A Strain-Energy Method for Determining Residual Stresses in Anodized Thin Films

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ABSTRACT

Residual stresses in thin films are usually evaluated either by measurement of elastic strains in the film or from the curvature or deflection of a film-coated substrate material (the Stoney technique). Both methods are prone to serious measurement errors particularly for thinner films or smaller curvatures or deflections. The Stoney technique is popular because the analysis does not require the elastic modulus of the film. However, residual stress can be determined more accurately using the film modulus. A simple strain-energy analysis using this modulus has been developed to investigate residual stresses in boric acid-sulphuric acid (BSA) anodized films, based on bending measurements of thin coupons. The method is an improvement over Stoney's equation because the square root of the thickness of the film, rather than the thickness itself, is involved, so reducing one of the larger sources of error. The modulus of the film was determined from nanoindentation measurements. The strain-energy method allows analysis of residual stress development in the coupons as functions of film thickness and time. The results show that the residual stress in BSA-anodized films formed on high strength Al-Cu alloy is highly tensile with stress levels up to 400 MPa. The effects of coupon geometry on stress development were also studied and were found to influence the final levels of residual stress developed. These results have implications for the measurement of residual stresses by beam deflection methods.

KEYWORDS Anodizing, residual stress, Stoney equation, strain energy.

1 INTRODUCTION: THE MEASUREMENT OF FILM RESIDUAL STRESS

Experimental techniques for measuring residual stresses in thin films on substrates fall into two classes:

- those based on the direct measurement of elastic strains in the film using X-ray diffraction and other similar techniques, and
- those based on the associated curvature or deflection of the substrate material.

In general, X-ray diffraction techniques are the most informative, allowing determination of all the principal stress components in the film, provided the elastic constants of both the film and the substrate material are known. X-ray diffraction can also be used to detect variations in stress within the film from grain to grain and to find stresses in films with unusual or irregular geometries. However, being based on diffraction, they are limited to crystalline materials of reasonable thickness, so accurate determination of residual stress in very thin films can be problematic. Similarly, thick coatings also pose problems due to X-ray absorption. The other drawback is the need for sophisticated and expensive X-ray equipment and for skilled operators to carry out measurements and analysis. Notwithstanding these problems, X-ray diffraction remains a popular and versatile means for determining residual stress in thin-film coatings.

When the elastic constants of the thin-film coating are not known, or the cost implications too great, the residual stress in films is usually determined using a specimen curvature technique based on a simple bending analysis first proposed by Stoney [1] in 1909. Even for crystalline materials where the elastic constants are known, this substrate curvature technique is often preferred since it is more convenient to use and easier to apply under difficult conditions. Such conditions include *in situ* heating or cooling or stress measurement during the course of film growth or subsequent processing.

1.1 Specimen Curvature Technique – The Stoney Analysis.

Stoney [1], working with electrodeposited nickel coatings on steel substrates, was the first to realise that the residual stress in the coating could be determined from the curvature of a long narrow specimen which had been coated on one side only. In his analysis he assumed that stress in the coating would curve the metal specimen into a circular arc of radius R (its equilibrium curvature). By taking moments about the specimen's neutral axis, he derived an expression for the stress in the coating, σ_c , as

$$\sigma_{\rm c} = \frac{E_{\rm s} t_{\rm s}^{2}}{6Rt_{\rm c}} \tag{1a}$$

where E is Young's modulus, t is thickness, and the subscripts 'c' and 's' refer to coating and substrate materials respectively. This equation can also be extended to the biaxial case by replacing E_s with its biaxial equivalent $E_s/(1-v_s)$, thus

$$\sigma_{\rm c} = \frac{E_{\rm s} t_s^2}{6R(1 - v_s)t_{\rm c}} \tag{1b}$$

where v_s is Poisson's ratio of the substrate material.

When using Equation (1) it is often more convenient, and easier to measure the end deflection of a long narrow specimen rather than its radius of curvature. For this case, $R \approx L^2/2\delta$, and Stoney's equation becomes

$$\sigma_{\rm c} = \frac{E_{\rm s} t_{\rm s}^2 \delta}{3L^2 (1 - \nu_{\rm s}) t_{\rm c}} \tag{1c}$$

where δ is the end deflection of a specimen of length *L*. The direction of the deflection or curvature of the specimen indicates whether the residual stress, σ_c , is tensile or compressive. Stoney assumed that only uniaxial elastic stresses were present and that the coating thickness was negligibly thin in relation to the substrate upon which it forms. His analysis also implicitly assumes that the stress developed in the film remains constant through its thickness. This is generally not the case. For example, Chiu [2] showed that a shallow stress gradient exists through the film thickness from a maximum value at the interface it shares with the substrate to a minimum value at its outer surface. However, although the residual stress in a film calculated using Stoney's equation is only a mean value, it is usually sufficient for most purposes.

