

International Conference on Advances in Manufacturing and Materials Engineering,
AMME 2014

A comparative study of different electrolytes for obtaining thick and well-ordered nano-porous anodic aluminium oxide (AAO) films.

M.K.Kushwaha

Deptt. of Mechanical Engg. S.B.S.State Technical Campus, Ferozepur, Punjab 152001, India

Abstract

A comparative study has been carried out to find best electrolyte for obtaining thick and well-ordered nano-porous Anodic Aluminium Oxide (AAO) films using diluted Chromic, Oxalic, Phosphoric and Sulphuric acid solutions. The top view pore structure ordering and thickness of the AAO films have been determined from Field-emission Scanning Electron Microscopy. Extent of ordering is evaluated by comparing Fast Fourier Transforms (FFT) of the top view SEM images. It was found that films anodized in Oxalic acid are thickest and degree of pore ordering in this case is also highest.

© 2014 Elsevier Ltd. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Selection and peer-review under responsibility of Organizing Committee of AMME 2014

Keywords: Anodic Aluminium Oxide (AAO) films, two-step Anodization, Self-ordering regime and Fast-Fourier Transform, Mild and hard anodization.

1. Introduction

Anodization of aluminium had started in the beginning of the last century [Thompson and Wood, 1983]. The nanoporous type of the Anodic Aluminium oxide film or layer has attracted enormous attention in the last two decades due to its unique and tunable structure which acts as a very useful and versatile template, mask or host for making various types of nanocomposite and nanodevices to be used in the fast growing field of nanotechnology [Masuda and Fukuda, 1995]. It is extensively researched these days and hence so many review papers pertaining to it have been published [Mutali et al., 2013; Chi and Zhi, 2011; Gerrard et al., 2011; Lei et al., 2007]. This film, hereinafter referred to as AAO (Anodic Oxide Film), consists of both upper longer porous part and lower or inner, shorter barrier or compact type nonporous part. The pores are parallel to each other and normal to the surface

Corresponding author. Tel.: +91 (0)8288005720; fax: +91 (0)1632 242138

E-mail address: kushwaha_m_61@yahoo.com

[Diggle et al., 1969]. Such structure has interpore spacing of 50 - 400 nm, pore diameter of 20 - 200 nm, uniform pore periodicity from 50 to 400 nm; and pore density of as high as 10^{11} pores cm^{-2} [Chik and Xu, 2004]. This porous structure is schematically represented as a honeycomb structure with a high aspect ratio (depth of pore divided by its diameter) as this is essential in a template for producing nanometric devices [Kushwaha et al., 2008]. It is viewed as fine channels characterized by a close-packed array of columnar hexagonal cells, each containing a central pore [Li et al., 2000; Masuda and Hasegawa, 1997]. The idealized structure of AAO film has been shown in Fig.1. However, the geometry of the AAO film, obtained generally is far from that of this idealized structure as the arrangement of the cells is not perfectly hexagonal [Masuda and Hasegawa, 1997]. It may be somewhat closer to ideal one when conditions for self-ordering are satisfied during its formation [Neilsch et al., 2002].

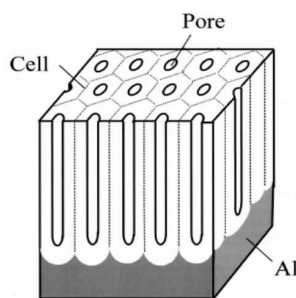


Fig. 1. The idealized structure of Anodic Aluminium Oxide (AAO) film [Asoh et al., 2001].

