Eng. & Tech. Journal, Vol. 28, No. 16, 2010

Laser Surface Treatment for Anodizing Process of Aluminum Alloy

Ali.A.Abdul Hadi*

Received on: 22/2/2010
Accepted on: 3/6/2010

Abstract

Laser material processing play important role to improve surface properties, in this work Aluminum AA1100 was used to build Al_2O_3 oxide layer on the main surface of the workpiece in H_2SO_4 acid at cell potential between 8-24 volts for 30 minutes after irradiated the surface test by pulsed Nd-YAG laser, fluctuating current was measured with time without laser treatement and after laser treatment, Pulsed Nd-YAG laser was used to test the resistance oxide layer to break. This paper gives results of the experimental research referring to the quality of surface indicator obtained by laser surface treatment.

تأثير المعاملة السطحية بالليزر على عملية انودة سبيكة الالمنيوم

الخلاصة

ان المعاملات السطحية بوساطة الليزر تلعب دور مهم في تحسين خواص السطح . في هذا البحث تم استخدام سبيكة الالمنيوم AA1100 لبناء طبقة اوكسيدية من AL_2O_3 في عملية الانودة على السطح الاصلي للسبيكة في محلول H_2SO_4 والمشوب بكريتات بوتاسيوم الالومونيوم المائية $KAl(SO4)_2.12H_2O$. جهد الخلية الكيميائية المستخدم لتكوين الطبقة بين 8-24 فولت لمدة 30 دقيقة. ليزر Nd-YAG النبضي استخدم في المعملة السطحية للسبيكة قبل عملية تكوين الطبقة الاوكسيدية.تم قياس تذبذب التيار مع الزمن للعينات المعاملة سطحيا بالليزر والغير معاملة. Nd-YAG ليزر استخدم في فحص قابلية الطبقة الاوكسيدية للتكسر للعينات المعاملة سطحيا بالليزر والغير معاملة. هذا البحث يعطي نتائج عملية لنوعية الطبقة الاوكسيدية الناتجة بعد المعاملة السطحية بالليزرمن حيث مقاومة التكسر تحت اشعة الليزر.

Introduction.

Laser can be characterized by physical parameters such as spatial and temporal properties of the output light, the active element producing the light, the pumping method and resonator design [1]. Laser can deliver very low (~mW) to extremely high(1-100kW) focused power with a precise spot size/dimension and interaction/pulse time(10^{-3} to 10^{-15}s) on to any kind of substrate through any medium [2]. As well as processing materials by thermal modes, the interaction between the photons of the laser beam and atoms in materials enables processes to be performed thermally (without heat): bonds can be made and broken. The beam can be manipulated with optical components to perform a variety of operations simultaneously, or switched between locations for sequential processing [3]. Laser has

* Laser and Optoelectronics Engineering Department, University of Technology/Baghdad

https://doi.org/10.30684/etj.28.16.2
2412-0758/University of Technology-Iraq, Baghdad, Iraq

some unique properties for surface heating. The electromagnetic radiation of the laser beam is absorbed within the few atomic layers for opaque materials, such as metals, and there are no associated hot gas jets, eddy currents or even radiation spillage outside the optically defined beam area [4].

The range of surface treatment processes available goes all the way from transformation hardening, annealing, shock hardening and bending (as processes which do not involve melting) to processes which involve melting such as surface melting, surface alloying, surface cladding and those processes which involve some form of photochemistry such as laser chemical vapor deposition, laser physical vapor deposition and stereo lithography. One of these processes laser annealing [5][6]

The intense heat that laser may produce on solid matter enables several types of ultrafast, and economical processing of material that are distinctly advantageous from the quality, productivity and efficiency point of view than that possible with their conventional counterparts. Laser processing of steel is well established in automotive industry [4] recently interests have focused on laser heat treatment of lightweight aluminum alloys. The attraction of lightweight metals is in the high strength to weight ratio and consequential improvement the mileage [7].

Laser material processing is depending on how much energy will absorb during the process. Absorption energy in other word is number of pulses or exposure time that related to the application and material surface properties. Each material has absorption curve according to wavelengths, at specific wavelength the absorbed energy will reach to the maximum value, under normal work condition the absorption energy will be less than what in the theoretical process because of the micro surface undulation and surface color have server effect on how much energy will really absorb inside material.

This paper will report on local laser heat treatment of aluminum and the investigation on the quality of anodizing oxide layer before and after laser annealing according to fluctuating of current at different voltage values.

Theory

Anodizing developed in the early 1930’s [8], it has greatly extended the applications of aluminum in products and uses where the metal might otherwise not be utilized. The finish is readily available from finishing job shops throughout the world and is relatively inexpensive.

