High Temperature Hard Anodizing with Tartaric Acid-Oxalic Acid-Triethanolamine Bath

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Tartaric acid does not produce uniform films on A6063 alloy (Al–Mg–Si). Uniform films are formed when oxalic acid is added to the tartaric acid bath, but hardness above Hv 400 cannot be obtained at a voltage below 100 V. When 1 mol dm^{-3} tartaric acid–0.4—0.6 mol dm^{-3} oxalic acid baths were adjusted with triethanolamine (0.26—0.54 mol dm^{-3}) to pH 1.00 and 1.25, crack-free films with hardness above Hv 430 were formed at 40 °C in the range 65—85 V. The hardness of the film is independent of the anion content of the film, increasing with increase in the thickness of cell wall and lowering in porosity.

In general, hard anodizing of aluminum has been carried out in sulfuric acid at low temperatures below 10 °C.[1] It is considered that compact films can be obtained at low temperatures because of high formation voltages and that thick films can be obtained because of the low rate of dissolution of porous layers during the course of anodization. However, this process requires special facilities for refrigeration, and the films are cracked. A process operating at moderate temperatures is desirable.

For this purpose, (a) dilute sulfuric acid or (b) organic acid whose solvent action on the oxide film is weak above ordinary temperatures, are suitable as electrolyte, because hard films which possess large cells and a small number of pores can be formed on account of high voltage. (a) is liable to produce pitting,[2] and (b) to produce uniform films.[3,4] However, study on hard anodizing above ordinary temperatures has seldom been reported. Although malonic acid yields hard films at temperatures 40—60 °C,[5] it is liable to decompose into CH_3COOH and CO_2 at high temperatures.[6]

Recently, it was found[7,8] that crack-free films with hardness above Hv 500 are formed in tartaric or malic acid baths at temperatures above 60 °C. However, the acids have the disadvantages that the bath voltage is too high (above 150 V for high purity aluminum) and uniform films cannot be formed on alloys such as A6063 (Al–Mg–Si). Additives for overcoming the difficulty were investigated.[9] By addition of 0.2 mol dm^{-3} oxalic acid to 1 mol dm^{-3} tartaric or malic acid, films with hardness Hv 300—420 were obtained on A6063 alloy at 40—50 °C.[10] However, the bath voltage was still high (105—140 V at 5.65 A dm^{-2}).

The bath voltage can be lowered by further addition of oxalic acid, but the dissolution of the cell wall during anodization is accelerated, leading to a decrease in the hardness of the film. Simultaneous attainment of the increase in hardness and decrease in bath voltage is impossible.

With the aim of producing film with hardness above Hv 400 at voltages below 100 V, tartaric–oxalic acid electrolyte was improved. The dependence of the hardness on the anion content and porous structure of the film was also investigated.

Effect of pH and Oxalic Acid Concentration

The rise in the pH of electrolyte is necessary to reduce the rate of chemical dissolution of the porous layer during the course of anodization above room temperature. However, the rise in bath voltage, which follows the rise in pH and induces burning, should be suppressed as much as possible. There are two means for raising the pH, dilution of acid and addition of a base without dilution. In a dilute oxalic acid bath of high pH, the bath voltage is so high that burning is liable to occur, whereas in a bath with high oxalic acid concentration, adjusted to the same pH, the voltage is lower than in the dilute acid bath.[11,12] The lower the pH and the higher the oxalic acid concentration, the more the oxalate is involved in the film. The chemical dissolution rate of the film is independent of the oxalate concentration of the bath, and the film becomes soluble when the oxalate content of the film is higher and the pH of the bath lower. It seems that the barrier layer formed in a bath with concentrated oxalic acid, adjusted to a high pH, contains more oxalate than that formed in a dilute acid bath of the same pH so that the electrochemical dissolution of the layer is accelerated, lowering the bath voltage at a constant current density. This might occur also in the case of oxalic acid mixed with tartaric or malic acid. In a tartaric or malic acid bath with high oxalic acid concentration, adjusted to a high pH, the bath voltage would be lower than that in a bath with low oxalic acid concentration. Even if the bath voltage is decreased, the rate of dissolution of the cell wall is relatively low because of a high pH so that the hardness of the film would not decrease remarkably.

