An overview of the potential of quantitative coating adhesion measurement by scratch testing

S.J. Bull and E.G-Berasetegui
Department of Mechanical, Materials and Manufacturing Engineering
University of Newcastle
Newcastle-upon-Tyne
NE1 7RU, U.K.

Abstract

The scratch test has been used to assess the adhesion of thin hard coatings for some time now and is a useful tool for coating development or quality assurance. However, the test is influenced by a number of intrinsic and extrinsic factors which are not adhesion-related and the results of the test are usually regarded as only semi-quantitative. The stress state around a moving indenter scratching a coating/substrate system is very complex and it is difficult to determine the stresses which lead to detachment. Furthermore the interfacial defect state responsible for failure is unknown. However, by a careful analysis of the observed failure modes in the scratch test (not all of which are related to adhesion) it is possible to identify adhesive failures and in some cases these occur in regions where the stress state is relatively simple and quantification can be attempted.

Ideally engineers would like a material parameter (such as work of adhesion or interfacial toughness) which can be used in an appropriate model of the coating-substrate system stress state to determine if detachment will occur under the loading conditions experienced in service. This data is not usually available and the development of such models must be seen as a long term goal. In modern indentation and scratch systems the work of friction (or indentation) can be directly measured and the relationship between this parameter and adhesive failure can be demonstrated in some cases. This paper reviews the main adhesion-related failure modes and the stresses responsible for them and indicates where quantification is possible illustrating this with results from hard coatings on steel, thermally grown oxide scales and optical coatings on glass. The use of empirical calibration studies, directly measured work of friction and quantification by finite element methods is discussed.

1 INTRODUCTION

The scratch test has been used for many years to provide a measure of coating/substrate adhesion [1-6]. In the normal configuration of the test a diamond stylus is drawn across the coated surface under an increasing load until some well-defined failure occurs at a load which is often termed the critical load, $L_c$. Many different failures are observed which include coating detachment, through-thickness cracking and plastic deformation or cracking in the coating or substrate [7-10]. In fact it is usual that several different failure modes occur at the same time and this can make results of the test difficult to interpret.
The failure modes observed in the scratch test depend on many factors and are most easily characterised in terms of the hardness of both substrate and coating (Figure 1). In the case of a typical Rockwell ‘C’ diamond indenter (120° cone with 200μm hemispherical tip), for soft coatings and soft substrates the test is dominated by plastic deformation and groove formation and little or no cracking is observed except at very high loads. For hard coatings on soft substrates deformation of the substrate is predominantly plastic whilst the coating may plastically deform or fracture as it is bent into the track created by plastic deformation of the substrate. Soft coatings on a harder substrate tend to deform by plastic deformation and some extrusion of the coating from between the stylus and the substrate may occur. Considerable thinning of the coating by plastic deformation will occur before plastic deformation and fracture of the substrate becomes significant. For hard coatings on hard substrates plastic deformation is minimal and fracture dominates the scratch response.

As the indenter becomes sharper, plastic deformation becomes more localised to the surface and it is easier to prevent plastic deformation of the substrate. In such cases the results of the test are easier to analyse and quantify, particularly for more modern depth sensing indentation and scratch systems. However, damage to the diamond stylus during the test becomes much more significant as its sharpness increases. The choice of stylus thus represents a compromise between damage and ease of data analysis – for industrial hard coatings of reasonable thickness (>1μm) the Rockwell ‘C’ stylus has proved very successful whilst for sub micron coatings a conical indenter with a tip radius of a few microns is more suitable.

The scratch test is not well-suited to measure the adhesion of soft coatings but can give some information if the interfacial shear strength is less than the shear strength of either the coating or substrate. In general, the scratch test is most effective if the substrate does not plastically deform to any great extent. In such cases the coating is effectively scraped from it and the uncovering of the substrate itself can be used as a guide to adhesion. However, it is difficult for this to be quantified. Detection of the uncovered substrate may be a problem unless post facto chemical analysis methods can be employed. However, some success is possible by measuring the change in friction during the scratch if the coating and substrate behave differently. For instance, an increase in friction may be observed if a high friction coefficient substrate in uncovered during the test.

The scratch adhesion test is much more useful for hard coatings, particularly when these are deposited on softer substrates. For a harder coating on a soft substrate the spallation and buckling failure modes arise from interfacial detachment [8,9,10] and can thus be used as the basis for an adhesion test. Both may be quantified in some circumstances and are discussed in this paper. The origin of these failure modes and the theoretical basis for analysing them is introduced in the next section, together with finite element results aimed at improving quantification.

2 OVERVIEW OF SCRATCH ADHESION TESTING

2.1 REQUIREMENTS FOR QUANTIFICATION OF THE SCRATCH TEST

If the scratch test is to be fully quantitative it must deliver a parameter which is representative of the state of adhesion of the interface but is not related to the other properties of the coating/substrate system such as hardness. The best parameter for this is work of adhesion which is a measure of the chemical bonding across the interface. However, most adhesion
tests do not measure this basic adhesion but produce a practical adhesion measurement conflating basic adhesion with other factors which can be specific to a given material pair or test method [11-13]. Film adhesion is often characterised by the strain energy released per unit increase in delamination area, \( G \), which is sometimes referred to as the interfacial fracture energy and can be used to generate an interfacial fracture toughness, \( K_i \). For most practical purposes this measurement of practical adhesion is sufficient but it should be corrected for method-specific factors to ensure that the test is widely applicable and the data produced can be compared with that from other test methods.

The scratch test is usually only regarded as semiquantitative as there are a number of intrinsic and extrinsic parameters which are known to affect the measured critical load (Table 1). Many of these intrinsic factors are instrument-specific and require a careful calibration approach if results are to be compared between instruments. However, the extrinsic factors such as coating thickness and substrate hardness must also be known if the results of the test are to be understood. These parameters, together with the residual stress in the coating and its Young’s modulus, are an important requirement for the models of the failure mode used to generate interfacial fracture toughness. There are thus four requirements for a quantitative scratch adhesion test:-

1) An adhesion-related failure mode,
2) A well-defined failure mechanism,
3) A method to identify that adhesion failure has occurred, where it is located and the size of the failure,
4) A method of determining the stresses which cause failure.

These will be discussed in more detail in the following sections.

