〈Review〉

양극산화피막 형성에 관한 연구(Ⅱ)

– 양극산화피막조성 –

한 성 호

한국기계연구소 표면공학연구실

Anodic Film Formation on Aluminum (Ⅱ)

– Anodic Film Composition –

SEONG-HO HAN

Surface Engineering Laboratory Korea Institute of
Machinery and Metals, Changwon, Kyung nam, Korea

초   록

양극산화피막의 조성은 현대 장비의 정밀도가 nano 영역까지의 성분 분석이 이루어 짐으로서, 최근에 와서 급속한 진전을 나타내고 있다. 특히 TEM/EDS System을 이용한 Ultramicrotomed 시편의 정밀 분석 기술은 이제 한계를 나타내고 있는 것 같다. 본고에서는 반응 Mechanism을 연구하는데 가장 필수적인 분야인 양극산화 피막의 조성에 관해 1950년대 이후 어떻게 연구되고 설명되었는가를 조명하므로 해서, 그 응용의 기반을 확고히 하고저 한다.

1. Barrier-Type Anodic Films

Recent work has emphasized the important contribution of detailed studies of film composition towards understanding barrier-type anodic film growth on aluminium over a wide range of forming conditions [1, 2, 3]. Whilst such films have long been considered to consist principally of amorphous anodic alumina, the incorporation of species, particular to a given electrolyte, during film growth is recognized, although the significance is far from clear.

It was found that characteristic anions of the anodizing electrolytes were incorporated into both barrier and porous films. The term acid anion is used to indicate the anion species such as SO^{2-} or PO^{3-}, which arise from the anodizing electrolyte, even though it is realized that for barrier film formation the electrolyte is generally not acidic but neutral. The early techniques available for these studies included radioactive tracer techniques allied with chemical sectioning (removal of the outer layers of the anodic film by uniform chemical dissolution) [4, 5], and observation of subtle changes which occurred in the rate of hydration for compositionally di-

fferent regions within a film[6]. Early work by Bernard and Randall[4], and Bernard[5], using radioactive tracer methods, reported that about 1 wt % boron and phosphate is detected in barrier-type films formed in corresponding electrolytes. Later, Randall and Bernard[6], using radioactive tracer techniques to study films formed in aqueous phosphate electrolyte, found that only one-third of the film near the metal/film interface was free of phosphate from the electrolyte, suggesting, at face value, that the oxyanions were mobile and involved in charge transfer along with metal cations. An important observation is that the 2:1 ratio of anion-containing film material to anion-free material always held, independent of the total film thickness.

Recent work by Rabbo, Richardson and Wood[3], using secondary ion mass spectrometry to analyse barrier films formed in phosphate solution, confirmed the general observations of Randall and Bernard[6].

More recently, Thompson, Wood and Shimizu[7], applying the techniques of ultramicrotomy allied with recent advances in analytical transmission electron microscopy i.e. scanning transmission electron microscopy (STEM) which had an X-ray analysis capability (EDX), have enabled the distribution of anions such as phosphate in anodic barrier films on aluminium to be determined. They performed indepth analysis of a film formed in a neutral phosphate electrolyte and obtained a similar conclusion to Rabbo et al[3]. In additon, the geometry and composition of such highly localized features as flaws in anodic barrier films formed on selected aluminium alloys, containing finely dispersed and only microscopically visible precipitates or intermetallic compounds, have been determined successfully[8].

Konno et al.[9] give the compositions of the inner, intermediate and outer parts of a film formed in phosphate solution as $A\ell O_{1.5}$ or $A\ell_2O_3$ (depth 60-75nm), $A\ell O_{1.463}(PO_4)_{0.025}$ (depth 20-50nm) and $A\ell O_{1.09}$ $(OH)_{0.74}$ $(PO_4)_{0.025}$ (depth 5-15nm) respectively, with the average film PO_4^{3-} content of 4.7%. Konno, Kobayashi, Takahashi and Nagayama[10] performed an X-ray photoelectron spectroscopy (XPS) analysis and obtained in-depth profiles of a film formed in neutral borate solution. They reported that the outer part of the film is slightly hydrated with a composition expressed at $A\ell O_{1.35}$ $(OH)_{0.28}$ $(BO_3)_{0.07}$, while the composition of inner part is $A\ell O_{1.5}$ $(B_2O_3)_{0.027}$. The average content of borate in the film is 5.8% B_2O_3. In their later report[9], the composition of the two parts are slightly different, being $A\ell O_{1.29}$ $(OH)_{0.28}$ $(BO_2)_{0.14}$ and $A\ell O_{1.473}$ $(BO_2)_{0.054}$ respectively.

