A New Model for the Formation of Anodic Coatings on Aluminum

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In a paper published in the November 2009 of this journal, the author challenged the validity of the "barrier layer" theory of coating formation in the anodizing of aluminum. It was shown that there is adequate evidence that the barrier layer was not a layer at all, but was instead a transition zone between the metal and the anodic oxide film. Additionally, the theory failed to account for the effect of material composition and structure on the formation, structure and growth processes. The author concluded that the theory is no longer valid. In this paper, a new model for the formation of anodic coatings is presented. This model is based on the initial formation, morphology and growth processes being highly dependent on the lattice vacancy and defect structures. These factors are further modified by the presence of alloying and impurity metals.

Keywords: *anodizing of aluminum, anodic coating formation, anodizing theory, barrier layer theory, lattice structure defects, pore structure*

Introduction

Anodic coatings are the most widely used means of producing an attractive functional finish on aluminum. Comprehensive details of the technology of producing anodized finishes have been given published previously.[1] Following the discovery of the process in 1927, attempts have been made to provide an explanation of the process of anodic oxide formation. The model of Keller, Hunter and Robinson[2] has been generally accepted by researchers and practical anodizers.

Outline of the present model

Their theory of the process is summarized in the following statement: "A barrier layer of oxide starts to form in the usual manner, but as soon as any oxide is formed, solvent action by the electrolyte also starts, which tends to reduce the thickness of the barrier layer. From observations of the voltage and current excursions which occur at the start of coating formation, these processes tend to reach a balance within a relatively short rime, after which coating formation proceeds at a uniform rate."

The essential concept of the authors was that of a uniform anodic coating made up of hexagonal cells consisting of a "barrier layer" and hexagonal cell walls with a central pore. It is this model which has been widely accepted by most investigators. Linked with this was the concept that the cell size (C) was:

$$C = (2 \times W) + P$$

where:
W = cell wall thickness
P = pore diameter.

The wall thickness was found to be voltage dependent and the pore diameter varied with the electrolyte. Although there has been work reported which has modified the understanding of the effect of the electrolyte and anodizing conditions on the composition and morphology of the oxide, its basic concept remains unchanged.

The theory assumed a uniform metal and developed an idealized model based on this assumption. This took no account of the possible effect of factors such as anisotropy and other metal structural features of the metal. This approach led to most research being focused on coating morphology and composition. The main research on alloys focused whether the metal present could anodically oxidize specific problem alloys, mainly in the 2000 and 7000 series, which have been widely investigated.

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The present author has previously published a detailed critique of the "barrier layer" theory[3] and considers it both inaccurate and inadequate for the following reasons:

- The cells produced are not uniform and a number are not hexagonal, but this is ignored.
- The idea of a "barrier layer" is a misconception, since it is not a uniform layer and does not function as a "barrier" in any meaningful way.
- The variation in film thickness on grains of different orientation is not considered.

This contribution has drawn attention to papers which are at variance with the "barrier layer" theory, but these have largely been ignored in academic research. Analysis of published data has shown that cell and pore sizes have a wide range of values when individual values of a population of cells or pores were examined. Further, a different mode of initial oxide growth has been established for all electrolytes and their associated conditions. Other investigators have shown that lattice structures, vacancies and defects can play a role in oxide formation.

Development of a new model

Whilst anodizing research focused on the minutiae of the anodic coating, in the 1960s, research on the structure of aluminum was adding significantly to knowledge of the effects of metal composition and metallurgical structure, which led to improved manufacturing techniques. These related especially to metal lattice structure and defects at the atomic lattice level. A book by Altenpohl, published in 1972, described various lattice defects resulting from hot and cold working.[4] He drew attention to the effect of dislocations produced by working, and the presence of "vacancies" (empty spaces) in the lattice structure. It appears that researchers on anodic coatings did not become interested in vacancies until the late 1980s which, even then, mainly concentrated on vacancies found in the anodic coating but did not consider the possibility that these vacancies could affect the formation process.