Experimental

Plates of extruded aluminium alloy A6063-T5,[13] 3 mm thick and 40 mm wide, were cut into 100 mm lengths (surface area =88.4 cm^2). Each of them was racked to a holder made of pre-anodized tantalum wire, 1 mm diam., and treated with an aqueous solution of 1.25 mol dm^{-3} NaOH at 80 °C for 30 s. They were then successively rinsed, neutralized with 15% HNO_3, rinsed and anodized. A 5 dm^3 beaker was used as an electrolytic cell, cathodes being made of two plates of carbon (250×50×10 mm).

Tartaric acid which can produce film at lower voltage than malic acid was used as the primary ingredient of the electrolyte

Table 1. Composition and pH of electrolytes

Tartaric acid mol dm^{-3}	Oxalic acid mol dm^{-3}	Triethanolamine mol dm^{-3}	pH (at 25 °C)
1	0.2	0	0.80
1	0.2	0.13	1.00
1	0.2	0.22	1.25
1	0.4	0	0.67
1	0.4	0.26	1.00
1	0.4	0.34	1.25
1	0.6	0	0.60
1	0.6	0.43	1.00
1	0.6	0.54	1.25
1	0	0	1.28

and was mixed with oxalic acid or oxalic acid and triethanolamine[14] (Table 1). The bath temperature was kept at 30, 40, and 50±1 °C. While the solution was stirred with a propeller at about 330 min^{-1}, galvanostatic anodization using a three-phase full-wave rectifier was carried out at 2.26 A dm^{-2} for 50 min and at 5.65 A dm^{-2} for 20 min. Current was controlled to a specified value within 15 s after switching on. The hardness was measured on the surfaces of two anodized specimens at three points each, using a micro Vickers hardness tester with a load of 100 g. The average of six readings was taken. The microstructure of the anodized surface was observed with an electron microscope using a one-step carbon replica at an accelerated voltage of 50 kV. The carbon content of the film was determined by analysis of CO_2 gas produced by combustion (1300 °C, carrier gas O_2) of the film.[12] The film was isolated by the cathodic reduction method.

Results

States of the Anodized Surface. When anodizing was carried out in a bath with 0.2 mol dm^{-3} oxalic acid, adjusted to pH 1.00 and 1.25, at 5.65 A dm^{-2}, burning occurred. Under all other conditions uniform films were formed. The thickness of each film was about 35 μm. Films were colored, no cracks being observed. The color of the films formed at 2.26 A dm^{-2} was grayish yellow and that of the films formed at 5.65 A dm^{-2} reddish dark yellow. The lightness of the color increased with increase in oxalic acid concentration and rise in temperature.

Bath Voltage. The time dependence of the bath voltage is shown in Fig. 1. The voltage dropped after

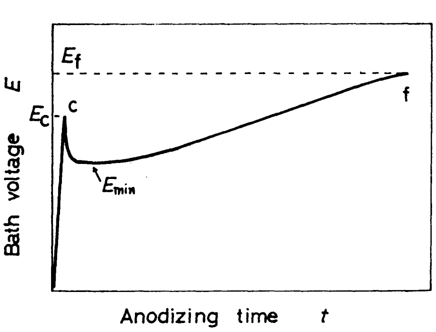

Fig. 1. Time dependence of bath voltage under galvanostatic anodizing.

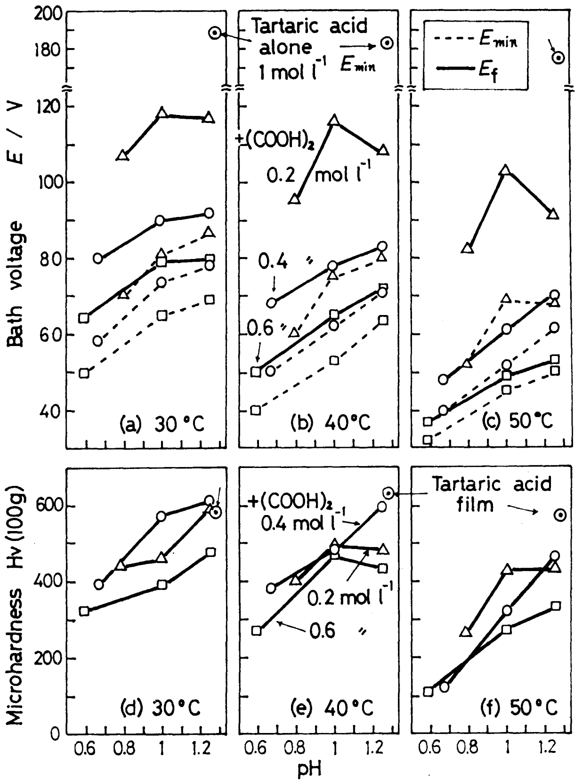

Fig. 2. Dependence of bath voltage and hardness of films on pH of electrolytes at various temperatures and oxalic acid concentrations(2.26 A dm^{-2}, 50 min, A6063 alloy).