Moderately ordered or disordered nanoporous structure on pure aluminium substrates with a controlled uniform pore diameter, interpore distance and aspect ratio have been formed by anodization in Sulphuric, Oxalic or Phosphoric acid electrolytes [Mutali et al., 2013]. Several studies have shown that other acids such as chromic, boric, citric and tartaric acids can also be used for preparation of AAO, but with inferior pore ordering in comparison with the three common electrolytes. Some ionic liquid additives enhance the oxide growth rate but decrease the degree of ordering. The technique of two-step anodization, invented by Masuda and Satoh in 1996, whose scheme has revolutionized the growth of nanotechnology, especially in the widespread applications of AAO, as the pores now can be arranged in near perfect ideally (hexagonally) ordered array structure using this novel method [Masuda and Satoh, 1996]. The depth of oxide layer increases with anodization time in the second step, but to a certain extent only. Some of the application areas of this well-ordered AAO films are molecular separation, catalysis, energy generation and storage, electronics, photonics, sensors, biosensors, drug delivery, solar cells, carbon nanotubes and template synthesis [Mutali et al., 2013]. Although AAO is successfully and widely used for the synthesis of well-ordered nanostructures, the growth mechanism of the porous alumina is still questionable. It is still not established that which physical factors control the pore ordering during the AAO growth [Thompson and Wood, 1983]. The oxide growth at the metal/oxide interface and electric-field-assisted local oxide dissolution at the oxide/electrolyte interface were supposed to be the driving forces for the growth of self-ordered porous structure [Sullivan and Wood, 1970]. Recently, it has been established that for obtaining well-ordered nanoporous structure, there is a self-ordering regime, i.e. a combination of anodization process parameters in which voltage is of utmost importance and these conditions are specific to the electrolyte used [Asoh et al., 2001]. The long-range ordering has been observed to occur under limited voltage conditions that were specific to the solution used for anodization, that is, long-range ordering takes place at 25-27 V in sulfuric acid solution [Masuda and Hasegawa, 1997], at 40 V in oxalic [Masuda and Fukuda, 1995; Masuda and Satoh, 1996] and chromic [Wojciech et al., 2014] acid solution and at 195 V in phosphoric acid solution [Masuda et al., 1998], corresponding to cell sizes of 63, 100, and 500 nm, respectively. Several groups have also reported similar results concerning the long-range ordering conditions for anodic porous alumina [Shingubara et al., 2004; Shingubara et al., 1997; Jessensky et al., 1998; Neilsch et al., 2002]. There is a need for qualitative and quantitative analysis of the ordering in AAO structure and hence Fast Fourier Transform (FFT) analysis of the top surface of the AAO film is done [Wojciech et al., 2014; Sulka and

Parkoła, 2007; Sulka and Parkoła, 2006; Ba and Li, 2000]. However thickness of these well-ordered oxide films reported in literature is generally in the range of 1 to 10 micrometer, e.g. 2 micrometer [Rabin, 2003], which may be considered as sufficiently thick for nanotechnological applications, but there are many applications which require both features in these films, i.e. greater thickness to increase strength, as well as well-ordered nanoporous structures, for deeper and uniform embedding of the lubricating material in the porous surface of the films. Few studies have been done to increase the oxide film thickness by varying anodization process parameters, but could succeed in obtaining only 20 micrometer thick films only [Wang and Wang, 2005] however in this case ordering of porous structure was not discussed at all. The anodic oxidation of aluminium under conventional so-called ‘mild anodization’ is tediously slow fabrication process with oxide formation speed 1–2 microns per hour and requires almost two working days to prepare an AAO membrane as against hard (HA) or high-field anodization method achieving considerably higher anodization speeds of 50–100 microns per hour. Another drawback of mild anodization is that self-ordering occurs only in narrow process window, i.e. in self-ordering regime, hence Lee and other co-workers modified the hard anodization or conventional type III anodization for fast fabrication of long-range ordered porous AAO membranes [Lee et al., 2006]. Hard anodization has been used by industries for last 50 years to get a thick, hard and wear resistant coating. The increase in hardness is attributed to reduced porosity and oxide hydration. This process has not been favored by academic research over the last four decades and has not been applied to the development of nanostructured materials because it is difficult to control structural parameters of the AAO, like pore diameter, interpore distance, etc. To address this problem, recently, some research work on combined hard anodization and mild anodization have been reported [Liu et al., 2014] so as to reduce longer time consumed in first step of two-step mild anodization process. However, they had to use two electrolytes, i.e. sulphuric acid for hard anodization in the first step and oxalic acid, for second mild anodization in the second step of anodization and hence the extent of self-ordering obtained is questionable as they have deviated from the self-ordering regime, recognized as necessary for well-ordering porous structure by many researchers.

In this study an attempt has been made to obtain thick and at the same time well-ordered nanoporous anodic alumina structure by using novel two-step anodization process invented by Masuda and Satoh, 1996, and anodization process parameters as per self-ordering regime. The effect of various electrolytes and anodization process time in the second step of two-step anodization have been compared to determine which electrolyte and process is more suitable to obtain the required structure in the AAO films. This maiden study will definitely help in growth of AAO applications for making such specific type of AAO nanostructures.

