

GLOBAL JOURNAL OF ENGINEERING SCIENCE AND RESEARCHES

OPTIMUM PRETREATMENT CONDITIONS FOR OBTAINING HIGHLY ORDERED ANODIZED ALUMINIUM OXIDE FILM

Harleen kaur^{*1}, Prabhjot Kaur², Lalit Sharma³, Sangeeta Sharma⁴, and Manoj Kushwaha⁵

^{*1,2} Research Scholar, I.K. Gujral Punjab Technical University, Kapurthala, Jalandhar

³ Associate Director, Shaheed Bhagat Singh State Technical Campus, Ferozepur

⁴ Associate Professor, Department of Applied Sciences and Humanities, Shaheed Bhagat Singh State Technical Campus, Ferozepur, Punjab, India

⁵ Professor, Department of Mechanical Engineering, Shaheed Bhagat Singh State Technical Campus, Ferozepur, Punjab, India

ABSTRACT

The surface roughness and surface brightness study of electropolished aluminum films formed by using different electrolytes is reported in present work. Different electrolytes produce films with different morphology and surface smoothness depending upon their nature. The electropolishing [EP] experiments were carried out at 298 K comprises of five types of electrolytes 100 % perchloric acid (HClO₄) [E1], mixture of 1:5 ratio of phosphoric acid (H₃PO₄) and ethanol (C₂H₅OH) [E2], mixture of 1:5 ratio of phosphoric acid and methanol (CH₃OH) [E3], 1:5 ratio of perchloric acid and ethanol [E4] and 2:1 ratio of methanol and nitric acid (HNO₃) [E5] at 15V and the electropolishing time was varied from 1 minute to 6minutes. It has been observed that maximum anodic brightening is obtained by using 100% perchloric acid, whereas maximum anodic leveling is attained by using a mixture of 2:1 ratio of methanol and nitric acid and 3 minutes is the optimum time for electropolishing. The formation of nano porous aluminum membranes by anodisation was also investigated. The regularity of nanopores was analysed after the pretreatment of aluminum.

Keywords: Electropolishing, Surface Roughness, Surface Brightness, Anodisation

I. INTRODUCTION

With escalating significance in the production of nanosized structures useful in electronic, optical, magnetic, sensors and optoelectronic devices, naturally occurring metals have been used as a host or a template. The anodic aluminum oxide (AAO) has been generally used to construct nanometer –sized structures through the template mediated process for the reason that of its quite low cost and simplicity of fabrication as compared to conventional materials which are lithography processed. To attain fine line lithography or ordered pore structure which is desirable for myriad applications, pretreatment step is desirable [1-5]. Several techniques such as degreasing, etching, chemical polishing, annealing and electropolishing, barrel polishing can be used for attaining surface planarization prior to anodisation. Among all the techniques, electropolishing is most effective technique [6-7]. Electropolishing is an electrochemical process which involves a combination of rectified current and a blended chemical electrolyte bath in order to eliminate flaws from the surface of metallic part. It is used to polish, passivate and deburr metallic parts. In basic terms, electropolishing replaces traditional mechanical finishing techniques, including grinding, milling, blasting and buffing [8-9]. The surface phenomenon of EP is usually separated into two categories: anodic leveling as well as anodic brightening. Anodic leveling comes out from a distinction in the dissolution rate in between peaks and valleys on a surface of rough metal which depends on the conditions of current distribution or mass transport. It is generally connected with a reduction of roughness in the micrometer or large array which directing to the ordered nanopore array. Alternatively Anodic brightening can only be realized under the circumstances in which the metal dissolution is mass transport controlled and the formation of a precipitated salt layer at the electrode surface is possible. The effect of crystallographic orientation and surface flaws on the dissolution method can be restrained by the existence of salt layer. This process leads to micro finishing in the scale of sub micrometer and specular reflectivity of metallic surface can be carried out [10-14]. The collective properties of high reflectivity lead to the

use of aluminum in a multiplicity of optical devices such as lasers, solar powered cells, interferometers, and biomedical instruments.

