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Behavior of Sulfate Ions during Formation of Anodic Oxide Film on Aluminium

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The incorporation of sulfate into anodic film formed on aluminium in an H_2SO_4–$MgSO_4$ solution was investigated by infrared spectroanalysis using the compensation method. The sulfate content of the film was very small at the initial stage of anodizing, but increased with time to a nearly constant value. This result is explained in terms of the variation of strength of electric field and the mobility of each anion in the barrier layer. The distribution of sulfate across the cell wall also was examined. The sulfate content was relatively small near the wall/solution interface, but increased with the distance across the wall from the surface, reached a maximum value on the intermediate layer between the wall/solution interface and the cell boundary, and decreased gradually. Such distribution is considered to be similar to that across the barrier layer. The SO_4 distribution and the transfer of anions from the barrier layer to the porous layer are explained.

When aluminium is anodized in an aqueous solution of an acid such as sulfuric or oxalic acid, porous-type films are formed. These films consist of hexagonal columnar cells, each of which contains a cylindrical pore. At the bottom of the pore there is a thin layer, called the "barrier layer."[1)] Probably only the barrier layer forms immediately after the start of electrolysis, but in a short time pores are developed by the solvent action of the electrolyte on the layer, and then close-packed cells are established. While the formation and dissolution of the barrier layer occur simultaneously, the porous layer grows toward the metal. Accordingly, the initially formed film is located near the outer surface. Such porous-type films contain more electrolyte anions than barrier-type films which are formed in neutral salt solutions.[2)] This fact suggests that the anions involved in the film affect the dissolution behavior of the film and determine the type of the film. Therefore, a study of the anodic behavior of electrolyte anions during the pore development is important to understand the pore-formation process and the properties of the films. From this point of view, the time dependence and distribution of the oxalate content of the film formed in oxalic acid were elucidated in a previous paper.[3)] The distribution of anions in the film formed with phosphoric acid also has been described.[4,5)]

Although the incorporation of sulfate into the initially formed film has been studied by Brace and Baker[6)] using ^{35}S as a radioactive tracer, the time dependence and distribution of sulfur content of the film are not obvious. Whether or not the behavior of anions at a constant current density is different from that of anions at a constant voltage also is not obvious.

The time dependence of sulfate content of the film during anodization in an H_2SO_4–$MgSO_4$ solution at a constant current density or a constant voltage was examined by infrared spectroanalysis using the compensation method. The anion distribution across the cell wall was examined by gravimetric analysis and the manner of transfer of anions from the barrier layer to the porous layer was speculated about.

Experimental

Foil specimens of 99.99% aluminium (annealed, 150 mm × 70 mm × 0.1 mm or 150 mm × 35 mm × 0.1 mm) were treated with a hot solution of mixture of phosphoric acid and chromic acid to remove natural oxide film, and then were anodized. For Auger electron spectroscopy and electron microscopic observation, electropolished aluminium sheets (25 mm × 10 mm × 0.5 mm) of the same purity were used. A 3 dm^3 beaker was used as an electrolytic cell, the cathodes being made of two plates of carbon (200 mm × 45 mm × 10 mm).

Anodizing was carried out in a mixed solution of 0.6 mol dm^{-3} H_2SO_4 and 0.4 mol dm^{-3} $MgSO_4$ at 30 °C for 3 s—30 min by applying a constant current density of 1 A dm^{-2} or a constant bath voltage of 18 V while the solution was stirred at a nearly constant rate. In every process, after the steady state was reached, the current density was 1 A dm^{-2} and the bath voltage was 18 V. Magnesium sulfate was added to sulfuric acid in order to retard the arrival at the critical point ('c' in Figs. 6 and 7) by suppression of the dissolution of the film.[7)] Since the Mg content of the film was extremely small and the sulfate content of the film was nearly the same as that of sulfuric acid film,[7)] the film-forming characteristics of this mixture are considered to be essentially the same as those of sulfuric acid alone.

