Evaluation techniques and improvements of adhesion strength for TiN coating in tool applications: a review

M.F. Othman\textsuperscript{a}, A.R. Bushroa\textsuperscript{ab} & Wan Normimi Roslini Abdullah\textsuperscript{a}

\textsuperscript{a} Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
\textsuperscript{b} Centre of Advanced Manufacturing and Material Processing (AMMP Centre), Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

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Evaluation techniques and improvements of adhesion strength for TiN coating in tool applications: a review

M.F. Othman\textsuperscript{a}, A.R. Bushroa\textsuperscript{a,b,*} and Wan Normimi Roslini Abdullah\textsuperscript{a}

\textsuperscript{a}Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia; \textsuperscript{b}Centre of Advanced Manufacturing and Material Processing (AMMP Centre), Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

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The adhesion between coating-substrate systems is an important factor in determining the performance and durability of coated engineering components. This paper reviews the microstructures and adhesion strength of titanium nitride (TiN) coating produced using two different processing methods: chemical vapor deposition and physical vapor deposition. Three methods to evaluate the adhesion strength of the coatings, namely the indentation test, laser spallation technique, and scratch test are presented and discussed in terms of their working principles, their advantages and disadvantages. The extrinsic and intrinsic factors influencing the adhesion strength of coating-substrate system, particularly for TiN coating, are also elaborated. The mechanisms and modes of coating failures in adhesion evaluation techniques are discussed with respect to the variation of coating-substrate system combination such as brittle, ductile, soft, and hard. Possible improvements on the adhesion strength of coating-substrate systems, focusing on the processing methods, compositions, and structures of coatings, are also reported.

Keywords: TiN coating; physical vapor deposition; chemical vapor deposition; adhesion; critical load

1. Introduction

Surface coatings are deposited onto steel-metal working tools, high-speed steel (HSS) drills, mills, and machine parts such as ball bearings to reduce friction, improve the hardness, and increase the wear and corrosion resistance of substrate materials. There are many types of surface coatings such as organic, glasses, ceramics, metallic, hard, soft, wear resistance, and corrosion resistance coatings. Most metals, alloys, ceramics, and some intermetallic compounds can be applied as surface coatings either individually or as mixtures. Proper selection of surface coatings is based on the component size and accessibility, corrosive environment, anticipated temperatures, component distortion, coating thickness, and costs.[1] The combination of hard and corrosion resistance coatings is most widely used means of protecting steel. Metals such as titanium (Ti) and silver (Ag) are deposited onto most tool steels in order to improve the hardness and increase the tool lifespan.

Titanium nitride (TiN) coatings are applied onto machine tooling such as drill bits and milling cutters for edge retention and corrosion resistance, often increasing their...
lifetime by a factor of three or more. These coatings deliver characteristics that are necessary for tool steels applications such as hard surfaces of 2400 HV to reduce abrasive wear, noble appearance in metallic golden and yellowish color, excellent adhesion to substrates, high chemical inertness, resistance to elevated temperatures, low maintenance cost, and high productivity.[2]

In tool applications, TiN coatings are also capable in providing the properties of improved ability to hold the tolerances and high temperature stability. Other than that, this coating is particularly used for tool steels due to its low coefficient of friction with most work piece materials, which improves the lubricity, results in excellent surface finish, and decreases horsepower requirements.[2]

A study by Zhang and Zhu [2] has shown that coating TiN onto drill bit increases the tool lifespan by over 1000% in the drilling of stainless steel work pieces. Furthermore, TiN coatings also provide corrosion protection for cutting tools, as reported by Chou et al. [3] and Lunarska et al. [4].

TiN film coatings are usually deposited onto cutting tools either by chemical vapor deposition (CVD) or by physical vapor deposition (PVD) techniques. Basic reaction in CVD process involves titanium tetrachloride, nitrogen (N), and hydrogen (H) at a high temperature range of 850–1100 °C.[2] In contrast, the PVD process relies on ion bombardment instead of high temperatures and operates at lower temperature range of 400–600 °C. In the PVD process, the substrate to be coated is placed in a vacuum chamber and heated to the required temperature. The Ti coating material is vaporized and reactive gases such as argon (Ar), nitrogen (N), and oxygen (O) are ionized to form TiN compound which then are deposited via ion bombardment onto the substrate materials.