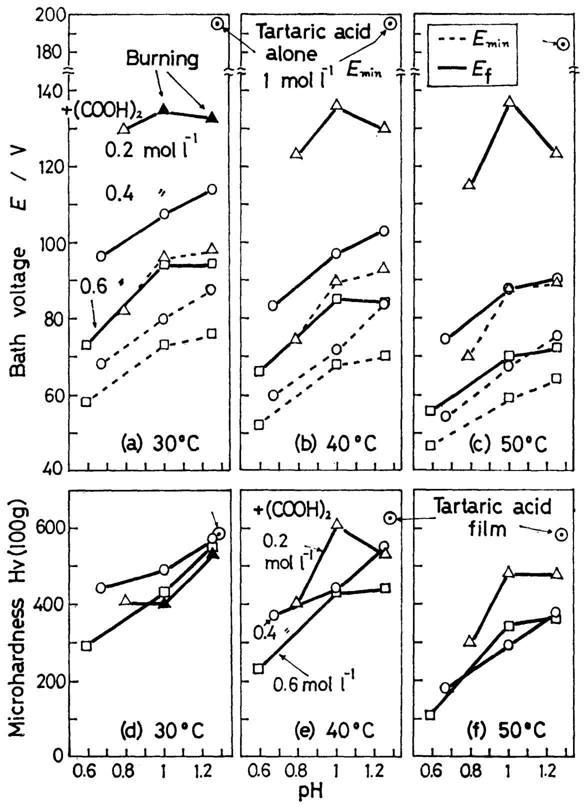

Fig. 3. Dependence of bath voltage and hardness of films on pH of electrolytes at various temperatures and oxalic acid concentrations(5.65 A dm^{-2}, 20 min, A6063 alloy).