2.2 SCRATCH TEST FAILURE MODES

2.2.1 Soft coatings

In general soft coatings (hardness<5GPa) fail by plastic deformation whether deposited on softer or harder substrates. Coatings deposited with a porous microstructure (e.g. the open columnar structures produced by vapour deposition at low temperatures) may also show some evidence of fracture but this is not widespread. The scratch test is not very useful for assessing adhesion unless the interfacial shear stress is less than the shear strength of the softer component. In such cases stripping or flaking of the coating may occur if the adhesion is very poor but often there is little to see but a plastic groove after the test is complete.

When a soft coating is deposited on a very different, harder substrate, such as aluminium or gold on glass, the detection of interfacial failure is much easier. As the load is increased in the scratch test the soft coating is progressively plastically deformed until at the critical load the substrate is uncovered. This can be detected by a colour change or by the use of surface analysis techniques such as x-ray photoelectron spectroscopy (XPS) which are surface sensitive. However, XPS analysis is not always practical since failure does not occur exactly at the interface - in such cases x-ray mapping or backscattered imaging in the SEM can be used to determine a critical load but this does not represent the load for interfacial detachment (Figure 2a), rather this is the load at which the coating has been scraped off the substrate. Unless there is a sharp transition when the coating is stripped, indicating some adhesive
failure, selecting a critical load for coating detachment is almost impossible in such cases but the scratch test critical load may give an indication of the resistance to scratch damage of the coated surface.

An alternative method to detect the appearance of the substrate is to analyse the friction traces developed during the scratch test. In the case of aluminium coatings on 304 stainless steel the friction coefficient increases when the substrate is uncovered (Figure 2b). The sharpness of the friction transition in the plot of friction coefficient versus load mimics the sharpness of the transition observed in backscattered electron images in the scanning electron microscope. However, such clear results are not often observed.

The earliest attempts at scratch test quantification by Benjamin and Weaver [7] are most applicable when thin coatings are plastically deformed in the scratch test. According to these authors the critical shearing force for coating removal, $\tau$, is a function of the scratch geometry, the substrate properties and the frictional force on the stylus. Thus, for a stylus of radius, $R$,  

$$\tau = \frac{kAH}{\left(R^2 - A^2\right)^{\frac{1}{2}}}$$

[1]

where the radius of the contact $A = (L_c/\pi H)^{1/2}$, $L_c$ is the critical load, $H$ is the hardness of the substrate material and $k$ is a constant varying between 0.2 and 1.0. The critical shear stress increases as the substrate hardness increases which agrees with experiment. This model assumes full plastic deformation (which is only applicable in a limited range of cases) and does not show the influence of coating thickness.

For soft polymeric coatings on harder metallic substrates the shear stress applied to the coating during the scratch test can lead to regions of delamination extending ahead of the stylus. In such cases a fracture mechanics model has been developed to assess adhesion based on the assumption that the stress field around a moving indenter can be given by the Boussinesq solution [14, 15]. This is clearly not a complete solution as it does not deal with elastic mismatch at the coating substrate interface but generates strain energy release rates comparable to those obtained by different adhesion test methods. However, the method requires knowledge of the area and geometry of delamination which is not always easy to determine if the coating is not transparent and the same mechanism of failure is not often observed for other coating systems. For this reason the model is not widely applicable.

In general only semiquantitative measurements of adhesion of soft coatings can be achieved by scratch testing and alternative adhesion test methods are preferred (e.g. tensile and peel tests [16], blister tests [17], superlayer tests [18]). Since soft coatings are usually quite ductile and may be mechanically manipulated without failure such mechanical tests are relatively easy to perform. The main problem is that the work done is not solely governed by the energy expended in detachment and deconvoluting the measurements in a way which separates the work of adhesion from other energy absorbing mechanisms is difficult [19].

### 2.2.2 Hard coatings
In the context of this paper hard coating refers to coating materials with a hardness of greater than 5GPa. The failure modes can be broadly split into four categories:

1. Through-thickness cracking - including tensile cracking behind the indenter [8,20], conformal cracking as the coating is bent into the scratch track [8,20] and Hertzian cracking [8]. These cracks may extend into the substrate if it is sufficiently brittle but are usually stopped at the interface in a hard coating on a softer substrate.

2. Coating detachment - including compressive spallation ahead of the indenter [8,20], buckling spallation ahead of the indenter [8] or elastic recovery-induced spallation behind the indenter [8, 21].

3. Chipping within the coating – usually observed for thick coatings on a softer substrate. The scratch test cannot practically measure the adhesion of coatings greater than 50μm thick in its conventional form since it is impossible to generate sufficiently large stresses at the interface before chipping of the coating occurs.

4. Chipping within the substrate – for brittle coatings on brittle substrates where the adhesion is good the system tends to behave in the same way as a brittle bulk material and unless the coating is sufficiently thick chipping of the substrate will occur.

The type of failure which is observed for a given coating/substrate system depends on the test load, the indenter radius, the coating thickness, the residual stress in the coating and the substrate hardness and interfacial adhesion. Generally the critical load at which a failure mode first occurs, or occurs regularly along the track, is used to assess the coating though there is a distribution of flaws and hence of failures in most cases [6]. Comparisons between different coatings are only valid if the mechanism of failure is the same which requires careful post facto microscopical examination for confirmation.

The adhesion related failures which are the basis of the scratch adhesion test for hard coatings are buckling and spallation [9,10] and are described in more detail in the next section.

2.3 FAILURE MECHANISMS RELATED TO ADHESION FOR HARD COATINGS

2.3.1 Buckling

This failure mode is most common for thin coatings (thickness typically <10μm) which are able to bend in response to applied stresses. Coatings much thicker than this limit will tend to show through-thickness fracture at stresses lower than those necessary to cause buckling and will fail by wedge spallation (see next section). Failure occurs in response to the compressive stresses generated ahead of the moving indenter (Figures 3a and 3b). Localised regions containing interfacial defects allow the coating to buckle in response to the stresses and individual buckles will then spread laterally by the propagation of an interfacial crack. Spallation occurs when through-thickness cracks form in regions of high tensile stress within the coating. Once the buckle has occurred the scratch stylus passes over the failed region crushing the coating into the surface of the scratch track formed in the substrate. Coating removal can be enhanced at this point or the failure may disappear completely depending on its size and the toughness of the coating.
Buckling failures typically appear as curved cracks or patches of damage extending to the edge of the scratch track or beyond. They are often delineated by considerable coating fragmentation and have major crack planes perpendicular to the coating/substrate interface. In most cases buckles form in the region of plastic pile-up ahead of the moving indenter (Figure 3c). The size of the buckle is typically less than or equal to the extent of pile-up. This would imply that the pile-up process controls the buckle failure mode to a great degree. This explains, to a large extent, the increase in critical load with substrate hardness for titanium nitride tool coatings on steel which is often reported [1] since in such coatings the buckle failure mode dominates. As the steel hardness increases plastic pile-up ahead of the indenter is reduced and the bending stresses induced in the coating by the pile-up are limited. A higher normal load is needed to develop equivalent pile-up and bending stresses and thus the critical load increases. The correlation between buckle diameter and pile-up diameter is very close for alumina scales on the oxide-dispersion strengthened alloy MA956 or TiN coating on stainless steel [10]. For TiN coatings on steel, changes in buckle diameter can be produced by changes in interfacial structure and adhesion but within limits defined by the size of pile-up.