After the anodized specimens were rinsed in running water for 10 min,[6)] the films were isolated by the mercury (II) chloride method. The films were rinsed, dried, and fully crushed. Thereafter, the SO_4 content of the films was determined by gravimetric analysis ($BaSO_4$) and by infrared spectroanalysis (KBr disk; sample = 3.5 mg, KBr = 800 mg). The chemical composition of the film near the surface and the film/metal interface were analyzed by a PHI Auger spectrometer during or after Ar^+ ion sputtering ($E_p = 3$ kV). The thin films isolated were observed directly with a transmission electron microscope at an accelerated voltage of 50 or 100 kV.

Results

Electron Microscopic Observation. At the constant current density, numerous pores of small radii were observed in the 3 s-film (Fig. 1). The radii of some pores increased with time and the number (surface density) of pores decreased (Fig. 2). The total area of pores decreased with time to a nearly constant value after 20 s.

At the constant bath voltage, the average radius of the pores and its variation with time were nearly the same as those obtained by the constant current process. Altough the number of pores in the 3 s and 10 s films was smaller than that obtained by the constant current process, the number decreased with time,

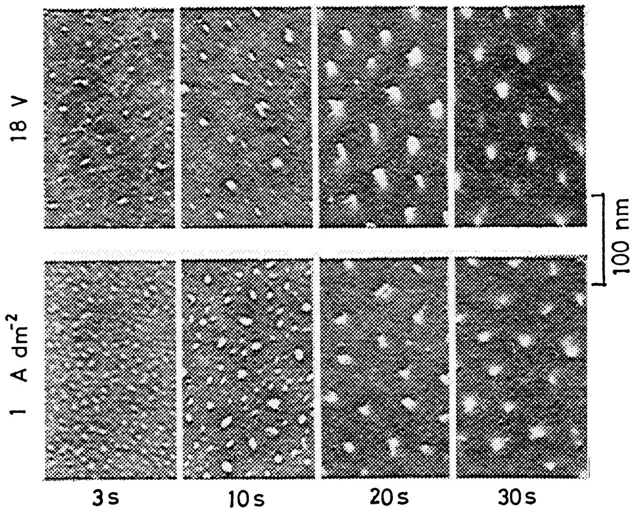

Fig. 1. Transmission electronmicro-photos showing the growth of pores at the initial stage of anodizing in 0.6 mol dm^{-3} H_2SO_4–0.4 mol dm^{-3} $MgSO_4$ at 30 °C (accelerated voltage=50 kV).

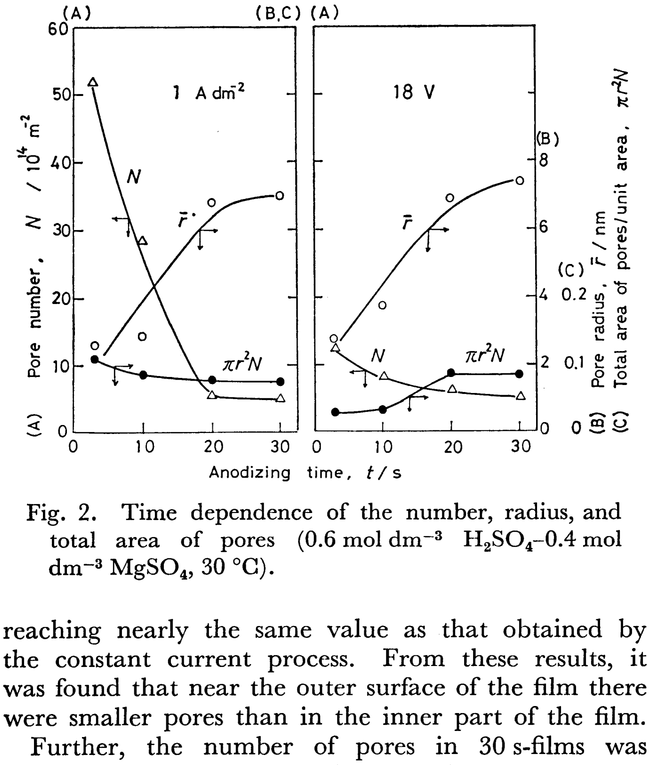

Fig. 2. Time dependence of the number, radius, and total area of pores (0.6 mol dm^{-3} H_2SO_4–0.4 mol dm^{-3} $MgSO_4$, 30 °C).

reaching nearly the same value as that obtained by the constant current process. From these results, it was found that near the outer surface of the film there were smaller pores than in the inner part of the film.