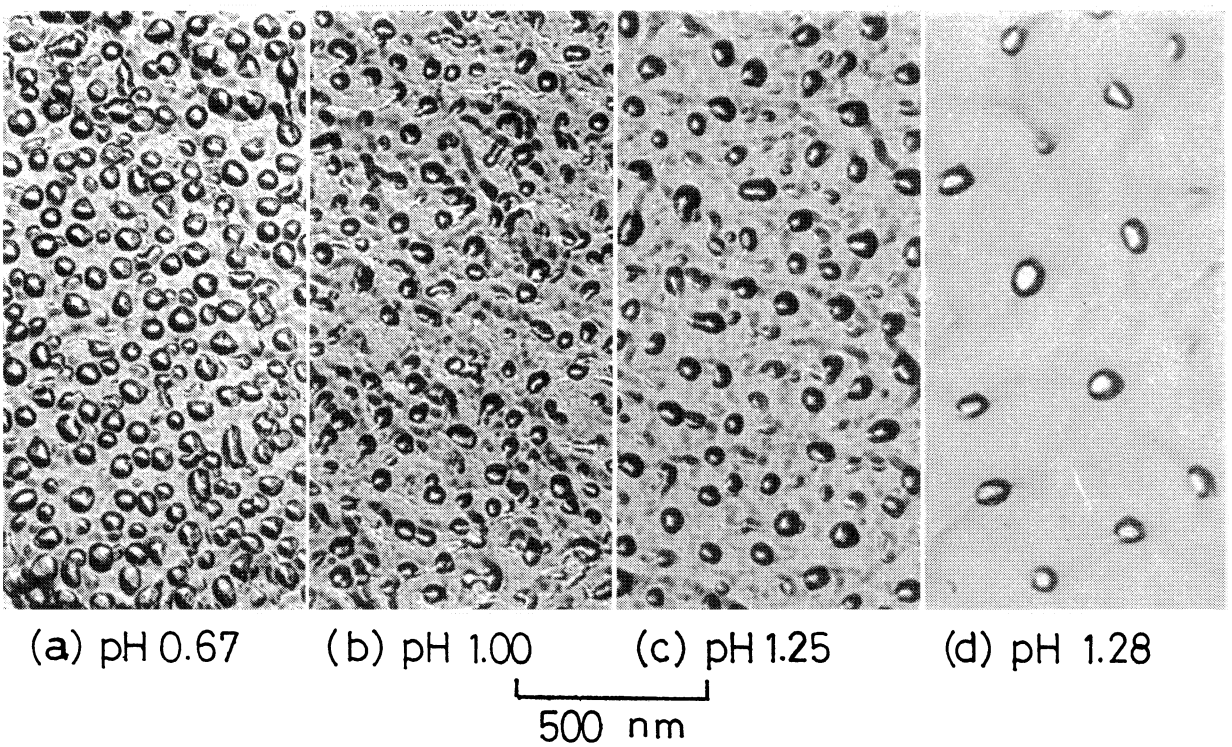

Fig. 4. Replica electron micrographs of film formed in (a) 1 mol dm^{-3} tartaric acid —0.4 mol dm^{-3} oxalic acid, (b) (a) +0.26 mol dm^{-3} triethanolamine, (c) (a) +0.34 mol dm^{-3} triethanolamine and (d) 1 mol dm^{-3} tartaric acid at 40 °C and 2.26 A dm^{-2} for 50 min.

the critical point "c" and then rose gradually. The slope of the voltage-time curve after point "c" decreased with increase in oxalic acid concentration, rise in temperature and lowering in current density.

The minimum bath voltage immediately after the critical point (E_{min}) increased with increase in pH and decreased with increase in oxalic acid concentration (broken line, Figs. 2a—c and 3a—c). The tendency was recognized also in the case of the final voltage (E_{f}, solid line). However, when oxalic acid concentration was 0.2 mol dm^{-3}, the E_{f} at pH 1.25 was lower than that at pH 1.00. The bath voltage decreased with rise in temperature and increased with increase in current density.

Hardness of the Film. As shown in Figs. 2d—f and 3d—f, the hardness increased with increase in pH and decreased with rise in temperature. At constant pH and temperature, the hardness decreased with

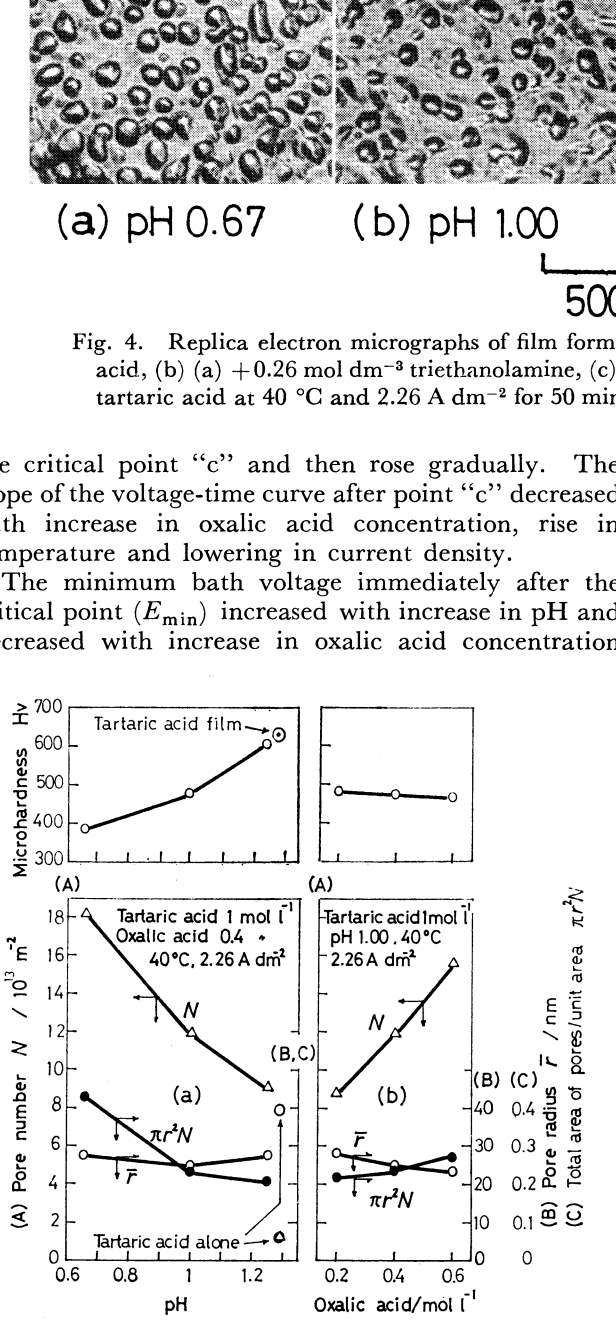

Fig. 5. Dependence of number, radius and total area of pores on pH and oxalic acid concentration of electrolytes.

