Strain–energy method for determining residual stresses in anodised thin films

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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) anodised 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, therefore 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 anodised 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: Anodising, Residual stress, Stoney equation, Strain energy

Introduction: measurement of film residual stress

Experimental techniques for measuring residual stresses in thin films on substrates fall into two classes:
(i) those based on the direct measurement of elastic strains in the film using X-ray diffraction and other similar techniques
(ii) 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, therefore accurate determination of residual stress in very thin films can be problematic. Similarly, thick coatings also pose problems owing 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 Stoney1 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.

Specimen curvature technique: 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 neutral axis of the specimen,
be derived an expression for the stress in the coating $\sigma_c$ as

$$\sigma_c = \frac{E_s t_s^2}{6R t_c} \quad (1a)$$

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 $E_c$ with its biaxial equivalent $E_s/(1-v_s)$, thus

$$\sigma_c = \frac{E_s t_s^2}{6(1-v_s)R t_c} \quad (1b)$$

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, $R = L^2/2\delta$, and Stoney’s equation becomes

$$\sigma_c = \frac{E_s t_s^2 \delta}{3L^2(1-v_s) t_c} \quad (1c)$$

where $\delta$ 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 $\sigma_c$ 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\textsuperscript{2} showed that a shallow stress gradient through its thickness. This is generally not the case. For example, Chiu\textsuperscript{2} showed that a shallow stress gradient

- Substituting into equation (3) gives the incremental strain energy as
  
  $$dU = \frac{2E_sL}{t^2} y_s^2 \max dy$$
  
  Then the total strain energy is
  
  $$U = \frac{2E_sL \max}{t^2} \int_{-1/2}^{1/2} y^2 dy$$
  
  giving
  
  $$U = \frac{E_sL^3}{6 t}$$

  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)

- Equating equations (7) and (8) and using subscripts ‘c’ and ‘s’ as before
  
  $$\sigma_s^2 \frac{V_c}{2E_c} = \frac{E_s \max}{6}$$

  giving the film residual stress as

  $$\sigma_c = \left[ \frac{E_c \max}{3E_c} \right]^{1/2}$$

  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

- Equation (11) requires 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.\textsuperscript{5-9} 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 one-tenth of the coating thickness.\textsuperscript{9} The substrate plays an important part in providing an elastic foundation for

### Strain energy method

**Strain energy method**

At equilibrium, the elastic strain energy in a bent substrate must be equal to, and balance, that in the coating the residual stress of which has imposed the bending. The strain energy per unit volume in an elastically strained body is $1/2E_e V$ and the total elastic strain energy $U$ in a body of volume $V$ is given by

$$U = \frac{1}{2} E_e V$$

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

$$dU = \frac{1}{2} E_e w L dy$$

For bending, and if a specimen with $w<<L$ is considered, so that the bending strains can be considered

**Unitary, 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

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

**Experimental procedure**

**Young’s modulus of 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.\textsuperscript{5-9} 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 one-tenth of the coating thickness.\textsuperscript{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. 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.

The nanoindentation measurements were performed using a Nano Indenter II 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 cabinet for at least 12 h. The sample mount forms part of the ‘load frame stiffness’ calibration constant. The machine had previously been calibrated using the method of Oliver and Pharr for indentations in fused silica. The data from digital voltmeters on the load and displacement in volts to load in mN and displacement in nm, and 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

\[ S = \frac{dP}{dh} = \frac{2}{\pi^{3/2}} \beta E_i A^{1/2} \]  

(12)

where \( S \) is the unloading stiffness, and \( A \) is the projected area of the indentation. \( \beta \) is a constant that depends on the geometry of the indenter (1.034 for a Berkovich indenter geometry). \( E_i \) is the reduced modulus and is given by

\[ \frac{1}{E_i} = \frac{1}{E} - \frac{1}{E_v} \]  

(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 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. 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.

Anodised coupons

Three different specimen configurations, as shown in Fig. 1, were anodised and used to test the effectiveness of equations (10) and (11). The specific anodising schedule used for the boric–sulphuric anodised (BSA) process is detailed elsewhere 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 Fig. 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 anodising or sealing of the coupons.