2. Experimental procedure

High purity aluminium coupons (99.997 % pure, Merck, Germany) of 50 mm x 30 mm x 0.4 mm size were taken. Only 1.0 cm² area was exposed to the electrolyte in electropolishing and anodization by masking the extra area using a tape and lacquer painting. Prior to anodization, two important pre-treatments, i.e. annealing and electropolishing were done. Annealing was done at 773 K for 3 hours in presence of nitrogen gas, in order to enhance grain size, eliminate residual stresses and obtain uniform conditions for pore growth over large areas of the samples. Al sheets were degreased in acetone and electropolished at constant voltage (20 V, d.c.) for 3 minutes in a mixed solution of 1:5 by volume of HClO₄ and C₂H₅OH respectively at 288 K to the level of mirror like surface finish having roughness number (Ra) of ~110 nm. The samples were anodized under constant cell potential condition as per the details given in table 1, which is as per self-ordering regime [Neilsch et al., 2002].

Table 1. Details of the anodization process parameters

S.N.	Electrolyte type	DC Voltage. (V)	Temp. (K)	Time (Hrs.) I step	Time (Hrs.) II step	Sample numbers
1	Sulphuric Acid 0.3 molar.	25	274	10	0.5,	S1 (3 nos.)
					1.0	S2 (3 nos.)
					1.5	S3 (3 nos.)
2	Oxalic Acid 0.3 molar.	40	290	10	0.5,	O1(3 nos.)
					1.0	O2(3 nos.)
					1.5	O3(3 nos.)
3	Chromic Acid 0.3 molar.	40	290	10	0.5,	C1(3 nos.)
					1.0	C2(3 nos.)
					1.5	C3(3 nos.)
4	Phosphoric Acid 0.1 molar.	195	285	10	0.5,	P1(3 nos.)
					1.0	P2(3 nos.)
					1.5	P3(3 nos.)

The solution was agitated using a mechanical stirrer in order to (1) dissipate heat that evolves during the process, (2) homogenize the electrolyte composition in the cell and (3) decrease the double layer thickness formed on the anode surface. The oxide films that formed in the first step was etched away in an aqueous solution of phosphoric acid (6 wt. %) and chromic acid (1.8 wt. %) by heating at 333 K for 10 minutes and this generated dimples on the metal surface. In the second step the anodization was carried out following the same conditions as those of the first anodization step and well-ordered pore structure was obtained in about 30, 60 and 90 minutes of the process. Fast Fourier Transform (FFT) of the FE-SEM images taken from the top surface of the AAO films on the anodized Al coupons were analyzed and for thickness measurement, cross-section of the AAO films were taken and again through FE-SEM the depth or thickness of AAO films were measured. All samples were clamped in a specially designed fixture, depicted in the Fig.2, for viewing cross-section and depth of oxide layer from the direction which was normal to the cross section, so as to eliminate chances of error in depth measurements.

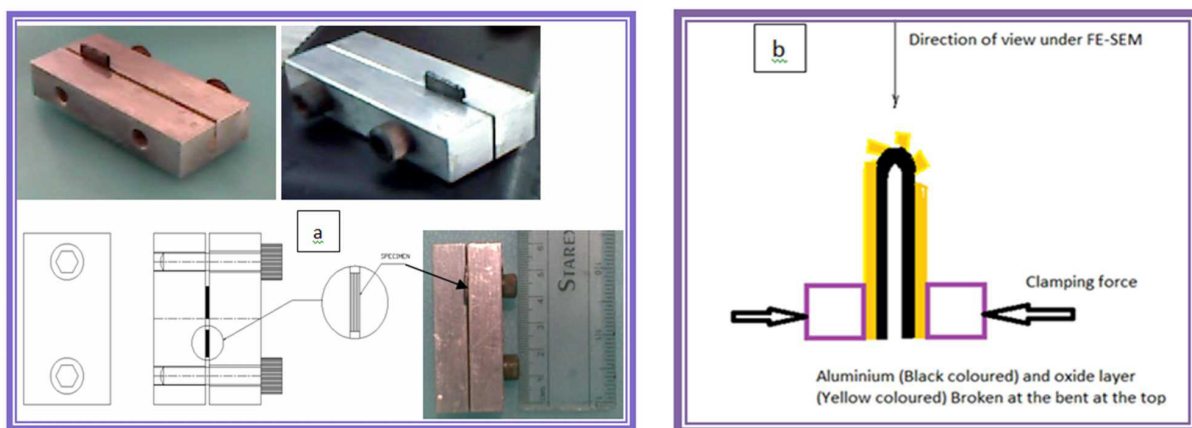


Fig. 2. A special aluminium fixture, as shown above in Fig. 2 (a) was designed and fabricated to secure the V-bent (fractured AAO) specimen for cross-sectional observation under FE-SEM. Fig. 2 (b) depicts the technique.