In literature, electropolishing (EP) technique by L1 solution i.e. mixture of 62cc perchloric acid, 700cc ethanol, 100cc butyl cellulose and 137cc distilled water has been studied extensively [15-17]. The problem remaining is whether the polishing of aluminum is restricted to a particular kind of film morphology or whether the Physico-chemical properties of the film are of prime significance. The present work depicts the study of variety of different electrolytes used on the brightness as well as surface smoothness on aluminum surface.

II. EXPERIMENTAL

2.1. Sample preparation

Aluminum specimens were cut from 99.99% pure sheet, 0.4 mm thick, into rectangular shape having the dimensions of 10 cm x 2 cm. After cutting; samples were first degreased in ethanol for 200 s, then washed in deionized water and air-dried. These samples were then annealed at 673 K for 2 hrs in temperature controlled silicon carbide tube furnace and then cooled for 22 hrs. Annealing is necessary to improve the homogeneity of the aluminum substrate for well ordered pore growth, by increasing grain size, thus minimizing grain boundary area which is considered as a defect and eliminating residual stresses obtained as a result of rolling. After annealing the specimens were coated with lacquer leaving an area of 1x1 cm and air dried for 12 hrs. To prevent the melting of lacquer during electropolishing the area was covered by firmly by black tape, except an exposed area, so that rest of the aluminum surface becomes insulator.

2.2. Potentiodynamic Measurements

Electropolishing tests were carried out in a rectangular container of borosilicate having the dimensions of 5 cm x 10 cm. During electropolishing the samples were used as the working electrodes with an exposed area 1 cm x 1 cm, the electrical circuit consisted of 15V D.C. potentiostat. Five types of solutions E1, E2, E3, E4, and E5 were used to study the effect on the surface of Aluminum during EP. The temperature was maintained at 25°C by thermo stated circulation of water by electrochemical cell and the time of electropolishing was varied from 1 minute to 6 minutes.

Table 1. Different Electrolytes used in Electropolishing

S. No.	Type of Solution	Composition of Solution
1.	E1	100% HClO ₄
2.	E2	Mixture of 1:5 ratio of H ₃ PO ₄ and C ₂ H ₅ OH
3.	E3	Mixture of 1:5 ratio of H ₃ PO ₄ and CH ₃ OH
4.	E4	Mixture of 1:5 ratio of HClO ₄ and C ₂ H ₅ OH
5.	E5	Mixture of 2:1 ratio of CH ₃ OH and HNO ₃

2.3. Anodization

The Anodization of aluminum was carried out in the 0.03M solution of phosphoric acid at direct current (DC) voltage of 160V at temperature 20±2 °C for about 1 hr after electropolishing with E1, E2, E3, E4 and E5; thereafter an anodic oxidized film with uniform thickness was obtained.

2.4. Characterization

The average surface roughness factor (R_a) was measured with the help of Surfest SJ-210, MITUTOYO portable surface roughness tester.

Morphology of electropolished and anodized alumina was analyzed by field-emission scanning electron microscope SEM JEOL, JSM-6610LV. Optical profilometer was used to analyse surface statistics of electropolished aluminum substrate. Formation of anodic film was investigated with the help of EDS (Energy Dispersive Spectroscopy) technique.

III. RESULTS AND DISCUSSION

3.1. Surface Roughness Testing

Electropolishing is a surface finishing process by which a metal surface is made smooth and bright by making it an anode in an appropriate electrolytic solution. Electropolishing involves mass transport control mechanism. As viscous layer of concentrated electrolyte is formed during electropolishing under which there lies an oxide layer.

This viscous layer conditions the high dissolution rate of the metal surface. The process involves the transition of metal ions over the phase boundary of metal surface and oxide layer through the oxide layer and finally through the viscous layer.

