

## **Measurement of the Poisson's ratio of Coatings**

Poisson's ratio is important for the characterisation of coatings, as it is required to determine their mechanical properties using techniques such as depth sensing indentation and surface acoustic wave spectroscopy. However, until now it has been extremely difficult to measure the Poisson's ratio of a coating and it is therefore commonly assumed, often incorrectly, to be the same as that of the bulk material.

This Measurement Note therefore describes a method by which the Poisson ratio can be determined by comparing the Young's modulus obtained from impact excitation to the plane strain modulus (indentation modulus) obtained from depth-sensing indentation. Impact excitation is used to determine the Young's modulus of the coating independent of Poisson's ratio. This result is then used in combination with nanoindentation results to determine the Poisson's ratio of the coating. This technique has been successfully used to determine the Poisson's ratio of titanium nitride coatings applied to different stainless steel and niobium substrates.

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## 1 Introduction

Knowledge of Poisson's ratio is extremely important for the characterisation of coatings, as it is needed to determine the mechanical properties of coatings in techniques such as depth-sensing indentation and surface acoustic wave spectroscopy. Measuring the Poisson's ratio of a coating is extremely difficult and for this reason it is often assumed that the Poisson's ratio of a coating is the same as that of the bulk material. However, this is often not the case. A method is therefore proposed by which the Poisson ratio,  $\nu$ , can be determined by comparing the Young's modulus,  $E$ , obtained from impact excitation to the plane strain modulus,  $E^*$ , (indentation modulus) obtained from depth-sensing indentation, assuming:

$$E^* = \frac{E}{(1 - \nu^2)}$$

Measurement of elastic properties of uncoated homogenous materials by impact excitation is a well-established technique<sup>1,2</sup>. When a specimen is caused to vibrate it emits an audible signal, the frequency of which depends on its elastic properties, mass and geometry. By measuring the fundamental frequency emitted it is possible to calculate the Young's modulus of the material. It is, however, necessary when using this technique to include a correction factor to take account of transverse shear, which is dependent upon the dimensions of the specimen and its Poisson's ratio.

Recently the above technique has been extended<sup>3</sup> using Euler-Bernoulli theory<sup>4</sup> to determine the Young's modulus from the harmonics as well as the fundamental frequency without using a material dependent correction factor. Euler-Bernoulli theory does not take account of transverse shear but previous studies<sup>3</sup> have shown that the influence of transverse shear becomes negligible, as the harmonic frequency tends to zero. This allows values of Young's modulus to be obtained from the zero frequency intercept of a plot of modulus against harmonic frequency. Further refinement of this method has

allowed this technique to be used to determine the Young's modulus of coatings. This is achieved by comparing the frequency spectra obtained from the coated material to that of the original substrate.

Once an accurate value of Young's modulus,  $E$ , is obtained from impact excitation (independent of a knowledge of Poisson's ratio) it is possible by combining this result with the indentation modulus obtained from depth-sensing indentation,  $E^*$ , to calculate the Poisson's ratio,  $\nu$ , using the following expression<sup>5</sup>:

$$\nu = \sqrt{1 - \frac{E}{E^*}}$$

This paper describes how this technique has been used to determine the Poisson's ratio of thin (<3  $\mu\text{m}$ ) titanium nitride coatings that have been applied to a range of different stainless steel and niobium substrates.

## 2 Experimental Procedure

### 2.1 Specimens Preparation

#### 2.1.1 Substrate

The two substrates used in these experiments were 304 stainless steel and niobium. The length and width of the specimens were 70 mm and 15 mm, with three nominal thicknesses of 0.87 mm, 1.24 mm and 1.84 mm (Table 1). The dimensional accuracy of the substrates has a significant effect on the results, so particular care was taken to ensure that the sides of the specimen were parallel, and that the dimensions and mass were accurately measured.

#### 2.1.2 Coatings

Samples were coated with TiN by reactive sputter deposition. Prior to deposition, samples were ultrasonically cleaned and rinsed in iso-propanol. They were then sputter etched in Argon plasma. TiN was deposited from a titanium target in Argon/Nitrogen plasma at  $2 \times 10^{-2}$  mbar. A target power of 800W and a DC bias voltage of -80V were used. The Argon/Nitrogen ratio was controlled by optical emission spectroscopy to prevent

target poisoning. Samples were held at 400 °C and rotated at 8 rpm throughout.