The main advantage of the Stoney equation is that the Young's modulus of the film or coating, E_c , is not required to calculate residual stress from the observed deformation. Although there have been some criticisms of the technique [3], it is widely applied where its convenience outweighs its associated errors. The new, and relatively simple, technique presented here represents an alternative method which can be used when the Young's modulus of the coating is known.

1.2 The Strain Energy Method.

At equilibrium, the elastic strain energy in a bent substrate must be equal to, and balance, that in the coating whose residual stress has imposed the bending. The strain energy per unit volume in an elastically-strained body is $\frac{1}{2}\sigma\varepsilon$, or $\frac{1}{2}E\varepsilon^2$ and the total elastic strain energy U in a body of volume V is given by

$$U = \frac{1}{2} E \varepsilon^2 V \tag{2}$$

If the body is a rectangular strip of width w and length L, the total strain energy dU stored in an elemental strip of thickness dy is

$$dU = \frac{1}{2} E\varepsilon^2 w L dy$$
(3)

For bending, and if a specimen with $w \ll L$ is considered, so that the bending strains can be considered uniaxial, then $\varepsilon = 0$ when y = 0 and $\varepsilon = \pm \varepsilon_{\max}$ when $y = \pm t/2$. For a linear variation of strain with depth, the value of the strain at any point is

$$\varepsilon = \frac{2y}{t} \varepsilon_{\max} \tag{4}$$

Substituting into Equation (3) gives the incremental strain energy as

$$dU = \frac{2EwLy^2}{t^2}\varepsilon_{\max}^2 dy$$
(5)

Then the total strain energy is

$$U = \frac{2EwL\varepsilon_{\max}^2}{t^2} \int_{-t/2}^{+t/2} y^2 \, \mathrm{d}y$$
 (6)

giving

$$U = \frac{EwL\varepsilon_{\max}^2 t}{6} \tag{7}$$

For a system where the bending of a substrate results from a residual stress in a coating, the above strain energy must be balanced, for equilibrium, by the total elastic strain energy U_c in the coating. If the mechanism responsible for the residual stress acts uniformly through the film coating thickness, then the deformation should be akin to uniaxial (or biaxial) tension. If this is so, then from Equation (2)

$$U_{\rm c} = \frac{\sigma_{\rm c}^2 V_{\rm c}}{2E_{\rm c}} \tag{8}$$

Equating Equations (7) and (8), and using subscripts 'c' and 's' as before

$$\frac{\sigma_{\rm c}^2 V_{\rm c}}{2E_{\rm c}} = \frac{E_{\rm s} w L \varepsilon_{\rm s(max)}^2 t_{\rm s}}{6} \tag{9}$$

giving the film residual stress as

$$\sigma_{\rm c} = \sqrt{\frac{E_{\rm c} E_{\rm s} \varepsilon_{\rm s(max)}^2 t_{\rm s}}{3t_{\rm c}}} \tag{10}$$

Equation (10) allows the residual stress in the film to be determined simply from the output of strain gauge(s) attached to the substrate material. It applies to the uniaxial stress case, but can be extended to biaxial stresses, when it becomes

$$\sigma_{\rm c} = \sqrt{\frac{E_{\rm c} E_{\rm s} \varepsilon_{\rm s(max)}^2 t_{\rm s}}{3 \left(1 - v_{\rm s}\right) \left(1 - v_{\rm c}\right) t_{\rm c}}}$$
(11)

where v_c and v_s are the Poisson's ratios for the film coating and the substrate respectively.

2 EXPERIMENTAL PROCEDURES.

2.1 Young's Modulus of the Coating

Equations (10) and (11) require that E_c be known. This value can readily be obtained for most thin film materials using nanoindentation, a technique well-established for determining the

hardness and modulus of coated systems [4-9]. To determine the hardness of a coating in isolation of the substrate, the general 'rule of thumb' is that the indentation depth must be less than $1/10^{\text{th}}$ of the coating thickness [9]. The substrate plays an important part in providing an elastic foundation for coating and it is difficult to measure a coating-only modulus. The substrate continues to play a role in the measured indentation modulus even for indentations as shallow as 0.01% of the coating thickness [10]. However, for indentations that are a small proportion of the film thickness, the effect of the substrate modulus on the measured system response is relatively small and good correlation has been found between measured indentation modulus and moduli measured by other techniques [11].