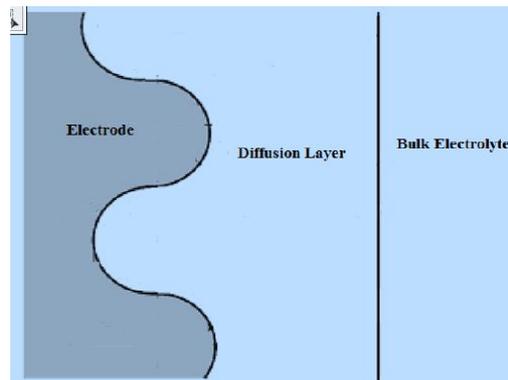


Figure 1. Schematic Diagram of Al during Electropolishing

To characterize and compare the surface roughness by using different electrolytes under same conditions, different techniques such as Surface roughness tester, FE-SEM and Optical profilometer was used. Table 2, 3, 4 and 5 shows the values of average roughness of electropolishing at 25°C by using E1, E2, E3, E4 and E5 respectively at 15V and time period ranging from 1 to 6 minutes. It has been observed that as the time increases roughness of the surface first decreases and then increases slightly. This may be due to the resistance to the rate of mass transfer of Al^{+3} ions from anode surface to bulk solution.

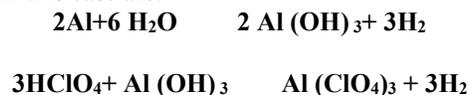
In first case, electropolishing was carried out by using E1 solution at 15V having temperature 308K and time period varying from 1 to 6 minutes. Minimum roughness value of $0.187\ \mu\text{m}$ is obtained at 3 minutes as shown in table 2.

Table 2. Surface Roughness Value by using 100% HClO₄

S. No.	Time (In minutes)	Surface roughness (R _a in μm)
1.	1 minute	0.388
2.	2 minutes	0.226
3.	3 minutes	0.187
4.	4 minutes	0.278
5.	5 minutes	0.279
6.	6 minutes	0.278

After 3 minutes, there is a slight increase in the roughness value and then becomes constant up to 6 minutes. This can be explained on the basis of super-saturation of the salt forming in case of the salt film mechanism of electropolishing. Oxygen bubbles formed may attach to the surface and cause occlusion of the surface at certain locations in differing dissolution rates.

Electrochemical reactions involved in this case are:



The perchloric acid is used to attain the lower pH to ensure that Aluminum ionizes into Al⁺³ and does not form other ions or oxides in the electrolytic bath. Thus, the perchloric acid acts essentially as a catalyst on the metal that release the Al⁺³ ions. Water molecules are the bulk acceptor molecules that provide the necessary ions to react with Al⁺³ released by the dissolving Aluminum anode during electropolishing.

Surface morphology of the substrate was determined by Scanning electron microscope as shown in figure 2. Strip like pattern is observed in this case.

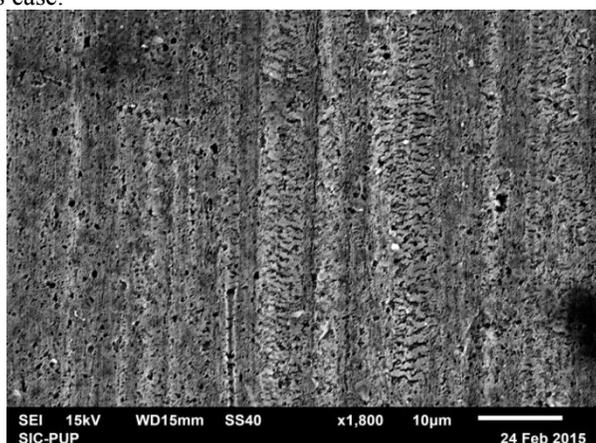


Figure 2. SEM Image of Electropolishing of Al by using 100% HClO₄ at 15V for 3 minutes