According to Evans [22] the critical buckling stress $\sigma_b$ is given by:

$$\sigma_b = \frac{122E_c}{1 - \nu_c^2} \left(\frac{t}{R}\right)^2$$

where $E_c$ and $\nu_c$ are Young’s modulus and Poisson’s ratio of the coating, $t$ is coating thickness and $R$ is the radius of the buckled region. This predicts that the critical buckle stress increases with coating thickness as is mostly observed. However, this equation assumes a planar interface which is not always the case. For a curved interface, Strawbridge et al [23] have shown that a tensile stress, $\sigma_t$, is generated normal to the interface by the action of the stress in the plane of the surface, $\sigma_0$, and the magnitude of this stress at the interface is given by:

$$\sigma_t = \sigma_0 \frac{t}{R_i}$$

where $R_i$ is the radius of curvature of the curved interface and $t$ is the coating thickness. In the scratch test the applied stress (i.e. the sum of any residual stress and the stresses introduced by the scratch stylus) determines $\sigma_0$ and, in the case of a coating bent over the pile-up ahead of the moving indenter, $R_i$ represents the radius of curvature of the pile-up. Since the amount of pile-up depends on the hardness of the substrate, the critical load in the scratch test should thus be proportional to $R_i$ and inversely proportional to $t$. As the hardness of the substrate increases so $R_i$ tends to increase and this behaviour is maintained for a fixed value of $t$ but the critical load is not inversely proportional to thickness. This is due to the fact that $R_i$ is actually a function of $t$ - the extent of pile-up decreases as $t$ increases as mentioned previously. In fact for thin TiN coatings on a range of steels experimental results indicate that $R_i$ is proportional to $t^2$ which would imply that the critical load is in fact proportional to coating thickness which is close to what is observed. However, much more data are necessary to determine the validity of this observation.
Buckling failures have been observed around static indentations and scratches in hard coatings on hard substrates produced by facetted indenters (e.g. by a Berkovich tip commonly used in nanoindentation testing). In such cases the detached buckle is often bounded by radial cracks and plastic deformation in the substrate is limited. This process can be analysed based on model suggested by Thouless [24] which assumes that: (i) the in-plane load on the delaminated sector due to indentation causes the growth of the delamination area, and (ii) the coating chips at the moment of buckling of the sector due to the same in-plane load. According to den Toonder et al [25] the interfacial fracture energy can be calculated using:

\[
\Gamma_i = 1.42 \frac{E t^3}{L^2} \left( \frac{\frac{a}{L} + \frac{\beta \pi}{2}}{a + \beta \pi} \right)^2 + \frac{t(1-\nu)\sigma_r^2}{E} + \frac{3.36(1-\nu)\kappa^2 \sigma_r}{L^2} \left( \frac{\frac{a}{L} + \frac{\beta \pi}{2}}{a + \beta \pi} \right)
\]  

(4)

where \(E\) is the Young’s modulus of the coating; \(t\) is the thickness of the coating; \(\nu\) is the Poisson’s ratio of the coating; \(\sigma_r\) is the residual stress in the coating and \(a, L\) and \(\beta\) define the geometry of the chipped piece (Figure 4). Reasonable values of interfacial toughness for hard films on silicon, glass and other hard substrates are produced by equation (4). This approach may be applied to cracks associated either with static indentations or scratches but the fracture energy is generally different in the two cases which implies that there is a frictional contribution to the failure in the scratch test which has not been considered.

2.3.2 Wedge Spallation

For thicker (>10 \(\mu\)m) coatings where bending is less common the buckling failure mode is not observed. In fact the coating can suppress the formation of a narrowly defined pile-up region (Figure 5d) and the stresses ahead of the indenter are less complex. Adhesive failure now occurs by a different mechanism (Figure 5a-c). Initially compressive shear cracks form some distance ahead of the indenter through the thickness of the coating. These propagate to the surface and interface and generally have sloping sides which can act like a wedge. Continued forward motion of the indenter drives the coating up the wedge causing an interfacial crack to propagate. As the extent of interfacial failure increases the wedge lifts the coating further away from the substrate creating bending stresses within it. Large enough displacements will cause a region ahead of the indenter to be detached in response to the tensile bending stresses created. When this happens the scratch diamond can drop into the hole left by removal of the coating (Figure 5d) and there is a dramatic increase in scratch width and scratch depth. Pile-up is then often seen beside the track until the stylus climbs up the wedge and out of the hole. Whereas such large failures are often observed for alumina scales on MA956, much smaller failures are often produced for vapour deposited TiN coatings and it is rare that the stylus drops into the hole left by the spalled coating. In this case the stylus passes over the edge of the spalled region creating considerable microfracture in the coating as it passes.

