for further use.

This study is concerned with aluminum etching, in which phosphoric acid is one of the basic components. Phosphoric acid solutions are used for steel etching, since specifically in this solution rust is removed more efficiently than in sulfuric or hydrochloric acid solutions [2]. Moreover, the iron phosphate crystals formed on the steel surface improve paint adhesion.

Under natural conditions, aluminum and its alloys are coated with a thin (thousandth fractions of micrometer-thick) layer of γ-AlOOH and bionite $Al_2O_3 \cdot H_2O$, which are stable in aqueous phosphate solutions at pH 4.5–8.5. Etching of nonferrous metals has a dual purpose of removing oxides from the surface and producing an active layer for improving the adhesion of coatings.

We carried out amorphous phosphating in weakly acid (pH 4.5–5.0) phosphate solutions. This requires thorough surface pretreatment in acid solutions (hydrochloric, sulfuric, phosphoric). Etching in phosphoric acid is studied inadequately.

When aluminum workpieces are dipped into the etchant bath (based on H_3PO_4), the oxide film is removed, and a part of Al passes into solution by the reaction

$$2Al + 6H_3PO_4 \rightarrow Al^{3+} + 6H_2PO_4^- + 3H_2\uparrow. \quad (1)$$

Rausch [3] studied steel etching in phosphoric acid and established an empirical relationship between the metal dissolution rate, on the one hand, and the reaction time, acid concentration, and temperature, on the other:

$$dr = \frac{\delta r}{\delta t} dt + \frac{\delta r}{\delta c} dc + \frac{\delta r}{\delta T} dT, \quad (2)$$

where r is the rate of metal dissolution in phosphoric acid; t, reaction time; c, acid concentration; and T, absolute temperature.

Another problem generated by aluminum etching consists in accumulation of aluminum ions in etching and phosphating solutions. This problem is eliminated by introducing fluoride ions which, in the presence of Na^+, convert aluminum ions into insoluble Na_3AlF_6 which is precipitated as the slurry by the reaction [4]

$$Al^{3+} + 3Na+ + 6H^- \rightarrow Na_3AlF_6\downarrow. \quad (3)$$

The uniformity of Al dissolution is increased by introducing additions (surfactants, complexes, inhibitors) [1].

There are published data on aluminum etching in phosphoric acid-based solutions with salt and inhibitor

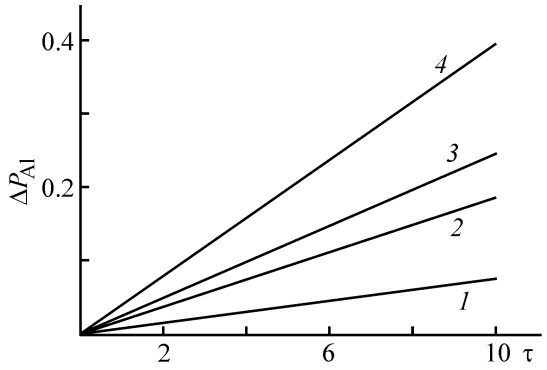

Fig. 1. Aluminum mass loss ΔP_{Al}, g m^{-2}, vs. time τ, min, in solutions with different H_3PO_4 concentrations at 20°C. $c_{H_3PO_4}$, M: (*1*) 0.085, (*2*) 0.425, (*3*) 0.85, and (*4*) 2.13.

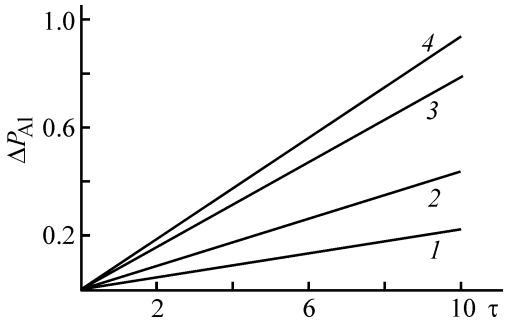

Fig. 2. Aluminum mass loss ΔP_{Al}, g m^{-2}, vs. time τ, min, Temperature, °C: (*1*) 20, (*2*) 30, (*3*) 40, and (*4*) 50.