Further, the number of pores in 30 s-films was smaller than that reported[1,8] previously. This is probably due to the low ability of transmission of the electron beam at 50 kV. Therefore, the values of the dissolution rate shown in Fig. 10 were calculated by using the data (r=7 nm, N=9.2×10^{14} m^{-2}) obtained with 100 kV-observation on the films formed for 80 s.

Infrared Spectra of the Films. Curve 1 in Fig. 3 shows a spectrum of a film formed in sulfuric acid, obtained by using KBr as reference. The absorption band 1150 cm^{-1} is considered to be due to sulfate, because it also exists in the spectrum of $Al_2(SO_4)_3$ (broken line). Dorsey[9] also assigned such bands to sulfate. However, the determination of the SO_4 content of the film using this band was difficult, because not only was its band weak, but also a strong and wide absorption band due to Al-OAl (stretching) was present below 900 cm^{-1}.[10] Therefore, the appropriate amount (1—3.5 mg) of the film formed in chromic acid, which did not absorb infrared rays over the 1400—1000 cm^{-1} region (curve 2), was added to the KBr reference so as to make the base line of the spectrum nearly horizontal, as shown by the curve 3, compensating the absorption by Al-OAl. When the amount of the film formed in chromic acid was in excess, such spectra as the curve 4 were obtained. However, the slight deviation of the base line from the horizontal did not appreciably change the absorbance at 1150 cm^{-1}. By such a compensation method, the IR spectra of the films whose SO_4 content had been already determined by gravimetric analysis were obtained. The absorbance at 1150 cm^{-1} was then calibrated against the SO_4 content of the film (Fig. 4). By using this relation, the SO_4 content of the film could be determined with errors below 10%.

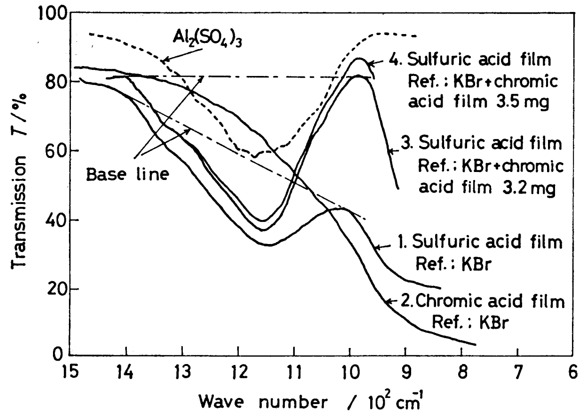

Fig. 3. Infrared spectra obtained by the compensation method.

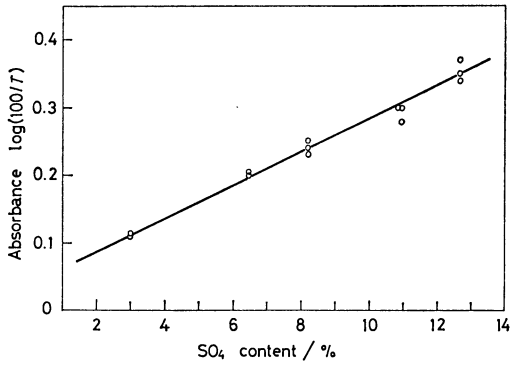

Fig. 4. Calibration of absorbance at 1150 cm^{-1} in IR spectra against the SO_4 content determined by gravimetric analysis ($BaSO_4$).