This omission had the consequence that most anodizing researchers did not realize that the conclusions of Franck[5] and Csokan[6] on the role of defects in initiating the growth of oxide nuclei were referring mainly to active centers containing an agglomeration of lattice defects and not the micro-level features with which they were familiar.

A perspective on growth of oxide

Having established the deficiencies of the "barrier layer" theory, it seemed relevant to consider the known features of the formation of oxide films on aluminum. This approach was based on the concept that although oxide films were formed in many environments, it seemed likely that there would be one or more characteristics in the initial formation which was common to all, or at least, to most. There is quite extensive literature, but the main common factor found is that the initial growth of oxide films was by the formation of nucleation centers. In more recent years, there seemed to be significant evidence that these centers were related to the presence of a local concentration of structural defects which resulted in the initial patterns of oxide formation being similar. Examples of the mode of initial oxide formation in other environments are displayed in Fig. 1.

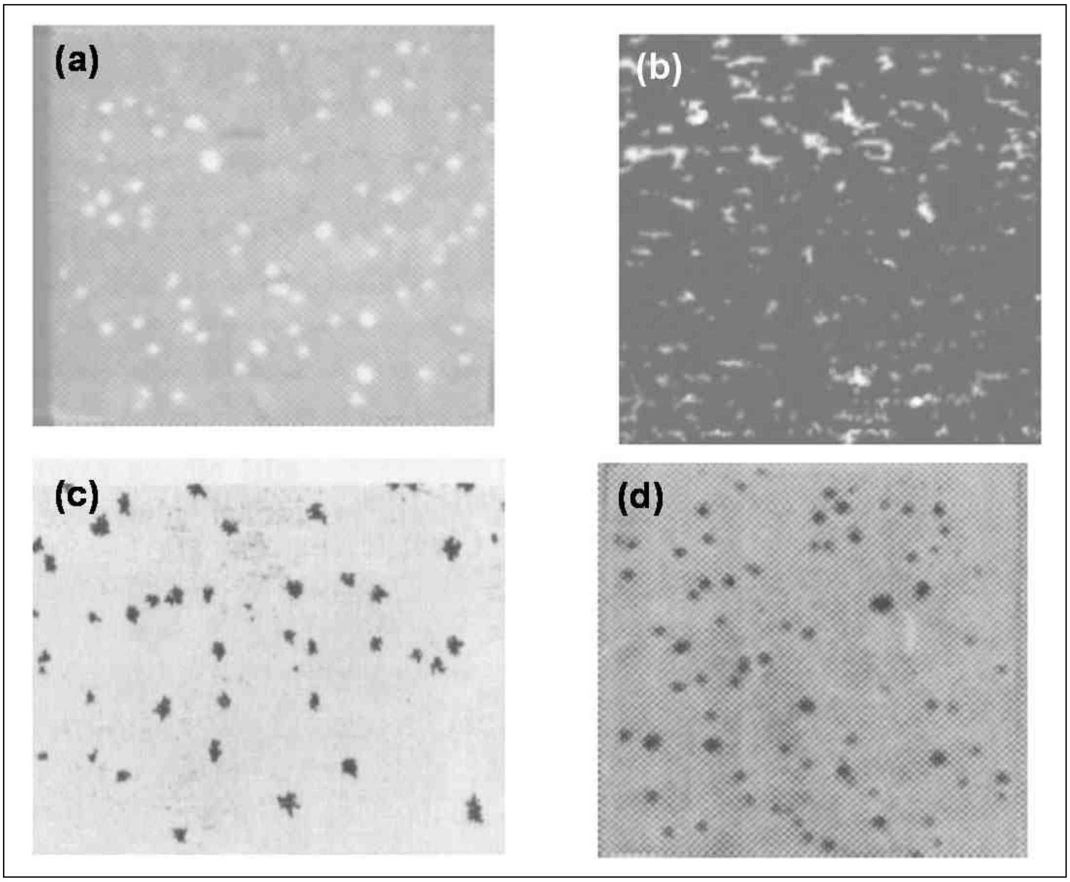


Figure 1—*Examples of initial oxide formation in typical environments: (a) heated in air to 250°C; (b) exposed in an urban atmosphere; (c) exposed in a marine atmosphere; (d) initial formation of anodic oxide.*[9]