Anodizing converts the surface of aluminum to an oxide. While aluminum naturally forms aluminum oxide on its surface, this is a very thin film. Anodizing provides a much thicker oxide coating several mils thick if required.

In anodizing process the voltage can have sever affect on the anodizing, a much higher voltage that of conventional anodizing is employed in a hard anodizing process, because the input resistance of the immersed system has as increased resistance at low temperature which required more voltage to a achieve a given current level in the system. Usually such voltage cannot be initially applied to the articles being anodized the initial voltage is usually more than about 10-20 volts since at higher voltage a deteriorated oxide coating is produced or the aluminum article can start burning which is the catastrophic dissolving of the aluminum[9].

Time of anodizing process, in other word the thickness of oxide layer is proportional with current density and on the total time of anodizing process [10]

The anodizing process itself is differ from metal to another for example the anodizing of Cu depends on the deposit the anodic layer on the cathode pole and in aluminum the anodic layer will deposit on the anode pole.

The process of anodizing is depending on the type of alloy, the respositvity of aluminum alloy is differing from alloy to another Table (1 & 2) [11].

The oxide layer (Al_2O_3) its shows high corrosion and wear resistance also high adhesive with material compare with other types like F_2O_3.

Corrosion is degradation of material properties or mass over time due to environmental effects [12]. The series sequences of the corrosion process have become a problem of worldwide significance. The costs attributed to corrosion damage of all kinds have been estimated to be of the order of 3 to 5 percent of industrialized countries gross national product.

Aluminum is a relatively expensive metal because its extraction from the mineral, bauxite, is energy intensive. Pure alumina is extracted from bauxite in the *Bayer* process, by dissolution in sodium hydroxide from which it is precipitated, calcined and used as feedstock in the *Hall-Herault* high temperature electrolytic reduction process to recover aluminum metal [13].

Aluminum oxide can be formed in air ascribed to the large negative Gibb's free energy changes [15].

$$2Al(s)+3/2O_2(g) \longrightarrow \alpha Al_2O_3(s) \; ; \; \Delta G° = -1582 \text{ kJ/mol}$$

$$2Al(s)+3H_2O(l) \longrightarrow \alpha Al_2O_3(s)+3H_2(g) \; ; \; \Delta G° = -871 \text{ kJ/mol}$$

If aluminum is electrochemically anodized, an oxide grows at the anode electrode.

$$2Al(s)+3H_2O(l) \; Al_2O_3(s)+6H^+ +6e^-$$

and hydrogen evolves at the cathode

$$6H^+ +6e^- =3H_2(g)$$

s is solid
l is liquid
g is gas

This explains that the reaction at the anode electrode (Al) [15].

Experimental Part.

The basic experimental procedure is Q switched Nd-YAG laser system, $3x10^{9}$ pulse duration with focal length 10 cm was used in heat treatment to the surface of AA 1100 of Aluminum. In this study samples were used in 1mm sheet unionized aluminum workpiece thickness, were half these samples subjected to 700mJ energy of laser beam before anodizing process can go up the surface temperature to 420°C equation (1)[19] and other part were not irradiated.

$$T_s = T_o + 2I\frac{(1-R)}{K}(\frac{Nt}{\pi})^{\frac{1}{2}} \quad \ldots(1)$$

Where T_o : initial surface temperature (K), I : power density $6.5*10^8$ (J/cm^2), R : reflectivity (%), K : thermal conductivity (W/m.k), N : thermal diffusivity (m^2/s) and t : pulse duration (s).

In anodizing process The electrolytic solution that was used to produce Al_2O_3 Layer was prepared by using 6.61×10^{-3} mole of H_2SO_4 and 2 mole of $KAI(SO4)2.12H_2O$ which are dissolved in 200 ml of distilled water. The electrolytic solution temperature started at 25C° and ended by 90C° during anodizing process. Multi voltages from DC power supply applied to the samples that immersed in electrolytic solution fig (A1).

The anodizing test time used for all samples is 30 minutes. Applied voltages are started at 8, 11, 13.5, 15.5, 19, 21, 24 volts before laser treatment and after laser treatment same applied voltages sequence was applied.

360mJ Pulsed Nd-YAG laser beam was used to destroy the Al_2O_3 layer.

The reflectivity of aluminum and other types of material fig (A2) explains how much light can absorb under different wavelengths [16].

Reflectivity is difficult to control due to the process its self causing variation in the surface reflectivity ,once the material becomes hot the reflectivity is reduce due to the increased phonon concentration, as is indicated in the Bramsen eqation[4]

$$\varepsilon_\lambda = 0.365\left(\frac{\rho_r(T)}{\lambda}\right)^{1/2} - 0.667\frac{\rho_r(T)}{\lambda} + 0.006\left(\frac{\rho_r(T)}{\lambda}\right)^{3/2} \quad \ldots.(2)$$

$Pr(T)$ Electrical resistivity at temperature T°C.