Time Dependence of the SO_4 Content. Figure 5 shows the IR spectra of the films formed at 1 A dm^{-2} for 5 s—30 min. Nearly the same spectra were obtained in the case of 18 V-anodizing. The time dependence of the SO_4 content obtained from these spectra is shown in Figs. 6 and 7. At the initial stage of every anodizing process, the SO_4 content was very small, but it increased with time to a nearly

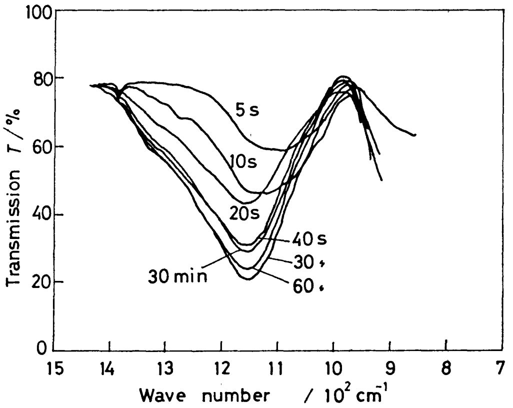

Fig. 5. Infrared spectra of films formed in 0.6 mol dm^{-3} H_2SO_4-0.4 mol dm^{-3} $MgSO_4$ at 30 °C and 1 A dm^{-2} for various times (Ref.; KBr+chromic acid film).

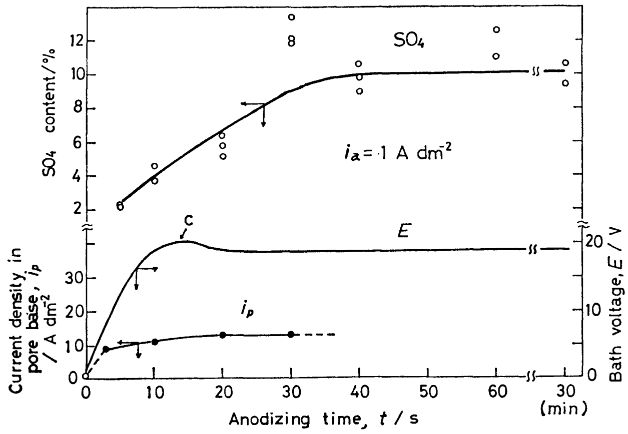

Fig. 6. Time dependence of the SO_4 content, current density in pore base, and bath voltage during constant current anodizing (0.6 mol dm^{-3} H_2SO_4-0.4 mol dm^{-3} $MgSO_4$, 30 °C).

constant value after 30 s at 1 A dm^{-2} and after 10 s at 18 V, respectively. These results were similar to those obtained with oxalic acid. However, in the case of 5 s and 10 s-films, the band due to sulfate shifted to a lower wave number. Perhaps the binding state of sulfate to the film is different. Therefore, strictly speaking, the relation between the absorbance at such a lower wave number and the SO_4 content may be different to some extent from that shown in Fig. 4. However, the results shown in Figs. 6 and 7 were consistent with the fact (Fig. 8) that the Auger peak to peak height of sulfur in the film near the outer surface, which was formed initially, was smaller than that of sulfur in the inner part of the film, which was formed later.

Anion Distribution across the Cell Wall. The distribution of electrolyte anions across the cell wall was examined in the same way as in the previous paper. Namely, after the specimen was anodized for 30 min, it was immersed in 1 mol dm^{-3} H_2SO_4, keeping the temperature at 30 °C. Then the time dependences of both the amount of the dissolved film and the SO_4 content of the remaining film were determined by weight measurement and gravimetric analysis, respectively (Fig. 9). From these results, the SO_4 content of the film dissolved for a certain period was calculated. Further, the rate of chemical dissolution of the film was calculated every 10 min with reference to the method by Nagayama and Tamura[11] and the thickness of the wall consumed was thereby determined. The SO_4 content and chemical dissolution rate of the film for a certain period were plotted against the mean distance from the surface of the wall (Fig. 10).