The wedge spallation failure mode depends on two distinct processes occurring [22]. Firstly a compressive shear crack must form and then interfacial detachment occurs. According to Evans [22] the biaxial stress necessary to cause the wedge crack, \(\sigma_w\), is given by
\[ \sigma_w = \left( \frac{4E_i G_f}{(1 - \nu_c)\lambda} \right)^{1/2} \]  \hspace{1cm} [5]

where \( G_f \) is the coating fracture energy and \( \lambda \) is the width of the wedge spalled region. The biaxial stress to produce the spall, \( \sigma_{sp} \), after shear cracking has occurred is given by

\[ \sigma_{sp} = \left( \frac{E_i G_i}{(1 - \nu_c)\lambda} \right)^{1/2} \]  \hspace{1cm} [6]

where \( G_i \) is the strain energy release rate for a crack in the interfacial region (i.e. the interfacial fracture energy) which, in an ideal case, can be equated with the crack surface energy, \( \gamma \), and hence basic adhesion. However, for all real interfaces other energy dissipation mechanisms are likely to be operating (e.g. plasticity, microfracture, heat generation, etc.) so \( G_i \) can be taken as a measure of practical adhesion. Since to get a visible wedge spall both the through-thickness and interfacial cracks must be formed the total failure stress, \( \sigma_F \), is given by the sum of equations (4) and (5). As Equation 5 has a \( 1/\sqrt{t} \) dependence the critical load for wedge spallation is expected to decrease as coating thickness increases. There is no requirement that the crack propagates exactly along the interface in this analysis though this is often the case if the adhesion is poor and the interface is sufficiently planar.

### 2.4 STRESSES RESPONSIBLE FOR FAILURE

The stresses around a moving indenter sliding across a coating/substrate system are complex and no analytical model exists which fully describes what is observed. Some progress has been made with finite element modelling, particularly in cases where both coating and substrate remain elastic, but this work is a simplification compared to what usually occurs in a real scratch test. A number of improvements to the approach are required and still need to be addressed:

1. Realistic materials models are required which include the elastic properties of coatings and substrate, their yield and fracture strength and work hardening characteristics.
2. Cracking and the modification of the stress state by the presence of cracking needs to be implemented for hard coatings or substrates.
3. Modification of the stress field by changes in indenter/coating friction requires data for each coating/substrate system of interest.
4. Roughness of the surfaces and interface causes localised stress concentrations which are often ignored in basic finite element models and can lead to considerable reductions in the normal load at which failure occurs.

The yield, work hardening and fracture properties of many coatings are not well known and getting good input data for finite element models can be problematic. Combinations of finite element modelling and experiment are attempting to address this problem. For instance, Jiang et al have developed finite element models of scratches using more realistic elastic-plastic materials models [26] and Holmberg and co-workers have developed a method for determining the fracture properties of coatings from the tensile cracking which occurs behind the indenter in the scratch test [27]. However, much more progress is needed, particularly as adhesion failures often arise after through-thickness fracture has already occurred and the modifications which this generates to the stress field around the moving indenter need to be incorporated in any finite element model if accurate failure stresses are to be determined. Also, any failure mode which occurs close to the indenter is likely to be in a region where the
stress field is changing rapidly and it will be difficult to determine exactly which stresses are responsible for failure. Therefore, finite element modelling can currently only be regarded as providing a guide to the stress fields around the moving indenter but can help to identify those failure modes which are generated by simple stress conditions.

If finite element modelling is to be used to predict failure in the scratch test a suitable failure criterion needs to be developed. Developing stresses is one part of this but the defect distribution in the coating and interfacial region will also need to be known if accurate predictions are to be made. Relatively little work has been done in this area to date.

2.5 DETECTION OF FAILURE

A number of techniques have been used to identify the onset of adhesion failure in the scratch test including post facto microscopy, acoustic emission and friction analysis. Perhaps the most useful and reliable is imaging the scratch by an appropriate microscopy technique. For the conventional scratch test where a Rockwell ‘C’ stylus is used to generate failure it is relatively easy to identify failure using reflected light microscopy or scanning electron microscopy as the failures are usually tens of microns across. In such cases adhesive failure detected by acoustic emission or friction changes usually correlates well with the failures visible by microscopy. However, it is often observed that acoustic emission detects failures which cannot be seen in the microscope, perhaps failures of the interface which are not associated with chipping.

AE signals result either from the sudden release of elastic energy or from surface interactions such as friction and adhesion. Sudden energy release occurs during unstable crack growth, high-speed phase transformations, and plastic instabilities. A transducer to measure the acoustic emission is attached to the scratch slider and its output can be correlated to events which occur along the scratch track. At constant load, as the scratch is created a baseline AE response is established due to plastic deformation and friction/adhesion and individual AE responses from fracture are superimposed upon this. The magnitude of the acoustic emission signal depends on the size of the crack produced since the energy in the AE signal scales with the energy released in the process [28]. For coatings thicker than a micron, the area of adhesive failure is large compared to the area of through-thickness cracks; a large jump in the acoustic signal is thus a reasonable indication of adhesive failure. However, as coating thicknesses reduce the size of the adhesive and through-thickness failures also reduce and are more comparable. The acoustic signal is reduced and it becomes much more difficult to determine what sort of failure has occurred. Indeed, at small scales the generation of acoustic emission can represent the emission of bursts of dislocations as well as fracture [29] and acoustic emission measurements from nanoindentation and nanoscratch tests can identify that these mechanisms are operating when combined with careful microscopy.

When nanoscratch testing is applied to coatings considerably less than 1µm thick, light microscopy is no longer suitable and other techniques are essential to assess failure mechanisms. High resolution scanning electron microscopy or atomic force microscopy can offer some information by there is a limit to what can be seen – adhesion failure may be visible but through-thickness cracking is often not unless the crack opening is significant. In such cases changes in the indentation load-displacement or friction curves are a good indication that failure has occurred but determining what failure mode still requires careful microscopy.
The advantage of using load-displacement or friction-displacement curves to determine the onset of failure is that this enables quantification of the failure in terms of the work done. This will be discussed in more detail later in the paper.

3 EXPERIMENTAL

In this study the scratch adhesion behaviour of relatively thick hard coatings on soft substrates (coating hardness >10GPa, Substrate hardness < 5GPa) and thin hard coatings on hard substrates has been investigated (coating and substrate hardness >7GPa). Similar samples have been investigated in previous work [10] but in this case the residual stress in the coating has been carefully determined and the quantification is expected to be more accurate.

3.1 Hard Coatings on soft substrates

Samples of 304 stainless steel and the oxide dispersion strengthened (ODS) alloy MA956 (composition in Table 2) were cut into 20 x 10 x 2mm sections, polished to a 1µm diamond finish, and cleaned and degreased in isopropyl alcohol prior to use. The stainless steel coupons were coated with TiN by sputter ion plating (SIP [30]) or arc evaporation [31] in commercial coating equipment at a temperature of 500°C. Coatings with thicknesses in the range 1 to 25µm were deposited with a 120 nm titanium interlayer to promote adhesion. The alloy samples were isothermally oxidised in air at temperatures between 1150°C and 1300°C for times up to 1400h to produce alumina scales up to 20µm in thickness. The thickness of all scales or coatings was measured by both ball cratering and metallographic cross sections.