The character of anodic oxide nucleation

As detailed previously, in the period 1967-1983, a series of investigations[3] reported the initiation of the growth of anodic oxide from random nucleation sites. Coatings appeared to be formed initially at high energy points, such as structural defects.[5] This led to an extensive series of investigations were started by Csokan[6] in the early 1960s, using a cine-camera linked to an electron microscope. These investigations included all types of electrolytes used industrially. This work continued into the 1970s.[7]

These studies demonstrated that film growth commenced with a nucleation process. Csokan observed that anodic coating formation took place by forming a series of initial active nuclei (Fig. 2), leading to the development a series of secondary centers, until the entire surface was covered. These nucleation sites were found to be associated with defect structures in the metal.

Pore formation

On the basis of Macdonald's evidence,[8,9] when the anodic current is applied, there is an agglomeration of vacancies (Fig. 3) whose spacing (on average) is voltage dependent. This agglomeration of vacancies is unlikely to result in an entirely empty lattice locally. To fulfill this is a function the structure still has to have a skeleton of aluminum atoms present, and thus some oxide will be formed. The vacancies provide the path needed to conduct current and allow for the high level of outflow of aluminum ions since, on average, only two out of every three aluminum atoms form anodic oxide.[10]

Initial coating formation

As the oxide nucleates and spreads to cover the whole of the aluminum surface, an anodic oxide coating develops with very specific characteristics. At the metal/electrolyte interface there is an excess of oxygen ions, giving an n-type oxide at the metal/oxide interface and a p-type oxide at the oxide/electrolyte interface. These zones were found by Sato and Kaminga[12] to be of 20 to 50Å in thickness. This is depicted diagrammatically in Fig. 4.

The defect structure, the presence of impurity atoms and the oxide solvency of the electrolyte, can be expected to affect the size of the coalesced vacancies. Although the average size of the pores formed will be around the values reported in the literature, because of these factors the values will vary significantly.

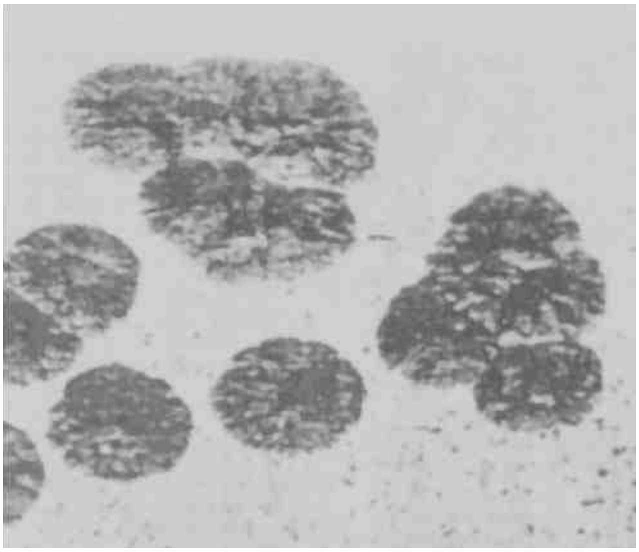


Figure 2—*Initial anodic oxide nucleation sites as observed by Csokan.*[8,9]

It has previously been pointed out that there is an increase in volume of the anodic coating compared with that of the metal from which it has been formed. This would account for the tendency of some pore diameters to be less than average. It may be that anodic coatings themselves develop a defect structure which limits the infilling of the larger pores. Alternately, it may be that the size of the coalesced vacancies at the base is smaller.

