Microstructure and indentation response of TiN coatings: the effect of measurement method

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ABSTRACT

The hardness and elastic modulus of thin films can generally only be determined directly using an ultra-low load indentation tester or indirectly using a modelling approach since there is usually a contribution from the substrate. Although the modelling approaches developed work reasonably well when there is sufficient load support from the substrate, if this shows appreciable plastic deformation during the indentation process there can be a change in the deformation mechanisms of the coating and direct and indirect measurements are less comparable. In this paper the changes in hardness and contact modulus of sputtered titanium nitride coatings deposited on stainless steel have been investigated using both direct and indirect measurement techniques as a function of thickness and applied substrate bias. The same trends in behaviour have been observed for each of the techniques though the absolute hardness values determined are not identical at low coating thickness. The usefulness of the two approaches is discussed in light of these observations.

1. Introduction

As the use of thin ceramic films, such as titanium nitride deposited by either physical vapour deposition (PVD) [1] or chemical vapour deposition (CVD) [2] techniques, has become more widespread the need to be able to routinely measure their mechanical properties has increased. This is necessary both for the development of coatings with suitable performance in a given application and in quality control of the coating process. For instance, the hardness of the film (or more realistically the load-bearing capacity of the coating/substrate composite system [3]) can be correlated with abrasive wear resistance

and thus coating hardness can be used for ranking purposes in situations where other factors are not important.

The problem in determining the indentation hardness or elastic modulus of a thin film arises from the fact that it is necessary to minimise the size of the indentation to ensure that there is no (or limited) contribution from the substrate in the measured data which is more challenging for softer substrates. For hardness, following the early work of Buckle [4], it is generally assumed that the penetration depth of the indenter must be less than one tenth the coating thickness in order to achieve this. For elastic properties the required penetration depth is a much smaller proportion of the coating thickness; strictly speaking the coating and substrate are springs in series and there will always be some contribution from the substrate but this is minimized when the indenter penetration is less than 1% of the coating thickness and the indenter tip end radius is less than 10% of the coating thickness.

Experimental analysis and finite element modelling have shown that the shape of the strained region below a hardness indenter is approximately hemispherical whether the strain is elastic or plastic. Finite element studies have shown that the radius of the hemispherical plastic zone around an indent, R_p, is given by [5]

$$\frac{R_p}{\delta_{max}} = -12.907\frac{H}{E_r} + 4.5451 \qquad (1)$$

where H is the hardness and E_r is the plain strain modulus of the coating and this can be used to assess the validity of this 10% rule-of-thumb. For a typical hard TiN coating where E_r=520GPa and H=30GPa so that E_r/H~17, the radius of the plastic zone is about four times the maximum displacement (i.e. the sum of the elastic and plastic deflections of the test surface) and five and a half times the contact depth of the indent (i.e. its plastic depth) which is consistent with the 10% rule. Outside the plastic zone, contact stresses decay with the inverse square of distance from the contact and only reach zero at effectively infinite distance. Thus, significant elastic strain occurs over a much larger volume (Figure 1) and for this reason it is much more difficult to measure the elastic properties of a coating independent of the substrate.

Thus there are two approaches to determining coating hardness:-

(1) **Direct measurement.** Conventional microhardness testers can only be used for relatively thick coatings (> 5 μm). The measurement of coating hardness

for thinner films requires the use of ultra-low load nanoindentation testers where the penetration depth of the indenter is continuously recorded to calculate a hardness value.

(2) **Indirect measurement.** A modelling approach is used to apportion the contributions to the measured hardness of the composite system from the substrate and coating respectively. This can often be performed for thinner coatings than can be directly measured.

There are advantages and disadvantages to each technique. Though conventional microhardness testers are available in a large number of industrial laboratories, nanoindentation testers that are commercially available represent a high cost investment at present and are mainly used in research labs. Conventional microhardness equipment is relatively robust and can be used in a wide range of working environments whereas the ultra-low load testers are more sensitive to vibration and temperature changes. For this reason, conventional microhardness testing systems are more likely to be found in quality assurance labs in industry. The nanoindentation tests have a distinct advantage that they do not rely on the subjective judgement of an operator to measure hardness and are able to measure elastic response as well. In this paper the results of conventional microhardness in conjunction with a modelling approach and nanoindentation tests are compared for sputter ion plated titanium nitride coatings.