For observing ordering in the porous structure, conventional method of SEM was followed and samples were viewed from the top surface. Four types of anodizing electrolytes, viz., Chromic, Oxalic, Phosphoric and Sulphuric acids have been used and anodization process parameters have been strictly followed as per self-ordering regime, reported earlier [Neilsch et al., 2002] and the details are given in table no. 1. For all these four electrolytes, nine samples [(3x3) for each electrolyte] were taken so that average of three samples, subjected to same treatment, may be taken for more reliable results. For a given electrolyte, samples were anodized for different time durations (0.5, 1.0 and 1.5 hours) in the second step of anodization so as to determine the optimum time for obtaining thickest films.

3. Results and discussion

The results of samples anodized in four commonly used electrolytes, i.e. chromic, oxalic, phosphoric and sulphuric acids have been presented in Fig. 3. The Top view FE-SEM images of the best one, out of the nine samples having given same treatment has been presented here. However there is no significant difference in the samples anodized in the same electrolyte under the same conditions, except one condition (different time duration in the second step of anodization), i.e. samples S1, S2 and S3 (Pl. refer table 1) have more or less same pore structure and ordering. The figure 3 shows Top views of the samples and their FFTs (Fast Fourier Transforms) in the inset. It can be seen that best pore-ordering is obtained when oxalic acid is used as electrolyte. The FFT in that case is also showing six distinct spots, which the characteristic is of hexagonally ordered porous structure.

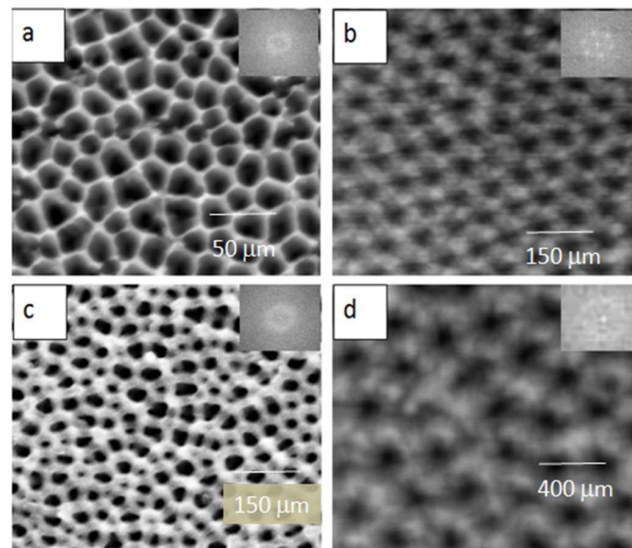


Fig. 3. Selected FE-SEM images of the samples anodized in four electrolytes and their corresponding Fast Fourier Transforms (FFT) in the insets. (a; sulphuric acid, b; chromic acid, c; oxalic acid and d; phosphoric acid).

The second best ordering is achieved when phosphoric acid has been used. The FFT shows a hazy ring type structure. This hazy ring is the result of overlapping of many hexagons. The results of the samples anodized in chromic and sulphuric acid are similar. In both of the cases, the degree of ordered porous structure obtained is lower, which is also evident from their FFTs. The FFTs of both samples are dull rings of greater thickness indicating that the interpore distance distribution is wide and not as narrow as in the case of phosphoric acid. The incorporation of acid anion in the formed AAO film may be the reason for the obtained difference in the degree of ordering. Although it is widely accepted fact that anodization process is very easy to perform but very complex to understand as there are many factors which may affect it. The sizes of the formed pores and interpore distances were approximately same as per the empirical relationship in the open literature, i.e. the pore diameter and interpore