More investigations are needed before it will be possible to evaluate fully the factors responsible. The results in the previous paper[4] reported a ± 25% variability. The variability of the size of individual cells was thought likely to be similar.

Factors influencing cell morphology

This variation in individual cell sizes can be readily seen in Fig. 5, where the predominant cell shape is that of an irregular hexagon. However, values measured of a limited sample[4] showed a ± 27% variability around the mean of the areas of the cells referred to. It is appropriate to consider the cause of this variability.

The model being developed accepts the basic finding of Keller, Hunter and Robinson that the (mean) cell size is voltage dependent, but they did not appear to recognize or explain the factors giving rise to this variability.

Runge[14] has pointed out that "the hexagonal structure of anodic oxide is the result of entropy, the natural thermodynamic state of being at the lowest energy state. Structural defects, even pre-deforming the surface, can dictate an even-lower energy state, orienting the anodic oxide structure. This explains why naturally occurring non-hexagonal cells can be among the population."

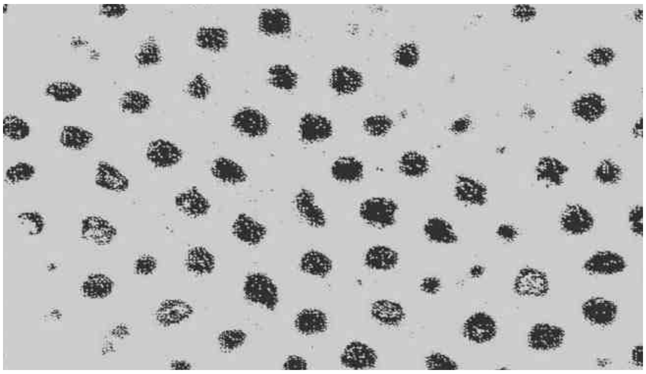


Figure 3—*Transmission electron micrograph of a stripped film showing where an agglomeration of vacancies has occurred after anodizing for 30 sec in a 1.5M H_2SO_4 electrolyte at 20°C*[11] *(Original b/w image reversed).*

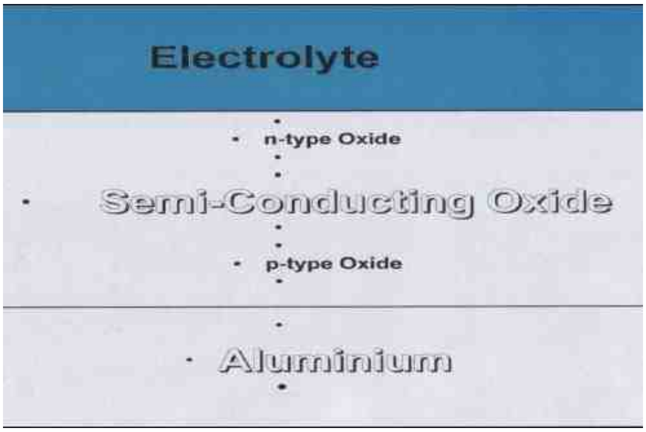


Figure 4—*Portrayal of the structure of the transition zone.*

This is a relevant consideration, since it is a reminder that each individual cell is at the same state of entropy. However, to explain the variations between individual cells, it seems necessary to consider the configuration of atoms within the lattice. With the presence of foreign atoms, lattice vacancies, lattice distortion from manufacturing operations and different packing density configurations on various planes at the metal/oxide interface, it is not difficult to conceive of the net effect being the variable morphology seen in the literature.

Formation of the pore structure

As soon as this incipient pore structure is established, a cell structure develops, since further growth can only take place vertically and thus a pore structure is established. The average spacing between the pores is voltage dependent, but the distance between individual pores may vary, depending on the strength of the field surrounding them. This is affected by the presence of foreign atoms and lattice defects.