The desired property of coating, which is known as adhesion, can be achieved by sum of all interatomic interactions at the interface between coating and substrate materials and the combination of coating-substrate elastic properties, fracture toughness, distribution of pores and other defects in the material, load conditions, and friction behavior.[5]

Adhesion strength is defined as a measure of coating resistance to coating failure and can be determined by the measurement of the critical load. The adhesion strength can be measured by various techniques, either by mechanical or by non-mechanical methods. Mechanical methods include the tape test, indentation test, laser spalling test, and scratch test. Examples of non-mechanical methods are X-ray diffractions, capacity test, and thermal methods. Among these techniques, the scratch test is preferable due to the simple sample preparation and capability in observing many different failures which include coating detachment, through-thickness cracking, plastic deformation, and cracking in the coating or substrate.[6] It has been widely used to evaluate relatively well-adhered surface coatings and is now an essential tool for use in industry for quality control purposes in order to study the mechanical strength and adhesion of coatings on machine components.[7]

The measurements of adhesion strength for TiN thin films using the scratch test have been broadly reported in several literatures.[7–9] Evaluation using this technique depends on both intrinsic and extrinsic parameters. Intrinsic parameters relate to the scratch testing procedure such as the scratching speed, loading rate, diamond tip radius, and diamond wear. In contrast, examples of extrinsic parameters are substrate temperature, pre-treatment process, lubrications, substrate hardness, coating thickness, substrate and coating roughness, friction coefficient, and frictional force.

The accuracy of scratch testing has been improved throughout the years with enhancements such as utilization of acoustic emission (AE) and tangential friction force
to detect coating failure. In addition, the energy description model of coating removal by scratch test has also been developed. Mechanism of coating failures can be detected and categorized during adhesion evaluation techniques according to the type of coatings; either ductile or brittle. The failures also rely on the substrate materials and stresses during adhesion test.

Incorporation of an interface layer in the coating structure can enhance the adhesion of coating deposited by PVD. The interface layer would act as a transition layer, which can improve both chemical and mechanical bonding between coating layers. In the TiN coating system, the adhesion strength can be increased by the inclusion of other metallic coating layer such as pure Ti deposited in between TiN coating and substrate materials. Oxide metals can also be used as the interface layer to improve the adhesion strength. The oxide layer creates strong intermediate or inter diffusion layer at coating layer interfaces. Thus, the presence of Ti and TiO₂ interlayers in the deposition process of TiN is expected to improve the adhesion strengths. Consequently, a Ti/TiO₂/TiN compositional gradient coating is expected to have better adhesion strength than Ti/TiN or TiN coatings.

The objective of this paper was to review the various evaluation techniques for measuring adhesion strengths in tool applications, particularly for TiN coatings. The mechanism of failure will be presented especially for scratch adhesion test. Past studies on the methods to enhance adhesion strength for TiN coatings will also be discussed in this paper.

2. Microstructures and adhesions of TiN coating

TiN coatings are widely applied to the cutting tools such as cemented carbide tungsten that has been reported previously and wear parts due to their excellent properties such as high hardness, excellent strength, low wear resistance, and high temperature stability.

The coating thickness of TiN film on tool steels is generally between 2 and 10 μm. TiN coatings deposited using CVD method tend to be thicker (approximately 7–9 μm thick) than coatings deposited by PVD (3–5 μm thick). It was shown that the hardness of coating tends to increase as film thickness increases, which is believed to increase tool life span.

The microstructure in TiN film deposited by CVD method appears to have equiaxed submicron grains with a tendency to form columnar morphology on approaching the outer TiN surface as the grain size increases. In contrast, the surface morphology of TiN coating deposited by PVD is characterized as being entirely columnar with grains extending through the coating thickness. Figure 1(a) shows the microstructure of TiN coating deposited on cemented carbide substrates by CVD method, while Figure 1(b) shows the columnar structures of PVD TiN coating.

The adhesion strength of a coating is dependent on both chemical and physical interactions between the coating-substrate system and microstructure of the interface region. A good adhesion is characterized by strong bonding across the interfacial region, low stress gradients either from intrinsic or applied stress, absence of easy fracture mode, and no long-term degradation modes. Poorly adhered coatings have low degree of chemical bonding and poor interfacial contact between the coatings and substrates.

The adhesion strengths of coating-substrate system can be represented by the critical load values measured by various adhesion evaluation methods. Testing conditions
such as scratch speed, loading rate, diamond tip radius, and diamond wear may influence the value of critical load. Parameters related to coating-substrate system, which can affect the determination of critical load value are substrate hardness, coating thickness, substrate and coating roughness, friction coefficient, and friction force.[17]

Laugier [15] has reported that the adhesion strength of TiN coating deposited using PVD method was significantly poorer as compared to TiN coatings deposited by CVD. It was shown that the PVD TiN coating had spalled at a critical load of 1.2 kgf, whereas CVD TiN coatings were preserved even at applied load as high as 3.5 kgf.[15] It is believed that the poor adhesion strength was due to the absence of interfacial

Figure 1. SEM micrograph of TiN coatings using different deposition processing. (a) PVD and (b) CVD.[15]
bonding layer and the formation of columnar morphology in PVD TiN coatings which had resulted in low toughness.

