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An analysis of the elastic properties of a porous aluminium oxide film by means of indentation techniques

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ABSTRACT

The elastic modulus of thin films can be directly determined by instrumented indentation when the indenter penetration does not exceed a fraction of the film thickness, depending on the mechanical properties of both film and substrate. When it is not possible, application of models for separating the contribution of the substrate is necessary. In this work, the robustness of several models is analyzed in the case of the elastic modulus determination of a porous aluminium oxide film produced by anodization of an aluminium alloy. Instrumented indentation tests employing a Berkovich indenter were performed at a nanometric scale, which allowed a direct determination of the film elastic modulus, whose value was found to be approximately 11 GPa. However, at a micrometric scale the elastic modulus tends toward the value corresponding to the substrate, of approximately 73 GPa. The objective of the present work is to apply different models for testing their consistency over the complete set of indentation data obtained from both classical tests in microindentation and the continuous stiffness measurement mode in nanoindentation. This approach shows the continuity between the two scales of measurement thus allowing a better representation of the elastic modulus variation between two limits corresponding to the substrate and film elastic moduli. Gao's function proved to be the best to represent the elastic modulus variation.

1. Introduction

Aluminium and its alloys have a natural surface heterogeneous oxide film, which is not enough corrosion resistant for many applications [1]. In these conditions, an anodising treatment leading to the formation of a more corrosion resistant thin film is used. The anodising treatment is usually performed in sulphuric acid solutions, giving rise to a porous structure consisting in hexagonal columnar cells like a honeycomb. Each cell consists of a central pore surrounded by alumina walls having both 10–20 nm in dimension. The cells grow normally to the surface of the aluminium substrate, which is separated from the cells by a thin barrier layer of 15 nm of thickness [1]. The structure of such an anodized material has been largely studied [1,2], but only few investigations on the mechanical properties of the porous oxide film have been reported in the past [3,4].

From the investigation of the performance of coated materials it has been determined that the elastic modulus of the film is an important parameter [5–7]. One of the most suitable techniques for determining its value is the instrumented indentation tests by employing the methodology of Oliver and Pharr [8]. The choice of the scale of measurement, *i.e.* nanoindentation and/or microindentation, mainly resides in the nature (*global mechanical properties*, *heterogeneity*, *and presence of porosity*…) and the geometrical parameters (*thickness*, *roughness*, *and pores size*…) of the film. Nevertheless, a direct determination of the elastic modulus is possible by means of nanoindentation when the indenter displacement is less than a limiting value depending on the mechanical properties of the film and of the substrate. This criterion is usually defined in terms of critical ratio of coating thickness to indentation depth. Sun et al. [9] show that this critical ratio is a function of the yield strength ratio and also that it depends on the tip radius. This

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critical ratio is around 1% for a hard film on soft substrate [10,11] but this value can reach up to 20% for a soft film on hard substrate [12,13]. Consequently, a direct determination can be unachievable for very thin films or in microindentation due to the range of applied loads which are not low enough to only affect the film behaviour. In these conditions, models are required for separating the contributions of the film and of the substrate from the measured or, often called, composite reduced modulus. These models have been formerly developed for analysing nanoindentation data by Gao et al. [14], Menčik et al. [15], Perriot and Barthel [16], Antunes et al. [17], Doerner and Nix [18] and Bec et al. [19] on the basis of the best fit of the elastic modulus variation as a function of the indenter displacement, film thickness and some adjusting parameters.

In order to analyze their reliability, all these models were applied in this work on indentation data ranging from nanoindentation to microindentation. For a sound discussion, these models must be applied on proper indentation data which are obtained after calibration of the instrument principally depending on the indentation mode and on the scale of measurement. Usually, the calibration must consider two aspects which can be analyzed separately: (*i*) the rounded-tip-effect on the contact area calculation and (*ii*) the determination of the frame compliance of the instrument/specimen couple. For the contact area calibration, Oliver and Pharr [8] suggested the use of a complex iteration function, which is justified in nanoindentation for the first nanometres of the indenter penetration, typically lower than 200 nm. For higher penetration depths, the correction introduced by Troyon and Huang [20], which consists in adding a constant value to the indenter displacement is enough precise regarding the magnitude of displacements in microindentation.

On the other hand, the frame compliance is considered to have a constant value in nanoindentation, whereas Chicot et al. [21] have shown that, in microindentation, the compliance term depends on the specimen mounting, shape and nature of the sample and testing conditions. Consequently, the frame compliance does not have a constant value for relative high loads and its value must be taken into account for each set of indentation data analyses. For this reason, Tricoteaux et al. [5] developed a model valuable for microindentation experiments, taking into account explicitly the frame compliance [22].