distances are proportional to anodization voltage and the values of these two are 1.3nm per volt and 2.5 nm per volt respectively. In this experiment, anodization voltage for sulphuric acid was 25 V and hence diameter of pores is approx. 33 nm and interpore distance is approx. 63 nm. Similarly the diameter and interpore distances in case of Oxalic and Chromic acids have been found in as 52 and 100 nm respectively. Pore diameter and interpore distance in case of Phosphoric acid have been found as 254 nm and 490 nm respectively, which very well correspond to the empirical relation. The results of thickness measurements for the four types of electrolytes have been shown in the Fig.4 and Fig.5. Fig.4 shows the cross sectional FE-SEM images of the samples, while Fig.5 shows the effect of electrolyte and time of second step of anodization on the thickness of AAO films. The thickest AAO films (15 μm) have been obtained when Oxalic acid has been used as the electrolyte and the duration of second step of anodization is 1 hour. The thickness of AAO in all the four cases have been found to be maximum or constant after one hour of anodization in the second step, indicating that one hour is the optimum time for the process to get thickest films. When anodization is started after dissolution of the formed AAO film that was obtained during the first step of anodization, the pores nucleate from the dimples left in the metal. Initially thickness of nanoporous AAO film is very less. It increases with a constant growth rate, which is higher as compared to dissolution rate. In all of the four electrolytes, Aluminium Oxide is soluble and the chemical reaction decreases the AAO thickness from the top surface which is in direct contact with the electrolyte. After some time, there is dynamic equilibrium in the growth rate and dissolution rate of AAO films and the process attains steady state and it is found that after one hour, the dissolution rate takes over formation rate and hence thickness starts decreasing.

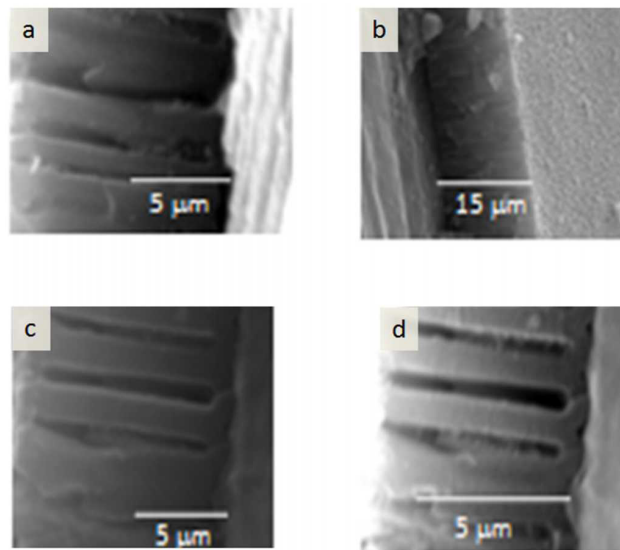


Fig. 4. Selected cross-sectional FE-SEM images of the samples anodized in four electrolytes (a; Sulphuric acid, b; Oxalic acid, c; Chromic acid and d; Phosphoric acid).

Fig.5 shows Plot of the average thicknesses of the AAO films anodized in four electrolytes viz. a; Sulphuric acid, b; Oxalic acid, c; Chromic acid and d; Phosphoric acid vs. anodization time in the second step of anodization. It is found that thickest AAO films have been obtained when electrolyte is oxalic acid and the time in the second step of anodization is 1 hour. Even if anodization is continued for another 30 minutes, there is no increase in thickness as the electrochemical formation rate by anodization is neutralized by chemical dissolution rate of the AAO in this acid.