The thickness of each coating was determined using a gravimetric technique. This involved weighing the specimen before and after coating to determine the mass of TiN deposited on the surface. The mass,  $m$ , density,  $\rho$ , and surface area,  $A$ , of the coating were used to calculate the average thickness,  $h$ , using the following expression:

$$h = \frac{m}{A\rho}$$

**Table 1** Thickness for TiN coatings.

| Code | Substrate material | Substrate thickness (mm) | Coating thickness ( $\mu\text{m}$ ) |
|------|--------------------|--------------------------|-------------------------------------|
| A    | Steel              | 0.87                     | 0.95                                |
| B    | Steel              | 0.87                     | 2.28                                |
| C    | Steel              | 0.87                     | 2.66                                |
| D    | Steel              | 1.24                     | 2.07                                |
| E    | Steel              | 1.84                     | 1.67                                |
| F    | Niobium            | 0.81                     | 1.34                                |

To verify the gravimetric results the coating thickness of specimen B was determined by sectioning the specimen and measuring the coating thickness using a Scanning Electron Microscope (SEM). The result, 2.34  $\mu\text{m}$ , confirms that there is good agreement between the average thickness obtained by the gravimetric technique and the average thickness measured using SEM.

## 2.2 Impact Excitation

Tests were performed using an IMCE Resonant Frequency Damping Analyser (RFDA). A schematic diagram of the apparatus is shown in Figure 1. The specimen was supported by two thin wires located at the fundamental nodal points a distance of  $0.224 \times l$  from each end, where  $l$  is the length of the specimen. An automatic impulser was used to excite flexural vibrations in the specimen by striking lightly at the centre of the specimen. A non-contacting microphone placed near the end of the specimen was used to pick-up the specimen's response. The RFDA was used to obtain the frequency spectrum and identify between 6 and 10 overtones for each specimen. Frequency spectra were obtained for each specimen both before and after deposition of the TiN coating.

## 2.3 Nano-indentation

Values for the indentation modulus of the TiN coatings were determined using depth-sensing nanoindentation. This was conducted using an MTS-Nano Instruments Nanoindenter II with a Berkovich diamond indenter. Specimens were mounted on aluminium stubs using thermoplastic wax (mp. 80 °C). Indentation experiments were conducted at three different test forces to determine the composite modulus from both substrate and coating as a function of contact depth. The rates at which the force was applied to the indenter and the maximum forces applied are given in Table 2.

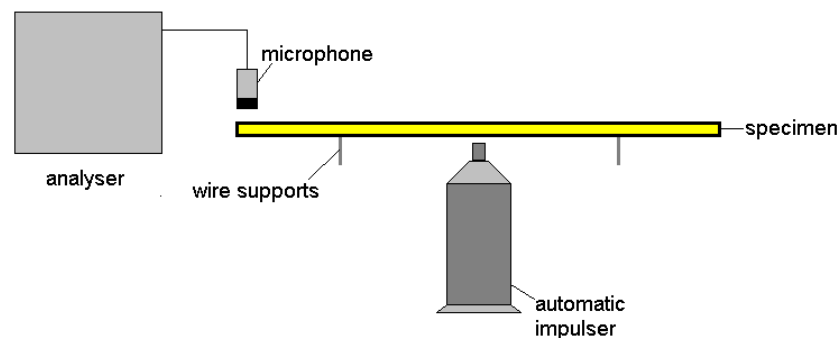


**Figure 1: Diagram of the RFDA Test Apparatus**

In each case the maximum applied force was held for 60 seconds to minimise the influence that creep has upon the measurement of contact stiffness. To obtain a reliable estimate of indentation modulus, each indentation experiment was repeated 20 times at 50  $\mu\text{m}$  intervals. The laboratory temperature was controlled throughout the experiments at  $22 \pm 0.2^\circ\text{C}$  and the instrument further protected from short-term temperature fluctuations by two passive enclosures. Thermal drift corrections calculated from a 60 second hold period at the beginning of each indent experiment were used to correct for residual drift, which was typically less than  $0.1 \text{ nm s}^{-1}$ .