Brightness has been attained I at utmost level just like mirror surface. Figure 3 depicts optical profilometry view and detailed statistics of the surface of electropolished aluminum substrate by using E1

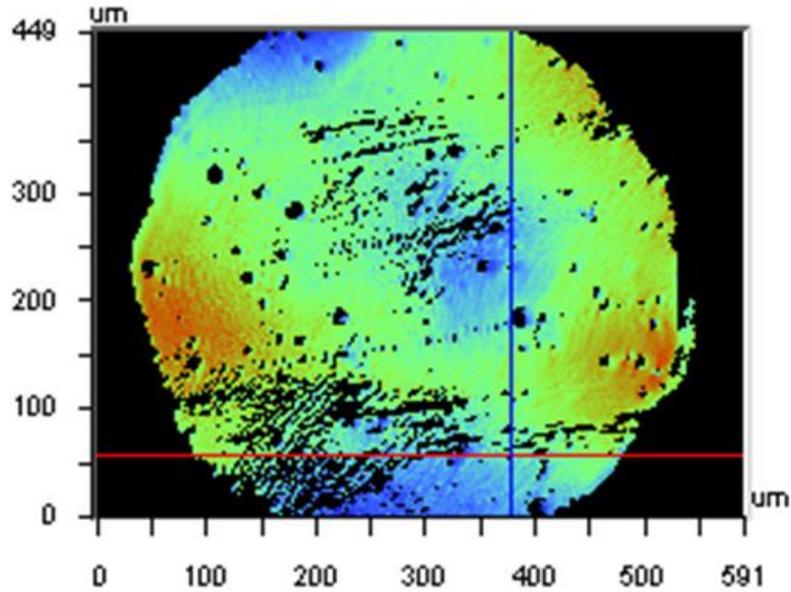


Figure 3. Optical Profilometry View of Electropolished Sample by using 100% HClO₄

Table 3. Surface Statistics Analysis from Optical Profilometer

Surface Statistics	Set-up Parameters
Ra: 280.80 nm	Size: 368 x 240
Rq: 357.16 nm	Sampling: 1.61 μm
Rz: 2.58 nm	
Rt: 2.85 μm	

In second case, a process of electropolishing was carried out by using E2 and E3 at 15V with temperature of 308K. Minimum surface roughness value of 0.040 μm and 0.283 μm has been achieved after 3 minutes by using E2 solution and by using E3 respectively as shown in table 4.

TABLE 4. Surface Roughness Value by using a Mixture of 1:5 Ratio of H_3PO_4 and C_2H_5OH and by using Mixture of 1:5 Ratio of H_3PO_4 and CH_3OH .

S. No.	Time (In minutes)	Surface roughness (R_a in μm) by E2	Surface roughness (R_a in μm) by using E3
1.	1 minute	0.037	0.454
2.	2 minutes	0.044	0.325
3.	3 minutes	0.040	0.283
4.	4 minutes	0.042	0.293
5.	5 minutes	0.043	0.293
6.	6 minutes	0.043	0.295

In both cases phosphoric acid supports the metal dissolution and together with ethanol and methanol facilitates the formation of the viscous layer.



Surface brightness obtained by using E2 and E3 in both the cases is dull as compared to surface obtained in case of E1 but a slight difference in the surface smoothness values obtained after the electropolishing by using E2 and E3 as shown in table 4. This comparison shows that electropolishing by using ethanol with phosphoric acid gives more smoothness than that of methanol.

In fourth case, electropolishing was carried out by using E4 mixture at 15 V with electrolyte temperature 308 K which is mostly used by the researchers as a pretreatment of Aluminum prior to anodisation for attaining ordered nanopore array. Table 4 shows that the minimum surface roughness value of 0.186 μm is obtained after 3 minutes.