The microstructure of a thin film exerts a considerable influence on its properties. For vapour deposited materials deposited under most conditions the coating is comprised of columns which are aligned perpendicular to the coating/substrate interface and it is this columnar microstructure which controls the mechanical and physical properties of the film [6]. Due to the aligned growth process the structure of the coating is very anisotropic which leads to anisotropy in many film properties. Furthermore, a certain amount of microstructural control is possible since manipulation of the process parameters during deposition can lead to changes in the microstructure of the deposited coating (for example by variations in the packing density of the columns and the grain boundary strength which holds them together).

The application of a substrate bias has a profound effect on the growth and microstructure of PVD thin films [7-10]. Figure 2 shows the microstructure of sputter ion plated titanium nitride deposited under two different bias conditions. The -20V bias film (Figure 2a) has an open columnar structure (zone 1 according to the Thornton structure model [11]) whereas the -60V biased film (Figure 2b) is much denser, the

individual columns being much less well-defined (zone T). Coatings with these microstructures will have substantially different physical properties due predominantly to changes in the packing density of the columns which make up the coating [12]. In this study we have investigated the variations in microhardness going from zone 1 to zone T microstructures and compared this to the results of nanoindentation testing.

Both zone 1 and zone T microstructures are associated with the preferred orientation of the growing columns and this development of texture leads to variations in coating properties with coating thickness. The development of texture in PVD coatings occurs in three stages [10]:-

(1) **Nucleation -** crystallites are nucleated on the substrate from the vapour phase. The distribution and size of these will depend on the nature of the substrate.

(2) **Competitive growth -** certain favourably oriented nuclei will grow faster than the remainder of the crystallites. These may not constitute the majority of the nuclei population.

(3) **Steady growth -** once a preferred orientation has achieved dominance steady state growth will occur.

These stages in coating growth lead to changes in microstructure of titanium nitride coatings with increasing thickness. Initially at the interface region a very fine grain size is established and little or no preferred growth orientation is observed [13]. With increasing thickness there is an increase in average column size towards the outer region of the coating. For this reason, the hardness and residual stress in the film decrease with distance from the interface since due to the increase in grain size the average yield strength of the coating will decrease towards its outer surface. This behaviour is also modified by changes in film density produced by the competitive growth process [13]. In this study we have investigated the variation hardness and elastic modulus with coating thickness for titanium nitride coatings produced by sputter ion plating and relate the results to changes in the microstructure of the coating arising from the growth process.

2. Indentation Measurement Techniques

2.1 Direct Measurement

Hardness testing involves pressing of an indenter of known geometry into the surface of a material under a given load. Beneath the indenter shear stresses can be developed which are large enough to cause local yielding, elsewhere the deformation is predominantly elastic and stress relief can only occur by other mechanisms such as fracture. On unloading there is some elastic recovery of the impression, but because of the plastic deformation complete recovery is not possible and the region around the impression is left in a state of residual stress.

In general, the hardness, H, is defined as

$$H=P/A \qquad (2)$$

where P is the applied load and A is the projected area of the impression. For the commonly used Vickers indenter this needs to be modified slightly as the hardness is defined as load divided by the surface area of the impression but both areas can be determined from the indentation diagonal, d, knowing the geometry of the indenter; it is usually assumed that these diagonals do not change due to the elastic recovery. However, ignoring the effects of elastic recovery can lead to appreciable errors in the measured hardness for low load indentations [14-15]. It is generally found for brittle materials that, as the size of the impression is reduced (i.e. the load is reduced), then the measured hardness increases; this is the so-called indentation size effect which incorporates the effects of elastic recovery with other factors such as the effects of work hardened layers, the decreasing effects of defects, the spacing of geometrically necessary dislocations and indentation fracture, etc. [15-17]. In general, the hardness may be expressed as

$$H=kd^{m-2} \qquad (3)$$

where d is the indentation diagonal length, k is a constant and m is the indentation size effect (ISE) index.

For a Vickers indenter both the diagonals can be used to determine the hardness and the penetration depth is d/7. This penetration can be reduced by using the Knoop indenter where the penetration depth is only d/30.5 where d is the long diagonal. However, even with such reduced penetration it is not possible to ensure that the deformation is confined to the coating if post facto measurements using the optical systems of a conventional microhardness tester are used to determine hardness. On polished surfaces it is difficult to measure impressions with $d<10\mu m$ by this method and the errors dramatically increase as the indent size is reduced; it is not possible to measure impressions with $d<3\mu m$ without resorting to a scanning electron microscope. For rough surfaces these measurement limits increase in size.