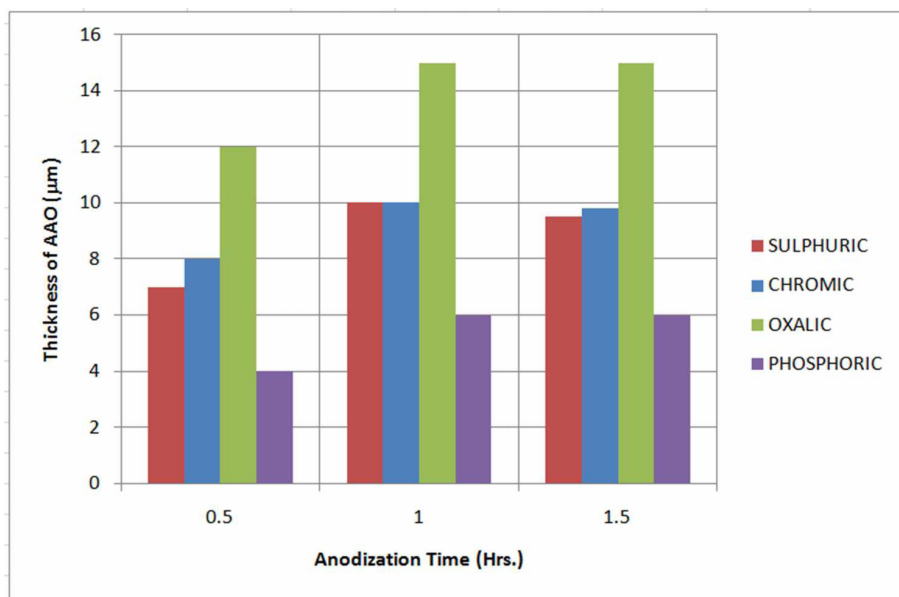


Fig. 5. Plot of the average thicknesses of the AAO films anodized in four electrolytes (a; Sulphuric acid, b; Oxalic acid, c; Chromic acid and d; Phosphoric acid) vs. anodization time in the second step of anodization.

There is decrease in the thickness of the AAO films if anodization is continued after one hour in case of Sulphuric acid and Chromic acid solutions. This may be attributed to the increase in the dissolution rate as compared to the formation rate in these cases, because both of these acids are comparatively more aggressive than the other acids. The AAO thickness decreases from maximum of 10 μm to 9.5 μm and from maximum of 10 μm to 9.8 μm in case of Sulphuric and Chromic acids respectively.

4. Conclusion

Anodization in four commonly used electrolytes was conducted to determine which is the best electrolyte out of Sulphuric acid, Oxalic acid, Chromic acid and Phosphoric acids to get the highest degree of pore ordering and what is the optimum time in the second step of anodization to get the thickest AAO films. It was found that Oxalic acid is the best out of these four electrolytes, giving best ordering and thickest AAO layer and one hour is the optimum time to get maximum thickness under conditions of self-ordering regime for all electrolytes.

Acknowledgements

The author is thankful to late Dr. H.B. Sharda, Ex-Principal, S.B.S. College of Engineering and technology, now renamed as S.B.S. State Technical Campus, Ferozepur, Punjab, India, for relieving him from duty for three years under Quality Improvement Programme (Q.I.P.), for his Ph.D. at I.I.T. Roorkee, India, Q.I.P. centre I.I.T. Roorkee and A.I.C.T.E. (All India Council for Technical Education, India.) for sponsoring him under Q.I.P.

References

- Thompson, G.E. and Wood, G.C. 1983 "Anodic films on aluminium." In treatise on materials science and technology, Vol. 23: Corrosion: Aqueous Process and Passive Films; Scully, J. C., Ed.; Academic Press Inc.: New York, 1983; Chapter 5, 205-329.
- Masuda H, Fukuda K., 1995. Ordered Metal Nanohole arrays made by a two-step replication of honeycomb structure of anodic alumina. *Science*, 268 1466.
- Mutalib, A., Md J., Dusan L., Nicolas, H. Voelcker. 2013. Nanoporous anodic aluminium oxide: Advances in surface engineering and emerging applications, *Progress in Materials Science* 58 636–704,