The nanoindentation measurements were performed using a Nano Indenter II^{TM} at the University of Newcastle. The coated samples were firmly waxed to aluminium sample holders with a high purity thermoplastic wax (Lakeside 60). The thin wax layer appears 'stiff' to the indenter. In order to eliminate as much thermal drift as possible, specimens were then allowed to thermally equilibrate within the thermally-lagged Nano Indenter II^{TM} cabinet for at least 12 hours. The sample mount forms part of the 'load frame stiffness' calibration constant. The machine had previously been calibrated using the method of Oliver & Pharr [13, 14] for indentations in fused silica. The data from digital volt meters on the load coil and capacitor were processed using propriety software which converts the load and displacement in volts to load in mN and displacement in nm and corrects for load frame stiffness, thermal drift, and spring constants etc. The load-displacement data can then be plotted and the unloading stiffness can be used to obtain the indentation modulus of the material.

The modulus is found using the equation

$$S = \frac{\mathrm{d}P}{\mathrm{d}h} = \frac{2}{\sqrt{\partial}} \,\hat{\mathrm{a}} E_{\mathrm{r}} \sqrt{A} \tag{12}$$

where S is the unloading stiffness, and A is the projected area of the indentation [13-17]. β is a constant that depends on the geometry of the indenter (1.034 for a Berkovich indenter geometry). $E_{\rm r}$ is the reduced modulus and is given by

$$\frac{1}{E_{\rm r}} = \frac{\left(1 - v^2\right)}{E} + \frac{\left(1 - v_i^2\right)}{E_i}$$
(13)

where E and v are the Young's modulus and Poisson's ratio for the specimen and E_i and v_i are the same parameters for the indenter. Equation (12) originates from Sneddon's [18] analysis of load-displacement and contact area for any punch that can be described as a solid of revolution of a smooth function.

The modulus for the sample is obtained from estimating the plastic contact area from the plastic contact depth (after subtracting any elastic displacement) and then using this in Equation (12) with the known Young's modulus and Poisson's ratio for the indenter. The exact modulus and hardness depend critically on the calibration of the machine and the values chosen for Poisson's ratio. This is discussed in more depth by Hay *et al* [19]. To check that the values for contact area calculated from the unloading curves were correct, the indentations were imaged in an FEI Sirion 200 FEG scanning electron microscope (SEM) and the areas measured using Image Pro v4.0 (Media Cybernetics, Inc., Silver Spring, USA). This allowed any effects owing to pile-

up/sink-in of the underlying aluminium substrate to be accounted for. A value of 0.25 was used for the Poisson's ratio in the calculations [20].

2.2 Anodized Coupons

Three different specimen configurations, as shown in Figure 1, were anodized and used to test the effectiveness of Equations (10) and (11). The specific anodizing schedule used for the boric-sulphuric anodized (BSA) process is detailed elsewhere [12], and the specimen material used for these tests was a 2000 series Al-Cu alloy in the T4 or T6 condition. To ensure adequate bending of the substrate material, in response to the film residual stress, a 22-gauge specimen thickness (0.68 mm) was used.

The film-induced bending strains which developed in each of the specimens were determined using standard foil-type strain gauges, of gauge length 3.18 mm and resistance 120 Ω , bonded in the locations shown in Figure 1. These gauges were bonded in place using a high-temperature, heat-curing, epoxy resin to ensure that the strain gauges did not detach during the anodizing or sealing of the coupons.



Figure 1 Specimen geometries and strain gauge locations

To protect the strain gauges from the electrolyte, and to allow anodizing on one side only, each specimen was coated, on the strain-gauged side, with a thin layer of a proprietary silicone rubber sealing compound. This rubber compound was very flexible (low modulus) and so had very little effect on the film-induced bending of the substrate material. It also adhered sufficiently well to it to prevent ingress of the electrolyte to the strain gauge locations. A section through a specimen, in the vicinity of the strain gauges, is shown in Figure 2.

To compensate for any changes in temperature, each active strain gauge had a similar dummy gauge connected in a half-bridge arrangement. This ensured that the measured strain values

were due only to the film-induced bending and not to the presence of any stray temperature effects. Before the specimens were anodized and sealed, each strain gauge was zeroed, with the reference environment being standard laboratory conditions.



Figure 2 Strain gauge locations relative to anodic oxide film

After processing, the specimens were removed from the sealing bath and the readings from the gauges monitored continuously using a chart recorder over a period of approximately fifty to sixty hours. At the end of this monitored period, the thickness of the anodic oxide films was measured using an eddy current meter and the results checked in an SEM. The specimen and film property details are given in Table 1.