Given the subjective nature of the diagonal measurement process and the difficulty in viewing such small impressions the need for a more reliable measurement system is clear. A number of instruments were developed to allow the making of impressions at very low loads [18-21] that are the basis of a number of commercially available instrumented indentation testers; the common feature of all of these high resolution instruments is that load and indenter displacement is continuously monitored during the indentation cycle. This enables the properties of thin films to be determined from the measured data without the need to optically measure indentation diagonals dramatically improving the accuracy of the hardness data determined for small impressions. These instruments are often termed nanoindentation testers because the indenter displacements that are being routinely measured are of the order of nanometers.

In order to obtain the hardness from such depth-sensing indentation tests, the projected area in contact with the indenter needs to be determined from the load-displacement data. Since the measured displacements will include elastic and plastic contribution, the elastic effects must be removed to obtain the plastic or contact depth. This can be achieved from the extrapolation of the initial unloading slope of the load-displacement curve [22-23]. From the contact depth the projected area of the contact can be determined if the indenter geometry is known. This generally requires experimental calibration of the indenter shape [23].

The data obtained during unloading of the indentation can also be used to obtain the elastic properties of the coating [22-23]. Since elastic response is a longer range effect than plasticity it may be necessary to apply a correction to the measured data to account

for elastic deformation of the substrate [22, 24] using an appropriate model even if a direct measurement of plasticity (hardness) is possible.

Since the nanoindentation test was first introduced and the data analysis approach was successfully developed the availability of reliable, cost-effective nanoindentation systems from different manufacturers has increased in laboratories around the world. The use of the technique for coatings assessment is now commonplace. Interest has moved from basic coating assessment (i.e. hardness and elastic modulus measurements) to using the systems for assessment of other key properties such as dynamic mechanical response [25-27], fracture toughness [28-31] and time-dependent properties such as creep [32-34]. For titanium nitride coatings the focus on understanding the relationship between single layer coating properties, process parameters and failure modes [35-36] has developed to include multilayer and graded coatings of which TiN is a part [e.g. 37]. The effect of coating thickness and length-scale effects in plasticity and fracture has also been a research issue [38-39]. A discussion of all aspects of nanoindentation testing is thus very broad and more information can be found in these references and other review papers [40-42].

2.2 Indirect measurement

Early models of composite hardness based on apportioning hardness contributions to different layers [43-44] using deforming area [45] or deforming volume arguments [46] do not describe very well the available experimental data in most circumstances. However, in the volume law-of-mixtures hardness model introduced by Burnett and Rickerby [45-46] and extended by Bull and Rickerby [47], it was realized that deformation of the harder material (coating or substrate) could constrain deformation in the softer one, reducing the deforming volumes in the softer layer and generally increasing the composite hardness. The use of this volume law-of-mixtures hardness model incorporating indentation size effects for both coating and substrate [47] allows a good description of experimental data but requires a complicated fitting approach. For this reason, a simplified model based on work of indentation was developed by Korsunsky and co-workers [48-49]. In its most simplistic version

$$H_c = H_s + \frac{H_f - H_s}{1 - k\beta^2} \qquad (4)$$

where H_s is the substrate hardness, H_f the coating hardness, H_c the composite hardness, k is a constant, β is the relative indentation depth, RID, (ð/t) where ô is the indenter displacement and t is the coating thickness. The constant k in Eq. (4) controls how the hardness changes in the region where $\beta < 1$.

When modeling the coating—substrate system hardness, it has been customary to start with the basic definition of hardness, H, as a pressure, though an alternative but equivalent definition of hardness is [50]

$$H=W/V \tag{5}$$

where W is the plastic work of indentation and V is the deforming volume. Any mechanism that contributes to energy dissipation in the indentation cycle is automatically included in the work of indentation, which is just the sum of these contributions. In instrumented indentation testers where load and indenter displacement are continuously monitored, W can be measured directly. However, a direct measurement of V is not possible, and, if the deforming volume is to be used as a basis for modeling, it needs to be related to something that is measurable, such as the indenter displacement. Since the deforming volume is approximately hemispherical, Eq. (1) can be used to determine V for bulk materials.