ε_λ (T) Emissivity at T°C to radiation of wavelength . λ.

The emissivity It is a measure of a material's ability to radiate absorbed energy, A true black body would have an $\varepsilon = 1$ while any real object would have $\varepsilon < 1$, if The electrical resistivity of aluminum at 25°C (starting temperature) is $2.8*10^{-8}$ Ω.m and the electrical resistivity of aluminum at 420°C (aluminum annealing temperature) is $7.2*10^{-8}$ Ω.m, the emissivity at 25°C is 0.0417 and at 420°C is 0.0437.

The predominant adhesion force of tiny particles smaller than 50 µm on a dry surface is due to Van der Waals force [17]. The adhesion force, *Fa*, for a spherical particle on a flat substrate surface with a certain deformation at the particle-substrate interface is given by [17].

$$F_a = \frac{h\,r}{8\pi Z^2} + \frac{h\,r_a^{\,2}}{8\pi Z^3} \qquad \ldots(3)$$

Where *h* is the material-dependent for Al_2O_3, *r* is the particle radius, *ra* is the radius of the adhesion surface area and *Z* is the atomic separation between the substrate surface and the bottom surface of the particle respectively. The Lifshitz-Van der Waals constant, *h*, for a aluminum oxide particle on aluminum substrate is 4.68 eV [17], which corresponds to 7.498189904e-19 J. For Van der Waals bonded crystals, *Z* is approximately equal to 4A° [17]. Assuming that the diameter of the aluminum particle is 10 µm and the diameter of adhesion area between an aluminum oxide particle and aluminum substrate is 5% of particle diameter, then *r*, *ra* are 5.0×10-4 cm and 0.25×10-4 cm respectively. From Eq. (3) and the above values, the adhesion force between the aluminum oxide particle and the aluminum substrate is approximately 2.3 dyne.

The current density passing across the oxide film can be written as [18]

$$j = j_a + j_c + j_e \qquad \ldots(4)$$

where j_a, j_c and j_e are the anion-contributing, cation-contributing and electron-contributing current density, respectively. Since the electronic conductivity in the aluminum oxide is very low, the ionic current density ($j_i = j_a + j_c$) is the predominant mode to transport the charges. The relationship between the ionic current, j_i, and the electric field, *E*, can be expressed in terms of the Guntherschultze-Betz equation

$$j_i = j_0 \exp(\beta E) \qquad \ldots(4)$$

where both j_0 and β are temperature- and metal-dependent parameters. For the aluminum oxide, the electric field *E*, j_0 and β are in the range of 106 to 107 V/cm, 1 × 10−16 to 3 × 10−2 mA/cm2 and 1×10^{-7} to 5.1×10^{-6} cm/V, respectively. Based on the Guntherschultze-Betz equation[18], the rate-limiting steps of the film formation are determined by the ionic transport either at the metal/oxide interface, within the bulk oxide or at the oxide/electrolyte interface.

Results and Discussion.

When the two dissimilar metals come into contact, the electrical loop is closed, and the natural voltage differential between them causes electron flow. One metal will become the anode (negative) and one will become the cathode (positive) In the simplest terms, this electrical circuit causes the anode to lose ions and the cathode to gain ions. This process slowly consumes the anode (galvanic or dissimilar metal corrosion) and effectively strengthens the cathode against corrosion.

The result obtained after laser treatment there is significant change in quality of Al_2O_3 Figure (16) shows from (1-2) pulses are needs to destroy oxide layer according to applied voltage, after laser treatment Figure (17) illustrated (1-3) pulses to destroy the oxide layer according to applied voltage. Al_2O_3 layer prove strong resistance to the laser beam compare to it before laser treatment especially at the higher volts, laser beam before anodizing process play an important role to make the surface microstructure almost free from all the surface stress and close most of micro vacancies that formed during manufacture process and that give homogeneous distribution of ions on the surface.

Figure(1) there is no change in current level also the oxide layer can easily to removed by laser , Figure(8) after laser treatment some changes in current level was appeared after 20 minutes but still below the threshold line and ineffective growth of the oxide layer.

The anodizing process at low applied voltage which is compose of DC component leads to cooled electrolyte solution which can have relatively low acid concentration, Strong anodized layer are provided from homogeneous structure. Increasing bath temperature during anodizing process will not effect on degradation of layer.

Figure (9,10, and 11) it shows current fluctuating, oxide layer forming still easy to remove, increasing applied voltage to 19 volts Figure (12) shows after 10 minutes past of anodizing time there is steady in increasing current, oxide layer shows more strong to laser power because of layer homogeneous and start become thick.