Matzuzawa, Baba and Tajima[11] performed an in-depth profile analysis for a film formed in neutral borate electrolyte, on a single crystal of aluminium, using auger spectroscopy. They reported that the boron is uniformly distributed through the film sections.

Recently, observation in the transmission electron microscope of electron-beam induced crystallization of ultramicrotomed sections of anodic barrier films formed on aluminium in neutral phosphate or borate electrolytes, without current decay, have shown that the films consist of two distinct layers having markedly different susceptibilities to electron beam induced cry-

stallization[12, 13]. Basically, the induced cry-
stallization of the amorphous film to crystalline
γ-Al_2O_3 occurs, accompanied by apparent
texture changes in the film section, more freely
in the inner layer of virtually pure oxide next to
the metal than in the outer layer contaminated
with the electrolyte anion. The difference in the
rates of crystallization of the various layers is
sufficiently large that usually no crystals can be
identified in the outer layer even after the
crystallization of the inner layer has been com-
pleted. Shimizu, Thompson and Wood[12], using
ultramicrotomy allied with transmission electron
microscopy, observed directly the duplex struc-
ture of barrier-type films formed in borate
solution. The inner part of the film, with little,
if any, incorporation of borate, can be readily
crystallized when the film section is exposed to
the electron beam in the electron microscope;
the outer part of the film, where anions are
incorporated, remained unchanged. Further-
more, if the forming electrolyte contained anions
of a heavy metal such as tungstate, its incor-
poration into the film material was shown to be
observed upon initial examination, due to its
darker appearance in the TEM caused by its
greater electron scattering corss section. Data
derived from the techniques considered above
suggest, at face value, that the relative thicknesses
of the anion-containing regions are about 0.7,
0.4, 0.3 and 0.2 for anodizing in neutral el-
ectrolytes of phosphate[13], borate[12], tung-
state[14] and chromate[15] respectively.

　　More recently, Skeldon et al.[16, 17] using
Rutherford backscattering spectometry (RBS)
and nuclear reaction techniques, reported that
films formed in aqueous borate electrolyte

consist of an inner region of relatively pure
alumina and outer region of relatively pure
alumina contaminated with about 1.5 wt %
boron probably as B_2O_3. The boundary
between the regions lies at a relative depth of
about 0.41 within the film and an oxygen
excess in the outer region of the film compared
with Al_2O_3 can be attributed to oxygen
associated with the boron.

　　Rabbo, Richardson and Wood[3] measured
the in-depth profile of chromium in a film
formed in neutral chromate electrolyte and
reported that chromium is rich in the surface
layer over a thickness of a few nanometres;
the chromium content then falls relatively
quickly to a very low but detectable level.
The average content of the incorporated
chromate is considerably low. It was thought
that the incorporated chromium decorated
likely flaws within the anodic film.

　　In general, the amount of water incorpora-
ted in anodic films depends upon the film
formation conditions and treatment during
anodizing, such as the concentration and
temperature of the electrolytes. Diggle et al.[18]
proposed that the water in anodic film is not
present in the free form, but occurs either
as hydroxide or hydrated oxide or both.
Lichtenberger[19] using a chemical analysis
method, which cannot provide knowledge of
the hydrogen distribution throughout the anodic
film, has indicated that 2.5% water, present
in the structure of boehmite, was necessary
to stabilize the spinel-type structure of alumina.
Rabbo, Richardson and Wood[3], using secondary
ion mass spectroscopy (SIMS) which is a rela-
tively new tool for the study of the hydrogen