For a single layer coated system it can be shown that [51]

$$H=\left(\frac{3t}{2R}-\frac{1}{2}\frac{t^3}{R^3}\right)H_0^F+\left(1-\frac{3t}{2R}+\frac{1}{2}\frac{t^3}{R^3}\right)H_0^S+\frac{3\gamma_s}{2R}+\left(\frac{3}{2R}-\frac{3t^3}{2R^3}\right)\gamma_i \tag{6}$$

where R is the radius of the plastic zone, $H_0(f)$ and $H_0(s)$ are the bulk hardnesses of coating and substrate and γ_s and γ_i are the energies of deformation of the surface and interface, respectively. For a hard coating on a soft substrate, such as TiN on steel, the radius of the plastic zone in the substrate can be more than three times that in the coating at the same test load. As plastic deformation expands from the coating into the substrate, there must be a rapid expansion of the plastic zone since at large loads the substrate will dominate indentation behavior. As the indenter penetration increases there is a smooth growth of the plastic zone radius from the coating-dictated size to that of the substrate. Deviations from the hemispherical shape can be accounted for by the interfacial energy, γ_i, whereas indentation size effects can be accounts for by the surface energy γ_s. Equation (6) may be combined with equation

(1) to get an expression for hardness in terms of indenter displacement which may be fitted to experimental data to determine the H_0 and γ terms. However, the fitting process is very sensitive to the amount and quality of the experimental data and it is not suitable for routine use.

The complexity of the processes occurring during the deformation of a coating— substrate system makes it difficult to produce a generic model for the behavior of the coating substrate system that can be used to extract coating properties from system property data. For this reason, a simplified approach is adopted in ISO14577 Part 4 [52]. To determine coating elastic properties from nanoindentation, the contact modulus is measured at a range of indentation loads and plotted as a function of contact depth. A linear fit to the data is extrapolated to zero contact depth to give the properties of the coating. This approach is based on the fact that there will always be an elastic contribution from the substrate which becomes increasingly important as the contact load increases and effectively the coating/substrate system may be treated as springs in series. This approach works well if there are no large changes in coating properties with contact depth—when the coating and substrate have very different properties, any results generated by this method should be treated with caution. Plotting hardness versus contact depth may also be used for hardness determination. The choice of the depth range for this is critical [52]; data at low contact depth (<10% coating thickness) often shows a plateau in hardness and extrapolation is accurate in this range but data from larger relative indentation depths includes differing substrate contributions that can lead to poor extrapolation fits and inaccurate coating hardness assessment. If a constant maximum value of hardness (a plateau) is observed over this range, this is the coating indentation hardness. If only a maximum in hardness occurs and indentation of a thicker coating yields the same value, then this is a strong indicator that this is the value for the coating, otherwise, this is only the minimum estimate of the coating indentation hardness. Plastic deformation must occur in the coating for the approach to be valid which necessitates sharp indenters with a tip end-radius less than the coating thickness when testing hard coatings like titanium nitride.

In this study the indentation properties of titanium nitride coatings on stainless steel obtained by direct and indirect methods have been determined to investigate the validity of the modelling approaches based on the volume law-of-mixtures and work of indentation models. The modelling methods have been based on data from microhardness tests. The ISO14577 extrapolation method has been applied to data produced by nanoindentation for comparison.

3. Experimental Procedures

3.1 Deposition of titanium nitride coatings

The TiN coatings were produced by sputter ion plating [53] which is a soft vacuum direct current sputtering process developed at Harwell Laboratory. Further details of the process can be found in the literature [54]. For this study TiN coatings were deposited onto a soft austenitic stainless steel substrate (1.4541 SS) to a thickness of around 2μm at a deposition temperature of 500^{o}C with in a range of applied substrate bias voltages from 0 to -120V. In addition, another set of TiN coatings were deposited at -60V bias voltage in the range 1-10μm thickness. Finally, a small number of coatings were deposited onto hardened M2 steel at different bias voltages and thicknesses for comparison. Uncoated substrates were polished to a 3μm diamond finish, sputter cleaned and a thin (150nm) titanium interlayer was then deposited to promote coating/substrate adhesion prior to TiN coating. Coating thickness was determined from metallographic cross sections (coatings >5μm thick) or ball cratering (coatings <5μm thick). The crystallographic orientation of the coating was obtained using electron backscatter diffraction and the coating grain size from transmission electron microscopy.