Scratch testing was performed using a CSEM scratch tester fitted with a Rockwell ‘C’ diamond (200µm tip radius). This is a dead-loaded machine where a separate scratch is made for each applied load. A 3mm scratch was made at each load. For the tests reported here scratches were made at 2N intervals starting at 2N. Care was taken to place the scratches sufficiently far apart so that their deformation regions did not overlap. Critical loads for each failure mode were determined by post facto microscope examination of the scratch tracks. The critical load criterion used was the lowest load at which the failure occurred more than twice along the scratch track. Since the total number of wedge cracks produced was low it was not possible to perform a full Weibull statistics analysis [6].

3.2 Hard coatings on hard substrates

400nm thick titania coatings were deposited on glass by sputtering. The 10cm by 10cm float glass samples were 4mm thick and were coated on the air side. Titania was sputtered from a metal target with a pulsed DC mode (2.43KW) in an argon/nitrogen/oxygen mixture and is referred to as TiO$_x$N$_y$ hereafter.

Nanoscratch testing was performed using a Hysitron Triboindenter - scratch tests were performed with a Berkovich indenter (200nm tip end radius) in the edge leading configuration. The total scratch length was 10µm. Along the length of the scratch the load was ramped to the maximum (10mN) at 1mN/µm over 30 seconds. At the end of the test it was ramped down to zero in the same time with the indenter nominally stationary. AFM traces were carried out with the same tip which made the scratch – the relatively blunt tip means that these images have limited resolution when compared to conventional AFM
Scratches were viewed by scanning electron microscopy and energy dispersive x-ray microanalysis was used to determine if spallation of the coating around the scratch had occurred. It was only possible to find those scratches where spallation had occurred in the SEM as through-thickness fracture is almost invisible even at the highest practical magnification. The image quality is poor due to the effects of charging – gold or carbon coating could not be used as this covers the cracks and reduces their visibility even further.

### 3.3 Finite Element Modelling

Previously finite element modelling of the scratch test for 2µm TiN on stainless steel had been undertaken by the authors using DYNA3D [32] but this analysis has been repeated using better substrate mechanical properties obtained from tensile tests on small samples cut from the substrate after coating. A two-dimensional plane strain model, which models the indentation as a cylinder rather than a sphere, was implemented in the ANSYS commercial Finite Element code in order to achieve reasonable run times. The mesh was chosen to be symmetric about the y axis and was refined in the region below the indenter. The coating thickness was set at 2µm and reasonable materials properties were used for both substrate and coating. For the stainless steel substrate plastic deformation and work hardening was allowed (yield stress, $\sigma_y=450$MPa; work hardening exponent, $n=0.26$) whereas for the TiN coating deformation is elastic up to 8GPa with no work hardening. The indenter/coating friction coefficient was fixed at 0.15. This is an approximation to the mechanical response of the system because it is expected that the TiN coating will undergo fracture if relatively modest tensile stresses (~500MPa) are generated.

As in the previous work models were run for comparison: a static indentation where the maximum vertical indenter displacement was 2µm and a simulated scratch where the indenter was allowed to indent to 2µm and was then moved tangentially 10µm. The new FE results are very similar to those obtained previously. Given the uncertainties about the difference between cylindrical and spherical indentations, as well as questions about the quality of the materials data, the absolute stress values generated must be questionable. However, the difference between static indentation and scratches is instructive.

### 3.4 Data for Modelling

In order to calculate the practical adhesion in terms of the interfacial fracture energies Young’s modulus and Poisson’s ratio of the coating are necessary. For all the scales and coatings investigated on soft substrates in this study the Young’s modulus was determined by nanoindentation testing on coatings that were at least 8µm thick using a Berkovich indenter using the method of Oliver and Pharr [33]. In order to reduce the scatter in the data the sample surface was polished prior to testing at a maximum load of 10mN; under these test conditions the contribution from the substrate is expected to be minimal. Properties for the coatings on glass were obtained from very low load indentation testing (<100µN) on the 400nm coating using a very sharp cube corner indenter (tip end radius <50nm). Young’s modulus was again extracted from the unloading curve by the method of Oliver and Pharr [33] – the measured moduli values were extrapolated to zero depth to account for the effect of the substrate. Indents were imaged after testing using the tip that made them to confirm that
no detectable pile-up occurred and that the measured area of the indent was close to that
determined from the Oliver and Pharr approach – in such circumstances the Elastic Modulus
determined by the Oliver and Pharr method is the same whether a well-calibrated Berkovich
or cube corner indenter is used. However, if significant pile-up occurs it can cause errors in
the data obtained using either indenter and this may be worse for the cube-corner indenter.
Correction of the areas for pile-up is essential in such circumstances. Quoted values in Table
2 are the average of ten measurements and are similar to what is expected for such coatings.
There was a small variation in Young’s modulus of the oxide scale on MA956 depending on
the oxidation temperature but this was not significant in the temperature ranges investigated
here. Handbook values have been used for Poisson’s ratio in all cases.

4 RESULTS

4.1 Hard Coating on Soft Substrate

4.1.1 Scratch Test Failure Load Regimes

For all coatings investigated the critical load for buckle formation increases as the coating
thickness increases (Figure 6a and 6b). Wedge spallation does not occur until higher coating
thicknesses and the critical load for wedge spallation decreases as thickness increases. This is
exactly the same as has been observed previously [9,10] and is broadly in agreement with the
theoretical predictions in Section 2.3. The critical load for buckle failure for the arc
evaporated TiN is lower than that for the Sputtered coatings which might imply poorer
adhesion but the wedge spallation critical loads are more comparable.

4.1.2 Finite Element Results

The main stress components in the coating at the coating/substrate interface have been
extracted from the finite element data for both static indentation and scratching and are
plotted in Figure 7. $\sigma_{xx}$ (parallel to the surface) is tensile beneath the indenter in static
indentation due to the stretching and bending of the coating as it is dragged into the
impression as the substrate plastically deforms beneath it. At the edge of the contact the
bending is in the opposite sense and compressive stresses are observed. This is exacerbated
by pile-up. $\sigma_{xx}$ quickly falls to zero outside the pile-up region. On moving the indenter the
compressive stress is increased ahead of the indenter and reduced behind it, probably due to
changes in the amount of bending in the coating. Well outside the contact region a
compressive stress exists ahead of the indenter which approximates to a state of pure
compression. In the region of bending at the edge of the contact the shear stress component
$\tau_{xy}$ is also significant and the values at the leading edge of the indenter are increased by
sliding. The stresses perpendicular to the interface $\sigma_{yy}$ are compressive in the contact region
as expected with tensile stress regions just outside in the bending zone. These tensile stresses
are much reduced in the scratch case.