distribution in barrier films, examined the in-depth profile of hydrogen and hydroxyl ions in films formed over a wide pH range in a study of film hydration characteristics and likely film formation mechanism. The results suggested that the extent of hydration increases with pH, particularly from acidic to neutral pH values. Hydrogen was detected throught the film, and the apparent concentration depended on the pH of the electrolyte. The degree of hydration in the outer regions of the film, particularly for films formed in neutral and alkaline solutions, was of higher value than the inner regions. Lanford, Alwitt and Dyer[20] used a nuclear reaction technique to study the hydrogen profiles through various forms of alumina. They investigated the hydrogen profiles in films formed in aqueous phosphate, tartrate and glycol borate electrolytes. For films formed in phosphate electrolyte, the outer regions are enriched in hydrogen to about 60 nm; calculation of the likely extent of phosphorus incorporation, compared with the low level of hydrogen incorporation, suggested that they were introduced by independent processes and not the result of HPO^{2-} or $H_2PO^-_4$ incorporation. Such a calculation thus assumed that phosphate incorporation as the mono or di-hydrogen species did not change during anodizing. They also claimed that the hydrogen content is dependent on the pH values of the electrolytes. The higher the solution pH, the higher the hydrogen content in the film. For composite films formed after hydrothermal treatment, they suggested that the hydrogen profiles give evidence for water penetration and accumulation in the barrier

layer of the composite film, i.e. hydrated and anodic films.

2. Porous-Type Anodic Films

A considerable amount of work has been done to elucidate the precise chemical composition of these films, the knowledge gained giving significant insight into the growth mechanism and likely chemical behaviour of such films. It is widely known that porous anodic films are contaminated by acid anion species and reference in this survey has been made to anodic film material since it is realized that pure oxide is not always developed. The literature shows reasonable agreement with respect to the levels of acid anion incorporation within the bulk films. The highly contaminated films formed in sulphuric acid have attracted wide study because of their commercial importance and relatively readily detected acid anion species.

Pullen[21] round 13 wt % SO^{2-}_4 ion which is often expressed as SO_3, Liechti and Treadwell[22] quoted 8-13% SO_3 and Spooner[23] obtained 17.7% SO^{2-}_4, which could be increased by forming films at lower temperature and higher current density. Similar observations have been made by Mason and Raub et al.[25] who reported 10-17% SO_3. Hoar[26] has proposed that these conditions favour the dissociation and SO_3 absorbed by the electrolyte, prior to incorporation below the compact surface of the film. Ginsberg and Wefers[27,28] reported a sulphur content corresponding to 13 wt % SO_3, which was reduced to 8 wt % by prolonged washing. They concluded that sulphur-containing anions present in anodic films can be either free (i.e. capable of removal by washing)

or 'chemically bound'. Brace and Baker[29] used a radiotracer method to show that the sulphate is incorporated into the bulk alumina, and is not just a surface effect. Lau et al.[30], using infrared spectroscopy, reported that the sulphur is present as the sulphate anion. Dorsey[31, 32] reported a band in the infrared spectrum due to Aℓ-O-S bonding as well as the normal sulphate band, and proposed a model showing how sulphur could be bound into a cross linked helical Al-O-Al network. Electron probe microanalysis has also been used to determine sulphur in sulphuric acid-formed films, a typical level of 4 wt % S (i.e. 12 wt % SO_4^{2-}) was found to be distributed uniformly throughout the 50 μm film section. More recently, surface sensitive techniques, allied with ion etching, have been used to analyse the sulphur content across film sections. Treverton and Davis[33], using XPS, analysed the sulphur content of films formed in sulphuric acid by ac and dc anodizing. They found that films contain suphates in the surface region and, elsewhere in the film, the sulphur was in a form that results in sulphides in the ion etched surfaces. The resultant composition of the ac and dc films are slightly different. Tajima et al.[34, 35] have used infrared spectrosocpy, differential thermal analysis, allied with optical techniques to detect incorporated anions. Their results indicate that initially the film resistivity is anion indpependent, but decreases with time due to anion incorporation. They found that the anion content increased with increased current density, confirming the results of Mason[24].

Dormony and Lichtenberger-Bajza[36] showed

that hard anodic coatings formed in sulphuric acid contain slightly more sulphur (13.5-15.2% SO_3) than normal coatings (12.8-13.7% SO_3). Mason[24] found that the SO_3 content of the film could be reduced by electrodialysis or by hydrothermal treatment in boiling water.