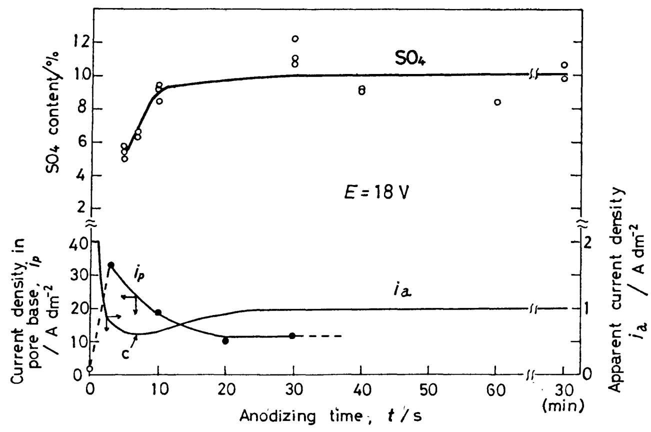

Fig. 7. Time dependence of the SO_4 content, current density in pore base, and apparent current density during constant voltage anodizing (0.6 mol dm^{-3} H_2SO_4-0.4 mol dm^{-3} $MgSO_4$, 30 °C).

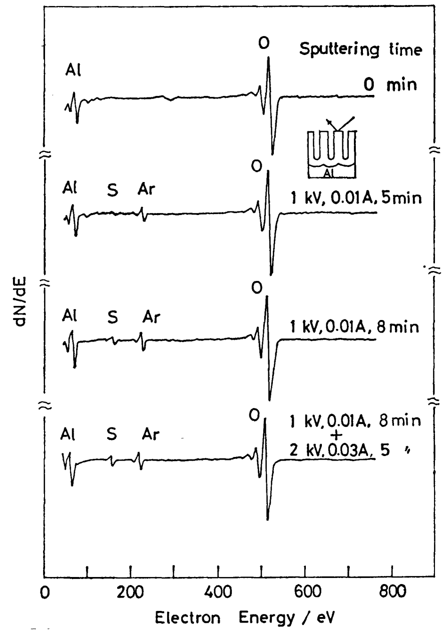

Fig. 8. Auger spectra obtained during Ar^+ ion sputtering from the surface of the film (0.6 mol dm^{-3} H_2SO_4-0.4 mol dm^{-3} $MgSO_4$, 30 °C, 1 A dm^{-2}, 30 s).

The SO_4 content was relatively small near the wall/solution interface, but increased with the distance across the wall from the surface, reached a maximum value on the intermediate layer between the wall/solution interface and the cell boundary, and decreased gradually. This result is similar to that obtained with phosphoric acid[4] or oxalic acid.[3]

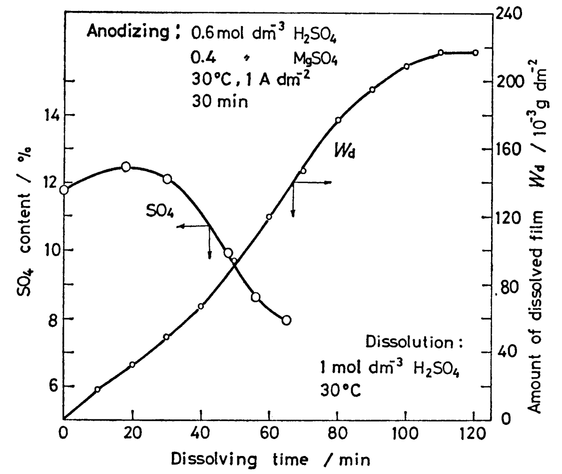

Fig. 9. Variation of the amount of the dissolved film and the SO_4 content of the remaining film with dissolving time.

