Materials Letters 179 (2016) 82–85

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Young's modulus of anodic oxide layers formed on aluminum in sulphuric acid bath

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ARTICLE INFO

Article history:
Received 23 December 2015
Received in revised form
24 April 2016
Accepted 7 May 2016
Available online 9 May 2016

Keywords:
Porous materials
Thick Films
Indentation and hardness

ABSTRACT

The Young's modulus of anodic oxide layers formed on pure aluminum in sulphuric acid electrolyte was measured using nanoindentation tests. A model that accounts the anodizing conditions effect on this response was developed using the experimental design methodology. For this purpose, a three variables Doehlert design (bath temperature, anodic current density, sulphuric acid concentration), was implemented. The surface response analysis showed that the high values of the Young's modulus are obtained at low temperatures and high current densities. It was demonstrated that the established model can be used to well estimate the porosity of the oxide layer.

1. Introduction

The formation of porous anodic oxide layer on aluminum has been widely studied [1]. These oxides have attracted considerable interest due to their unique porous structures. These nanostructures can be used as templates for preparing a wide range of materials (photonic crystals, micropolarizers, polymeric nanostructures, nanometals, polymeric and carbon nanotubes) [2].

The mechanical properties of porous oxide layer have been extensively investigated using experimental and numerical studies including microhardness, wear, friction, scratch, nanoindentation, bending and tensile tests [3–6]. Among these works, some authors have focused their attention on the measure of the Young's modulus of the anodic oxide layer using nanoindentation technique [3,6]. These authors have reported the presence of a high relationship between the Young's modulus and the porosity of the anodic layer. On the other hand, Li et al. [2] have demonstrated that the porosity itself strongly depends on the elaboration conditions.

To the author knowledge there is no direct relation between the Young's modulus of the nanoporous oxide layer and the anodizing conditions.

In order to develop a relation between the anodizing parameters and the Young's modulus of the anodic layer, the methodology of experimental design was used [7–9]. An experimental design is the best technique to reach conclusions with a minimum of experiments [7–9]. The multivariate experimental design techniques are becoming extensively used in several research fields due to many well known advantages [7–9].

In the present paper, the Doehlert experimental design [10] was implemented in order to develop a direct relationship between the Young's modulus E(GPa) and the anodizing parameters (bath temperature (T), anodic current density (J) and sulphuric acid concentration (C_{sul})).

2. Experimental

2.1. Materials and procedures

Al1050A coupons with dimensions of 20 mm x 20 mm x 3 mm were used for sulphuric anodizing. Prior to anodizing, these coupons were mechanically polished up to P1000 grade paper. Then, they were: (i) chemically polished in 15:85 (v/v) mixture of concentrated HNO_3 and H_3PO_4 at 85 °C for 2 min; (ii) etched in 1 M NaOH solution at 25 °C for 1 min and (iii) chemically pickled in 30% (v/v) HNO_3 solution for 30 s The deionised water rinsing was applied between the different operations. Afterwards, the coupons were anodized in vigorously stirred sulphuric acid solution. The anodizing time was chosen so that to obtain a constant thickness of 30 μm. In the anodizing cell, the used cathodes were aluminum sheets. Sulphuric, nitric and phosphoric acids are of analytical grade.

The Young's modulus of the anodic oxide layer was measured using CSM-instruments equipped with a Vickers tip nanoindentation tester. The contact force was 25 mN and the

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http://dx.doi.org/10.1016/j.matlet.2016.05.035

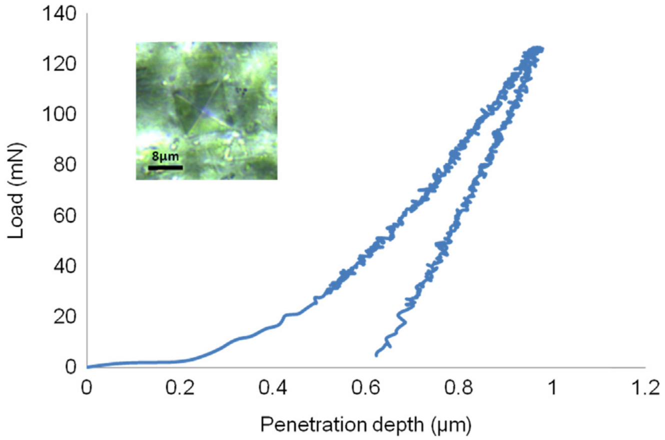

Fig. 1. Typical load-unload nanoindentation curve and optical microscopy of the indent after test.

Table1
Doehlert experimental design in natural variables and the Young's modulus measured responses.