Figure (13, 14) shows there is dropping in current level this explain during oxide layer formation with time it become much thicker and more homogeneous and that will gives higher resistance to workpiece.

In general there is degradation of measuring current after laser surface treatment, according to OHM law there is increasing in resistance that related to thickness.

Anodizing surface and removed area of aluminum oxide layer are shown Figure (A3 &A4) the bright surface it appears after laser treatment.

Conclusions.

1) The anodizing process is depending on the applied voltage during the process
2) Laser surface heat treatment before anodizing to the AA1100 alloys will increase the quality of anodizing process especially at high voltage.
3) At low voltage there is possibility to form oxide layer but it's very thin and easily to remove.
4) At high voltage the value of fluctuating current become less than low voltage.
5) $KAI(SO4)2.12H_2O$ play very important role in forming and the quality of oxide layer.

Refrences.

[1]- J.Ready, "Hand Book of Laser Materials Processing", Laser Institute of Amerca,(2001).

[2]- J.Dutta, I. Mann, "Laser Processing of Materials" , Sadhana, Vol.28, Parts 3 & 4, June/August 2003, pp. 495–562.

[3]- J.Ion, "laser processing of Engineering Materials", Elsevier,(2005)

[4]- W.Steen, "laser material processing", springer,(1991).

[5]- E. Kannatey, "Principles of Laser Material Processing", Willy. (2009).

[6]- W.M. Steen, K.G.Watkins, "Coating by laser surface treatment",

Journal de Physique 111, Volume 3, December,(1993)

[7] - K. H. Leonga, K.R.Saboa, "Laser Welding of Aluminum Alloys", Tecnology Development,Cp 90783, Feb.(1997).

[8]- Anodic oxidation of aluminum and its alloys, In Information Bulletin, vol. 14. London: The Aluminum development association, (1948).

[9]- M. Lerner,B. James, " Low voltage Hard Anodizing Process" , United State Patent.(4,133,725), jun.(1979).

[10]-R. Forneaux, W.Ragby, "Porous Anodic Aluminum Oxide Film", United state Patent.(4,859,288), Aug.(1989).

[11]-V.F.Henley, "Anodic Oxidation of Aluminum & its Alloys", Pergamon Press,(1982).

[12]-P. Schweitzer, "Fundamentals of Metallic Corrosion" CRC Press, 2ed.(2007).

[13]-B. Ralph, "Corrosion Since and Technology" ,CRC Press.(1998).

[14]- Shakhashiri ,"Bauxite and Alumina Statistics and Information". USGS Retrieved (2009-05-05).

[15]- U.Gosele,H. Foll, "Fabrication of monodomain Porous aluminum using nanoimprint lithography and its application" Hall.(2003).

[16]- B. Mellish,"wavelength curves for aluminium (Al), silver (Ag), and gold (Au) metal mirrors at normal incidence", Optical Coating, (2005).

[17]- R. A. Bowling, "A theoretical review of particle adhesion" in *Particles on Surfaces*, K. L. Mittal, ed. (Plenum,New York, 1988), Vol. 1, pp. 129-142.

[18]- P. A. M. E. A. J. Bard), Encyclopedia of electrochemistry of the elements, vol. 6. New York and Basel: Marcel Dekker, 1973

[19]- Walaa .W.J.,"Methods of Low Carbon Steel and stainless Hardening with Laser " , thesis of Ph. D in applied physics , University of Technology,pp.1,2,10,11,13,16,22-26.(1999) .

Table (1) Anodizing Ability of Shaped Aluminum Alloy

MATERIAL	PROTECTIVE	COLOR	BRIGHT	HARD
1080A-0	E	E	v-E	E
-H8	E	E	v-E	E
1050-0	E	E	v	E
-H8	E	E	V	E
1200 -0	V	V	G	E
-H4	V	V	G	E
-H8	V	V	G	E
2011 -TD	F	F(D)	U	G
-TF	F	F(D)	U	G
2014A-TB	F	F(D)	U	G
-TF	F	F(D)	U	G
2024-TB	F	F(D)	U	G
-TD	F	F(D)	U	G
2618A-TF	F	F	U	F
3103 -0	G	G	P-F	E
-H4	G	G	P-F	E
-H8	G	G	P-F	E
3105 -0	G	G	P-F	E
-H4	G	G	P-F	E
-H8	E	E	E	E
5005 -0	E	E	E	E
-H4	E	E	E	E
-H8	V	V	G	E
5083 -0	V	V	G	E
-H2	V	V	G	E
-H4	V	V	G	E
5154 A-0	V	V	G	E
-H2	V	V	G	E
-H4	V	V	G-V	E
5251 -0	V	V	G-V	E
-H3	V	V	G-V	E
-H6	V	V	G	E
5454 -0	V	V	G	E