Further, the diameter of the pores will be affected by the oxide-solvency of the electrolyte and anodizing conditions, as has been documented in the literature. The work of Franklin showing how pore size diminishes with pH in a boric acid electrolyte also suggests that a similar effect will be found with sulfuric acid. Size measurements on pores in sulfuric and oxalic acid electrolytes indicate generally that the pores remain parallel, except near the electrolyte interface (Fig. 6). Oxide solvency exhibits itself as an attack on the outer layers of the coating, particularly architectural coatings, which leads to "chalking" in service.

The effect of alloying additions and impurity elements

The effect of alloying and impurities has been considered in the previous paper but relates to effects at the micro and macro level. It is known that magnesium and zinc atoms diffuse rapidly through the anodic coating, thereby increasing the number of vacancies in the oxide structure. Elements such iron, manganese and silicon, when present in amounts forming a solid solution, increase in electrical resistance and appear to form anodic oxide. However, the concept that the presence of these atoms may affect the cell morphology or pore size is a new concept, but it follows the reasoning of this model. For the present it remains an area where there is only conjecture on offer.

Features within a population of cells

The previous contribution focused attention on the fact that if size measurements are made of a number of cells or pores, the values recorded fall within a statistical normal distribution curve. It would therefore be desirable to report accordingly on the characteristics of a population of cells. This is a new concept and one which has received almost no attention.

Variability of the cell structure throughout its thickness

One of the inadequacies of the Keller, Hunter and Robinson model is that it conveys the impression to many practical anodizers that the pore extends from above the "barrier layer" to the surface of the coating. What is overlooked is that all cells grow normal (vertically) to the surface of the metal from which they are formed. The problem is that the size of the cells is small in relation to the surface finish of the material being anodized. The surface variations over a machined or extruded surface are such that there will be many places where adjacent cells are inclined to or away from each other.

This was well demonstrated by Arrowsmith and Moth[15] using a StereoScan™ electron microscope. Fig. 7 shows the inclination of cell growth leading to pore branching and the termination of cell growth due to this factor when anodizing in a phosphoric acid electrolyte.

Effect of insoluble intermetallics on coating structure and growth

The above work also included examples of the effect of insoluble intermetallic particles on the structure of anodic coatings. Figure 8 shows a large amorphous intermetallic trapped in a hard anodic coating. He also showed how some intermetallics were soluble in the electrolyte and left voids in the film.

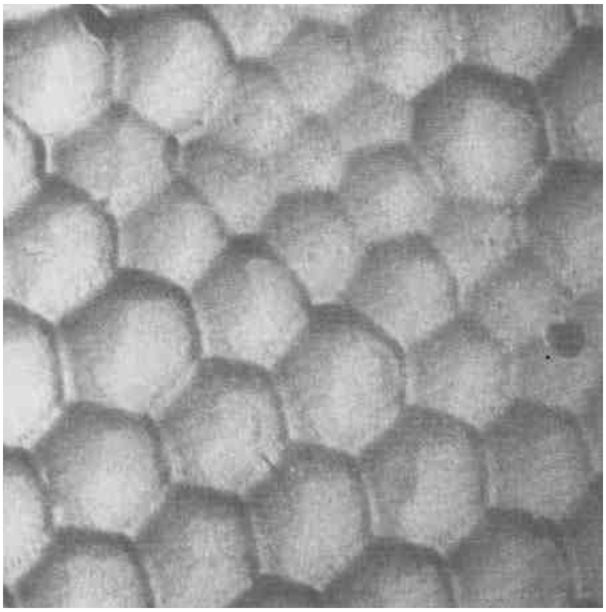


Figure 5—*Anodic cell base pattern for a coating formed for 70 min at 25 mA/cm^2 to 120V in 0.25M oxalic acid at 15°C.*[13]