Coatings were originally deposited in the early1990s and have been used as equipment testing and training standards at Newcastle for the past 20 years. This has enabled the reliability of the measured indentation data from a given tester to be assessed and comparisons between different test systems to be made over time. Figure 3 shows the variation of measured hardness with time over a 20 year period. It can be seen that there is no change in the microhardness measured by the conventional hardness tester but there is a gradual increase in the hardness measured by nanoindentation. This is not due to sample changes but an increase in the bluntness of the Berkovich indenter used (see next section). Dense and stoichiometric samples were used for these studies – the TiN coating used was developed to be good diffusion barrier in corrosion applications and shows good stability at room temperature [55]. Samples were kept in a vacuum desiccator in a temperature-controlled lab (20±2^{o}C) when not in use. Changes in coating structure and properties were assessed and limited to surface oxidation (thickness increases from ~2nm to 7nm in 20 years) which has a minimal effect on the indentation properties measured here. The coating residual stress (~6.5GPa) did not change (within experimental error) over the period.

3.2 Hardness Testing

Vickers microhardness measurements were made on all samples and the uncoated substrate at loads ranging from 15 g to 1 kg. Five indents were made at each load and the average value of the ten measured indentation diagonals was used to determine the hardness. Standard testing conditions were used in all cases (15 s dwell time, tests in laboratory air, 50-80% humidity). The indentation diagonals were measured with the optical system of the microhardness tester. No problems with measurement of diagonals down to 5 μm were experienced due to the good state of the polish on all samples, but the accuracy of the measured data is reduced as the contact size becomes smaller. The Vickers hardness is defined as load divided by surface area of the impression and this has been corrected to load divided by projected area of the impression to match the Berkovich hardness values reported here and is therefore quoted as hardness in GPa in Figures 3, 4, 6, 8 and 11.

These data were used in conjunction with the volume law-of-mixtures hardness model to determine the coating hardness. The model produces best fit values of the coating hardness at a constant diagonal size (in this case 10 μm), the coating ISE index, and parameters defining the functional fitting of the plastic zone shape. In this study only the 10 μm hardness has been used for comparison since the other parameters are known to show a much larger dependence on the quality of the measured hardness data.

The hardness and elastic modulus of the films was also determined using a commercially available Nanoindenter (Nanoindenter 2). Although the samples had macroscopically smooth surfaces as deposited, it was necessary to employ a dimpling technique in order to obtain surfaces smooth enough for random placement of the nanoindentations [56]. A 25.4mm diameter steel ball which was coated with 0.25μm diamond paste was rotated against the coating surface under a normal load of 1N for ~180s in order to polish a spherical cap dimple of ~0.5mm diameter into the coating surface with a roughness of about 40nm. Indentation tests were carried out in the polished zone at the edge of the dimple; the slope angle of the polished surface is about 1^{o} from the horizontal and this does not appreciably effect the hardness and contact modulus determined from these indentations. The displacement of the indenter is measured with a capacitance displacement gauge with a resolution of 0.16 nm. The load is applied by passing a current through a coil which is positioned in a magnetic field. The resolution of the system is 0.3 pN. A minimum of ten indentations were made on

each sample to fixed depth in the range of 25 to 1000 nm. The hardness and contact modulus were calculated using the method of Oliver and Pharr [23]. The contact modulus was converted to Young's Modulus using a Poisson's ratio of 0.25 in all cases. The impressions showed no evidence for pile-up and no further correction was applied to the data presented in this study. The hardness and modulus of the uncoated stainless steel substrate were measured at 10 mN peak load using a Berkovich indenter fitted to a Hysitron Triboindenter. Considerable pile-up was observed and AFM images from the tip used to make the indentations were used to correct the area of the impressions. At this load the impressions were very much smaller than the steel grain size (~10 μm) and were positioned well away from grain boundaries so the main source of variability was the orientation of the austenite grains. The average hardness of the stainless steel substrate was about 2.4 GPa. The indentation modulus varied from 210 to 240 GPa with a mean value of 220 GPa. These results are in agreement with the work of Hauslid et al [57]. The hardness of the M2 steel was about 6.0 GPa and the indentation modulus was 205±14 GPa using the same approach.