-H2	V	V	G	E
-H4	G	G	F	V
6061 -TB	G	G	F	V
-TF	V	V	G-V	E
6063 -TB	V	V	G-V	E
-TF	G	G	F	G-P
6082 -TB	G	G	F	G-P
-TF	F	F	*	G
7020 -TB	F	F	*	G
-TF	F	F	*	F

Table (2) Anodizing Ability of Cast Aluminum Alloy

BS	ALLOY TYPE	PROTECTIVE COLOR BRIGHT	COLOR	BRIGHT
LM0	AL99.5	E	E	E
LM2	AL Si 10Cu 2Fe	F	U	U
LM4	AL Si 5Cu 3	G	F(D)	U
LM5	AL Mg 5	E	E	G
LM6	AL Si 12	F	U	U
LM9	AL Si 12 Mg	F	U	U
LM 10	AL Mg 10	E	F	U
LM 12	AL Cu 10 Si 2Mg	F	F	U
LM 13	AL Si 11 Mg Cu	F	U	U
LM 16	AL Si 5 Cu 1Mg	G	F(D)	U
LM 18	AL Si 5	G	F(D)	U
LM 20	AL Si 12 CuFe	G	F(D)	U
LM 21	AL Si 6 Cu 4 Zn	F	U	U
LM 22	AL Si 5 Cu 3 Mn	G	F	U
LM 24	AL Si 8 Cu 3 Fe	F	F(D)	U
LM 25	AL Si 7 Mg	G	F(D)	U
LM 26	AL Si 9Cu 3Mg	F	U	U
LM 27	AL Si 7Cu 2	G	F(D)	U
LM 28	AL Si 19 Cu Mg Ni	U	U	U
LM 29	AL Si 23 Cu Mg Ni	U	U	U
LM 30	AL Si 17 Cu 4 Mg	U	U	U

E ……. Excellent
V ……. Very good
G ……. Good
F ……..Fair
P …….Poor
U ……. Unsuitable
D ……..Dark Colors