Incorporation of acid anions other than sulphate has also been reported and quantified. Plumb[37], using a radioactive tracer method, reported 6 wt % PO_4^{3-} ions in films formed in phosphoric acid; the amount of phosphorus in the film varied in direct proportion with the film thicknesss, showing that the phosphorus is present within the film rather than adsorbed merely at the surface. Infrared spectrometry studies by Dorsey[38] suggested that a 2μm film formed in phosphoric acid contained 6% PO_4^{3-}, whereas a 5.3μm film contained 8% PO_4^{3-}. Nagayama et al.[39], in a chemical dissolution study of films formed in 4% phosphoric acid, proposed a compositional model comprising three regions. The first two layers of the cell material adjacent to the pore contained phosphorus. The compositions were claimed to be $Al_{2-X/3} H_X O_{3-Y/2} (PO_4)_Y$ and $Al_2O_{3-Y/2} (PO_4)_Y$ respectively. The third layer, near the film substrate interface, was considered to be relatively pure alumina region. Alvey[40] reported the phosphorus content of a film formed in phosphoric acid, measured colorimetrically from a solution containing leached phosphate, to be about 7.6 wt % PO_4^{3-}. Electron probe microanalysis was employed ion beam thinned[43, 44] and ultramicrotomed sections[45], separated from the electrolyte in the pores by the differently textured acid anion-incorporated material. Furthermore, for a given
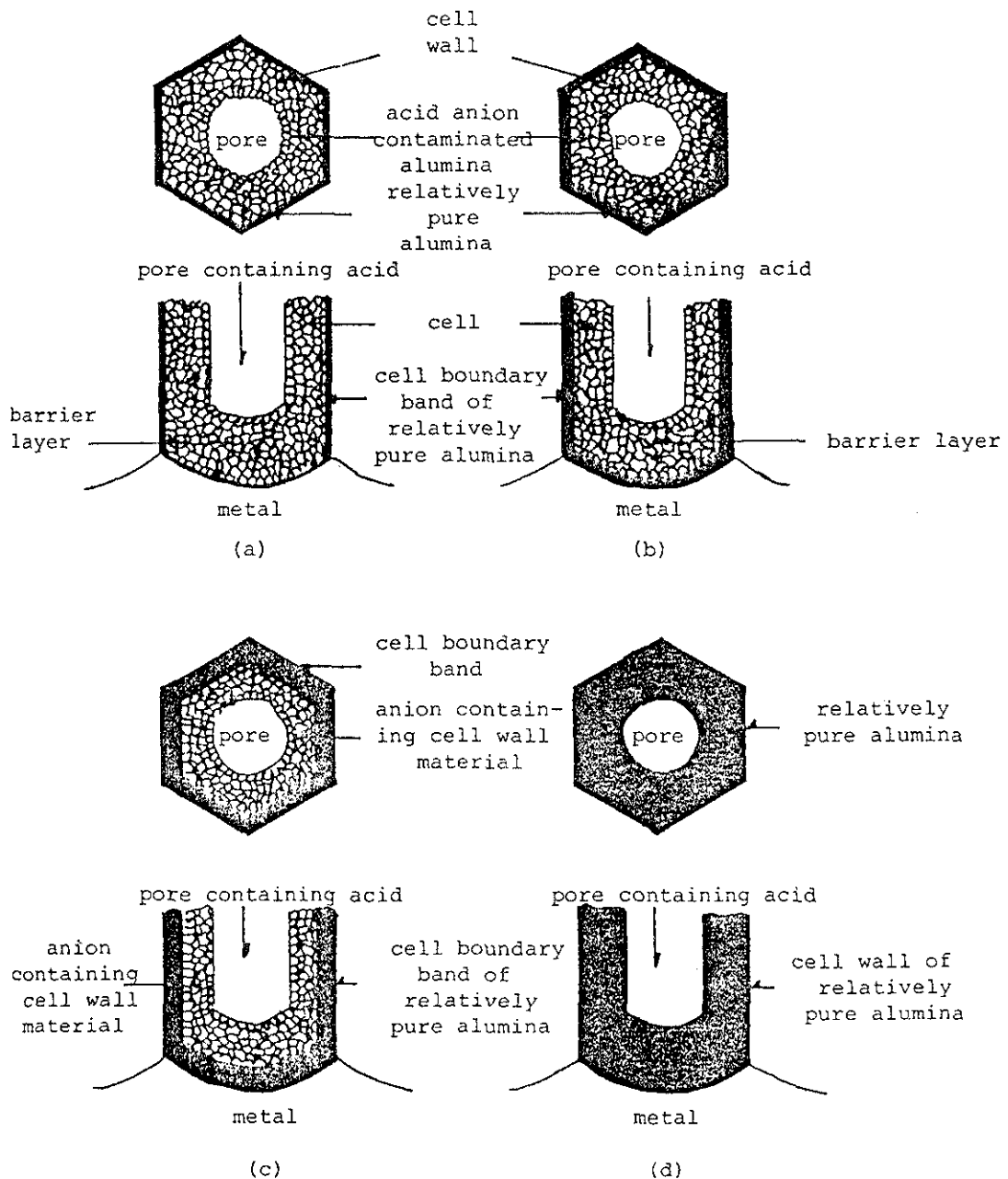
Fig. 1 The plan and sectional view of a pore and adjacent cell for films formed in each
of the major acids: (a) sulphuric acid, (b) oxalic acid, (c) phosphoric acid,
(d) chromic acid. The cell comprises acid anion contaminated film material adjacent
to the pore and relatively pure alumina, where cells meet: from Thompson and Wood[44]