The variation of hardness with contact depth for a 2 μm TiN coating deposited at -60V bias in shown in Figure 4. Measurements were made with three different diamond indenters on adjacent areas of the same sample. There is clear evidence of an indentation size effect with hardness increasing as the load is reduced. The effect depends on the bluntness of the tip with the very blunt microhardness Vickers diamond showing the highest hardness and the blunter Berkovich indenter leading to a higher hardness at lower loads in the nanoindentation tests. The high load nanoindentation hardness of TiN tends to 22GPa whatever the tip bluntness. As a tip is used for testing more samples in general it becomes blunter (Figure 5) and thus leads to higher hardnesses when tests are carried out at contact depths less than 200nm (as would be necessary for measuring the hardness of a 2μm coating independent of the substrate) even after the tip-shape is recalibrated using indentations in fused silica to account for the wear. Testing a hard coating with a blunter tip results in a higher load needed to initiate plastic deformation and a delayed transition from elastic to fully elastic-plastic behaviour leading to enhanced indentation size effect behaviour and higher hardness at lower loads. Thus for testing coatings of a lower thickness than this it is essential to use a sharp tip for reliable results. The gradual increase in hardness with time in the data in Figure 3 is therefore a reflection of the blunting of a tip which was used for general

purpose testing – for accurate work sharp tips are required and these are not loaded onto the machine unless accuracy and repeatability is necessary.

4. Results

4.1 Effect of Applied Substrate Bias

Figure 6 shows the variation in hardness determined from nanoindentation and the volume law-of-mixtures hardness model for the films with varying applied substrate bias deposited on stainless steel. There is a considerable increase in hardness with bias up to about -60 V when the rate of increase is much reduced. Such trends have also been observed for the residual stress in the films measured by X-ray techniques [58]. Both the modelling approach and the direct hardness measurements show the same trends, though the absolute hardness values are different. The increase in hardness is associated with the increase in coating density as a result of the ion polishing effects of ion bombardment during deposition [10]. The unbiased film shows a zone 1 type structure (according to Thornton's structure model [11]; see Figure 2a) whereas this is progressively converted to an increasingly dense zone T structure (Figure 2b) as the negative voltage on the samples during deposition is increased. In the unbiased film the columns which comprise the coating are separated from their neighbours but the application of a small substrate bias forces them into contact leading to a rapid increase in hardness. Once some intercolumnar contact has been achieved further densification of the coating becomes more difficult and the rate of hardness increase is reduced. By an applied bias of -60V the coating has virtually reached full density.

In parallel with the hardness increase there is an increase in elastic modulus (determined by nanoindentation (Figure 7)) over the same bias range. The greatest increase is again observed at low bias voltage and the measured modulus is constant above -60V. The modulus above this bias voltage is close to 460GPa which is similar to other nanoindentation measurements [59] but lower than the values measured by resonance methods on similar TiN coatings [60].

4.2 Effect of coating thickness

The grain size of all the films deposited in this study is very small near to the coating/substrate interface (<20nm). With increasing thickness there is an increase in

average column size and a tendency towards the adoption of a {111} texture in the outer regions of the coating. Individual grains are tapered with larger grain diameters measured at the surface than at the interface and the surface grain size increases with coating thickness. Due to the effect of boundaries impeding dislocation motion the fine grained material near the interface has a higher yield strength than the coarser-grained material near the surface. Higher yield strength material can support larger residual stresses without plastic deformation and thus the stresses supported by the outer regions of the coating will be smaller than those which can be supported near the coating/substrate interface [13]. For this reason, it is expected that the hardness will be reduced as coating thickness increases and larger grain size material contributes more to the overall measurement; this is observed for films less than ~4μm thick (Figure 8). A similar result can be seen in the Modulus data (Figure 9).

This behaviour is modified by the changes in density produced by the competitive growth process. Figure 10 shows a fracture section through the 6μm TiN film. In the interface region the coating is dense, but the density is much reduced at 3-4μm from the interface. The coating shows a minimum in hardness between 2 and 5μm in thickness. Both direct and indirect measurements show the same general trend but the absolute values of the measured hardness are different in each case.

5. Discussion

5.1 Validity of the indirect hardness measurement approach

The fact that the volume law-of-mixtures model based on the microhardness data and the directly measured nanoindentation data shown the same trends as a function of substrate bias and coating thickness is reasonable evidence that either approach can be used for quality control processes but absolute comparisons between measurements should not be attempted. The relatively good agreement for the direct and indirect measurements when the thickness of the TiN is greater than 5μm in Figure 8 indicates that this is related to the load support from the stainless steel substrate.