Specimen type	Alloy	t _c /μm	t _s /mm
1	2014:T6	2.31	0.68
2	2024:T4	2.03	0.68
3	2014:T4	1.75	0.68

Table 1 Specimen details for residual stress experiments

2.3 Radius of Curvature Measurement.

To check the validity of the results obtained using the strain energy method, against the standard Stoney analysis, an additional specimen (type 3^*) was anodized and sealed in the manner described. Once removed from the sealing bath, this specimen was clamped at one end and its curvature measured from the deflections at six positions in the *x*-*y* plane along its length, as

shown in Figure 3, using a travelling microscope. The specimen was confirmed as being nominally flat before anodizing and the developing substrate strain was monitored as before after the specimen was removed from the sealing bath.



Figure 3 Radius of curvature and coupon deflection

Using a non-linear regression analysis, the best-fit circle was obtained from these data so providing the radius of curvature, R, of the specimen. In addition, the end deflection of the specimen, δ , was also measured. These results together with all other specimen details for the deflection experiment are shown in Table 2.

Specimen type	Alloy	t _c /μm	t _s /mm		
3*	2014:T4	2.98	0.68		
Radius of curvature, $R = 8.38$ m					
Deflection, $\delta = 1.41 \text{ mm}$					

 Table 2 Specimen details and results for deflection experiment

3 EXPERIMENTAL RESULTS AND DISCUSSION.

The BSA anodizing process produces a very thin barrier type film, generally $2.0-3.0 \mu m$ thick depending on processing time. This type of film is much more compact than that usually obtained from conventional sulphuric acid or chromic acid anodizing processes. As shown in Figure 4, the structure of this type of film coating contains few crack-like defects. The lack of porosity and associated stress-relieving mechanisms mean that the residual stress developed in the film is likely to be tensile.



Figure 4 Scanning electron micrograph of film-substrate interface

3.1 Nanoindentation Measurements

Figure 5 shows two typical indentations into an anodized coupon.



Figure 5 (a) 500 mN and (b) 50 mN maximum load indentation into an anodized coupon

It can be seen that there is extensive cracking around the indentation at 500 mN load as the coating has bent and flexed to accommodate the deformation in the substrate. Extensive cracks are evident at the indentation corners and edges and inside the indentation itself indicating that the coating has a low inherent fracture toughness. The residual depth of indentation at this load was approximately $3.2 \,\mu$ m, which is substantial given that the film thicknesses were of the order of 2-3 μ m. Lower load indentations made to 50 mN peak load (which generally did not show cracking) were used to calculate the modulus and hardness of the films. Figure 5 shows a typical 50 mN indentation into the coated sample.



Figure 6 A typical load-displacement curve for a 50mN indentation into an anodized sample

The 50 mN indentation shown in Figure 6 penetrated to a maximum depth of 1.13 μ m. This is greater than the recommended value of indentation depth to film thickness ratio of $\sim t/10$ for the values to truly represent the coating-only properties. However, at lower peak loads, effects from film roughness and residual porosity gave unacceptable scatter in the mechanical property data. The load-displacement curve shown in Figure 6 does not show any evidence of pop-in which might be related to cracking events and combined with the evidence from the microscopy confirms the absence of cracks. The values for indentation (Young's) modulus and hardness that were calculated from these indentations were 97 (± 4) GPa and 2.5 (±0.2) GPa (or 231 VHN) respectively. These values have been corrected for any pile-up/sink-in as the areas used were those measured from the scanning electron micrographs. The modulus value reported here correlates well with values of modulus previously reported by Alwitt *et al* [20].

3.2 Coupon Residual Stress Measurements.

To calculate the magnitude of the residual stress in a film from Equations (10) and (11) the Young's modulus, E_{c} , of 97 GPa measured using nanoindentation was used. The value of Poisson's ratio, $v_{c} = 0.25$, was obtained from the literature, [20]. The calculated stresses thus obtained are shown in Figure 5 for coupon types (1), (2) and (3) for both the x and y directions (as defined in Figure 1). These results show that the residual stress developed in BSA films is indeed tensile for both the uniaxial and the biaxial case. The maximum residual stress developed varied according to the specimen geometry, with the largest residual stress, $\sigma_c = 410$ MPa, being developed in type (3), i.e. the long, narrow specimen. Such a variation was to be expected since the shape of the specimen would largely determine the degree of bending taking place in the x and v directions. The least amount of bending developed in specimen type (1) and was essentially biaxial due to the equal geometric (Poisson's) constraint offered by this shape in the two directions. The measured strains were approximately equal in both the x and y directions and hence the residual stress causing this deformation is isotropic and planar within the film with the maximum calculated values being $\sigma_{c(x)} = 250$ MPa and $\sigma_{c(y)} = 230$ MPa respectively. Between these two extremes, the bending that developed in specimen type (2) was again biaxial, although the stresses which developed were not identical, $\sigma_{c(x)} = 150$ MPa and $\sigma_{c(y)} = 280$ MPa, due to the unequal constraint offered by this shape of specimen in the two axis directions. Thus, within the context of the present work the tensile residual stress which develops in BSA anodised films lies in the range 150 - 410 MPa with the largest stress being developed in the long axes. The results obtained for all three specimen geometries compare favourably with the values obtained using the traditional Stoney approach, viz. using the radius of curvature and end deflection measurements for specimen 3* the residual stress in the film was calculated as σ_c = 350 MPa and $\sigma_c = 360$ MPa respectively.