**Table 2** *Loads and rates used in the indentation experiments.*

| Experiment number | Maximum Load (mN) | Loading Rate (mN/sec) |
|-------------------|-------------------|-----------------------|
| 1                 | 10                | 0.5                   |
| 2                 | 20                | 1.0                   |
| 3                 | 40                | 2.0                   |

### 3 Results and Discussion

#### 3.1 Impact Excitation

##### 3.1.1 Modulus of substrates

Theoretical values for the modulus of the substrate,  $E_{s(i)}$ , were determined from the fundamental frequency and all the harmonics using Euler-Bernoulli theory. This uses non-dimensional Eigen-frequencies,  $f_{s(i)}$ , to calculate the modulus at each peak in the spectra thereby avoiding the use of material dependent parameters such as Poisson's ratio. The fundamental resonant peak is designated as eigen-frequency  $i=1$  and subsequent harmonics are numbered in order of frequency. The equation derived from Euler-Bernoulli theory to calculate the modulus values for the uncoated substrates is:

$$E_{s(i)} = \frac{48\pi^2 l_s^3 m_s f_{s(i)}^2}{X_{(i)}^2 b_s h_s^3}$$

where  $l_s$ ,  $b_s$ ,  $h_s$  are length, breadth and height of the substrate and  $m_s$  is substrate

mass.  $X_{(i)}$  indicates the non-dimensional eigen-frequencies of order  $i$  (Table 3).

**Table 3** *Non-dimensional Eigen-frequencies*

| $i$ | $X_i$             |
|-----|-------------------|
| 1   | 22.373            |
| 2   | 61.670            |
| 3   | 120.912           |
| 4   | 199.895           |
| $i$ | $[(2i+1)\pi/2]^2$ |

A modulus value was computed for each of the harmonics using the above equation. Figures 2 shows typical plots of these values as a function of frequency. It can be seen from these curves that the modulus first increases at low frequencies and then decreases at the higher frequencies. In practice, the modulus of stainless steel should be independent of frequency. This difference results from the fact that the Euler-Bernoulli equations fail to take into account transverse shear. It can, however, be seen that by fitting a second order polynomial to the impact excitation data and extrapolating the curves back to zero frequency, it is possible to obtain repeatable values of modulus. Moreover, the values that have been obtained (Table 4) for both the stainless steel and niobium substrates are consistent with those given in the literature<sup>6</sup> (Stainless steel, 200-207 GPa; Niobium, 103 GPa).

**Table 4** *Young's modulus of the uncoated specimens.*

| Code | $h_s$ (mm) | $E_s$ (GPa) |
|------|------------|-------------|
| A    | 0.87       | 204         |
| B    | 0.87       | 206         |
| C    | 0.87       | 205         |
| D    | 1.24       | 204         |
| E    | 1.84       | 199         |
| F    | 0.81       | 109         |

The results that have been obtained are consistent with the findings from previous studies by Nivoit<sup>3,7</sup>, in which a numerical simulation was used to examine the effect transverse shear has on the modulus results obtained from Euler-Bernoulli

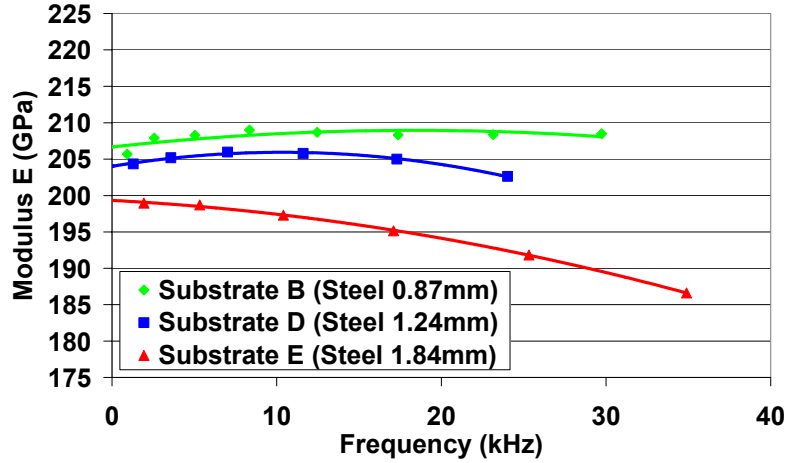


**Figure 2:** Calculated modulus as a function of harmonic frequency for three stainless steel substrates of different thicknesses.

theory. This simulation indicated that the modulus results decrease as the thickness of the specimens increases, which is consistent with the impact excitation results reported here (Figure 2). It was also observed in the numerical stimulation that as the frequency tends to zero the effect of transverse shear on the modulus becomes negligible. Again this is consistent with the results obtained in Figure 2, where it can be seen that the modulus results from all the specimens converge to a single point at zero frequency indicating that the effects of transverse shear at this point are negligible. Nivoit<sup>3</sup> concluded that as transverse shear was negligible at zero frequency an exact value of Young's modulus could be obtained at this point. Again this would appear to have been verified as the results obtained for stainless steel and niobium at the y-axis (Table 4) are both consistent with relevant Young's modulus values in the literature.