anodizing voltage the cell boundary band thickness was dependent on the acid employed. Thus, the film material adjacent to the pores contained the acid anion, and the relative extent of this region compared to the anion free material decreased in the order; sulphuric acid > oxalic acid > phosphoric acid > chromic acid.

The anion content of films formed in oxalic acid has received little attention. Pullen[21] determined 3 wt % oxalate in the film formed in oxalic acid, similar to that of Liechti and Tread-well[22], 3-3.3% oxalate. Wefers[46] measured 8.6% oxalate, equivalent to 2.3% carbon, from the analytical determination of carbon in films formed to 60V in oxalic acid, in broad agreement with the 7% oxalate determined by Fukuda[47] who also showed that the oxalate content of the film decreased with bulk electrolyte temperature. Fukuda and Fukushima[48] obtained a distribution of oxalate anions in the cell wall as well as in the barrier layer. The oxalate content in the inner layer (0-20nm) adjacent to the film/electrolyte interface was 9%; after increasing to a maximum value of 11% at a depth of 23nm from the film/electrolyte interface, the oxalate content quickly fell to zero towards the film/substrate interface and in the regions where cells meet.

Compared with films formed in the other major acids, films formed in chromic acid contain relatively low levels of chromate incorporation. Early work by Bengough and Sutton[49] reported a value of 0.4-0.7% chromium, whereas later work by Pullen[21] found less than 0.1% chromium in the film. Electron probe and CTEM/EDX analysis allied with ion-beam thinning techniques[50] dem-

onstrated that the chromium incorporation in the film is lower than the detection limit of the fine electron microprobe (< 0.1 wt %).

The water content of the film material has been investigated widely, although the results have differed considerably due presumable to variations in both anodizing and subsequent handling and measuring techniques. Cited values ranged from 1-15% for films formed in sulphuric acid, whereas the film formed in chromic acid has been said to be anhydrous[19, 30]. Liechti and Treadwell[22] suggested 5-6% water in films formed in oxalic acid, and 1-2% tightly bound water and 3-5% loosely bound water in films formed in sulphuric acid. Philips[51] considered that the water content of films formed in oxalic acid is equivalent to the compound $2 Al_2O_3 \cdot H_2O$. Dorsey[52, 53, 31], in many studies using infrared spectroscopy, has suggested the presence of decyclic alumina trihydrate[53] in the barrier layer of porous anodic films, although the sensitivity of the technique has since been questioned. Other studies have used the concept of adsorbed water on the pore walls to explain both electrical characteristics and ageing effects of the films[54, 55]; ageing may be defined as a gradual change in film properties with time of storage. The extent of protons and hydroxyl ions within the films were studied using SIMS for barrier films, which showed their presence throughout the films[3].