However, in the case of porous film the porosity is a very important parameter which can have a considerable influence on the elastic properties of the film and, consequently, on its elastic modulus value. The relationship between porosity and elastic modulus has been already proposed by Jernot et al. [23] who have connected the elastic modulus of a porous material to the massive one for sintered materials. This model has been modified by Tancret et al. [24] to take into account the size of the pores by separating the role of macro and microporosity. As an example for determining the elastic modulus of a microporous beta-TCP bioceramic, the model of Jernot et al. [23] has been successfully applied by Tricoteaux et al. [25] by neglecting the influence of the macroporosity. From a mathematical point of view, this model relates the elastic modulus of the porous material to the elastic modulus of the massive one, the degree of porosity and the number of grain boundaries connections.

In the present paper, the elastic modulus of a porous aluminium oxide film is determined by means of the instrumented indentation techniques at nano and micrometric scales. In nanoindentation, the continuous stiffness measurement mode is used to plot the elastic modulus as a function of the indenter displacement. In microindentation, the elastic modulus is determined by analyzing the unloading part of a load–depth curve. In this case, a unique value for the elastic modulus is obtained from each indentation curve. Both in nano and in microindentation, the same Berkovich indenter type is used. For analysing the load–displacement curve, the models of Oliver and Pharr [8] and Loubet et al. [26–28] are applied to take into account the deformation around the indent, sinking-in or piling-up, respectively. Indeed, this differentiation of the deformation mode is necessary since it affects the contact depth calculation and consequently, the contact area calculation. Afterwards, all the models are critically applied for determining the elastic modulus of the porous film and the porosity effect is studied by using the model of Jernot et al. [23]. For the tested material, the porosity of the film is associated to the presence of the pores inside the cells. Since the pores have a regular shape, the model of Jernot et al. [23] can be validly applied to compare the elastic modulus of the porous film to that of the massive aluminium oxide [3,4,29].

2. Experimental details

2.1. Material preparation

The experiments were conducted employing samples of a commercial 2017A-T4 aluminium alloy provided as sheet, whose chemical composition is given in Table 1. The metallurgical state T4 indicates that the material was solution treated at 500 °C during 50 min and water quenched at a temperature less than 40 °C. Following this heat treatment, the material was naturally aged for 4 days. After that, the specimens were degreased in an aqueous solution of sodium trisodiumphosphate Na_3PO_4 (60 g/l), sodium carbonate Na_2CO_3 (30 g/l) and sodium dodecylsulphate $C_{12}H_{25}NaO_4S$ (1.5 g/l) at 65 °C for 2 min, followed by rinsing with demineralised water. Then, pickling was done during a period of 5 min at 65 °C in an alkaline bath (10 g/l of NaOH) and neutralized in a sulphuric/chromic mixture (H_2SO_4: 180 ml/l, Cr_2O_3: 60 g/l) for 10 min at 65 °C. Finally, the specimens were anodized during 30 min in an aqueous solution of 180 g/l H_2SO_4 at 20 °C under a current of 1.5 A/dm^2. After anodizing, specimens were washed in distilled water and sealed in boiling water for 30 min at 96 °C.

Fig. 1a shows the scanning electronic microscopy (SEM) observation of the surface of the anodic oxide layer formed on 2017A-T4 aluminium alloy. This figure shows the grain boundaries (*white lines*) which results of the epitaxial growth of the oxides from each grain of the aluminium alloy substrate. Fig. 1b shows at a higher magnification the droplets of aluminium hydroxide which have grown at the surface of the aluminium oxide cells. The presence of the droplets hinders the visualization of the pores inside the cells. These droplets are the natural result of the sealing in boiling water for 30 min at 96 °C after anodization.

Fig. 2 illustrates a cross section of the film obtained after fracture by fatigue of an anodized sample. This figure shows that the mean value of the oxide film thickness is close to 12.5 ± 1.5 μm. This relative high standard deviation is due to the initial roughness of the sample before anodization. Note that in the following, the influence of the underlayer located between the substrate and the aluminium oxide film, having 15 nm of thickness, is neglected in the elastic modulus analysis. This approach is possible due to its relatively low thickness compared to that of the film.

Table 1
Chemical composition of 2017A-T4 aluminium alloy (wt%).

Element	Si	Cu	Ni	Fe	Zn	Mg	Mn	Cr	Ti	Al
wt%	0.57	4.19	0.07	0.47	0.01	0.61	0.29	0.04	0.04	Bal.