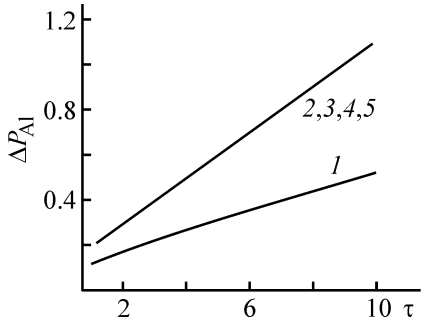

Fig. 3. Aluminum mass loss ΔP_{Al}, g m^{-2}, vs. time τ, min, in solutions with different compositions. Phosphoric acid concentration, M: (*1, 4*) 0.85, (*2*) 0.085, (*3*) 0.425, and (*4*) 2.13. Fluoride (H_2SiF_6) concentration, M: (*1*) 0 and (*2–5*) 0.05.

additions [5], in nitric and acetic acids in the presence of surfactants [6], and salts and surfactants [7], as well as with Fe^{3+} salt solutions in nitric acid in the presence of fluoride ions [8].

Here, we studied aluminum etching as influenced by various factors and elucidated the composition of the phosphate solution, suitable for obtaining a uniform surface.

EXPERIMENTAL

We used AD1N aluminum alloy (Al 99; Fe 0.6; Cu, Zn, Mg, Mn < 0.1 wt%) in the form of a plate with the total area of 60 cm^2. Degreasing was carried out with a solution containing 0.25 M sodium carbonate, 0.05 M trisodium phosphate, 0.02 M sodium silicate, and 2.5 g l^{-1} surfactants for 3–5 min at 50–90°C.

The samples were rinsed with water and etched in phosphoric acid solutions into which fluorides and sulfuric, nitric, or citric acid were added.

Deoxidation of Al was characterized by the degree of brightening as estimated with an FB-2 glossmeter (Russia). The glossmeter was calibrated against the standard (white) reference by fixing at the reference point of 30%.

The mass of the dissolved Al, ΔP_{Al}, was determined gravimetrically using a VLK-200 analytical balance (Russia) accurately to within 0.0005 g. The presented ΔP_{Al} values are the averages of 3–5 weighting data. The ΔP_{Al} values were used for calculating the corrosion current i_{cor}.

The i_{cor}–τ dependences were established by varying the nature of fluorides, concentration, temperature of solution, acidity, and process time. For tests we chose 0.85 M H_3PO_4 solution to which various fluoride species, SiF_6^{2-}, BF_4^-, and F^-, were added. Aluminum etching was examined at pH within 0.5–1.5 and temperature of 20–50°C. To increase the acidity we replaced a portion of phosphoric acid, specifically 0.1 mol l^{-1}, with sulfuric, nitric, or hydrochloric acid, respectively.

The aluminum surface morphology and roughness were examined with a VEECO-Thermomicroscopes atomic-force microscope.

The time dependence of the aluminum mass lost by etching in neat phosphoric acid solutions (0.085–2.125 M) is represented by a straight line (Fig. 1). Such dependence is described in the literature as the true, or instantaneous, corrosion at the given moment. At 0.8–2.0 M concentrations etching is not vigorous. The observed aluminum surface is uniform and bright. Further increase in the phosphoric acid concentration has little influence on the corrosion current and etching process.

Figure 2 shows how the etching proceeds at different temperatures. Within 20–50°C ΔP_{Al} linearly varies with τ in all the cases. Over the examined range, the etching rate increases 5 times.

Table 1. Corrosion current i_{cor} in relation to the nature of fluoride ions c_{H3PO4}=0.085 M; c_{F-}=0.05 M; T = 20°C; τ = 10 min

Fluorine-containing compounds	pH	i_{cor}, mA cm^{-2}
NH_4HF_2	2.0	15.9
HF	0.9	2.2
H_2SiF_6	1.0	1.6
HBF_4	1.1	1.2

Table 2. Corrosion current i_{cor} in relation to the H_3PO_4-based solution composition 4)

Composition of solution,[a] M	pH	i_{cor}, mA cm^{-2}
H_3P0_4 – 0.85, H_2SiF_6 – 0.05 [basic solution (1)]	1.05	1.62
(1)+H_2S0_4	0.80	2.52
(1)+$HN0_3$	0.75	3.35
(1)+HC1	0.60	2.80
(l)+ citric acid	0.92	2.52
(l)+ oxalic acid	1.10	3.33

[a] In all the solutions, 0.1 mol l^{-1} H_3PO_4 is replaced by 0.1 mol l^{-1} of the appropriate acid.

