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# Pilling–Bedworth ratio of thick anodic aluminium porous films prepared at high voltages in H<sub>2</sub>SO<sub>4</sub> based electrolyte

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Thick porous anodic films have been prepared using high voltages in a sulphuric acid based electrolyte. The use of H<sub>2</sub>SO<sub>4</sub> low concentration, low bath temperature and the boric acid as modifier allows the anodic porous film to be significantly thickened preventing its chemical dissolution. A new relation including the Pilling–Bedworth ratio, especially of the thick anodic porous films, is proposed here to take into account the nanoporosity and the anodic current efficiency.

**Keywords:** Aluminium, Thick anodic films, Porosity, Pilling–Bedworth ratio

## Introduction

The porous anodising of aluminium and its alloys is a well established process, discovered in 1857 by H. Buff and developed in 1911 by de Saint Martin. The first anodising process using sulphuric acid as electrolyte was patented in England in 1927.<sup>1</sup> Since then it has rapidly acquired a great industrial importance due to the various applications in different applicational fields such as aeronautic, architectural decoration, etc. The sulphuric acid remains the most used anodising bath due to its low cost, large range of potential applications and easy control of the operational parameters. These parameters vary with the final applications but their ranges are usually:<sup>1</sup> 1.0–1.5 A dm<sup>-2</sup> for the current density, 8.5–10 vol.-% (160–200 g L<sup>-1</sup>) for the electrolyte concentration and a typical voltage from 14 to 40 V. According to the final applications the anodic film thickness is usually limited to 20–30 µm, but higher values are sometimes required (~120–150 µm and sometimes up to 250 µm (Ref. 1)) in order to obtain maximum wear resistance. These thickest anodic films are always obtained using 'hard anodising' conditions, i.e. sulphuric acid solution but at low temperatures (from -5 to 5°C). Moreover, previous studies clearly show that the addition of boric acid as a modifier in sulphuric anodising bath induces significant increases in the microhardness and the thickness of the anodic film,<sup>2</sup> while the fatigue resistance does not significantly differ from the one obtained with the traditional chromic acid anodising.<sup>3</sup>

About twenty years ago, there was a renewal of interest for the anodising process due to the possibility to observe the nanoporosity inside the anodic film using microscope techniques like field emission gun scanning

electron microscopy (FEG–SEM) or transmission electron microscopy (TEM). Furthermore, the innovating research works of both Masuda in Japan<sup>4</sup> and Gösele in Germany<sup>5</sup> opened new ways to obtain highly nanoordered templates based on the anodic aluminium oxide (AAO). A later impregnation of metal or oxide and the possible final removal of the AAO template makes it possible to prepare nanodevices, such as dots or wires,<sup>6</sup> the sizes of which directly depend on the previous geometrical characteristics of AAO pores. Until now, since the thickness of AAO films is usually limited to 20–30 µm, the nanowires are restricted to this maximum length. Furthermore, authors<sup>5,7,8</sup> have claimed that the preparation of nanoordered AAO templates, especially hexagonal ordered pore arrays, require only moderate Pilling–Bedworth ratios (~1.4) whatever the electrolyte used for the anodising.

The aim of this work is to prepare thick aluminium anodic porous films using high voltages in a sulphuric acid based electrolyte in order to elaborate self-lubricating surface composites or to obtain eventually nanowires with a high ratio of length versus diameter. The Pilling–Bedworth ratio (PBR) will be particularly discussed here in the case of these thick anodic porous films.

## Experimental

All chemical species were analytical grade products (PROLABO) and the electrolyte aqueous solutions were obtained using deionised water.

Experiments were carried out using 1050 A aluminium alloy (99.5%Al) as substrate material. Each sample was a disc of 1 mm thickness and 1.04 cm<sup>2</sup> of surface area. The samples were degreased for 1 min in an aqueous alkaline bath containing Na<sub>2</sub>CO<sub>3</sub> (5 g L<sup>-1</sup>), Na<sub>3</sub>PO<sub>4</sub> (4.3 g L<sup>-1</sup>), Na<sub>2</sub>SiO<sub>3</sub> (0.5 g L<sup>-1</sup>) and NaC<sub>6</sub>H<sub>11</sub>O<sub>7</sub> (10 g L<sup>-1</sup>), then etched in aqueous NaOH (25 g L<sup>-1</sup>) for 1 min and neutralised in aqueous HNO<sub>3</sub> (20%v/v) for 2 min. After each step conducted at

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ambient temperature, the samples were rinsed in distilled water.