Table 5. Surface Roughness Value by using a Mixture of 1:5 Ratio of $HClO_4$ and C_2H_5OH

S. No.	Time (In minutes)	Surface roughness (R_a in μm)
1.	1 minute	0.275
2.	2 minutes	0.225
3.	3 minutes	0.186
4.	4 minutes	0.212
5.	5 minutes	0.212
6.	6 minutes	0.213

The role of perchloric acid is to attain the low pH to make certain that Al ionizes into Al³⁺ and does not form other ions in the anodic reaction, water and ethanol molecules are the shielding molecules that can reduce ion flux and/or stabilize surface Al atoms. Brightness obtained in this case is more as compared to second and third case but lesser than that of case 1.

In last case, electropolishing was carried out by using E5 mixture again at 15 V with electrolytic temperature of 308K. Table 6 shows that minimum surface roughness value of 0.030 μm is obtained again at 3 minutes which is maximum smoothness as compared to other electrolytes used as shown in table 5.

Aluminum reacts with Nitric acid to give aluminum nitrate and hydrogen gas is evolved at cathode.

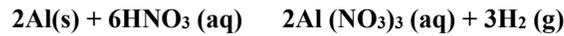


Table 6. Surface Roughness Value by using a Mixture of 2:1 Ratio of CH₃OH and HNO₃

S. No.	Time (In minutes)	Surface roughness (R _a in μm)
1.	1 minute	0.046
2.	2 minutes	0.036
3.	3 minutes	0.030
4.	4 minutes	0.052
5.	5 minutes	0.053
6.	6 minutes	0.053

Brightness of the surface obtained in this case is lesser than by using 100% HClO₄, but surface smoothness obtained is maximum in this case as shown in above table. The surface morphology of electropolished Aluminium by using E5 was studied by SEM, as shown in Figure 2. Sponge like particles due to the accumulation of electrolyte at some places has been obtained.

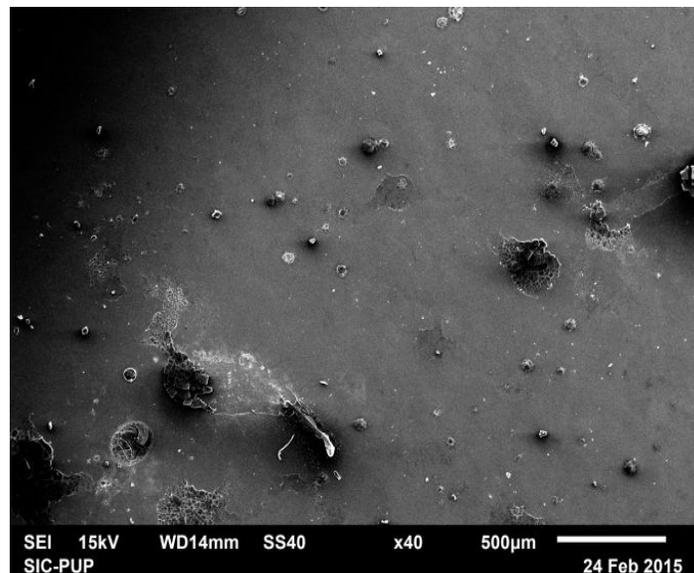


Figure 4. SEM image of Electropolished surface by using 100% HClO₄

Comparison of surface smoothness with time by using different electrolytes as explained above is shown in figure 3. Graph clearly shows that 3 minutes is the optimum time for electropolishing. Maximum depth in curve is obtained in case of electropolishing by using 2:1 ratio of CH₃OH and HNO₃.