One of the major factors governing the Al etching is the presence of fluoride ions in solution. Figure 3 characterizes the specific influence of fluoride ions on Al etching in phosphoric acid solutions. It is seen that, upon introduction into solution of 0.05 M F$^-$, the etching rate is independent of the H_3PO_4 concentration. Thus, equation (2) is supplemented with the $\delta r/\delta c^- dc^-$ term, where c^- is the fluoride concentration.

To elucidate the role played by fluoride ions, we applied both simple (HF, NH_4HF_2), and complex (H_2SiF_6, HBF_4) compounds (Fig. 4). We found that, at identical etching times and the fluoride concentration of 0.05, i_{cor} varies depending on the nature of F$^-$ as NH_4HF_2 > HF > H_2SiF_6 > HBF_4 (Table 1).

Introduction of NH_4HF_2 into the etching solution causes the mass of the dissolved metal to increase tens of times. This is evidently associated with electrochemical reactions involving NH_4^+ and formation of complexes accelerating the depletion of the near-electrode layer in

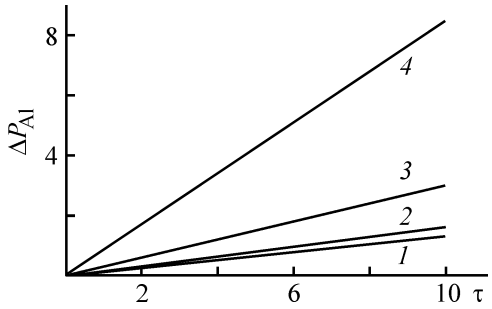

Fig. 4. Aluminum mass loss ΔP_{Al}, g m^{-2}, vs. time τ, min, in the presence of different F$^-$ species. c_{H3PO4} = 0.85 M; c_{F^-} = 0.05 M; T = 20°C (*1*) HBF_4 (*2*) H_2SiF_6, (*3*) HF, and (*4*) NH_4F–HF.

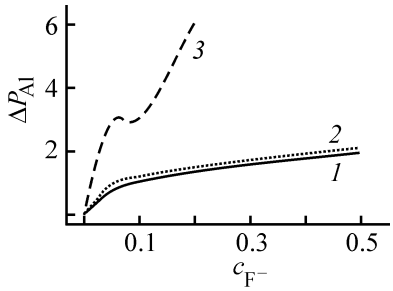

Fig. 5. Aluminum mass loss ΔP_{Al}, g m^{-2}, vs. c_{F-}, M, in the presence of different F$^-$ species. c_{H3PO4}=0.85 M; T=20°C; τ = 10 min. (*1*) HBF_4 (*2*) H_2SiF_6, and (*3*) HF.

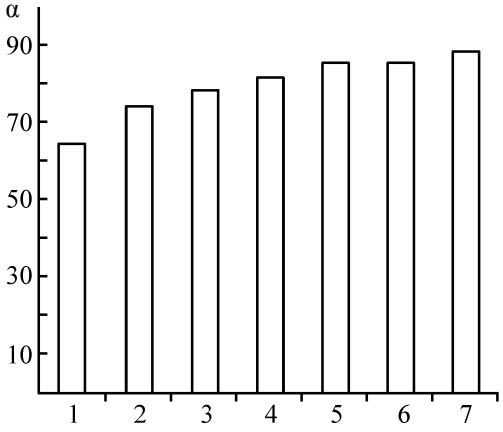

Fig. 6. Degree of aluminum brightening α, %, in relation to the etching solution composition. (1) Alkaline pretreatment; solution: (2) 0.85 M H_3PO_4; (3) 0.85 M H_3PO_4 + 0.05 M HF; (4) 0.85 M H_3PO_4 + 0.05 M H_2SiF_6; (5) 0.85 M H_3PO_4 + 0.05 M H_2SiF_6 + surfactant; (6) 0.85 M H_3PO_4 + 0.05 M H_2SiF_6 + surfactant + oxalic acid; and (*7*) 0.85 M H_3PO_4 + 0.05 M H_2SiF_6 + surfactant + oxalic acid + inhibitor.