To protect the strain gauges from the electrolyte and to allow anodising 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 Fig. 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 anodised and sealed, each strain gauge was zeroed, with the reference environment being standard laboratory conditions.

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 50–60 h. 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.

**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 anodised 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 Fig. 3, using a travelling microscope. The specimen was confirmed as being nominally flat before anodising and the developing substrate strain was monitored as before after the specimen was removed from the sealing bath.

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

**Results and discussion**

The BSA anodising 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 anodising processes. As shown in Fig. 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.

**Nanoindentation measurements**

Figure 5 shows two typical indentations into an anodised 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 $\sim 3.2 \mu m$, which is substantial given that the film thicknesses were of the order of 2–3 $\mu m$. 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.

The 50 mN indentation shown in Fig. 5 penetrated to a maximum depth of 1.13 $\mu m$. 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 Fig. 6 does not show any evidence of pop-in which might be related to cracking events and combined with the evidence from the microscopy that confirms the absence of cracks. The values for indentation (Young’s) modulus and hardness that were calculated from these indentations were $97 (\pm 4)$ GPa and $2.5 (\pm 0.2)$ GPa (or 231 HV) 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.19

**Table 1** Specimen details for residual stress experiments

| Specimen type | Alloy     | $t_b, \mu m$ | $t_s, \mu m$ |
|---------------|-----------|--------------|--------------|
| 1             | 2014:T6   | 2.31         | 0.68         |
| 2             | 2024:T4   | 2.03         | 0.68         |
| 3             | 2014:T4   | 1.75         | 0.68         |

**Table 2** Specimen details and results for deflection experiment

| Specimen type | Alloy     | $t_b, \mu m$ | $t_s, \mu m$ |
|---------------|-----------|--------------|--------------|
| 3*            | 2014:T4   | 2.98         | 0.68         |

Radius of curvature $R=8.38$ m, deflection $\delta=1.41$ mm.
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, \( \nu_c = 0.25 \), was obtained from the literature.\(^{19}\) The calculated stresses thus obtained are shown in Fig. 7 for coupon types 1, 2 and 3 for both the \( x \) and \( y \) directions (as defined in Fig. 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 \( y \) directions. The least amount of bending developed in specimen type 1 and was essentially biaxial owing 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, owing 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 of 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, namely using the radius of curvature and end deflection measurements for specimen 3\(^*\), the residual stress in the film was calculated as \( \sigma_c = 350 \) MPa and \( \sigma_c = 360 \) MPa respectively.

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, namely Alwitt \textit{et al.} \(^{19}\) Bradhurst and Leach.\(^{21}\) Alwitt \textit{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 aging 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 owing 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 co-workers reported that the coating stress, in anodised films measured in air (using the standard end deflection technique), was tensile after anodising 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 anodised film. Hockenhull et al.\(^{22}\) showed that the modulus of sulphuric acid anodised 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 \(\sim 99\) GPa for a 5 \(\mu\)m film, \(\sim 67\) GPa for a 10 \(\mu\)m film and \(\sim 54\) GPa for a 20 \(\mu\)m film. These workers concluded that the increase in the stiffness of the film as a 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 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 \(\sim 99\) GPa for a 5 \(\mu\)m film, \(\sim 67\) GPa for a 10 \(\mu\)m film and \(\sim 54\) GPa for a 20 \(\mu\)m film. These workers concluded that the increase in the stiffness of the film as a 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.

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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 regard to the specimen geometries employed. In particular, the following major conclusions were reached.

1. The residual stress that develops in a thin anodic oxide film produced by the boric–sulphuric acid anodising process is highly tensile after sealing.
2. Residual stress development in the film is gradual, with a maximum, and reasonably stable, value being reached after \(\sim 50\) h. This gradual increase in the residual stress is related to the dehydration of the film, post-sealing, and to the aging and structural changes that take place during this period.
3. The strain–energy method developed in the present 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 of 150–400 MPa. This range compares favourably with those obtained from the established Stoney method.

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