Clearly a very complicated stress state exists in the pile-up region close to the indenter where
bending of the coating occurs. This is the region where buckling occurs and it makes the
relationship between $\sigma_b$ and $L_c$ difficult to define. The stress state well ahead of the indenter
where wedge cracking occurs is much simpler and a linear relationship between $L_c$ and $\sigma_F$
is expected for a given coating/substrate/indenter combination. The compressive stress is
reduced the further ahead of the indenter it is determined but the rate of change is relatively
small. For a precise knowledge of the stresses responsible for detachment an interface fracture criterion is required. The FE results here imply that failure will occur just ahead of the moving indenter where the compressive stresses are highest. Two distinct stress maxima are observed in $\sigma_{xx}$, one at the edge of the contact where bending stresses and compression ahead of the moving indenter combine which is where buckle failure is most likely and a second maximum some distance ahead of the contact where wedge spallation is the preferred failure mode. For the 2µm thick coatings examined here the buckling failure is most likely as the stresses at the contact edge are highest as expected. For thicker coatings where the second moment of area is larger and bending is reduced the compressive stress maximum further away from the contact is largest and wedge spallation occurs. At intermediate coating thicknesses, the stresses are more comparable and either failure mode is possible, depending on the interfacial defect distribution.

4.1.3 Quantification of Failure Stresses

The stresses responsible for coating detachment, $\sigma_F$, are a combination of the residual stresses remaining in the coating at room temperature, $\sigma_R$, and the stresses introduced by the scratch stylus, $\sigma_s$. Thus

$$\sigma_F = \sigma_R + \sigma_s$$

[6]

$\sigma_R$ can be measured for both TiN and alumina coatings by x-ray diffraction using the $\sin^2 \psi$ method [34].

The stresses induced by the indenter have been determined empirically. The critical load for coating detachment is known to decrease as the residual stress in the coating increases for a wide range of coatings such as TiN [35]. In the case of TiN coatings the residual stress can be increased by increasing the energy or flux of ion bombardment during deposition [36]. Equating the change in scratch test critical load with the difference in measured residual stress enables a calibration factor to be determined. For sputtered TiN 1g normal load in the scratch test equates to a 2.3 MPa compressive stress ahead of the indenter whereas for Arc TiN this rises to 4MPa with an error of about 10% in both cases. For the alumina scales grown on MA956 the residual stress can be changed by altering the oxidation temperature. Plotting the measured residual stress against critical load allows a calibration coefficient to be determined from the slope of the graph (Figure 8). Experiments have been performed at three different oxide thicknesses. The calibration constant is almost the same in each case and is effectively constant within experimental error. Thus, for this material 1g normal load in the scratch test equates to an average value of 0.40±0.04 MPa. In all cases a linear relationship between critical load and stress is assumed which appears reasonable in these systems but may not be valid in all cases. Calculated failure stresses for alumina scales on MA956 and TiN on stainless steel are shown in Figure 9 where the stress introduced by the scratch stylus has been added to the residual stress in the coating to give the failure stress. It is clear that the failure stresses for arc evaporated TiN are now higher than for sputtered material since the scratch calibration constant is higher and the residual stress in the arc coatings is also much higher (7.0GPa compressive as opposed to 2.1GPa compressive for the sputtered TiN film).

The wedge failure stresses in Figure 9 can then be used to determine the work of adhesion by plotting the calculated $\sigma_F$ against the reciprocal of the square root of coating thickness (Figure 10). It is then possible to separate the two components contributing to wedging failure.
(Equations 5 and 6); the slope of this curve can be used to determine the interfacial fracture energy, $G_i$, using the coating data in Table 2, whereas the intercept gives a measure of coating fracture strength, $\sigma_w$. These values are presented in Table 3. It is clear that the fracture strengths of the coatings or scales are quite similar but that there is a much greater difference in the interfacial adhesion.

It is important to determine if failure is really interfacial if the scratch test is to be used for adhesion assessment, so Auger Electron Spectroscopy (AES) was used to identify the locus of interfacial failure for both materials. In the case of the alumina scales there is always a thin layer of oxide on the uncovered substrate at the bottom of the wedge-spalled pit. However, this may have been formed after scratch testing due to the exposure of the bare metal substrate to the atmosphere. There is no evidence for substrate material on the underside of any spalled debris that was collected. It is therefore reasonably certain that failure occurs at or very near to the interface once the wedge crack reaches the interfacial region. Assessing the failure locus of the TiN coatings is more complex since a thin (~100nm) titanium interlayer was used to promote coating adhesion which dissolves a considerable amount of carbon and oxygen from the substrate surface in the early stages of deposition [37]. In the coating processes used ion bombardment of the growing coating is used to promote adhesion by forming a pseudodiffusion zone in the interface region giving a metallurgical bond with no well-defined interface plane. The gold TiN was clearly removed at the bottom of wedge spalls but there was still considerable titanium present on the surface of the substrate. SIMS images of the surface showed that the nitrogen content of this surface layer is very low compared to the carbon and oxygen levels. It thus seems likely that failure has occurred within the titanium interlayer.

For both materials the interfacial fracture energies are higher than that expected from the fracture energy of the coating (~ 1J/m$^2$) but lower than or comparable to typical substrate values (~ 10$^3$J/m$^2$). This also indicates that the failure crack is propagating at or near the interface with at least some crack tip plasticity occurring within the substrate. As $G_i$ increases the effective coating/substrate adhesion increases so the results here indicate that the TiN/stainless adhesion is better than that for alumina/MA956 since the mechanical properties of the substrates, and hence the energy dissipated in crack-tip plasticity processes, are very similar. Since the TiN coated stainless steel has much smaller spalled regions and the coating is considerably more resistant to detachment during abrasion than the alumina scale the relative values of the fracture energies are as expected.