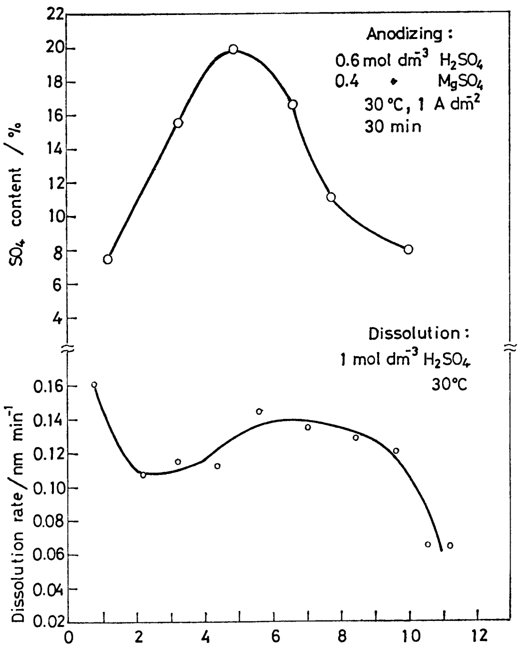

Fig. 10. Distribution of anions across the cell wall (upper) and the variation of dissolution rate of the film with the distance from the surface of the wall (lower).

As shown in Fig. 10 (lower), the chemical dissolution rate of the wall was highest near the surface, decreased with the distance from the surface, increased slightly, and decreased again near the boundary of the cells.

Little sulfur was detected near the barrier layer/metal interface (Fig. 11). The rate of sputtering of the film near the barrier layer/metal interface was lower than that of the bulk of the film.

Discussion

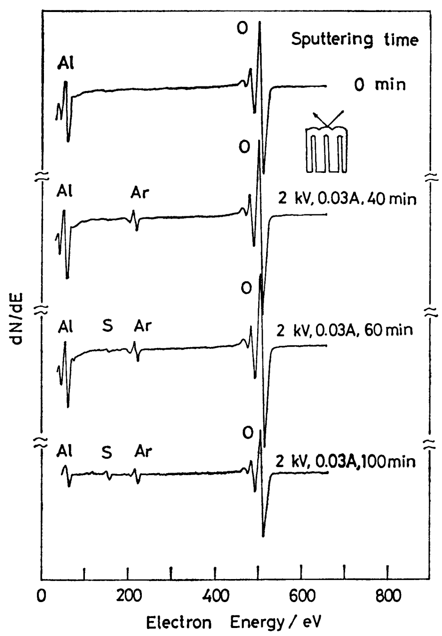

Fig. 11. Auger spectra obtained after Ar^+ ion sputtering from the barrier layer/metal interface (0.6 mol dm^{-3} H_2SO_4–0.4 mol dm^{-3} $MgSO_4$, 30 °C, 18 V, 30 min).

Mobility of Electrolyte Anions. It is impossible that the sulfate ions enter from the surface of the cell wall to which no electric field is applied. It is considered that the anions are pulled under the electric field from the surface of the barrier layer into the bulk of the layer, migrate through the layer, and remain in the porous layer by being released from the electric field.

Although the mechanism of movement of electrolyte anions is not known well, if the anions are mobile, the anion content of the film would increase with the strength of the electric field. This seems to be reasonable on the basis of the following two facts. (1) According to Hoar and Yahalom,[12] the electrical properties of the barrier layer formed in sulfuric acid and sulfate solutions are similar to those of the barrier layer formed in neutral borate solution, and the relation, $\log i$ (A m^{-2}) $\propto E/y$ (V m^{-1}), is not changed remarkably for different incorporated anions. In other words, as the current density becomes higher, the strength of the electric field increases. (2) According to Mason,[13] the SO_3 content of the film increases with the current density. Therefore, it can be said that the stronger electric field at the higher current density causes the increased SO_3 content of the film.