Alloying elements in the aluminium substrate have been identified in porous anodic films, by both X-ray emission spectroscopy and chemical analysis[56, 57, 58], and also by electron probe microanalysis[59]. The former work showed that magnesium, zinc, chromium and

especially silicon from the alloys were retained in porous film. Wood and Brock[59], using electron probe microanalysis, investigated the distribution of alloying elements and the apparent porosity through the anodic films. Copper is incorporated and retained in barrier-type films on a single phase A1-4% Cu alloy in approximiately its alloying proportions, but is leached out of porous films, causing extensive film thinning and pore enlargement. Silicon is oxidized much more slowly than aluminium and thus remains dispersed in the anodic film. Zinc remained in the film in the alloying ratio within the substrate. Many studies have considered porous film formation on both single and multi-phase aluminium alloys and determined the distribution of alloying elements in the resultant films. There are differences in the behaviour and this may be influenced by the relative sizes of the intermetallic particles considered and the different anodizing conditions employed. For instance, Shimizu et al.[60], using transmission electron microscopy of ultramicrotomed sections of an A1-1.5 Si alloy and the barrier-type film formed in borate electrolyte, have shown that relatively small silicon particles (10-20nm effective diameter) are "anodized" completely and incorporated into the amorphous alumina film.

REFERENCES

1. G.E. Thompson, R.C. Furneaux, G.C. Wood, J.A. Richardson and J.S. Goode, Nature, London, 272, (1978) 433.

2. M.F. Abd Rabbo, G.C. Woo, J.A. Richardson and C.K. Jackson, Corrosion Sci., 14, (1974) 645.

3. M.F. Abd Rabbo, J.A. Richardson and G.C. Wood, Corrosion Sci., 16, (1976) 689.

4. W.J. Bernard and J.J. Randall, J. Electrochem. Soc., 198, (1961) 822.

5. W.J. Bernard, J. Electrochem. Soc., 109, (1962) 1083.

6. J.J. Randall and W.J. Bernard, Electrochim. Acta, 20, (1975) 653.

7. G.E. Thompson, G.C. Wood and K. Shimizu, Electrochim. Acta, 26, (1981) 951.

8. G.E. Thompson, K. Shimizu and G.C. Wood, Nature, London, 286, (1980) 471.

9. H. Konno, S. Kobayashi, K. Fujimoto, H. Takahashi and M. Nagayama, Proceedings of INTERFINISH 80, Tokyo, Japan, (1980) 281.