The aluminium substrates were then used as anodes and a titanium sheet as cathode in the electrochemical cell thermally controlled at  $0 \pm 2^\circ\text{C}$ . The samples were anodised for one hour at a fixed voltage (50–300 V) in an aqueous mixed  $\text{H}_2\text{SO}_4$  ( $40 \text{ g L}^{-1}$ )– $\text{H}_3\text{BO}_3$  ( $10 \text{ g L}^{-1}$ ) electrolyte, using an electrical generator (Lambda Gen 300V-5A). The samples were finally rinsed with distilled water.

The micro and nanostructures of the coatings were finally observed by FEG–SEM with a JEOL JSM6700F device. The thickness of the anodic film was obtained from direct measurements on cross-sections using a MOTIC digital microscope (MOTIC DM 143) coupled with a microcomputer.

## Results and discussion

### High thicknesses

#### Results

The anodising process using sulphuric electrolyte at ambient temperature ( $18\text{--}25^\circ\text{C}$ ) is usually limited by the current density and the voltage at  $1.5 \text{ A dm}^{-2}$  and 40 V respectively. For example, Vrublevsky *et al.*<sup>9</sup> claimed that the anodising voltage in sulphuric acid (10 wt-%) cannot be higher than 30V at room temperature. Furthermore, Wang and Wang<sup>10</sup> recently claimed that it is difficult to prepare macroporous membranes in sulphuric acid and that phosphoric electrolyte is the only way of preparation to thicken the anodic macroporous layers.

By contrast, in the author's experimental conditions, the thickness of the anodic film varies from  $(179 \pm 7)$  to  $(269 \pm 34) \mu\text{m}$  in the 50–300 V voltage range (Table 1). However, it is important to note that these results, and especially the deviations, do not take into account some damaged samples, showing an important weight loss.

#### Discussion

These results are in agreement with the previous thicknesses, up to  $250 \mu\text{m}$  (Ref. 1), obtained for the 23–120 V voltage range with a 7% $\text{H}_2\text{SO}_4$  electrolyte regulated at  $0 \pm 5^\circ\text{C}$ . The high values could be mainly explained by both the low temperature of the anodising bath and the low concentration of the strong acid.

The electrochemical formation of the anodic porous film involves complex phenomena, including the growth of the layer by electrochemistry at the metal/anodic film interface and its chemical dissolution in contact with the

electrolyte. Nagayama and Tamura<sup>11</sup> demonstrated in particular that small changes in the bulk solution temperature have a significant influence on the chemical dissolution rate, a lower temperature (here  $0 \pm 2^\circ\text{C}$ ) reducing its kinetic.

Moreover, the chemical dissolution greatly decreases here because the concentration of sulphuric acid is low ( $40 \text{ g L}^{-1}$ ) in comparison with the usual contents ( $160\text{--}200 \text{ g L}^{-1}$ ). For example, the calculated ratio of the dissolved aluminium ion contents is

$$\frac{[Al^{3+}]_{40\text{g/L}}}{[Al^{3+}]_{160\text{g/L}}} = 1.56 \times 10^{-2} \quad (1)$$

for sulphuric acid concentrations respectively equal to 40 and  $160 \text{ g L}^{-1}$ . However, in some cases, the prevailing phenomenon is the electrochemical dissolution, instead of the anodising, damaging the sample.

These thick anodic films were then studied and compared with the previous results, using especially the PBR.