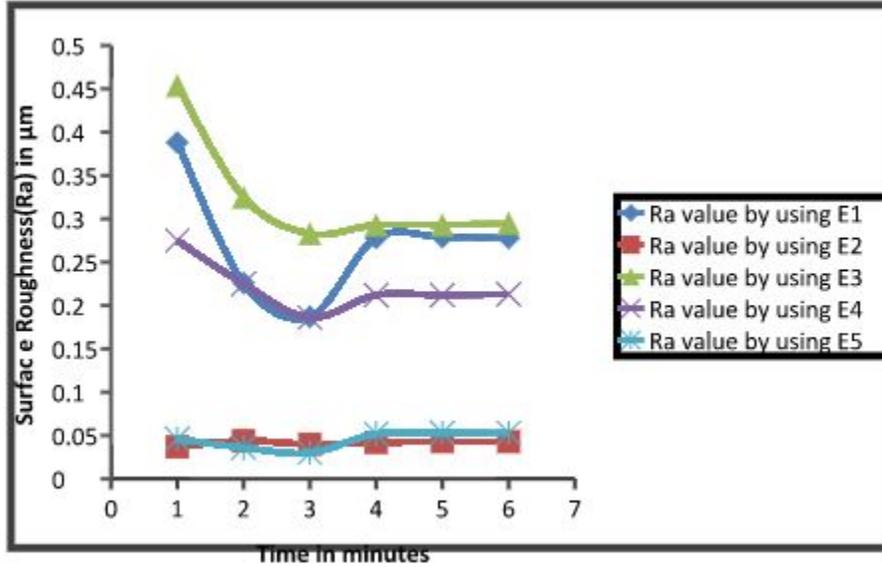
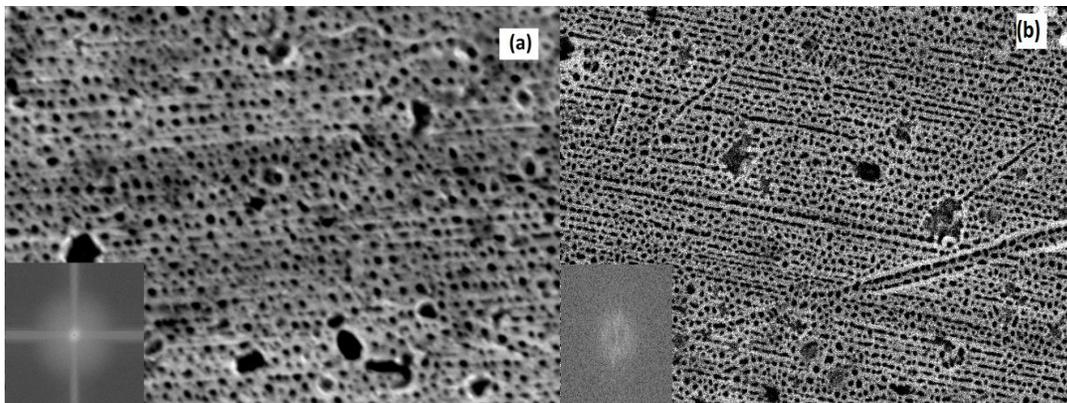


Figure 5. Graph Showing the Values of Surface Roughness by using Different Electrolyte

3.2. Scanning Electron Microscopy

The dependence of regularity of pores on pretreatment with different electrolytes has been studied by SEM. FFT (inset in the SEM image) clearly shows the morphology of the anodic porous alumina layer grown after electropolishing with E1, E2, E3, E4 and E5 respectively in figure 6. It is clearly observed that more the smooth surface provided by the electrolyte used in pretreatment, more will be the regularity ratio of pores formed during electrochemical oxidation as shown in figure e with six hexagonal spots confirmed by FFT with the help of Image J Software.