10. H. Konno, S. Kobayashi, H. Takahashi and M. Nagayama, Electrochim. Acta, 25, (1980) 1667.

11. S. Matzuzawa, N. Baba and S. Tajima, Electrochim. Acta, 24, (1979) 1199.

12. K. Shimizu, G.E. Thompson and G.C. Wood, Thin Solid Films, 77, (1981) 313.

13. G.E. Thompson, K. Shimizu and G.C. Wood, Electrochemical Society Meeting, Minneapolis (1981).

14. K. Shimizu, G. E. Thompson and G.C. Wood, Thin Solid Films, 81, (1981) 39.

15. P. Skeldon, K. Shimizu, G.E. Thompson and G.C. Wood, Unpublished work (1982).

16. P. Skeldon, K. Shimizu, G.E. Thompson and G.C. Wood, Surf. Interface Anal., 5, (1983) 247.

17. P. Skeldon, K. Shimizu, G.E. Thompson and G.C. Wood, Surf. Interface Anal., 5, (1983) 252.

18. J.W. Diggle, T.C. Downie and C.W. Goulding, J. Electrochem. Soc., *116*, (1969) 737.

19. E. Lichtenberger, Metalloberflache, *15*, (1961) 38.

20. W.A. Lanford, R.S. Alwitt and C.K. Dyer, J. Electrochem. Soc., *127*, (1980) 405.

21. N.D. Pullen, Meta. Ind., *54*, (1939) 327.

22. F. Liechti and W.D. Treadwell, Helv. Chim. Acta, *30*, (1947) 1024.

23. R.C. Spooner, Proc. Am. Electropl. Soc., *44*, (1951) 1321.

24. R.B. Mason, J. Electrochem. Soc., *102*, (1955) 671.

25. E. Raub, H. Kauser and A. van Krusenstjern, Metalloberflache, *21*, (1967) 144.

26. T.P. Hoar , "Modern Aspects of Electrochemistry", J.O'M Bockris, ed., vol.2, p. 262-342, Butterworth, London (1959).

27. H. Ginsberg and K. Wefers, Metall., *16*, (1962) 173.

28. H. Ginsberg and K. Wefers, Metall., *17*, (1963) 202.

29. A.W. Brace and H. Baker, Trans. Inst. Metal Finish., *40*, (1963) 31.

30. T.T. Lau, F. Naudin and P. Robbe-Bourget, J. Phys., (Paris) *25*, (1964) 11.

31. G.A. Dorsey, J. Electrochem. Soc., *115*, (1968) 1053.

32. G.A. Dorsey, Plating, *57*, (1970) 1117.

33. J.A. Treverton and N.C. Davies, Electrochim. Acta, *25*, (1980) 1571.

34. S. Tajima, N. Baba, T. Mori and M. Shimura; Proc. Symp. of Anodizing Aluminium, Birmingham, Aluminium Federation, London, p. 37 (1967).

35. S. Tajima, N. Baba and M. Shimura, Electro-chim. Acta, *12*, (1967) 955.

36. A. Dormony and E. Lichtenberger-Bajza, Metalloberflache, *15*, (1961) 134.

37. R.C. Plumb, J. Electrochem. Soc., *105*, (1958) 498.

38. G.A. Dorsey, J. Electrochem. Soc., *116*, (1969) 466.

39. M. Nagayama, H. Takahashi and M. Koda, Surface Finishing Tech of Metals, *30*, (1979) 438.

40. C.E. Alvey, Ph.D. Thesis, University of Manchester (1974).

41. G. Bailey, Ph.D. Thesis, University of Manchester (1978).

42. G. Bailey and G. C. Wood, Trans. Inst. Metal Finish., *52*, (1974) 187.

43. S.H. Tan, Ph.D. Thesis, University of Manchester (1982).

44. G.E. Thompson, R.C. Furneaux, G.C. Wood and R.J. Hutchings, J. Electrochem. Soc., *125*, (1978) 1480.

45. G.E. Thompson and G.C. Wood, Nature, London, *290*, (1981) 230.

46. K. Wefers, Aluminium, *49*, (1973) 553.

47. Y. Fukuda, Trans. natn. Res. Inst. Metals, *17*, (1975) 25.

48. Y. Fukuda and T. Fukushima, Bull. Chem. Soc. Japan, *53*, (1980) 3125.

49. G.C. Bengough and H. Sutton, Engineer, *122*, (1926) 274.

50. G.E. Thompson, G.C. Wood and R.J. Hutchings, Trans. Inst. Metal Finish., *58*, (1980) 21.

51. H.W. Phillips, Symposium on Properties of Metallic Surfaces, Institute of Metals, Monograph, *13*, (1952).

52. G.A. Dorsey, J. Electrochem. Soc., *113*,

(1966) 169,

53. G.A. Dorsey, J. Electrochem. Soc., *113,* (1966) 172.

54. A.C. Jason and J.L. Wood, Proc. Phys. Soc., *B68,* 1955) 1105.

55. C.J.L. Booker and J.L Wood, Proc. Phys. Soc., *B76,* (1960) 721.

56. R.C. Spponer, Plating, *63,* (1966) 451.

57. J. Cote, E.E. Howlett, M.J. Wheeler and

H.J. Lamb, Plating, *56,* (1969) 386.

58. R.D. Guminski, P.G. Sheasby and H.J. Lamb, Trans. Inst. Metal Finish., *46,* (1968) 44.

59. G.C. Wood and A.J. Brock, Trans. Inst. Metal Finish., *44,* (1966) 189.

60. K. Shimizu, G.E. Thompson and G.C. Wood, Electrochim. Acta, *27,* (1982) 245.