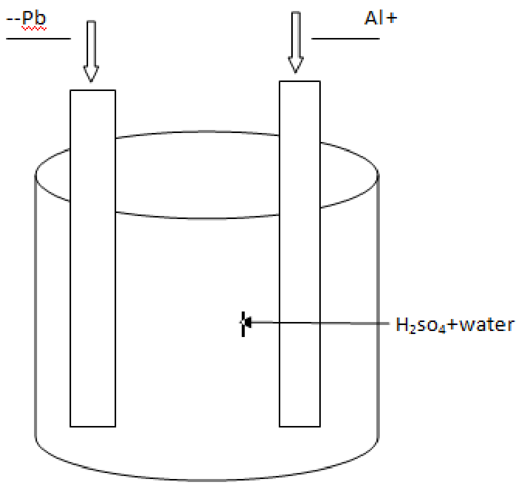


Figure (A1) showsthe experimental setup of anodizing

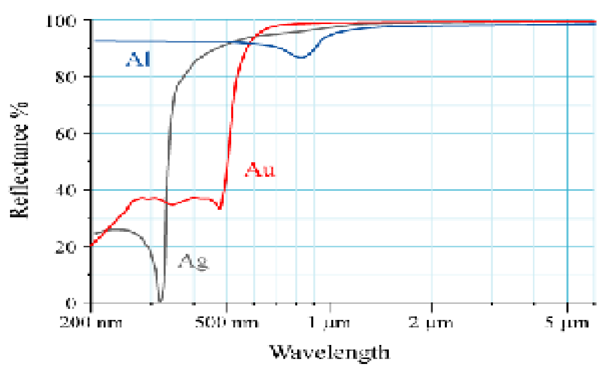


Figure (A2) shows the reflectivity of aluminum

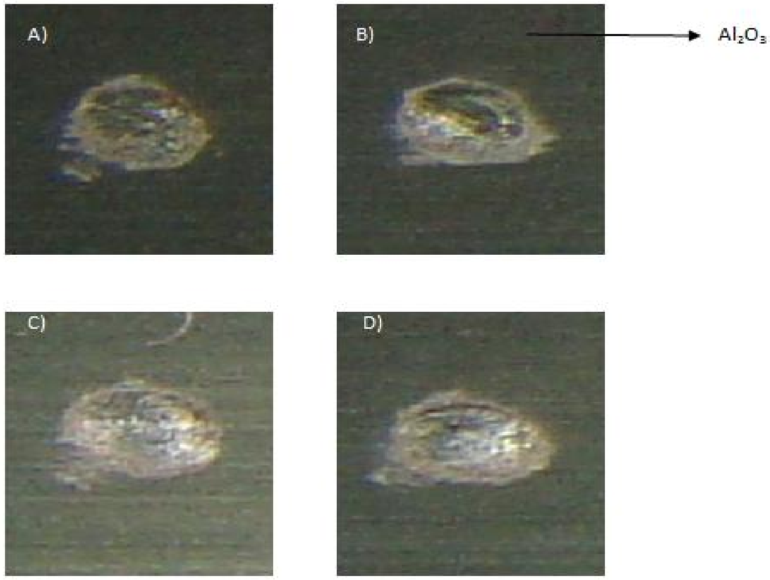


Figure (A3) Optical Images magnified (1x20) after Irradiated by Nd-YAG Pulsed laser A) 24 volts B) 21 volts C) 19 volts D)15.5 volts (Surface Treated by laser Before Anodizing) Anodizing Time is 30 Minutes, 360mJ energy, $3x10^{-9}$ pulsed duration

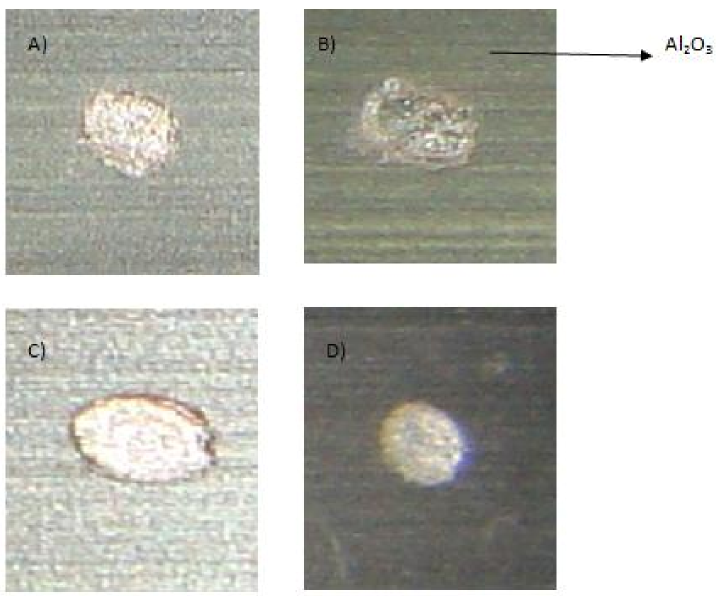
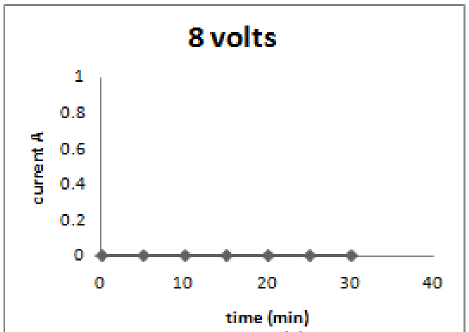
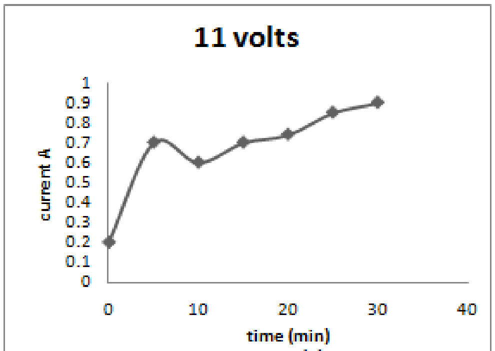


Fig (A4) Optical Images magnified (1x20) after Irradiated by Nd-YAG Pulsed Laser A) 24 volts B) 21 volts C) 19 volts D)15.5 volts (Surface was not Treated by Laser Before Anodizing)
Anodizing Time is 30 Minutes, 360mJ energy, $3x10^{-9}$ pulsed duration

Anodizing without laser treatment



Figure(1)



Figure(2)

