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New Method of Obtaining a Multilayer Anodized Film on 7075-T6 Al-Alloy Surface

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Abstract

It is well known that the anodized thin layer formed on Al-alloys surface are characterized with porosity of nanometric dimensions whatever acid or alkaline solutions are used. In this study, an attempt was made for the first time to develop a new method for obtaining anodized multilayer film by reinforcing the anodized oxide coating with incorporating nanosized graphite in the layer structure during anodizing process by means of anodizing Al- Alloy type 7075 T-6 in an electrolyte composed of water solution of chromic acid and graphite . This leads to obtain a multilayer anodized film having good thickness and high micro hardness properties. Nanosized particles of graphite have been formed into anodic oxide layer. The influence of anodizing process parameters (voltage and current density) on the thickness micro hardness and chemical composition of a multilayer oxide film are determined.

المستخلص

تتميز طبقة الانودة على سطوح سبائك الألمنيوم بشكل عام بظهور مساميات صغيرة الحجم سواء أجريت عملية الانودة في محاليل حامضية أو محاليل قاعدية .

أجريت في هذا البحث (ولأول مرة) محاولة تطوير طريقة جديدة تتلخص بالحصول على انودة متعدد الطبقات بإدخال جزيئات متناهية الصغر من الكرافيت في طبقات الانودة وذلك بإجراء عملية انودة لسبائك الألمنيوم من نوع 7075-T6 في محلول الكتروليتي يتكون من محلول مائي من حامض الكروميك وجزيئات صغيرة جدا من الكرافيت . أثبتت نتائج البحث تغلغل جزيئات الكرافيت في طبقات الانودة مما أدت إلى زيادة صلادتها وبسمك جيد. كما تضمن البحث حساب تأثيرات متغيرات عملية الانودة من الفولتية والتيار على كل من التركيب الكيميائي وسمك وصلادة طبقات الانودة.

1. Introduction

Anodizing or anodizing is an electrolytic passivation used to increase the thickness of the natural oxide layer on the surface of metals and alloys parts. The process is called anodizing because the object to be anodized is electrically positive part or anode, which is immersed in an electrolytic bath. Direct current is then applied and hydrolysis takes place releasing a high concentration of oxygen in a uniform manner[1,2] .

Anodizing can only be applied to metals and alloys which produces an insulating film under the anodizing conditions. This process is widely used and acceptable for the treatment of aluminum and its alloys. The oxygen reacts with the aluminum anode to form a greatly thickened, hard, and porous film of aluminum oxide[2]. Anodizing process increases corrosion resistance, surface hardness and wear resistance.

Anodizing process for aluminum & its alloys is electrochemical process by which Al or Al alloys are treated electrolytically in bath containing solutions of sulphuric acid, chromic acid or a mixture of sulphuric acid and oxalic acid to produce a uniform oxide coating on the surface. The sulphuric acid processes are most generally used for the production of decorative, protective and hard wear resistant coatings[3]. The chromic acid process is often employed, where a high resistance to corrosion is required with a minimum loss of metal section and the protection is the major consideration. The Military and aircraft assemblies are particular areas for this type of anodizing[4]. The sulphuric acid/oxalic acid solution is an anodizing solution which enables relatively "high temperatures" to be used. The properties of the anodized coating will vary with alloy composition, anodizing process employed and process time. Anodizing process changes the microscopic texture of the surface and changes the crystal structure of the metal near the surface[5]. Anodized aluminum alloys are multi-step process in which the Anodized layer is built up from the base of the film but the acids used for the anodic oxidation processes have a solvent action on the aluminum oxide film. Therefore, porous cell structure is formed; in anodic films which needs to be sealed. Sealing is a process used to close the porosity by treated the anodized articles by immersing them in boiling deionized water, salt solutions or in low pressure steam. The alumina of the anodized layer converts to aluminum monohydroxide $Al_2O_3.H_2O$, which enables to close the porous structure[6-8].

It is well known that the anodized thin layer is formed on the surface of aluminum characterizes with porosity whatever acid or alkaline solutions are used. Anodized oxide films on Al-alloys surface are characterized by relatively arrays of uniform pores of nanometric dimensions. In this study, an attempt was made for the first time to develop a new method for obtaining anodized multilayer by reinforcing the anodized oxide coating with incorporating nanosized graphite in the layer structure during anodizing process. This leads to obtain a multilayer with good thickness and high micro hardness properties for 7075T6Al-alloys.