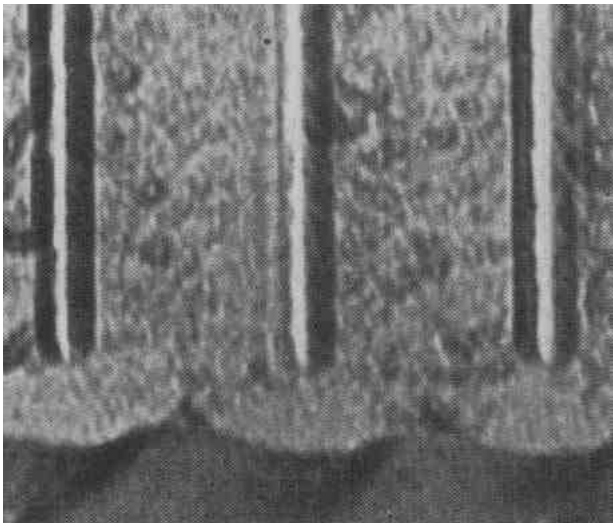


Figure 6—*Development of pores in an anodize coating produced in a 0.25M oxalic acid electrolyte at 0°C at 50mA/cm^2.*[13]

This feature had been previously investigated by Cooke,[16] who carried out a detailed investigation of the effect of such particles on the appearance and corrosion resistance of bright trim materials. The effect of these particles was that shown in Fig. 9. It can be seen that the final result is to produce a weak point on the anodic coating where corrosion is more likely to occur. An important consideration in terms of corrosion resistance is that as film thickness is increased, most of these intermetallics remain trapped within the anodic coating, but there is no easy path for penetration of corroding media, thus significantly reducing their effect on corrosion resistance.

Figure 7—*View of inclination of cells producing pore branching and termination due to machined surface.*

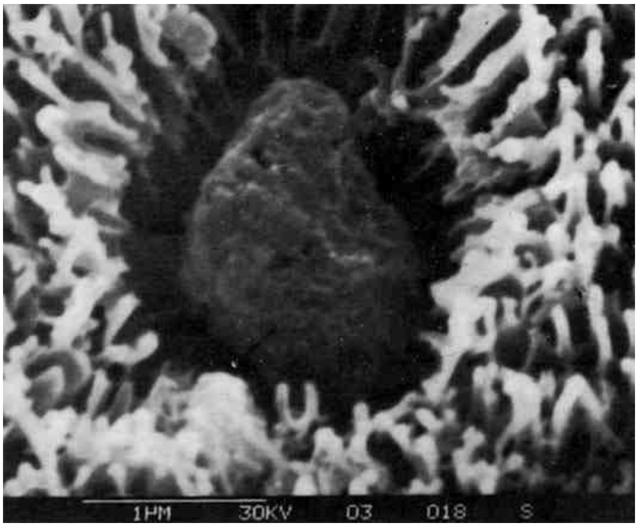
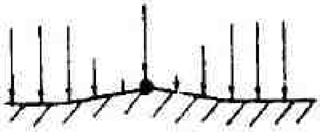
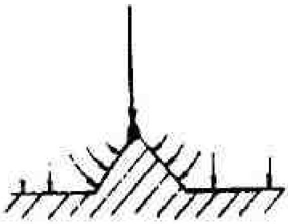


Figure 8—*A 3-D electron photomicrograph of trapped insoluble amorphous intermetallic particles.*

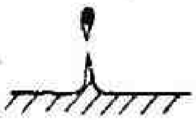
(a)
Particle on surface
(oxide not shown in sketches a-d)



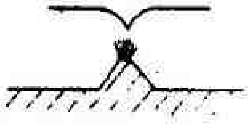
(b)
Initiation of cone formation
NOTE: length of arrows indicates magnitude
of current at each location



(c)
Condition where cone strongly
affects reflectance and image clarity
see note: for (b)



(d)
Isolation of particle
in film



(e)
Anodic film with dimple due to
unoxidized particle and aluminium

Figure 9—*Depiction of stages in the incorporation of an insoluble intermetallic into an anodic coating.*

Concluding remarks

The foregoing has shown the consequences of approaching an understanding of anodic coating formation from too restricted a basis. The oxide film present on aluminum is fundamental to understanding its surface chemistry. There are various environments which produce an oxide coating on aluminum. The evidence offered shows anodic oxide formation to be initially no different from that of other forms of oxide.