There is no reason to believe that the absolute hardness values determined by the two techniques should agree because they do not measure the same thing. In the direct hardness measurement by nanoindentation the plasticity associated with the indentation is

constrained within the coating and the deformation of the substrate is limited. However, the hardness determined from the model is averaged over the whole coating thickness throughout the contact area and is influenced by the deformation process. The plastic deformation of the substrate drives cracking of the coating as it is bent into the impression. In such circumstances it is not clear if the coating material in the deforming volume is plastically deforming at all. For this reason, the accuracy of the fitted hardness values is reduced as the coating thickness decreases. This can be regarded as a decrease in the load support of the coatings and it manifests itself in a reduction in the coating ISE index for thinner coatings. In this study all the fitted ISE indices were ~1.7 which is comparable with values reported for bulk ceramics [14-16] with the exception that for the 1μm film the value was 1.59.

For 2μm TiN on stainless steel at the lowest loads available the relative indentation depth (RID) is 0.25 and the majority of the composite hardness data occurs with RID>0.5. If the coating thickness increases to 5μm it is possible to have a relative indentation depth of 0.1 and the measurement satisfies the Buckle rule-of-thumb [4] for measuring coating hardness independent of the substrate. There is sufficient data in the critical RID range from 0.1 to 0.5 which make the modelled value for coating hardness agree with the directly measured value. Thus for testing sputtered TiN on stainless steel using microhardness measurement a coating thickness of greater than 5μm is required.

The substrate contribution to the deformation behaviour is also critical in determining the absolute value of hardness for the TiN samples deposited with different bias voltages in Figure 6. However, there is also a difference in what is reported as a representative hardness for the coating. In the case of the volume law-of-mixtures hardness model produced a lower hardness than the direct measurement. In part this is due to what is quoted as coating hardness in the two cases. The direct measurement nanoindentation data was obtained using the ISO14577 method from the plot of hardness again contact depth and is effectively dominated by the hardness at low penetration depth which contains any increases in hardness due to indentation size effects which are visible in nanoindentation data (e.g. see Figure 4). The volume law of mixtures model fits this indentation size effect according to equation (3) and the hardness is quoted at 10μm diagonal size (penetration depth 1.43μm) which is less inclusive of indentation size effects. The modelled hardness should be lower than the directly measured hardness for this reason as is observed.

There are alternative models which could be applied. For instance, the Korsunsky et al model in equation (4) does not explicitly include indentation size effects but can be used to fit microhardness data as a function of indent depth (Figure 11a). The modelled coating hardness from the volume law-of-mixtures model is plotted against the coating hardness obtained from the Korsunsky et al model fits (Figure 11b) and a linear relationship between the hardness values obtained by the two approaches is observed. The hardness obtained from the work of indentation model is lower and linearly related to that from the volume law-of-mixtures model. For hard substrates (M2 steel in this case with hardness about 6GPa) that give good load support to the coating the modelled hardness from both approaches is almost identical (hardness from the Korsunsky et al model is 89% of that from the volume law of mixtures model). In fact for hard substrates such as WC/Co there is no statistical different between either approach. For softer substrate materials like stainless steel the difference is much greater (hardness from the Korsunsky et al model is 63% of that from the volume law of mixtures model). Thus each different modelling technique produces different hardness values and the absolute values cannot be trusted for cases where significant plastic deformation of the substrate has occurred. The models do allow comparison between coatings and process development if not used on an absolute measurement basis.

5.2 Elastic properties and microstructure

The elastic modulus data for all the samples can be explained in terms of the density of the coating and its crystallographic texture. Electron backscatter diffraction texture analysis can be used to determine the percentage of material with (111), (110) and (100) planes normal to the coating surface which is the direction of indentation (Figure 12). The grain size in the plane of the coating is around 20nm for all the coatings tested here and thus the indentation is sampling many different columnar grains even at the lowest loads where plasticity occurs. In such cases an effective modulus can be defined as:

$$E_{eff} = \%(111)E_{[111]} + \%(110)E_{[110]} + \%(100)E_{[100]} \quad (7)$$

Equation (7) has been used to plot the effective modulus using the moduli in the different crystallographic directions calculated from the single crystal compliance data; E[200]=556GPa, E[110]=445GPa and E[111]=418GPa [61]. For bulk single crystals it has

been shown that the indentation modulus is typically different from the Young's Modulus in the indentation and is best approximated by a weighted average of the elastic constants in different directions around the impression and crystallographic correction factors have been calculated [62-63]. The approach here changes the weighting to the fraction of material with a given orientation present in the deforming volume below the indenter. When the coating is fully dense there is an excellent agreement between prediction and experiment. For the bias series this occurs at -60V bias and above (Figure 7) whereas for the thickness series the agreement is very good at thicknesses above 5μm and within experimental error for the lowest thickness where a dense layer is produced after initial nucleation. Taking the difference between the predicted and measured values for Young's Modulus and assuming that the measured modulus is proportional to coating density its can be estimated that the void volume fraction reduces from ~30% to zero as the bias increases from 0 to -60V. This is consistent with the change from 20% to zero measured for Magnetron sputtered TiN by Patsalas et al [64] in a similar bias range since the energy transfer to the growing film in magnetron sputtering is higher than that for simple DC sputtering (as investigated here) promoting coating densification.