Al^{3+} ions. However, experiments showed that application of NH_4HF_2 constitutes unacceptable practice because of stains observed on the Al surface.

To choose the adequate fluoride concentration, we examined the time dependence of ΔP_{Al} at fluoride

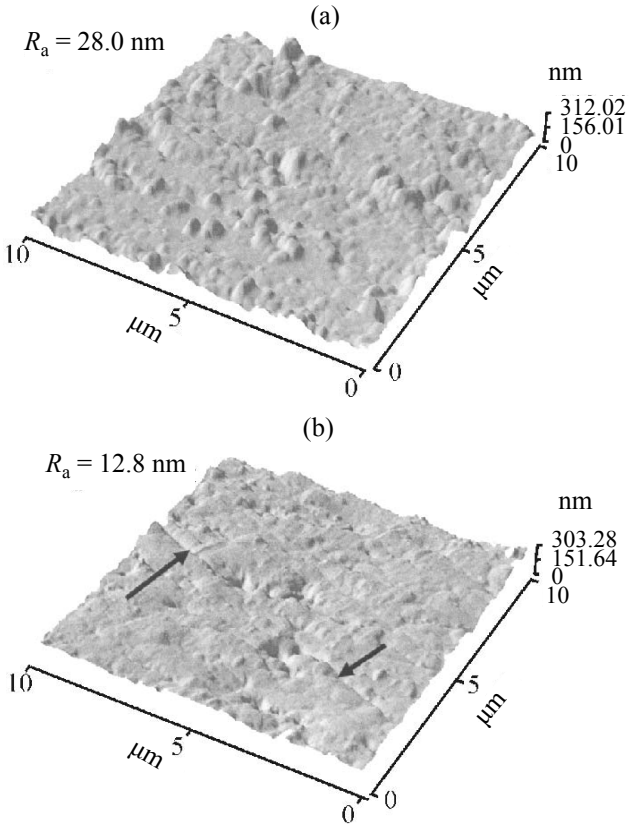

Fig. 7. Electron images of the aluminum surface: (a) no etching and (b) etching in 0.85 M H_3PO_4 + 0.05 M H_2SiF_6 + surfactant + oxalic acid + inhibitor solution. Rolling defects are shown with arrows.

concentrations within 0.01–0.5 M. The 0.01–0.05 M range was characterized by rapid acceleration of the metal dissolution; with c_{F^-} increasing further to 0.5 M the curve changed to exponential run (Fig. 5). Our data suggest that 0.05 M fluoride is sufficient for the working solutions.

For accelerating the metal dissolution for practical reasons phosphoric acid was partly replaced by a stronger acid. We found (Table 2) that, except for the case of the carboxylic acids, the metal dissolution is accelerated with increasing acidity of solution. At the same time, with oxalic acid introduced, pH of solution is 1.1, and the amount of dissolved metal is equal to that in the case of a stronger acid, HNO_3, with pH 0.75 (Table 2). This is evidently associated with formation of complexes. In all the examined solutions, metals preserved their fine-crystalline, light, semibright surface upon replacement of a portion of phosphoric acid with a different acid.

In an effort to achieve more uniform metal etching, we tested both nonionic and anionic surfactants.

We found that, with 0.1–0.2 g l^{-1} surfactant, a more uniform etching and a better surface brightening were achieved in both cases (Fig. 6).

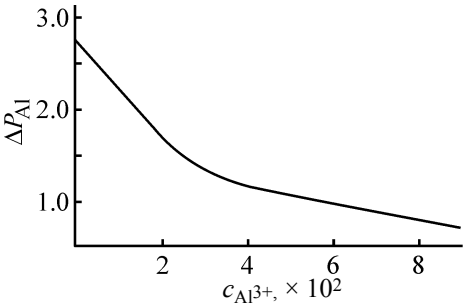

Fig. 8. Aluminum mass loss ΔP_{Al}, g m^{-2}, vs. $c_{Al^{3+}}$, M, in the basic solution. $c_{H_3PO_4}$ = 0.085 M; T = 20°C; τ = 10 min

Importantly, surfactants cause a parallel increase in detergency of solution.