### Pilling–Bedworth ratio

#### Definitions and results

The PBR, also called 'volume expansion factor' or 'volume growth coefficient', is rigorously defined by the ratio of grown oxide molar volume ( $V_{AAO}$ ) to the consumed metal molar volume ( $V_{Al}$ )

$$PBR = \frac{V_{AAO}}{V_{Al}} \quad (2)$$

In practice, the horizontal components are usually neglected in favour of the vertical one, reducing this calculation to the simple thicknesses ratio  $K_g^{9,12}$  (Fig. 1)

$$PBR \approx K_g = \frac{h_{AAO}}{h_{Al}} \quad (3)$$

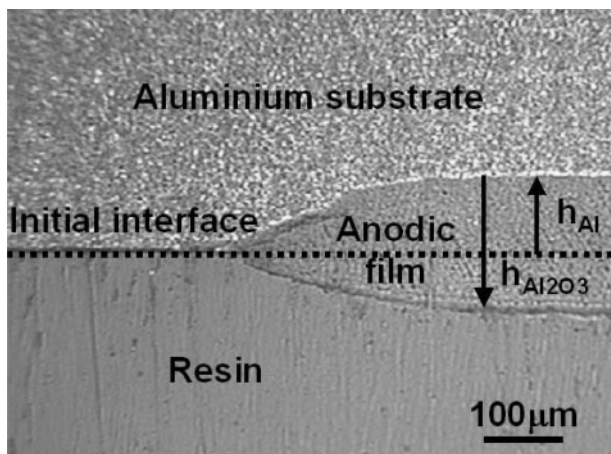
where  $h_{AAO}$  and  $h_{Al}$  are the vertical heights of the anodic aluminium oxide and of the consumed aluminium respectively.

The previous research studies mentioning the volume expansion factors showed a wide diversity of the PBR experimental results obtained in various anodising acid baths (Table 1): from 1.2 to 1.62 (Ref. 12) and from 0.91 to 1.71 (Ref. 13) in phosphoric acid, from 0.86 to 1.62 in 20 wt-% sulphuric acid,<sup>8</sup> from 1.36 to 1.45 in three different baths.<sup>5</sup>

Table 1 shows that in this study the  $K_g$  values increase from  $1.72 \pm 0.14$  to  $1.90 \pm 0.31$  as a function of the

**Table 1** Thickness and volume expansion factor obtained for different anodic porous films

Research studies	Electrolyte	Anodising cell voltage, V, or current density, $\text{mA cm}^{-2}$	Thickness of the anodic layer, $\mu\text{m}$	Volume expansion factor
Surganov <i>et al.</i> <sup>12</sup>	From 0.1 to 2.0M orthophosphoric acid at $18^\circ\text{C}$	From 2 to 13 $\text{mA cm}^{-2}$	–	From 1.2 to 1.62
Thompson <sup>13</sup>	Phosphoric acid	–	–	From 0.91 to 1.71
Jessensky <i>et al.</i> <sup>8</sup>	20 wt-% $\text{H}_2\text{SO}_4$ at $1^\circ\text{C}$	From 18 to 25 V	–	From 0.86 to 1.62
Li <i>et al.</i> <sup>5</sup>	2.7 wt-% oxalic acid at $1^\circ\text{C}$	40 V	–	1.42
	10 wt-% phosphoric acid at $1^\circ\text{C}$	160 V	–	1.45
	20 wt-% $\text{H}_2\text{SO}_4$ at $1^\circ\text{C}$	19 V	–	1.41
	1.7 wt-% $\text{H}_2\text{SO}_4$ at $10^\circ\text{C}$	25 V	–	1.40
	1.7 wt-% $\text{H}_2\text{SO}_4$ at $1^\circ\text{C}$	25 V	–	1.36
This study	$\text{H}_2\text{SO}_4$ ( $40 \text{ g L}^{-1}$ )– $\text{H}_3\text{BO}_3$ ( $10 \text{ g L}^{-1}$ ) at $0^\circ\text{C}$	50 V	$179 \pm 7$	$1.72 \pm 0.14$
		100 V	$233 \pm 10$	$1.76 \pm 0.17$
		300 V	$269 \pm 34$	$1.90 \pm 0.31$



1 Experimental calculation of volume expansion factor  $K_g$  from optical microscope cross-section view of anodic film prepared at 273 K using 50 V for 1 h

voltage (50–300 V) at a given bath's temperature ( $0 \pm 2^\circ\text{C}$ ) and for a constant anodising duration of one hour. These results are in accordance with the previous studies, underlining that the volume expansion factor of porous anodic films is proportional to the anodising voltage,<sup>8,14</sup> increasing typically from 1.38 to 1.62 for the 13–24 V voltage range.<sup>9</sup>