- Chi L., Zhi, C., 2011. Encyclopedia of Nanoscience and Nanotechnology edited by H.S.Nalwa, v 11 American Scientific Publishers.
- Gerrard, E. J. P., Ali, N. and Fawcett, D., 2011. Progress in Nano-Engineered Anodic Aluminum Oxide Membrane Development materials 4, 487-526.
- Lei, Y., Cai, W., Wilde, G. 2007 Highly ordered nanostructures with tunable size, shape and properties: A new way to surface nano-patterning using ultra-thin alumina masks, Progress in Materials Science 52 465–539
- Diggle, J. W., Downie, T. C., & Goulding, C. W., 1969. Anodic oxide films on aluminum. Chemical Reviews, 69(3), 365.
- Chik H., Xu J.M., 2004 Nanometric superlattices: non-lithographic fabrication, materials, and prospects, Materials Science and Engineering R, 43, 103
- Kushwaha, M.K., Sil, A. Ray, S. 2008. Carbon Nanotube/Nanofiber Embedded Nanoporous Anodized Aluminium Oxide Surface and Its Tribological Properties. Journal of Nanoscience and nanotechnology, American Scientific Publishers 8(8), 4152.
- Li, A. P., Muller, F. and Gosele, U., 2000. Polycrystalline and Monocrystalline Pore Arrays with Large Interpore Distance in Anodic Alumina. Electrochem. and Solid- State Letters, 3, 131.
- Masuda, H. and Hasegawa, F., 1997. Self-Ordering of Cell Arrangement of Anodic Porous Alumina Formed in Sulfuric Acid Solution. J. Electrochem. Soc., 144(5), 128.
- Nielsen, K., Choi, J., Schwirn, K., Wehrspohn, R. B. Gosele, U., 2002. Self-ordering regimes of porous alumina: the 10% porosity rule. Nano Lett. 2(7), 677.
- Masuda, H. and Satoh, M., 1996. Fabrication of Gold Nanodot Array Using Anodic Porous Alumina as an Evaporation Mask, Japanese Journal of Applied Physics, 35, L126.
- Thompson G. E., Wood, G. C. 1983. Treatise on Materials Science and Technology J. C. Scully, (Ed.) Vol. 23, Academic Press, New York, pp. 205-239.
- Sullivan J. P. O and Wood, G. C. 1970. The morphology and mechanism of formation of porous anodic films on aluminium. Proc. R. Soc. London, Ser. A, 317, 511.
- Asoh, H. Nishio, K., Nakao, M., Tamamura, T. and Masuda, H., 2001. Conditions for Fabrication of Ideally Ordered Anodic Porous Alumina Using Pretextured Al. J. of electrochemical society, 148, B152
- Masuda, H., Yada, K. and Osaka, A., 1998. Self-ordering of cell configuration of anodic porous alumina with large-size pores in phosphoric acid solution. Jpn. J. Appl. Phys., 37, L1340- L1342.
- Shingubara, S., Morimoto, K., Sakaue, H., Takahagi, T. 2004. Self-Organization of a Porous Alumina Nanohole Array Using a Sulfuric/Oxalic Acid Mixture as Electrolyte. Electrochem. Solid State Lett. 7, E15.
- Shingubara, S., Okino, O., Sayama, Y., Sakaue, H., and Takahagi, T., 1997. Ordered two-dimensional nanowire array formation using self-organized nanoholes of anodically oxidized aluminum. Jpn. J. Appl. Phys., 36(1) 12 B, 7791
- Jessensky, O., Müller, F., & Gösele, U., 1998. Self-organized formation of hexagonal pore arrays in anodic alumina, Applied Physics Letters, 72, 1173.
- Wojciech, J., Stepniowski, Marta Michalska-Domańska, Małgorzata Norek, Tomasz Czujko. 2014. Fast Fourier transform based arrangement analysis of poorly organized alumina nanopores formed via self-organized anodization in chromic acid. Materials Letters, 117, 69–73
- Sulka, G.D., Parkola, K.G., 2007. Temperature influence on well-ordered nanopore structures grown by anodization of aluminium in sulphuric acid, Electrochimica Acta 52 1880–1888,
- Sulka, G.D., Parkola, K.G., 2006. Anodising potential influence on well-ordered nanostructures formed by anodisation of aluminium in sulphuric acid, Thin Solid Films 515, 338 – 345
- Ba, L. and Li, W.S., 2000. Influence of anodizing conditions on the ordered pore formation in anodic alumina. J. Phys. D: Appl. Phys., 33, 2527
- Rabin, O. Herz, P.R., Lin, Y.m., Akintunde I, Cronin, S. B., Dresselhaus. M.S. 2003. Formation of thick porous Anodic Films and nanowire arrays on silicon wafers and glass. Advanced functional materials, 13, no.8, 631-638
- Wang, H. and Wang, H., 2005. Thick and macroporous anodic alumina membranes for self-lubricating surface composites. Applied Surface Science, 249, 151–156.
- Lee, W., Ji, R. Gosele, U., Nielsen, K., 2006. Fast fabrication of long-range ordered porous alumina membranes by hard anodization. Nature materials, 5, 741-747
- Liu, J., Liu, S., Zhou, H. Xie, C., Huang, Z., Fu, C., Kuang, Y., 2014. Preparation of self-ordered nanoporous anodic aluminum oxide membranes by combination of hard anodization and mild anodization. Thin Solid Films 552, 75–81,