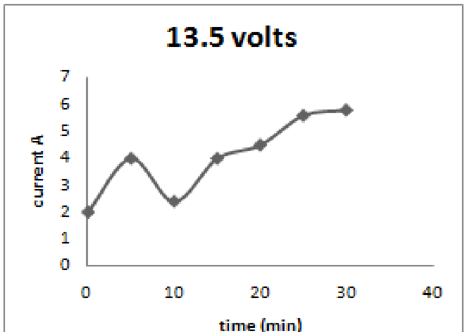
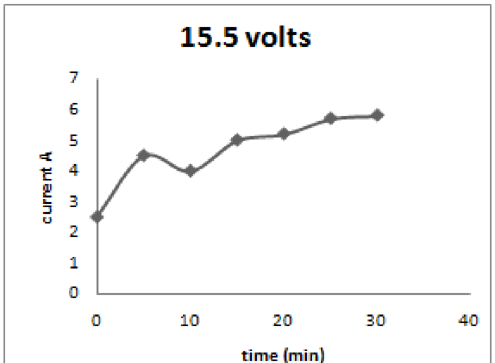
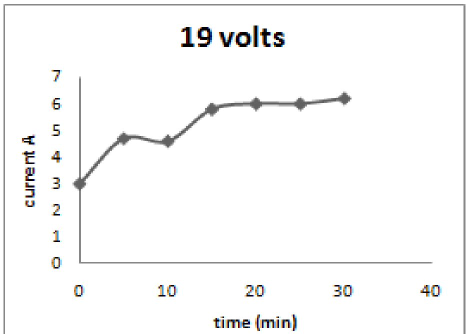


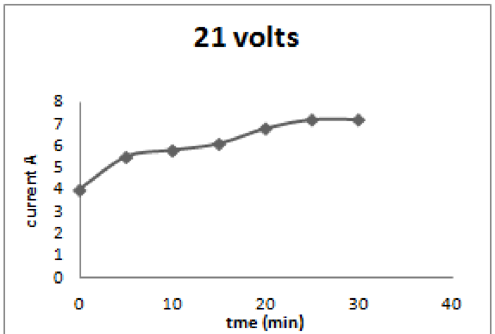
Figure (3)



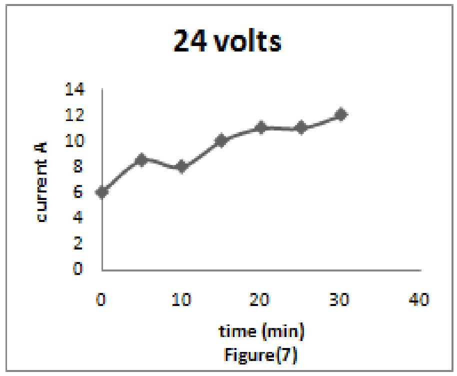
Figure(4)



Figure(5)

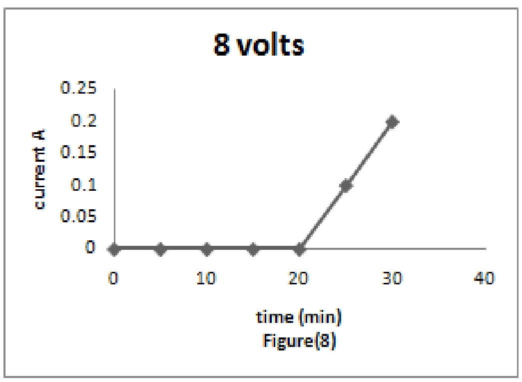


Figure(6)

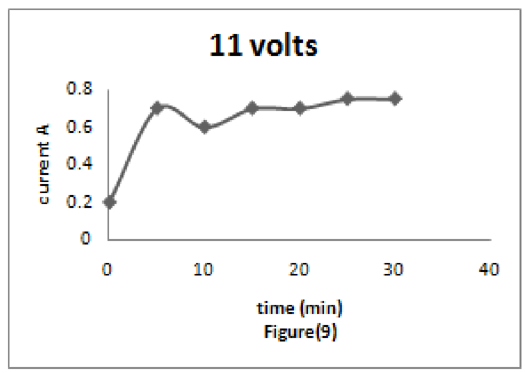


Figure(7)

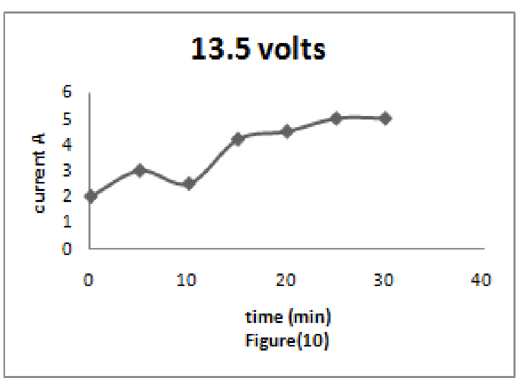
Anodizing after laser treatment



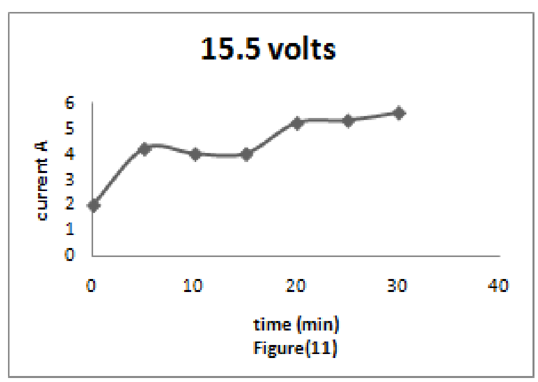
Figure(8)