N° run	T (°C)	J (A/dm^2)	Csul (g/L)	E (GPa)
1	25.0	2.00	160	49
2	3.0	2.00	160	62
3	19.5	2.87	160	52
4	8.5	1.13	160	56
5	19.5	1.13	160	50
6	8.5	2.87	160	66
7	19.5	2.29	193	61
8	8.5	1.71	127	72
9	19.5	1.71	127	60
10	14.0	2.58	127	76
11	8.5	2.29	193	60
12	14.0	1.42	193	64
13	14.0	2.00	160	74
14	14.0	2.00	160	69
15	14.0	2.00	160	67
16	14.0	2.00	160	72

maximum load was 120 mN. The loading and unloading velocities were 200 mN/min and the results are the average of 5 repeated tests. The obtained load-displacement data were evaluated according to the Olivier-Pharr method [11]. Fig. 1 shows a typical load-unload nanoindentation curve and optical microscopy of the indent after the test.

The morphology of the oxide layer was conducted using Jeol JSM-6400F Scanning Electron Microscopy machine.

2.2. *Doehlert experimental design implementation*

The Doehlert experimental design [10] was applied to establish the effect of the anodizing temperature (T(°C)), anodic current density (J(A/dm^2)) and sulphuric acid concentration (Csul (g/L)), and their interactions on the Young's modulus of the anodic oxide layer. Doehlert design is chosen for a number of advantages such as i) spherical experimental domain with a regularity in space filling, ii) ability to explore the whole retained domain and iii) sequentiality: the ability to re-use experiments when the domain boundaries have not been well chosen at the beginning.

The study domain is defined by giving to each parameters Uj, a centre Uj(0) and a variation step ΔUj. For the Doehlert design, the number of levels of each variable is: 5 for the first, 7 for the second and 3 for the remained k ones.

The selected parameters U_j were: .

1. U_1: the anodizing temperature, T (°C), with 5 number of levels.
2. U_2: the current density, J (A/dm^2), with 7 number of levels.
3. U_3: the sulphuric acid concentration, C_{sul} (g/L), with 3 number of levels.

Natural variables Uj were changed into coded variables Xj using the following equation [7–10]:

$$\mathbf{X_j} = \frac{\mathbf{U_j} - \mathbf{U_j}(0)}{\Delta \mathbf{U_j}} \tag{1}$$

In our case the centre $U_j(0)$ and the variation step ΔU_j for: (i) temperature were 14 and 11 °C respectively; (ii) for current density 2 and 1 A/dm^2 respectively and (iii) sulphuric acid concentration 160 and 40 g/L respectively.

A quadratic model with 10 coefficients, counting interaction terms, was supposed to describe the relationship between the Young's modulus response Y(GPa) and the experimental variables X_j:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + e \tag{2}$$

where b_0, b_j, b_{jk}, b_{jj} were the different coefficients of the model and “e” is the random experimental error.

The number of Doehlert design experiment can be computed according to $N = k^2 + k + N_0$, where k is the number of the variables and N_0 the number of experiments at the domain centre. In our case, the $N_0 = 4$ so we have to carry out 16 experiments according the Doehlert matrix. Replicates of experiment at the domain centre were undertaken in order to estimate the pure

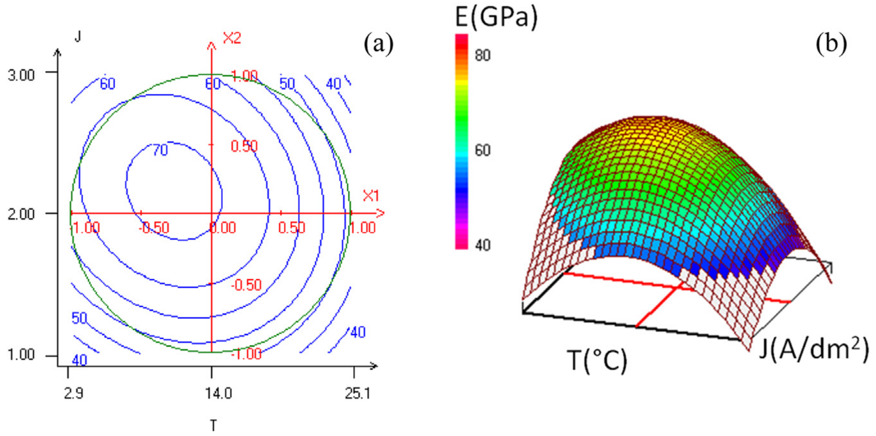

Fig. 2. Variation of the Young's modulus of the anodic oxide layer: (a) isoresponse versus (T, J) for $C_{sul} = 160$ g/L; (b) surface response versus (T, J) for $C_{sul} = 160$ g/L.