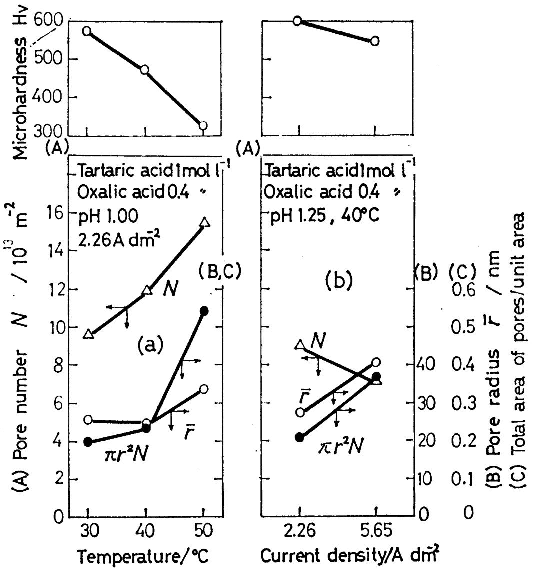

Fig. 6. Dependence of number, radius and total area of pores on temperature and current density.

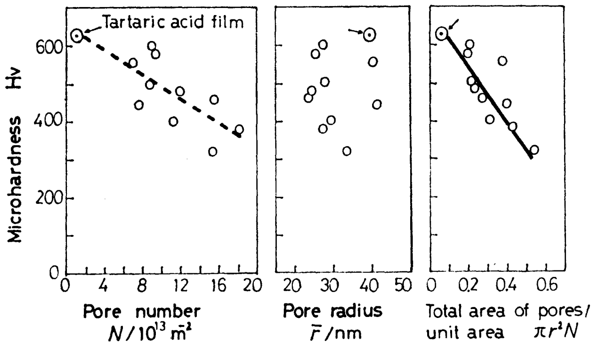

Fig. 7. Dependence of hardness of films on number, radius and total area of pores.

oxalic acid concentration. There was little change in the hardness with current density. By comparing the hardness with bath voltage, it was found that films with hardness above Hv 430 are formed in 1 mol dm^{-3} tartaric acid–0.4—0.6 mol dm^{-3} oxalic acid baths of pH 1.00 and 1.25 with voltage 65—85 V at 40 °C.

Carbon Content and Hardness of the Film. The carbon content of the film was determined in order to examine the effect of electrolyte anions on the hardness of the film. The hardness was independent of the carbon content of the film.

Microstructure and Hardness of the Film. Replica images of the film surface are given in Fig. 4. The number of pores in the films formed with mixed baths (a—c) is larger than that of pores in the film formed with tartaric acid alone (d). There is a difference in the number and radius of pores among the films shown in Figs. 4a—c. The number (surface density, m^{-2}) and radius (nm) of pores were measured on the photographs and the total area of pores was calculated. The parameters are plotted against the anodizing variables (Figs. 5 and 6) and the hardness of the film (Fig. 7). The hardness increased with decrease in the number and area of pores, but was not correlated with the radius of pores.

Discussion

When the pH of tartaric–oxalic acid electrolyte is raised by addition of triethanolamine, the electrochemical dissolution of the barrier layer is so suppressed that the bath voltage generally increases to maintain the current flow constant. The role of triethanolamine in this case is considered to be only the suppression of dissolution of the film by reducing the acidity of the tartaric–oxalic acid electrolyte as in the oxalic acid–triethanolamine bath.[12]