5.3 Effect of residual stress

The increase in hardness and elastic modulus with bias voltage is accompanied by an increase in compressive residual stress (Figure 13). At bias voltages less than -60V the change is significant for both hardness and residual stress but at higher bias voltages the hardness is almost constant whilst the residual stress increases significantly [6]. A correlation between indentation hardness analysed by standard nanoindentation methods and residual stress has been observed for aluminium alloys with a decrease in both hardness and elastic modulus with increasing stress from compression to tension [65]. Usually residual stress has a secondary effect on indentation properties because the residual stresses operate in a perpendicular direction to the major indentation loading direction. In soft materials the shape of pile-up and hence the indentation shape has been affected by residual stress leading to small changes in measured hardness (~10%) which is not real but a consequence of the measurement method. However, TiN does not show pile-up so the effect is minor, the major contribution to the increase in hardness with an increase in

compressive stress is the increase in density of the coating. This is true for both microhardness and nanoindentation measurements.

6. Conclusions

Both direct hardness measurement using the Nanoindenter 2 and indirect measurements using the volume law-of-mixtures hardness model have been successfully used to determine the hardness of titanium nitride films deposited on stainless steel as a function of processing conditions. Both techniques show the same hardness trends with substrate bias and coating thickness, though there is some variation in the absolute value of hardness determined. It is very dangerous to assess coating hardness on the basis of low load Vickers hardness measurements since these are almost always influenced by the substrate for thin films on soft substrates and comparisons between films should not be made like this if there is any variation in substrate hardness between samples. Hardness testing remains a useful technique in assessing the properties of deposited coatings but it is essential that considerable care is taken if reliable conclusions are to be drawn from measured data.

7. Acknowledgements

The author would like to thank Professor Trevor Page for useful discussions and helping to keep the Nanoindenter 2 working long beyond its expected life.

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Figure Captions

Figure 1 Comparison of elastic and plastic zones associated with an indentation in a coating/substrate system.

Figure 2 Scanning electron fractographs (secondary electron imaging) of (a) -20V bias and (b) -60V bias titanium nitride coatings deposited onto a stainless steel substrate by sputter ion plating.

Figure 3 Variation of hardness measured by different technique with time for a -60V bias TiN coating on stainless steel

Figure 4 Variation of hardness with contact depth for a 2μm TiN coating on stainless steel tested by a microhardness tester fitted with a Vickers indenter and a nanoindentation tester fitted with a blunt and a sharp Berkovich indenter.

Figure 5 Tip blunting with number of runs (50 indentation cycles) for a Berkovich indenter used to test TiN coated steel.

Figure 6 Variation of hardness with applied substrate bias as determined directly by nanoindentation compared to indirectly from microhardness by the volume law-of-mixtures hardness model.

Figure 7 Variation of Young's Modulus with applied substrate bias as determined by nanoindentation.

Figure 8 Variation of hardness with coating thickness as determined directly by nanoindentation and indirectly from microhardness data by the volume law-of-mixtures hardness model.

Figure 9 Variation of Young's Modulus with coating thickness as determined by nanoindentation.

Figure 10 Scanning electron fractograph of a 6 μm TiN coating on stainless steel deposited at -35 V bias. There is a reduction in density apparent in the centre of the coating though the interfacial and surface regions appear dense.

Figure 11 (a) Variation of microhardness with indent depth for 2μm sputtered TiN coatings on stainless steel deposited at different bias voltages fitted with the work of indentation model (equation (4)) and (b) comparison of coating hardness value from this model and the volume law-of-mixtures model.

Figure 12 Percentage of {111}, {110} and {100} texture from crystallographic orientation maps measured by electron backscatter diffraction (a) as a function of bias voltage for 2μm thick TiN and (b) as a function of thickness for sputter ion plated TiN deposited at -60V bias.

Figure 13 Variation of measured hardness with residual stress for 2μm sputter ion plated TiN deposited at a range of bias voltages.