**Discussion**

These very different values could be explained at first by the formation of aluminium oxyhydroxides with increasing hydration rate, rather than the obtaining of pure aluminium oxides, for example the so called alumina  $\text{Al}_2\text{O}_3$ . The corresponding theoretical values of  $K_g$  (excluding porosity) are indeed respectively

$$\frac{h_{\text{Al}_2\text{O}_3}}{h_{\text{Al}}} = \frac{\rho_{\text{Al}} \cdot M_{\text{Al}_2\text{O}_3}}{2 \cdot M_{\text{Al}} \cdot \rho_{\text{Al}_2\text{O}_3}} = 1.28 \quad (4)$$

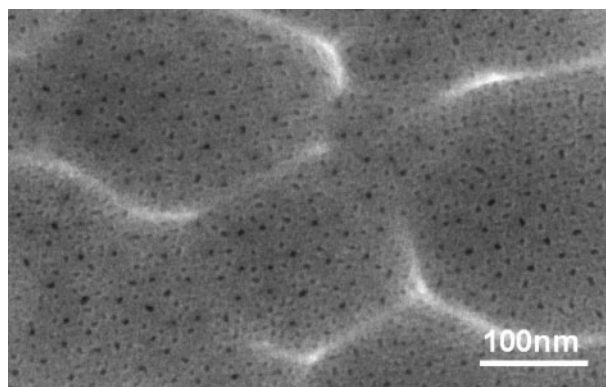
and

$$\frac{h_{\text{AlO(OH)}}}{h_{\text{Al}}} = \frac{\rho_{\text{Al}} \cdot M_{\text{AlO(OH)}}}{M_{\text{Al}} \cdot \rho_{\text{AlO(OH)}}} = 1.99 \quad (5)$$

where  $M_{\text{Al}_2\text{O}_3}$ ,  $M_{\text{Al}}$  and  $M_{\text{AlO(OH)}}$  are the molar masses of the alumina, the metallic aluminium and the aluminium oxyhydroxides respectively, while  $h_{\text{Al}_2\text{O}_3}$ ,  $h_{\text{Al}}$ ,  $h_{\text{AlO(OH)}}$  and  $\rho_{\text{Al}_2\text{O}_3}$ ,  $\rho_{\text{Al}}$ ,  $\rho_{\text{AlO(OH)}}$  are the corresponding vertical heights and densities respectively, with  $\rho_{\text{Al}_2\text{O}_3} = 3.97 \text{ g cm}^{-3}$  and  $\rho_{\text{AlO(OH)}} = 3.01 \text{ g cm}^{-3}$  according to the previous work of Gabe.<sup>15</sup>

This disparity of the volume expansion factors could also be normally explained by differences of the coating chemical composition due to the acid anion incorporation. For example, the anodic films formed in a sulphuric acid based electrolyte contain high levels of anion species incorporation (12–14 wt-% sulphate,<sup>13</sup> 13–17% minimum as  $\text{Al}_2(\text{SO}_4)_3$  (Ref. 1)), while the phosphate and oxalate contents are respectively 6–8 and 2.4 wt-% in the porous anodic films.<sup>13</sup> But these two previous arguments about the changeable chemical content of the anodic films cannot explain the experimental values lower than 1.28.

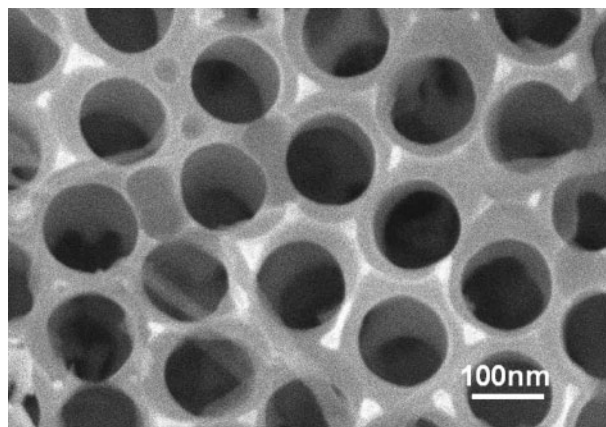
All the previous  $K_g$  values include hypotheses about the chemical composition of the anodic films but also, implicitly, about its porosity. The porosity is ~3–14% for the usual hard anodic films<sup>1,15</sup> but reaches sometimes