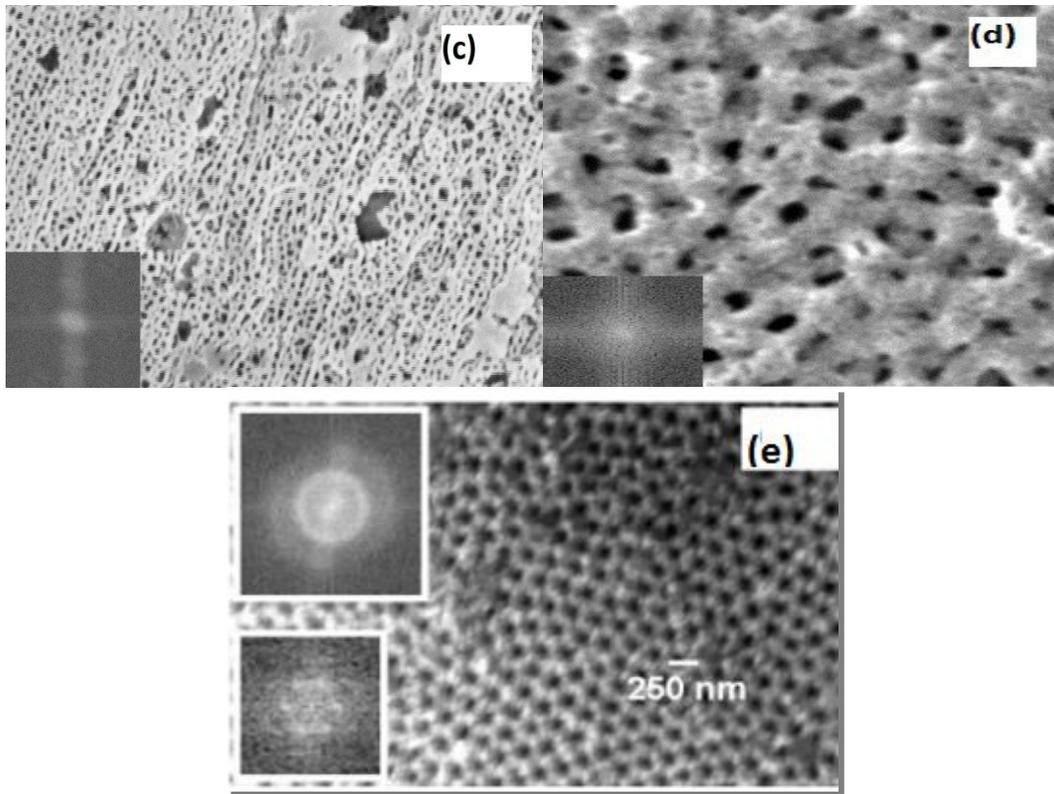


Figure 6. Anodized Sample Formed after Electropolishing by using (a) 100% HClO_4 (b) mixture of 1:5 ratio of H_3PO_4 and $\text{C}_2\text{H}_5\text{OH}$ (c) mixture of 1:5 ratio of H_3PO_4 and CH_3OH (d) mixture of 1:5 ratio of HClO_4 and $\text{C}_2\text{H}_5\text{OH}$ (e) mixture of 2:1 ratio of CH_3OH and HNO_3 (One Additional FFT taken from Selected Area Is Clearly Showing Six Distinct Hexagonal Spots)

3.3. Energy dispersive x-ray (EDX) spectroscopy

EDS Spectra confirmed the presence of Aluminum at 1.2 keV, because of pure aluminum metal template used. Peak of Phosphorus at 2 keV is also attributed which confirms the formation of nanopores with phosphoric acid. Beside of Al and P there are some other peaks of K, C, O, Na which appeared due to composition of Aluminum surface.

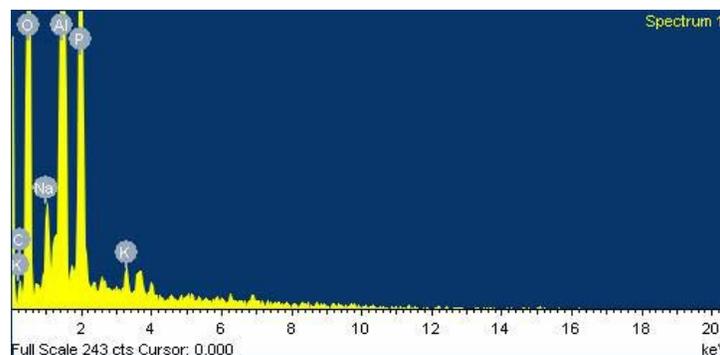


Figure 7. shows the Energy Dispersive Spectroscopy analysis of aluminum oxide. The EDS identifies that the anodic film contains the elements such as C, O, Na, Al, P and K. This proves that anodic layer was formed in the phosphoric acid solution