### 3.1.2 Modulus of coatings

Values for the Young's modulus of the titanium nitride coatings were obtained by comparing the dynamic response obtained from each coated specimen to that obtained from its substrate before coating. Using Euler-Bernoulli theory, the modulus of the coating,  $E_{c(i)}$ , at each Eigen-frequency is given by the equation:

$$A \left( \frac{E_{c(i)}}{E_{s(i)}} \right)^2 + B_{(i)} \left( \frac{E_{c(i)}}{E_{s(i)}} \right) + C_{(i)} = 0$$

where:

$$A = \left( \frac{h_c}{h_s} \right)^4$$

$$B_{(i)} = 4 \left( \frac{h_c}{h_s} \right)^3 + \left( 6 - \frac{h_s m_c f_{t(i)}^2}{h_c m_s f_{s(i)}^2} \right) \left( \frac{h_c}{h_s} \right)^2 + \left( 4 - \frac{f_{t(i)}^2}{f_{s(i)}^2} \right) \left( \frac{h_c}{h_s} \right)$$

$$C_i = 1 - \frac{f_{t(i)}^2}{f_{s(i)}^2} \left( 1 + \frac{m_c}{m_s} \right)$$

where:  $l$ ,  $h$  and  $m$  indicate length, height and mass, respectively and  $f_i$  and  $E_i$  represent the eigen-frequency and the corresponding modulus. The subscripts  $s$ ,  $c$  and  $t$  refer to the relevant values for the substrate, coating and total specimen.

Figure 3 shows typical results obtained for the moduli of the coatings,  $E_{c(i)}$ , calculated using the above equations. The results show that the coating modulus calculated from the Euler-Bernoulli equations increases with harmonic frequency. The modulus varying most rapidly when the coating is thin compared with the substrate. It should, however, be noted that the modulus values for each specimen

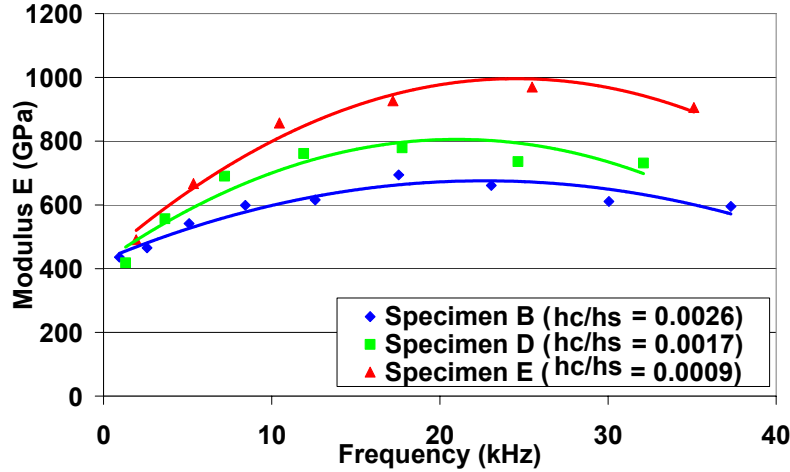


**Figure 3:** *Calculated modulus of TiN coatings on three stainless steel substrates of different thicknesses ( $h_c/h_s$  = coating/substrate thickness).*

converge to a single point, as the harmonic frequency tends to zero. Values for the modulus of the coating at zero frequency are given in table 5. Typical values of uncertainty for the impact excitation technique are quoted<sup>7</sup> at 6%. The average value of modulus in these experiments is 427 GPa. This value is in agreement with literature values for PVD titanium nitride obtained using acoustic microscopy<sup>7</sup> which quotes a modulus for this type of coating of  $409 \pm 5$  GPa.

### 3.2 Indentation Modulus of Coatings

Values for the indentation modulus,  $E^*$ , of the coated specimens were obtained by depth-sensing indentation<sup>8</sup> (DSI). Typical results are shown in Figures 4 as a function of the radius of contact area / coating thickness.

Each data point shown on the graphs represent the mean,  $\bar{x}$ , of 20 independent indentation experiments performed at different positions on the specimen. Repeatability has been calculated using the following equation for the standard uncertainty of the mean,  $U$ ,

$$U = k \frac{s}{\sqrt{n}}$$

where,  $n$  is the number of indentation experiments,  $s$  is the standard deviation and  $k$  is the coverage factor for 95% confidence limits from a t-distribution. It is this standard uncertainty of the mean,  $U$ , that has been used for the error bars in Figure 4.