Time Dependence of the SO_4 Content. In this experiment, even if the apparent current density (i_a) is constant, the real current density varied with the pore development at the initial stage (Fig. 6). Namely, when the anodizing is started, pores should not be present, so the current density is 1 A dm^{-2}. However, as pores were developed with time (3—20 s), the current density in the pore base (i_p) increased to a nearly constant value after 20 s (Fig. 6). Therefore, the strength of electric field would be small immediately after the start of anodizing, so that the SO_4 content is very small. Probably, this is due to small mobilities of HSO_4^- and SO_4^{2-} compared with

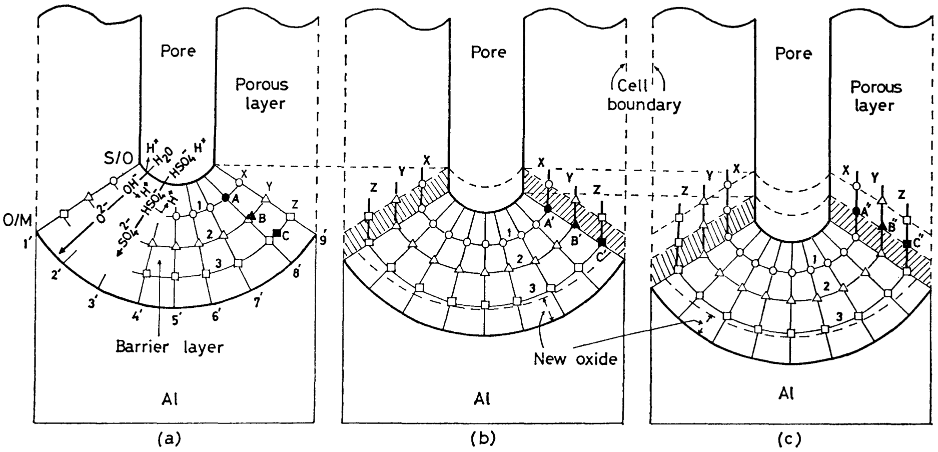

Fig. 12. Schematic representation of the transfer of anions from the barrier layer to the porous layer.

those of OH^- and O^{2-}. However, as pores are developed (3—20 s), the i_p increases and the strength of the electric field would increase, causing the increase of the SO_4 content. After 20 s, the i_p value is nearly constant. Therefore, it is considered that the film containing about 10% SO_4 (sulfate content of the 30 min-film) grows beneath the 20 s-film at a constant rate. The proportion of the initially formed film (outer layer) to the total film decreases with time so that the value of SO_4 content of the film, which was about 6% at 20 s, would approach with time to 10% as follows: $(6\% \times 20+10\% \times 10)/30=7.3\%$ at 30 s, $(6\% \times 20+10\% \times 40)/60=8.7\%$ at 60 s, and $(6\% \times 20+10\% \times 100)/120=9.3\%$ at 2 min. This is in fairly good agreement with the experimental result (Fig. 6).

In the case of constant voltage (Fig. 7), the i_a stayed at about 2 A dm^{-2} for the first 2 s, then abruptly decreased to a minimum value, and afterwards increased slightly to a constant value. For the first 2 s, the current density is low and the strength of electric field would be small, so that the SO_4 content of the film is small at the initial stage of anodizing. However, the i_p increases and the strength of the electric field would increase, so that the SO_4 content increases with time. In this case, the time to saturation of the SO_4 content was shorter than in the constant current process. This is due to the higher current density in the pore base at the initial stage of anodizing.

Anion Distribution across the Cell Wall. In steady state, the barrier layer, of constant thickness, moves toward the metal while it is renewed continuously. According to Siejka and Ortega,[14] the new oxide is formed at the oxide/metal (O/M) interface by the migration of oxygenated anions (O^{2-}, SO_4^{2-}), while at the solution/oxide (S/O, pore base), only the dissolution of the film occurs and there the oxide is not formed by the migration of cations.

Figure 12a shows the cross section of the barrier layer and its neighborhood in steady state. The curves 1, 2, and 3 show isopotential planes,[15] the lines of 1'—9' show the current flow (the direction of the electric field). The anion content is the same everywhere on a certain isopotential plane. Since the current density in the barrier layer decreases with the distance from the surface of the layer, the strength of the electric field is considered to decrease with the distance from the surface.