Porous layer contains a considerable amount of electrolyte anions,[15] the anion content of the phosphoric,[16] oxalic,[11] or sulfuric[17] acid film becoming maximum at a point between the wall/solution interface and the cell boundary. Electrolyte anions are considered to migrate through the barrier layer. Assuming that electrolyte anions are immobile, the porous layer arising from the barrier layer formed only by anion (O^{2-} and OH^-) migration[18] would contain no electrolyte anions. The radius of oxalate ions seems to be smaller than that of tartrate ions. Thus oxalate ions are more mobile in the barrier layer than tartrate ions. The solvent action of oxalic acid on the oxide film is stronger than that of tartaric acid. The bath voltage rises gradually with anodizing time (Fig. 1). As the porous layer grows, the supply of oxalic acid by diffusion from the bulk of the solution to the surface of the barrier layer is retarded[19] and the dissolution of the barrier layer is suppressed and the layer becomes thick gradually, leading to gradual rise in bath voltage. In baths with 0.2 mol dm^{-3} oxalic acid, the E_f at pH 1.25 is lower than that at pH 1.00. At pH 1.25, a local rise in temperature of the anode might occur[20] owing to uneven current distribution. However, apparently uniform films were formed.

According to the theory of ionic equilibria,[21] in the pH range 0—1.25, little tartaric acid dissociates, while 5—48% of the oxalic acid dissociates to $HC_2O_4^-$ ions. For instance, at pH 1.00, 99% of the tartaric acid remains undissociated, while 65% of the oxalic acid remains undissociated and 35% of the oxalic acid is present as $HC_2O_4^-$ ions. Even if this mixed acid has the same pH value, undissociated oxalic acid concentration increases with the addition of oxalic acid, causing the decrease in bath voltage.

No cracks were observed in the films obtained by high temperature process. From the fact[22] that cracks increase as the anode warms up to room temperature after withdrawal, the film formed by the low temperature process may easily be cracked under the influence of tensile stress caused by expansion of the anode. On the other hand, in the case of the high temperature process, when the anode is cooled to room temperature after withdrawal, the film undergoes compressive stress by contraction of the anode but it can withstand the stress.

The hardness of the film is controlled by the geometrical structure of the film, but not the carbon or anion content of the film. The hardness of the film is closely related to its porosity,[23] but the porosity varies with the number and radius of pores. Hardness seems to be related to the wall thickness. The relation between these parameters and the hardness was examined in detail.

Higher pH gave a harder film with a smaller number of pores and smaller area of pores, or lower porosity (Fig. 5a). The distance between the pores, or wall thickness, increases with increase in pH (Fig. 4). Lower oxalic acid concentration gave a harder film with a smaller number of pores and lower porosity (Fig. 5b), the cell wall becoming thick. Lower temperature also gave a harder film with a smaller number of pores and lower porosity (Fig. 6a). The cell wall became thick with fall in temperature, the parameters changing with current density (Fig. 6b). When the current density was high, the number of pores was small but the porosity was high and the hardness value small. In this case, the relation between the number of pores and the hardness was opposite to that obtained in the other cases. The bath voltage at 5.65 A dm^{-2} was higher than at 2.26 A dm^{-2} so that the cell wall near the pore base should be thicker. However, the thicknesses of the walls near