2. The Experiment

The samples used were 7075-T6 Al alloy in the form of plates of 3 mm thickness. The anodizing process of Al-Alloys 7075 T-6 was processed by removing all foreign materials from the surface area to be anodized. Abrade areas using a gray abrasive pad until a uniform abraded surface were obtained. Solvent was used to clean the area to be anodized using 5% KOH and a 10 % HNO_3 solutions.

The surfaces prepared were subject to electrolytic oxidation by the direct current method. The electrolysis was conducted in an electrolytic plastic tank of the dimensions: (20 X 20 X 15) cm with round edges. Pipes made of 7075 T-6 Al-alloy was used as the anode with 50 mm length , 81 mm diameter and 3 mm thickness. Table 1 lists the chemical composition for used & standard 7075 T6 Al-alloys. A stainless steel rod of the 1/ 5th of the anode area was used as the cathode. Electrodes were immersed to the depth of 3 cm from the tank bottom. Anodization was carried out in an the electrolytes solution of 10% chromic acid (CrO3) {100 g/ L} with an addition of 0.5% loose hexagonal graphite which grain size are less than 50-53 micron and had high purity of 99.9%.

During the anodizing process, the electrolyte was stirred in one direction with a mechanical stirrer at the constant speed of 150 r.p.m. This stirring speed enabled obtaining a homogeneous graphite suspension throughout the electrolyte volume. Graphitization was conducted during the electrolysis, producing a multilayer achieved by incorporating graphite into oxide structure. The anodizing process was conducted during a constant time period of 1 hr. at the current density of 2 or 3 A/dm^2 and at room temperature.

After completion of the anodizing process, the samples were rinsed for 1 hr. in the distilled water in order to remove remaining electrolyte. The samples, then sealed by immersion into a bath of boiling water to close the pores in a multilayer aluminum oxide. The thickness of all layers was measured with a Fischer's Dualscope thickness gauge. The analysis of the composition of the multilayer was performed using an X- ray diffractometer type a Philips PW3710 by using $\lambda_{Cu-k\alpha}$= 1.54 Å. Microhardness was determined by using a Hanemann micro hardness tester.

Operating conditions that may affect the anodizing process (electrolyte compos ion, voltage and current density) on the anodizing processing time, film thickness and its microhardness are studied in this work.

3. Results and discussion

Figure (1) illustrates the relations between the anodizing voltage and the anodizing time for Al_2O_3 layer and for Al_2O_3 + graphite. The value of anodizing voltage was varying with a growing oxide layer. At the beginning of the process, the voltage increased to a certain maximum value, called critical voltage; next it decreased slightly and having reached a certain minimum, then increased again. The reasons for this phenomenon are processes taking place during the oxide coating's formation[5-8]. The value of voltage was found proportional to the current density.

Table (2) shows that the current density and the electrolyte composition have a direct influence on the layer thickness during the anodizing process. Since anodizing is a balance between the chemical dissolution and the oxide formation processes, in the initial stage of anodizing, the total thickness of the composite coating was slightly decreased under a low current density due to a low deposition rate. It is assumed that the dissolution rate was greater than the deposition rate in this stage. The thickness of the anodic film then increased with the operating time.

Thickness of Al_2O_3 formed at room temperature amounted to 33 µm at current density of 2 A/dm and 45.5 µm at 3A/dm^2, while thickness of Al_2O_3 + graphite a multilayer amounted to 30.5 µm at 2 A/dm^2 current density and 41 µm at 3 A/dm^2. This means that, the thickness of Al_2O_3 were was by 5-10%higher than those of a multilayer, which results from a better access of the electrolyte ions to the oxidized material.

Proper current density for a given application is dependent on the purpose of the coating. The higher the current density, the faster the coating is applied. Too high of a current density, however, resulted in overheating of the work area and soft, thin coatings. On the other hand a low current density needs a long anodizing time.

Table (2) also shows that, microhardness of oxide layer formed on Al alloys depends on the conditions of the anodizing process, decreasing upon increasing the surface porosity. All layers formed in the electrolyte containing graphite have higher microhardness than those formed in the basic electrolyte. The difference in microhardness between the Al_2O_3 coatings and the Al_2O_3 + graphite coatings varies between 150 and 500 MPa respectively, depending on the current conditions. The layers had higher microhardness during anodizing at current density of 2 A/dm^2 than that at current density of 3 A/dm$^{2.}$ These results imply the filling of the aluminum oxide fibrous structure results in its enhanced hardness. From the difference in size of graphite grains and oxide nanopores it results that the mechanism of obtaining a composite layer consists in simultaneous building in of graphite into the structure of oxide layer during the formation[6].