These data support the conclusion made by Käsche [9] that surfactants favor surface blocking and etching proceeds over bumps and irregularities on the metal sample. Also, surfactants cause the surface tension to decrease and favor wetting of the metal surface. This is validated by morphological examinations (Fig. 7). The surface roughness parameter R_a (as calculated using three measured values) for the etched sample was estimated at 12.8 against 28.0 nm for the initial sample.

In the case of large-sized equipment, etching takes up to several hours or days, which necessitates introducing corrosion inhibitors into solution. Also, inhibitors are needed in the case of etching workpieces with strictly specified micrometer characteristics. This favors protection of the metal freed from oxides against further etching without interfering with the action of acid on oxide layers that remain to be removed. Although our focus was on deceleration of etching rather than on protective power, we can with a good reason apply the well-known equation [9]

$$Z = \frac{m - m_1}{m} \times 100\% \quad , \qquad (4)$$

where m and m_1 are the masses of the metal dissolved without and with inhibitor, respectively.

The most extensively applied inhibitor is thiocarbamide (Z = 80%) [10]. When choosing more efficient inhibitors to be applied in phosphoric acid, preference should be given to a pyridinecarboxylic acid derivative (Z=92%).

Another problem is posed by a decrease in the Al^{3+}

concentration in solution during etching of the aluminum surface. Figure 8 shows how ΔP_{Al} varies with c_{Al3+}. It is seen that, with increasing Al^{3+} concentration in solution, the aluminum surface etching is decelerated. The amount of Al^{3+} accumulated near the surface exceeds its concentration in the bulk of the bath, which complicates diffusion of acids and auxiliary chemicals into the working zone. This causes deterioration of the etching uniformity (surface planarization), thereby affecting the degree of brightening of the aluminum surface. The quality indicator will correspond to cases 2 and 3 in Figs. 6.

CONCLUSIONS

(1) In solutions with different H_3PO_4 concentrations (without F^-) the time dependence of the mass of the dissolved metal ΔP_{Al} is represented by a straight line; ΔP_{Al} increases proportionally to the increase in the H_3PO_4 concentration.

(2) Upon introduction into solution of fluoride ions (0.05 M) the mass of the dissolved metal is independent of the H_3PO_4 concentrations within 0.085–0.213 M.

(3) Depending on the nature of the fluoride ions introduced, the corrosion current i_{cor} varies as $NH_4HF_2 > HF > H_2SiF_6 > HBF_4$.

(4) The surface smoothness decreases insignificantly with increasing Al^{3+} concentration in solution.

(5) With temperature increasing from 20 to 50°C the metal dissolution rate increases by a factor of ca. 1.3 per 10°C.

(6) Introduction into solution of surfactants (nonionic or anionic) favors uniform etching of the aluminum surface.

(7) A suitable etching inhibitor was found in a pyridiniumcarboxylic acid derivative characterized by the protective power of 92%.

ACKNOWLEDGMENTS

The authors are grateful to V. Pakshtas for recording images and determination of the surface roughness of the aluminum samples on an atomic-force microscope.

REFERENCES

1. Wernic, S. and Pinner, R., *Surface Treatment and Finishing of Aluminum and its Alloys*, Teddington: Middlesex, 1996.
2. Freeman, D.B., *Phosphating and Metal Pre-Treatment*, New York: Industrial Press, 1986.
3. Rausch, W., *Die Phosphatierung von Metallen*, Sulgau (Germany): Eugen G. Leuze, 1988.
4. Giles, T.R., *Metal Finishing*, 2001, v. 99, p. 10.
5. Japan Patent 58 120 781.
6. US Patent 4970014.
7. Branch, L.C., *Metal Finishing*, 1998, vol. 96, pp. 24–29.
8. Chambers, B., *Metal Finishing*, 2000, vol. 98, pp. 26–29.
9. Кдsche, H., *Die Korrosion der Metalle*, Berlin: Springer, 1979.
10. Yukhnevich, R., *Tekhnika bor'by s korroziei* (Corrosion Prevention Techniques), Leningrad: Khimiya, 1989,