The higher value for $G_i$ for the arc evaporated TiN compared to the sputtered material indicates that the adhesion of the arc coatings is actually much better than their sputtered counterparts, a conclusion which is opposite to that which might be drawn from the scratch test critical loads. The coating flux in arc evaporation is highly ionised compared to sputtering and the bombardment of the substrate with these highly ionised particles in the early stage of deposition is much more effective at cleaning the surface and forming strong chemical bonds [31].

The interfacial fracture energy for alumina on MA956 is reduced as the oxidation temperature increases (Figure 11) but the fracture strength of the coating is actually increased. During the long exposures necessary to grow thick scales on the alloy at low temperatures void-like defects are known to grow in the scale. These will act as the crack nucleation sites that lead to failure [38]. If the scale has a constant toughness then the more defective low temperature
scales would be expected to fail at a lower stress level. The better adhesion of the low temperature scales is more difficult to explain but may be due to different chemistry of the interfacial regions.

4.2 Hard coating on hard substrate

For the TiO$_x$N$_y$ coating on glass the AFM image does not show a clear sign of adhesion failure though some damage at the side of the track is visible (Figure 12a). The edge on orientation is not perfect – more of the indenter face is involved in forming the left side of the scratch. There are no obvious through-thickness cracks in the AFM images, but the sharp edges delineating the scratch in the SEM image imply that through thickness cracking has occurred (Figure 12b). Energy dispersive x-ray microanalysis in the SEM confirms that coating detachment has occurred.

There is a smooth increase in friction force with scratch length (Figure 13a) up to a normal load of 3.2mN when some oscillations in the friction trace are observed. Such oscillations are also visible in the friction coefficient trace (Figure 13b). However, the clearest indication of failure is seen in the work of friction plot (Figure 13c) when jumps are observed associated with each failure event. The work of friction, which is the integral of the friction coefficient up to the given displacement, represents the irreversible work done during scratching. The smooth increase in work of friction is related to the increased work necessary to plastically deform the coating/substrate system to create the scratch track. However, the rapid increase in work of friction correlates with the onset of coating fracture. Both through-thickness and adhesive failure can generate such jumps.

For through thickness cracking the crack length is typically of the order of a few microns and the coating thickness is 400nm giving a crack area of $\sim 10^{-12}$ m$^2$. Given typical surface energies of 1J/m$^2$ the size of a jump in the work of friction trace might be expected to be of the order of 1pNm which is much smaller than observed in Figure 13c. Given that the area of adhesion failure is typically two orders of magnitude greater it is likely that these jumps are due to adhesive failure. The adhesion failure is visible in the scanning electron micrograph (Figure 12b) and it appears that this failure occurred in several stages from the jumps in the work of friction trace.

The total work represented in the jumps is 855pNm and the area of delamination is approximately 18µm$^2$. This would predict an interfacial fracture energy of 47.5J/m$^2$ which is comparable to results obtained for brittle coatings on brittle substrates by other methods. However, without improvements in the measurement of area this value must be regarded as tentative.

The work of friction could, in theory, be used to characterise the failure of hard coatings on soft substrates. However, given the size of the failures and the likely interfacial fracture energies the work of friction resolution of conventional scratch testing equipment is insufficient to resolve the failures.

5 CONCLUSIONS

The scratch test is a good method for quality assurance/quality control testing of the adhesion of hard coatings and is useful in the development of new coatings for process optimisation.
However, at present, quantitative adhesion data from the test which might be used as the basis of a performance model is difficult to extract from the test data. In most cases the stresses around the moving indenter are too complicated to be predicted accurately and therefore the stresses driving coating failure are not known. However, some failure modes occur sufficiently far away from the indenter that the stress states are likely to be simpler and quantification is a possibility.

The two main adhesion related failure modes in the scratch testing of hard coatings are wedge spallation and buckling. Buckling occurs for thin coatings which are able to bend in response to applied stresses. The stresses responsible for failure are complex due to the fact that buckling is confined within the region of pile-up close to the indenter. For thicker, stiffer coatings wedge spallation becomes the dominant failure mechanism. This occurs well ahead of the moving indenter and the stresses which are responsible for failure approximate to a state of pure compression. Wedge spallation stresses can, therefore, be quantified by calibration enabling an interfacial fracture energy to be determined.

To derive the maximum benefit from the scratch test better theoretical models for the stress fields associated with a moving indenter in a coating/substrate system are needed. These are most likely to be based on finite element analysis, but the modelling approach would need to include a large number of factors if the true stress state is to be predicted accurately enough. The use of good constitutive equations for coating and substrate, the incorporation of a suitable fracture model and a mechanism for handling interfacial and surface roughness will be essential if this is to be achieved. If a model is to be developed which can predict the onset of fracture then a method of representing the defect distribution in the system is also necessary. Furthermore the incorporation of residual stresses into the model is essential for accurate results. A considerable amount of development and validation work is thus required for any new system under investigation.

With the emergence of depth sensing indentation and scratch systems with high resolution of applied load, friction force and lateral displacement it is possible to make more direct measurements of interfacial fracture energy for thin coatings. This approach needs investigating on a wider range of systems and critically requires a very accurate assessment of the delamination area but offers a more quantitative evaluation method when compared to the traditional scratch test.

6 ACKNOWLEDGEMENTS

The author would like to thank Ian Gilbert for some SEM images and colleagues at Newcastle University for useful discussions.
References

### Tables

#### Table 1  
Intrinsic and Extrinsic factors in the scratch test.

<table>
<thead>
<tr>
<th>Intrinsic</th>
<th>Extrinsic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loading rate [3, 39, 40]</td>
<td>Substrate properties (hardness, elastic modulus) [40]</td>
</tr>
<tr>
<td>Scratching speed [3, 39, 40]</td>
<td>Coating properties (thickness, hardness, modulus, residual stress) [39, 40]</td>
</tr>
<tr>
<td>Indenter wear [39]</td>
<td>Surface roughness [40]</td>
</tr>
<tr>
<td>Machine stiffness/design</td>
<td></td>
</tr>
</tbody>
</table>

#### Table 2  
Composition and properties of the materials investigated in this study

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Coating</th>
<th>Young’s modulus (GPa)</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>304 stainless</td>
<td>Fe-18Ni-9Cr-1Ti</td>
<td>SIP TiN</td>
<td>450±35</td>
<td>0.28</td>
</tr>
<tr>
<td>MA956</td>
<td>Fe-20Cr-5Al-0.4Ti-0.5Y$_2$O$_3$</td>
<td>Arc TiN</td>
<td>500±62</td>
<td>0.28</td>
</tr>
<tr>
<td>Float glass</td>
<td>73%SiO$_2$, 15%Na$_2$O, 10%CaO+</td>
<td>TiOxNy</td>
<td>388±51</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>traces MgO, Al$_2$O$_3$ and K$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Wedge fracture stress and interfacial fracture energy determined from the scratch test.