An examination conducted on the substrate and the anodized layers using XRD reveal the presence of Al and graphite. Figure (2) shows the diffract s of loose graphite belongs to the polytypic 2H. The basic reflex 002, whose value a mounts to 3.367 Aº & the intensity I=100. Figure (3) is dominated by two intense peaks 1.435 Aº belong to the substrate, whereas the reflex 3.361 Aº belongs to graphite , with the number of counts amounting to 116 counts/s, which indicates the largest amount of graphite in the Al_2O_3 layer among the investigated surfaces when the anodizing processes were done at 2 and 3 A/dm^2 respectively.

4. Conclusions

The developed technology enables obtaining a multilayer of aluminum oxide and graphite during one technological process. The largest amount of graphite in the Al_2O_3 layer was obtained at the current density of 3 A/dm^2 Al_2O_3 + graphite a multilayer film having a smaller thickness(30.5 to 41 µm) but higher microhardness (4600 to 5010) , when compared to the film obtaining after anodizing without graphite in the same condition, which have 33-45.5 µm thickness and 4500- 4900 micro hardness.

5. References

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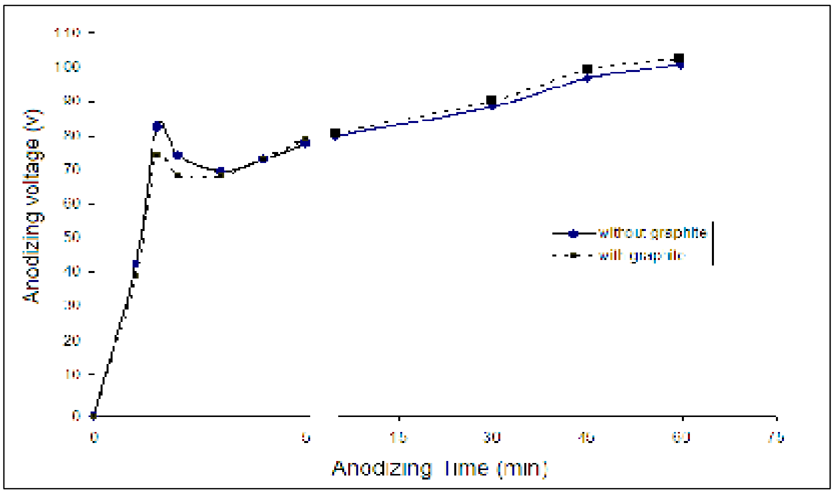
Table (1).The chemical composition of used Al-alloy compared with its standard composition .

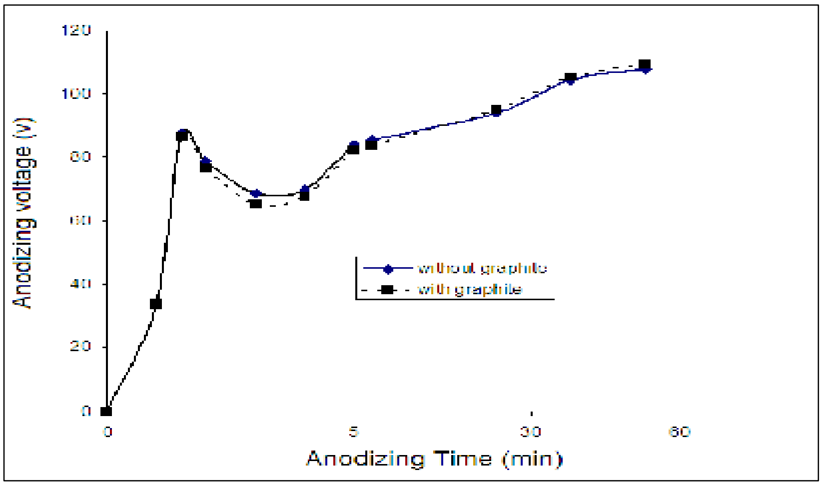
Element	Zn	Mg	Cu	Cr	Fe	Si	Mn	Ti	Al
wt% Measured	5.62	2.65	1.3	0.17	0.34	0.085	0.40	0.022	Balance
wt% Standard	5.1-6.1	2.1-2.9	1.2-2.0	0.18-0.35	0.5 Max.	0.4 Max.	0.3 Max.	0.2 Max.	Balance

Table (2).The influence of electrolyte composition & current density on the thickness & micro hardness on an anodized film.