IV. CONCLUSION

Polishing by using different electrolytes produces films having different surface roughness and brightness depending on the electrolyte used. It has been concluded that 3 minutes are sufficient to obtain best surface smoothness as well as brightness by using different electrolytes. The present results shows that maximum surface smoothness is obtained by using 2:1 ratio of CH₃OH and HNO₃ at 15V with electrolytic temperature of 308 K at 3 minutes which leads to ordered nanoporous structure. On the other hand best surface brightness is obtained by using 100% HClO₄ at 15V with electrolytic temperature of 308 K at 3 minutes. Thus, it has been observed that sufficient ionic conductivity is required in the surface film to produce smooth and bright surface.

V. ACKNOWLEDGEMENTS

The authors gratefully acknowledge to I.K. Gujral Punjab Technical University, Kapurthala, Jalandhar for its valuable inputs on presented research. Also, the support given by Dr. T.S. Sidhu, Director of Shaheed Bhagat Singh State Technical Campus, is appreciatively acknowledged for build up experimental setup.

REFERENCES

1. H. Masuda, M. Satoh, *Japanese Journal of Applied Physics.*, **35**, (1996), L126.
2. P.R. Evans, G. Yi, W. Schwarzacher, *Applied Physics Letter.*, **76**, (2000), 481.
3. F. Li, R.M. Metzger, W.D. Doyle, *IEEE Transaction of magnetics.*, **33**, (1997), 3715.
4. O.K. Varghese, D. Gong, M. Paulose, K.G. Ong, C.A. Grimes, E.C. Dickey, *Journal of Material Research.*, **17**, (2002), 1162.
5. H. Asoh, M. Matsuo, M. Yoshihama, S. Ono, *Applied Physics Letter.*, **83**, (2003), 4408.
6. P. Neufeld, D.M. Southall, *Electrodeposition of Aluminium.*, **3**, (1975), 159.
7. H. Adelhani, S. Nasoodi, A.H. Jafari, *International Journal of Electrochemical Science.*, **4**, (2009), 238.
8. K.M. Alam, A.P. Singh, S. Bodepudi, S.Pramanik, *Surface Science.*, **605**, (2011), 441.
9. K.Saito, H. Inoue, E. Kako, T. Fujino, S. Noguchi, M. Ono, T. Shishido, *Particle Accelerators.*, **60**, (1998), 193.
10. G. kwon, Y. Kim, E. Moyon, D-H Keum, Y-H Lee, S. Baik, D. Pribat, *Applied Surface Science.*, **307**, (2014), 731 .
11. J.Tousek, *Electrochimica Acta.*, **22**, (1977), 47.
12. A-A Taha, A.-M. Ahmed, H-H Rahman, F-M Abouzeid, *Applied Surface Science.*, **277**, (2013), 155.
13. K.Kontturi, *Journal of Applied Electrochemistry.*, **19**, (1989), 76.
14. W.C.Elmore, *Journal of Applied Physics.*, **10**, (1939), 724.

15. S. Bandyopadhyay, A. Miller, H. Chang, G. Banerjee, V. Yuzhakov, D. -F. Yue, R. Ricker, S. Jones, J. Eastman, E. Baugher, M. Chandrasekhar, *Nanotechnology.*, 7, (1996), 360.
16. R. Ricker, A. Miller, D.F. Yue, G. Banerjee, S. Bandyopadhyay, *Journal of Electronic Materials.*, 25, (1996), 1585.
17. D. Ma, S. Li, C. Liang, *Corrosion Science.*, 51, (2009), 713.