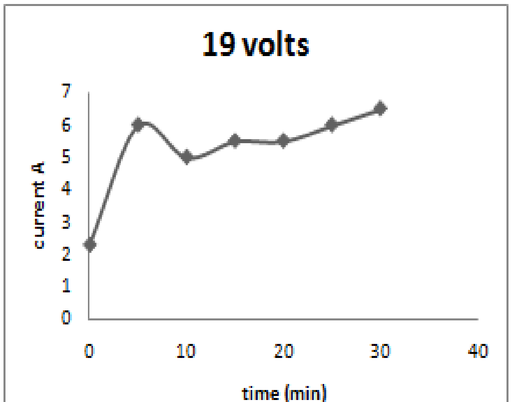
Figure(9)



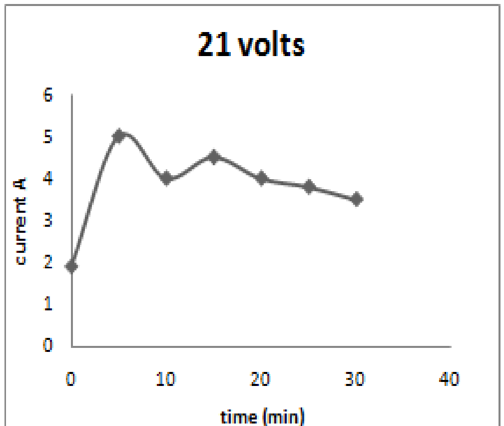
Figure(10)



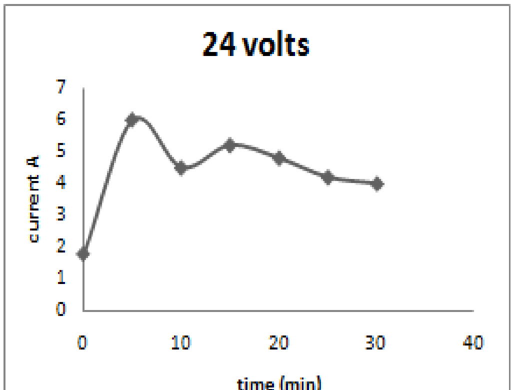
Figure(11)



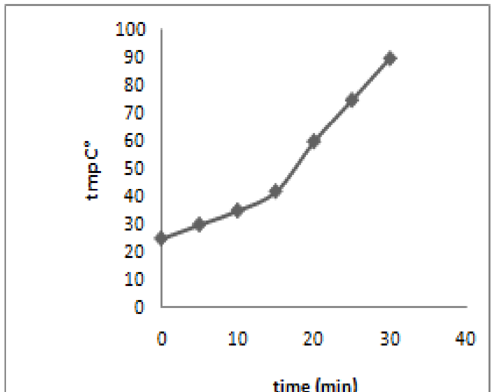
Figure(12)



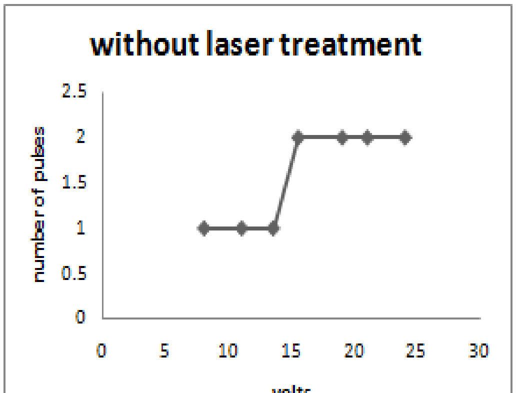
Figure(13)



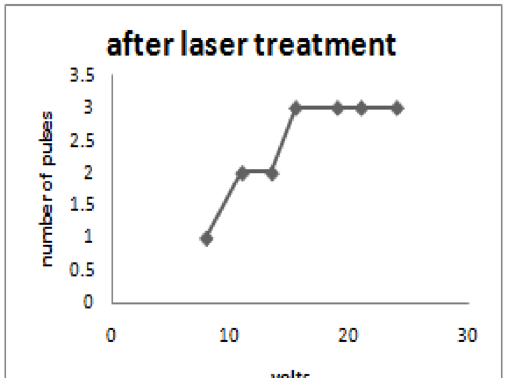
Figure(14)



Figure(15)



Figure(16)



Figure(17)