Electrolyte Composition	Current Density(A/dm^2)	Thickness of film (μm)	Micro hardness of film
Without Graphite	2	33	4500
	3	45.5	4900
With Graphite	2	30.5	4600
	3	41	5010



Figure(1- a)



Figure(1- b)

Figure (1). The relations between anodizing voltage and time of process depended on the electrolyte composition. A) at 2 A/dm^2 , b) 3A/dm^2.

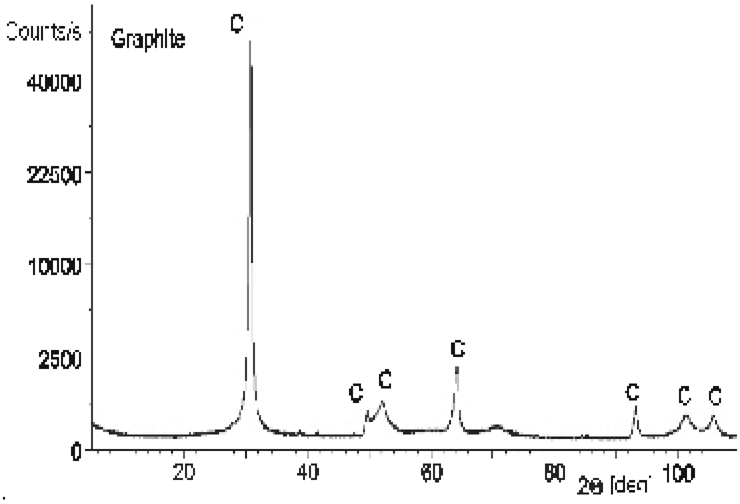
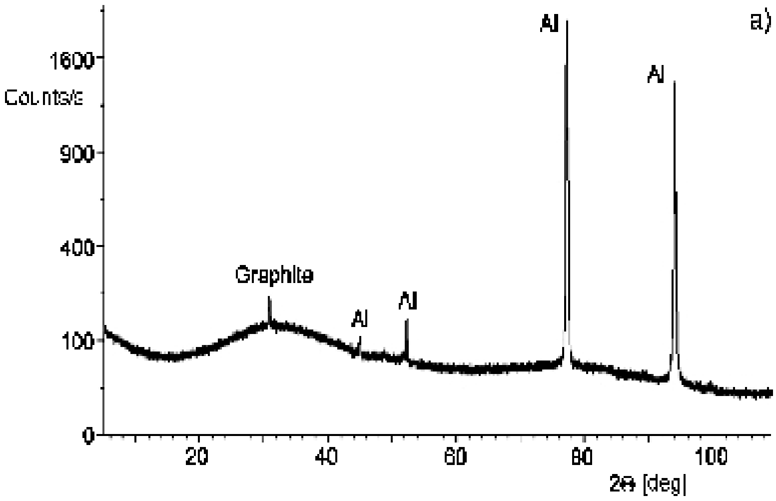
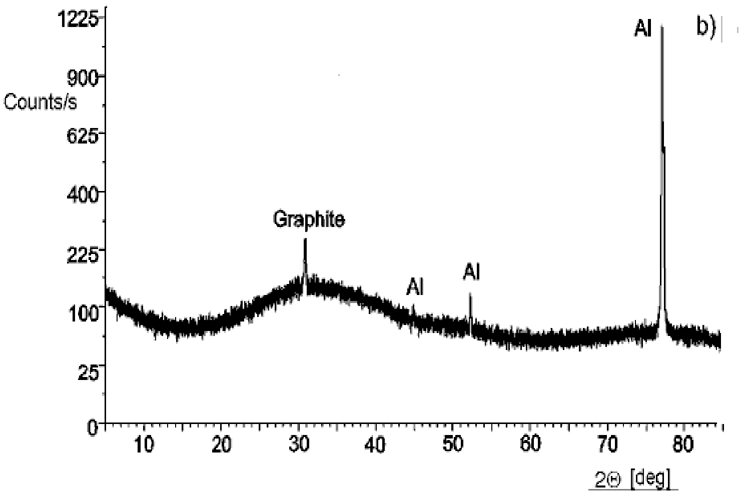


Figure (2) . XRD of graphite.



Figure(3-a)



Figure(3-b)

Figure (3) . XRD of the a multilayer film on anodized 7075-T6 Al-alloy. a) at current density 2 A/dm^2,b) at current density 3 A/dm^2.