In the steady state, OH^- (by decomposition of H_2O) and HSO_4^- ions are supplied from the solution into the barrier layer. The former is dissociated into O^{2-} and the latter is dissociated into SO_4^{2-} by releasing H^+, and then they migrate into the barrier layer. However, SO_4^{2-}, which is larger than O^{2-}, becomes gradually immobile since the strength of electric field decreases with the distance from the surface. On the intermediate layer between the interfaces of O/M and S/O, the strength of electric field is probably so small that SO_4^{2-} ions are delayed and accumulated there. On the contrary, O^{2-} ions migrate farther inward, so that the film with a very small SO_4 content is formed near the O/M interface (Fig. 11).

When the electrolysis is continued, the interfaces of S/O and O/M move gradually, while the distance between these interfaces is kept constant and the shaded portions become porous, as shown in Figs. 12b and 12c. During this period, the direction and strength of electric field applied to the anions at the position of A turn to the cell boundary and increase, so that the anions migrate toward the cell boundary and the metal, resulting in the movement on the isopotential plane 1 to A' in Fig. 12b. Al^{3+} ions which take part in the formation of the film are replaced continuously by new cations transported from the metal. Most anions located at A may be transferred to A'; however, some anions may migrate inward further than the isopotential plane 1 and some anions may be supplied from the solution. The SO_4 content on the plane 1 is always kept constant. Thereafter, the anions at A' remain in the porous layer by being released from the electric field, as shown by A'' in Fig. 12c. In the same manner, most anions located at the positions B and C in Fig. 12a are transferred to B' and C' in Fig. 12b, and remain in the porous layer as B'' and C'' in Fig. 12c, respectively. Accordingly, the anions located nearer to the surface of the barrier layer and farther from the center (5' in Fig. 12a) of the layer are more rapidly transferred to the porous layer. The SO_4 contents on the planes X, Y, and Z in the porous layer are the same as those on the planes 1, 2, and 3 in the barrier layer, respectively. The composition of the wall surface is the same as that of the barrier layer surface.

The surface of the wall is soluble, since HSO_4^- ions would be incorporated into the oxide. The chemical dissolution rate of the wall decreases with the distance from the surface of the wall as the number of HSO_4^- ions became fewer, increases owing to the increase in the SO_4 content of the film, and decreases again near the cell boundary owing to the decrease in the SO_4 content.

Thus, the distribution of anions across the cell wall is considered to be similar to that established in the barrier layer.

Conclusions

The time dependence and distribution of SO_4 content of the anodic oxide film formed on aluminium in an H_2SO_4–$MgSO_4$ solution were the same as those of the film formed in oxalic acid and in phosphoric acid. From these results, it is speculated that the behavior of sulfate ions during anodizing was as follows.

(1) Immediately after the start of anodizing, a film containing a number of micropores and a small quantity of SO_4 was formed, and then the number of pores decreased. During this period, the current density in the pore base increased and the strength of electric field increased so that the SO_4 content of the film increased. When the current and voltage were in steady state, the SO_4 content of the film became constant.

(2) Under the electric field, HSO_4^- ions were pulled from the surface of the barrier layer into the layer, were dissociated into SO_4^{2-} by releasing H^+, and then migrated into the layer. However, since the strength of electric field was smaller with the distance from the surface of the barrier layer, SO_4^{2-} ions gradually became immobile and accumulated. Therefore, the SO_4 content of the film reached a maximum value on the intermediate layer between the pore base and the barrier layer/metal interface. When the barrier layer became porous by being released from the electric field, the distribution of anions across the barrier layer remained in the porous layer across the cell wall.

(3) The surface of the wall was soluble since HSO_4^- ions would be incorporated into the oxide. The chemical dissolution rate of the wall decreased with the distance from the surface of the wall as the number of HSO_4^- ions became fewer, increased owing to the increase in the SO_4 content of the film, and decreased again near the cell boundary owing to the decrease in the SO_4 content.

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15) Although the exact shapes of S/O and O/M interfaces are not obvious, they are drawn as concentric.