Indentations were made at three different depths to assess the influence the substrate has on the modulus. The deeper the indenter penetrates into the specimen the more the substrate influences the modulus results. Low forces were therefore desirable to reduce the depth the indenter penetrates into the specimen. The minimum depth that could be used was, however, limited to 50 nm due to uncertainties in the area function of the indenter close to the end of the tip. Loads of 10, 20 and 40 mN were therefore chosen to give indentation contact depths,  $h_c$ , of between 76 and 240 nm. To determine the indentation modulus of the coating independent of the properties of the substrate a linear fit was used to determine the intercept of the line with the y-axis (Table 5).

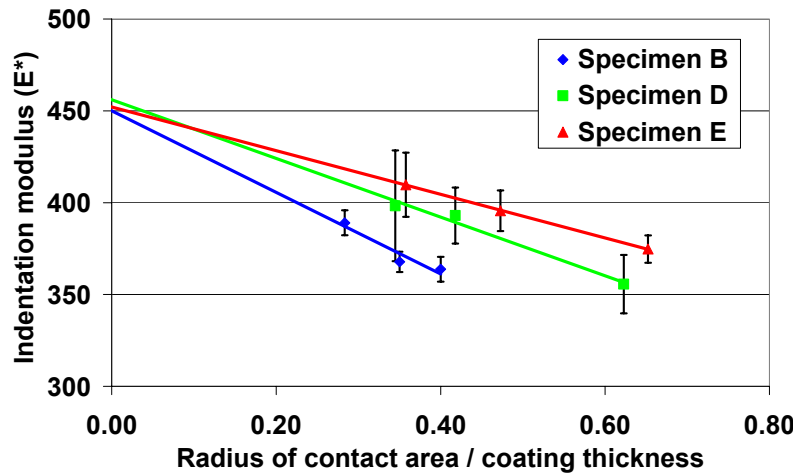


**Figure 4:** Indentation modulus ( $E^*$ ) of three TiN coated stainless steel specimens of different substrate thicknesses.

### 3.3 Poisson's Ratio

By combining the values of Young's modulus,  $E$ , obtained from impact excitation and the coating plane strain indentation modulus obtained from depth-sensing indentation,  $E^*$ , it was possible to calculate the Poisson's ratio,  $\nu$ , using the following expression<sup>7</sup>:

$$\nu = \sqrt{1 - \frac{E}{E^*}}$$

Values for the Poisson's ratio of each TiN coating are given in Table 5. It can be seen that the Poisson's ratio of all the specimens are similar with an average value of  $0.23 \pm 0.03$ . This is consistent with a value of Poisson's ratio of 0.20 in the FASTE project<sup>7</sup> obtained by acoustic microscopy on similar but thicker coatings.

## 4 Conclusions

Young's modulus results from impact excitation used in combination with indentation modulus results from depth sensing indentation yielded consistent values of Poisson's ratio for coatings of different thicknesses deposited on 2 different substrates of 3 different thicknesses. The Poisson's ratio obtained for the coatings  $0.23 \pm 0.03$  was in agreement with literature values, 0.20, obtained from similar but thicker coatings measured using acoustic microscopy<sup>7</sup>.

Impact excitation values for the Young's modulus of the substrates agreed with literature values measured using mechanical tensile tests<sup>6</sup> and the Young's modulus of the coatings was in agreement with values obtained for a similar but thicker coating using acoustic microscopy<sup>7</sup>.

**Table 5** Determination of Poisson's ratio from values obtained for indentation modulus  $E^*$  and the Young's modulus  $E$  from impact excitation

| Code           | $h_s$<br>(mm) | $h_c$<br>( $\mu\text{m}$ ) | Indentation<br>Modulus $E^*$ | Impact Excitation<br>Modulus $E$ | Poisson's ratio ( $\nu$ ) |
|----------------|---------------|----------------------------|------------------------------|----------------------------------|---------------------------|
| A              | 0.87          | 0.95                       | 456                          | 425                              | 0.26                      |
| B              | 0.87          | 2.28                       | 449                          | 427                              | 0.22                      |
| C              | 0.87          | 2.66                       | 464                          | 440                              | 0.23                      |
| D              | 1.24          | 2.07                       | 456                          | 421                              | 0.28                      |
| E              | 1.84          | 1.67                       | 452                          | 434                              | 0.20                      |
| F              | 0.81          | 1.34                       | 436                          | 417                              | 0.21                      |
| Average values |               |                            | 452                          | 427                              | 0.23                      |

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