2 Field emission gun scanning electron microscopy plan view of anodic film prepared at 273 K using 30 V for 15 min

more than 50% for some highly nanoordered AAO films, the average pore diameter being directly proportional to the anodising duration and voltage.<sup>16</sup> For example, Figs. 2 and 3 show the FEG–SEM plan views of two anodic films obtained at 30 and 200 V, the corresponding void area fractions being lower than 5% and equal to 45% respectively. Usually the previous authors did not specify the void percentage in relation to the  $K_g$  values, thus considering that the porosity results only from the chemical dissolution. But some previous discussions<sup>5,8</sup> regarding the formation of the most porous anodic films mentioned the influence of large compressive stresses in the anodic films, inducing probable changes in their mechanical properties and density. Thus, a rigorous comparison between anodic films with different porosities actually appears difficult. From this perspective, the use of  $K_g$  values is more adequate and useful for the comparison of the compact anodic films obtained under the barrier anodising conditions.

Furthermore, the calculation of  $K_g$  is based on the measurement of the thickness of the anodic film ( $h_{\text{AAO}}$ ) which directly depends on the growth rate of the anodic film. The anodic current is used partly to form the anodic film, but it is also implicated in the dioxygen gas evolution and in the anodic dissolution, i.e. the egress of aluminium ions through the anodic film to the electrolyte, both phenomena being closely linked to the current



3 Field emission gun scanning electron microscopy plan view of anodic film prepared at 273 K using 200 V for 1 h

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density. For example, the anodic current density logarithm is clearly proportional to the inverse of the volume expansion factor.<sup>14</sup> The anodic current efficiency appears as the last but not least parameter.

Thus, as a result of this study, it could be considered incorrect to identify the experimental  $K_g$  ratio with the theoretical PBR. To account for the porosity of the anodic film, as well as the anodic current efficiency, a new relation could be now proposed

$$K_g = \frac{h_{AAO}}{h_{Al}} = PBR(1+P)\Phi^e = \frac{V_{AAO}}{V_{Al}}(1+P)\Phi^e \quad (6)$$

where  $P$  is the porosity percentage ( $0 \leq P < 1$ ) and  $\Phi^e$  is the anodic current efficiency.

For the special case of the highly nano-ordered AAO templates, i.e. anodic films including a straight porosity perpendicular to the substrate surface, this previous relation becomes

$$K_g = \frac{h_{AAO}}{h_{Al}} = PBR \left( 1 + \frac{S_{\text{pore}}}{S_{AAO}} \right) \Phi^e \quad (7)$$

where  $S_{\text{pore}}$  is the global surface area of the pores and  $S_{AAO}$  is the geometrical surface of the anodic film. From the experimental point of view, both surfaces could be obtained using the image analysis of the TEM or FEG–SEM pictures, while a rigorous measurement of the experimental anodic current efficiency seems more difficult to obtain. Indeed, it would be required either to measure the gas evolution and the aluminium ions content in the electrolyte, or to weigh precisely the samples before and after the anodising, and forming a hypothesis about the chemical composition of the anodic film in spite of the electrolyte nature.

## Conclusions

This study has shown the possibility of preparing thick anodic aluminium porous films using high voltages in a sulphuric acid based electrolyte. The use of strong acid low concentration, low bath temperature and boric acid as modifier allows the author to significantly thicken the anodic porous film preventing its chemical dissolution. The Pilling–Bedworth ratio was analysed and discussed,

especially in the case of these thick anodic porous films. It appeared that the experimental vertical growth coefficient  $K_g$  actually depends on the chemical composition of the anodic films, the porosity percentage and mainly on the anodic current efficiency, impeding a rigorous comparison between different studies. A new relation including  $K_g$  and the theoretical PBR has been finally proposed to take into account the nanoporosity and the anodic current efficiency.

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