<table>
<thead>
<tr>
<th>Substrate/coating</th>
<th>Interfacial fracture energy, $G_i$ (J/m$^2$)</th>
<th>Wedge fracture stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIP TiN/304</td>
<td>538</td>
<td>4.64</td>
</tr>
<tr>
<td>Arc TiN/304</td>
<td>2578</td>
<td>4.89</td>
</tr>
<tr>
<td>Al$_2$O$_3$/MA956</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1150°C</td>
<td>35.0</td>
<td>7.59</td>
</tr>
<tr>
<td>1250°C</td>
<td>16.9</td>
<td>8.06</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1  Schematic showing the various scratch test failure modes which dominate as a function of coating and substrate hardness (H_c and H_s, respectively).

Figure 2  (a) Scanning electron micrographs (backscattered image) of scratch tracks in a 100nm aluminium coating on 304 stainless steel showing the stripping of the coating at the critical load with a sharp change (top scratch) and a more gradual change as the aluminium coating is thinned (lower scratch). (b) Associated friction traces showing a sharp and gradual transition in the friction coefficient.

Figure 3  Buckling failure mode in the scratch test; (a) pile-up ahead of the moving indenter and (b) interfacial failure leading to buckling. Through-thickness cracking results in removal of coating material. Scanning electron micrograph (c) of buckle failures in TiN coated stainless steel.

Figure 4  Schematic diagram of the geometry of a chipped segment of coating

Figure 5  Wedge spallation failure mode in the scratch test; (a) wedge crack forms some way ahead of the moving indenter; (b) continued forward motion drives the coating up the wedge opening up an interfacial crack; (c) through-thickness cracking close to the indenter leads to spallation. (d) Scanning electron micrograph of a wedge spallation failure in an alumina scale on MA956 oxidised at 1250°C for 100h.

Figure 6  Variation of critical load for wedge or buckle formation as a function of coating thickness for (a) Alumina on MA956 and (b) TiN on stainless steel.

Figure 7  Stress components in the coating next to the coating/substrate interface determined for static indentation and scratching using the Finite Element code ANSYS (a) axis and scratch directions, (b) \( \sigma_{xx} \), (c) \( \sigma_{yy} \) and (d) \( \tau_{xy} \).

Figure 8  Variation of critical load with residual stress for 8µm and 20µm alumina scales grown on MA956 at a range of oxidation temperatures.

Figure 9  Variation of compressive failure stress with coating thickness for alumina on MA956 and TiN on 304 stainless steel. The scratch induced stress has been added to the residual stress in the scales and coatings.

Figure 10  Variation of critical failure stress, \( \sigma_F \) with the reciprocal of the square root of coating thickness \( t \), for (a) alumina scales on MA956 at different oxidation temperatures, (b) TiN on stainless steel.

Figure 11  Variation of interfacial fracture energy with wedge fracture strength of alumina scales on MA956 as a function of oxidation temperature.
Figure 12  (a) AFM image of a 10mN scratch in TiO$_x$Ny. (b) SEM image of the same scratch.

Figure 13  Variation of (a) friction force, (b) friction coefficient and (c) work of friction with scratch displacement for 400nm TiO$_x$Ny on float glass.
Figures

Figure 1 Schematic showing the various scratch test failure modes which dominate as a function of coating and substrate hardness ($H_c$ and $H_s$, respectively).
Figure 2  (a) Scanning electron micrographs (backscattered image) of scratch tracks in a 100nm aluminium coating on 304 stainless steel showing the stripping of the coating at the critical load with a sharp change (top scratch) and a more gradual change as the aluminium coating is thinned (lower scratch). (b) Associated friction traces showing a sharp and gradual transition in the friction coefficient.
Figure 3  Buckling failure mode in the scratch test; (a) pile-up ahead of the moving indenter and (b) interfacial failure leading to buckling. Through-thickness cracking results in removal of coating material. Scanning electron micrograph (c) of buckle failures in TiN coated stainless steel.
Figure 4  Schematic diagram of the geometry of a chipped segment of coating
Figure 5  Wedge spallation failure mode in the scratch test; (a) wedge crack forms some way ahead of the moving indenter; (b) continued forward motion drives the coating up the wedge opening up an interfacial crack; (c) through-thickness cracking close to the indenter leads to spallation. (d) Scanning electron micrograph of a wedge spallation failure in an alumina scale on MA956 oxidised at 1250°C for 100h.
Figure 6  Variation of critical load for wedge or buckle formation as a function of coating thickness for (a) Alumina on MA956 and (b) TiN on stainless steel
(a)

(b)

\[ \sigma_{xx} \, (\text{MPa}) \]

Load

Scratch direction

\[ x \, (\mu m) \]

\[ \sigma_{xx} \] vs. \( x \) (\( \mu \text{m} \))

- Indent
- Scratch
Figure 7  Stress components in the coating next to the coating/substrate interface determined for static indentation and scratching using the Finite Element code ANSYS (a) axis and scratch directions (b) $\sigma_{xx}$, (c) $\sigma_{yy}$ and (d) $\tau_{xy}$. 
Alumina Scales on MA956

Figure 8 Variation of critical load with residual stress for 8µm and 20µm alumina scales grown on MA956 at a range of oxidation temperatures.
Figure 9  Variation of compressive failure stress with coating thickness for alumina on MA956 and TiN on 304 stainless steel. The scratch induced stress has been added to the residual stress in the scales and coatings.
Figure 10  Variation of critical failure stress, $\sigma_F$ with the reciprocal of the square root of coating thickness, $t$, for (a) alumina scales on MA956 at different oxidation temperatures, (b) TiN on stainless steel.
Figure 11  
Variation of interfacial fracture energy with wedge fracture strength of alumina scales on MA956 as a function of oxidation temperature.
Figure 12: (a) AFM image of a 10mN scratch in TiO$_x$N$_y$. (b) SEM image of the same scratch.
Figure 13 Variation of (a) friction force, (b) friction coefficient and (c) work of friction with scratch displacement for 400nm TiO$_x$N$_y$ on float glass.