Figure 5 Development of residual stress with time after anodizing and sealing

3.3 Origins of Thin-Film Residual Stress

The most noticeable feature of these results was the fact that in all cases it was indicated that initially the strain values increased rapidly before levelling out to a maximum, and fairly stable, value towards the end of the test period. This observation suggests that the residual stress develops quite quickly in the film after processing. These results are similar to those obtained by others viz. Alwitt *et al* [20], Bradhurst and Leach [21]. Alwitt *et al* postulated that the stress introduced during sealing is the sum of three distinct contributory stages:

- i. the process stress resulting from the seal reaction at 100°C,
- ii. rapid ageing and structural changes in the freshly sealed oxide on going from an aqueous to an air environment,
- iii. the thermal stress due to cooling from the sealing temperature of 100°C to room temperature.

They suggested the following: the process stress would be compressive due to the introduction of water into the film. This would cause structural changes to take place in the oxide as its pore volume filled up but with no increase in the coating thickness itself. The stress brought about by the transfer from an aqueous to an air environment is of unknown magnitude but is most likely tensile as excess water is lost. The stress that develops during cooling must be compressive since it is caused by the difference in the thermal expansion coefficients of the coating and the underlying substrate. Finally, Alwitt and his co-workers reported that the coating stress, in anodized films measured in air (using the standard end deflection technique), was tensile after anodizing and compressive following sealing in boiling water. However the stress in this oxide coating was also found to be highly dependent upon humidity, with a large tensile residual stress (~110 MPa) being present in dry air. The influence of environmental humidity has also been shown to affect the elastic modulus of the anodized film. Hockenhull et al [22] showed that the modulus of sulphuric acid-anodized films in situ could vary markedly as a function of both relative humidity and film thickness. Under normal atmospheric conditions (taken here as 65 % relative humidity) the Young's modulus for these porous films was found to be ~99 GPa for a 5 μm film, ~67 GPa for a 10 μm film, and ~54 GPa for a 20 μm film. These workers concluded that the increase in the stiffness of the film as function of relative humidity was due to the dehydration of the aluminium oxide monohydrate (boehmite) which occurred during, and continued after, sealing. This conclusion is borne out by the results of the present study.

Thus, a considerable variation has been reported in the literature for the type of residual stress present in anodic oxide films, with both tensile and compressive stresses being possible. However, this variability may be rationalised if one invokes the notions of internal stress development put forward by Alwitt *et al.* [20]. The final residual stress state of sealed anodic oxide films is dependent upon the relative magnitude of the stresses developed during stages (i) to (iii) above. The type of stress developed, either tensile or compressive, is dictated by the largest of these contributory factors. For unsealed oxide films a mechanism similar to stage (ii) will be largely responsible for the type of film stress developed as the oxide ages after anodizing, with its magnitude depending upon the relative humidity of its environment.

4 CONCLUSIONS

The results of these experiments show that the strain-energy method is a simple and viable method for determining the residual stress developed in anodic oxide films. The results obtained were reproducible and self-consistent with regards to the specimen geometries employed. In particular, the following major conclusions were reached.

- The residual stress that develops in a thin anodic oxide film produced by the boricsulphuric acid anodizing process is highly tensile after sealing.
- Residual stress development in the film is gradual, with a maximum, and reasonably stable, value being reached after approximately fifty hours. This gradual increase in the residual stress is related to the dehydration of the film, post-sealing, and to the ageing and structural changes that take place during this period.
- The strain-energy method developed in this work is a viable means of determining the sign and magnitude of the residual stresses developed in anodic oxide films with the indicated values of calculated residual stress being in the range 150–400 MPa. This range compares favourably to those obtained from the established Stoney method.

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