The "barrier layer" approach treats an anodic coating as a film, but in so doing has failed to recognize that, as with other oxide films, its formation and properties are dependent on the composition and structure of the metal from which it is formed. This has lead to a concentration of effort on film formation and morphology.

During the 1960s, a significant advance in understanding of the metal lattice structure was made by the aluminum industry and its implications for metal fabrication procedures and properties. Although pioneering work was carried out in this period which linked lattice defect structures to the mode of initial oxide formation and growth, the results were either ignored or regarded as a minor modification to the "barrier layer" theory. This has led to a lack of critical examination of these findings by anodizing researchers.

The neglect of the advances in metallurgy meant that it was only in the 1990s that there was a recognition that features such as vacancies, dislocations and atomic packing densities might have a significant effect on anodic coatings. It is considered that the foregoing model reveals much of the complex reactions taking place at the metal/oxide interface and provides a better understanding of the process than hitherto prevailed. At this point in time it should lead to a better understanding of the process and stimulate ideas for further advances.

Acknowledgements

Over a period of two years, I had the privilege of intermittently exchanging ideas on anodic coating formation with Dr. Jude Runge of Compcote International Inc. This was most helpful to me in preparing this paper. I would also express my thanks to Ted Short (formerly of Alcan R&D Ltd., Banbury, U.K.) for reading the draft of this paper and for helpful comments.

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About the author

Dr. Arthur Brace, CPE, AESF Fellow, FIMF, FIMMM, was born in Bristol, England and attended a local grammar school, leaving at 16 to become a laboratory assistant in a plant producing aluminum and magnesium castings. He remained associated with aluminum for most of his subsequent career. In the late 1940s, he joined the Aluminum Development Association, being involved is several projects promoting the use of aluminum. In this period he first became involved in anodizing and a few years later joined Alcan's Laboratories at Banbury, where he built up an anodizing R & D team which subsequently established itself as one of the leading centers for anodizing. This led to his promotion as Head of the Chemistry Division, Several years later he left Alcan and became a plant manager, gaining experience in architectural and hard anodizing. He went on to establish himself as a professional consulting engineer. He assisted a number of companies in setting up anodizing plants. Over the years he also established a reputation for problem solving in anodizing.

Noting the large increase in the use of hard anodizing and the growth of offshore contracts, he played a leading role in setting up the International Hard Anodizing Association to provide a forum for its members to discuss issues of mutual interest. He was one of a small committee that formed the Aluminum Anodizers Association. He also served as President of the International Branch of the American Electroplaters and Surface Finishers Society and was a member of its Light Metals Committee. He also served on the Council of the Institute of Metal Finishing and as Chairman of its Aluminum Finishing Committee. He was author of two books, and numerous papers relating to aluminum and anodizing.

He holds a B.Sc. (Economics) from the London School of Economics and a Ph.D. from the University of Aston in Birmingham. He has also received the following awards:

- *City and Guilds of London Institute Insignia Award in Technology (1956).*
- *Institute of Metal Finishing Jim Kape Memorial Award for Best Paper (1987).*
- *Sam Wyman Memorial Award (AESF) for outstanding paper (1990).*
- *AESF Award for outstanding contribution to the Aluminum Finishing Industry (1994).*
- *Institute of Metal Finishing A.W. Hothersall Memorial Award (1995).*
- *Aluminum Anodizers Association, Robert L Kersman Award of Excellence for Best Paper (2002).*