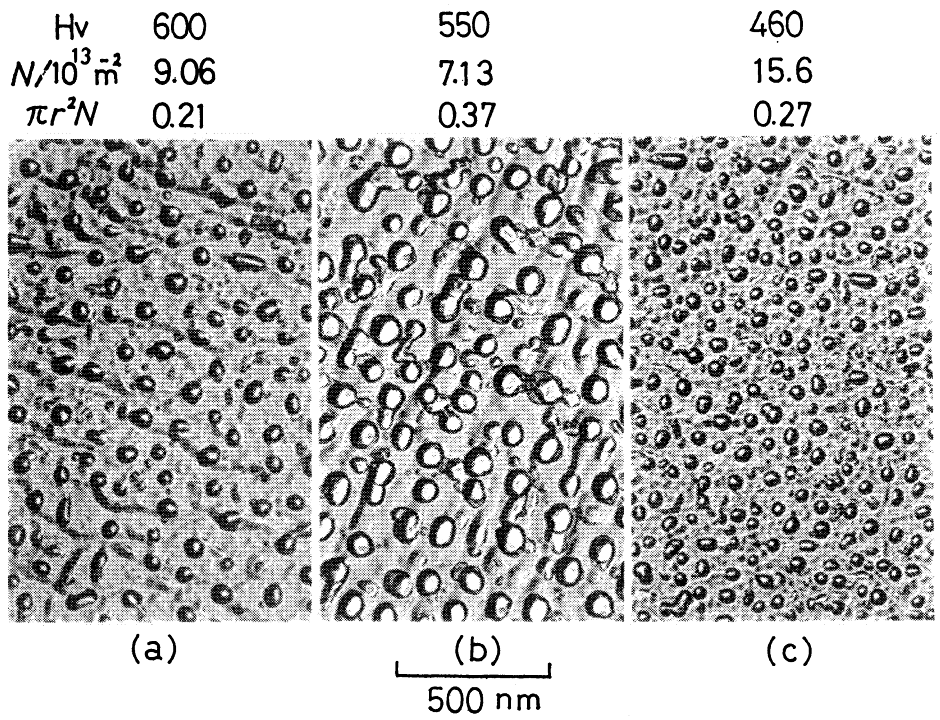

Fig. 8. Porous structure (replica image) and hardness of film.
(a) 1 mol dm^{-3} tartaric acid —0.4 mol dm^{-3} oxalic acid —0.34 mol dm^{-3} triethanolamine, pH 1.25, 40 °C, 2.26 A dm^{-2}, 50 min.
(b) The same bath as (a), 5.65 A dm^{-2}, 20 min.
(c) 1 mol dm^{-3} tartaric acid—0.6 mol dm^{-3} oxalic acid—0.43 mol dm^{-3} triethanolamine, pH 1.00, 40 °C, 2.26 A dm^{-2}, 50 min.

the surface were nearly the same as those of the walls of the film formed at 2.26 A dm^{-2} (Fig. 8b). When the current density is high, considerable heat is generated from the anode, making heat transmission insufficient and causing easy dissolution of the film. No definite relation exists between hardness and the radius of pores (Fig. 7).

When the bath voltage was raised, the cell wall as well as the barrier layer became thick and the number of pores decreased (Fig. 9), leading to a decrease in porosity and increase in hardness. Thus, in many cases, hardness was related to pore number, wall thickness and porosity. However, the number of pores is not closely related to hardness (Fig. 7). As shown in Fig. 8, film (a) is harder than film (b), while (a) has a larger number of pores than (b). This is due to the lower porosity of (a). Film (b) is harder than film (c), while (b) has a higher porosity than (c). This is due to the thicker wall of (b).

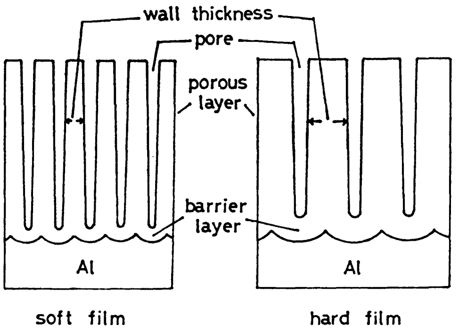

Fig. 9. Porous structure (cross section) and hardness of film.

The hardness of the film is controlled by wall thickness and porosity of the film, but not the anion content of the film; the thicker the wall and the lower the porosity, the harder the film.

Conclusions

High temperature hard anodizing of A6063 alloy was tested in 1 mol dm^{-3} tartaric acid–0.2—0.6 mol dm^{-3} oxalic acid–0—0.54 mol dm^{-3} triethanolamine baths at temperatures 30—50 °C and current densities 2.26 and 5.65 A dm^{-2}. The results are as follows:

1) In tartaric–oxalic acid baths, the films formed by addition of 0.2 mol dm^{-3} oxalic acid gave hardness above Hv 400, but the bath voltage was too high (above 100 V). When oxalic acid concentration was increased to 0.4—0.6 mol dm^{-3}, the hardness of film as well as the bath voltage decreased.

2) When 1 mol dm^{-3} tartaric acid–0.4—0.6 mol dm^{-3} oxalic acid baths were adjusted with triethanolamine (0.26—0.54 mol dm^{-3}) to pH 1.00 and 1.25, crack-free films with hardness above Hv 430 were formed at 40 °C with voltage 65—85 V.

3) The hardness of the film is independent of the anion content of the film, increasing with increase in the thickness of cell wall and decrease in porosity.

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13) JIS-H4100, alloy composition; Mg, 0.57; Fe, 0.19; Si, 0.23; Mn, 0.03; Cu, 0.008%. T 5; quenched from high temperature during extrusion and followed by tempering (*ca.* 205 °C, 1 h).

14) When NaOH was added to solutions containing 0.2 mol dm^{-3} or more oxalic acid, precipitate was observed.

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