3. Adhesion evaluation techniques
The adhesion between coating and substrate can be measured to quantify the performance and reliability of coated materials. The calculations to determine substrate-coating adhesion can be based on either:

1. The maximum force per unit area exerted when the two materials are separated or
2. The work done in separating two materials from one another.[18]

The methods for adhesion evaluation are classified into qualitative and quantitative techniques that can either be based on mechanical and non-mechanical approach. Table 1 shows several methods to measure the adhesion strength. The simplest evaluation method is the tape test, although the result obtained is less precise and accurate. The indentation, laser spallation, and scratch adhesion test are the most practical and widely used methods for coating adhesions analysis. A comprehensive review, comparing the advantages and limitations of these three methods, will be presented in this section.

3.1. Indentation test
In the indentation adhesion test, stable cracks with the introduction of plastic zone are generated into the coating-substrate interface using either Brale or Vickers indenters.[18] It is believed that the interface within the vicinity of created plastic zone produces lower toughness as compared to film and substrate materials and subsequently causes the occurrence of preferential lateral crack area.

Figure 2 shows the schematic view of crack size measurement induced from the indenter loads. The values of critical normal loads for the complete removal of coating from substrate material are known as adhesion strength of coating-substrate systems. This adhesion evaluation technique can be used for a variety of coating-substrate systems. For example, it can be applied to both soft flexible coatings on metals and hard brittle coatings on silicon (Si). This technique delivers qualitative and quantitative results and requires simple test sample preparation. It is popularly used in the industry due to the availability of commercial equipment with digital interferometers which

<table>
<thead>
<tr>
<th>Classification</th>
<th>Qualitative</th>
<th>Quantitative</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Bend and scratch test [19]</td>
<td>Laser spallation technique [25–30]</td>
</tr>
<tr>
<td></td>
<td>Scotch tape test [20]</td>
<td>Indentation test [22,31,32]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Direct pull-off method [33]</td>
</tr>
<tr>
<td>Non-mechanical methods</td>
<td>X-ray diffraction [34]</td>
<td>Thermal method [18]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nucleation test [18]</td>
</tr>
</tbody>
</table>
enable rapid identification of damage and deformation of substrates.[35] Limitations of the indentation adhesion test include the complex mode of loading conditions such as high compressive stress and large shear stress which may produce significant hoop stress, leading to radial cracking in substrate and coating.

Figure 3 shows the results of a series of indentions made at different loads [36] where the average change in lateral cracking is monitored as a function of load. The interfacial fracture toughness, $K_{II}$ is derived from the linear portion of indentation load vs. lateral crack length plot as presented in Figure 3 according to Equation (1).

$$K_{II} = \left( \frac{G_{II}E_c}{1 - v_c^2} \right)^{1/2}$$  \hspace{1cm} (1)

Figure 2. Schematic diagram of coating indentation using adhesion test.

Figure 3. Plot of crack size, $a$ vs. indentation load for series of indentions made at different loads.[36]
where $A$ is a constant which can be seen in Figure 3 for calculation of slope, $E_c$, $v_c$, and $G_{li}$, are Young’s modulus, Poisson’s ratio (i.e. of the coating) and strain energy released per unit area, respectively. It is also observed that in this technique, $K_{II}$ is relatively insensitive to the substrate hardness.

The Brale indentation test was used to measure the interface adhesion toughness of diamond thin films,[37] deposited on a ductile aluminum alloy, Ti–6Al–4V. The Brale indentation utilized Rockwell hardness test with diamond Brale ‘C’ indenter. The results show delamination in area of indentation for large loads of 60–150 kg. The findings also show that the interface toughness obtained was at a high value of 50 J/m² and more than 80% of delamination occurred during the application of 150 kg load.

### 3.2. Laser spallation technique

The interface tensile strength of various thin coatings such as ceramics, polymeric, and metallic materials deposited on substrates can be measured using laser spallation method with the required coating thickness from 0.3 to 3 μm.[27] Figure 4 presents the basic laser spallation test setup.[25] The aluminum (Al) film is sandwiched between the back surface of the substrate and a 50–100-mm thick layer of solid water glass. A 2.5 ns Nd:YAG laser pulse is focused onto an area of 3 mm in diameter on a 0.5-mm Al film. The induced expansion of Al would generate a compressive stress pulse with 1 ns rise time directed toward the coating that is deposited on the substrate’s front surface. The compressive stress wave is reflected into tensile pulse from the coating’s free surface and is completely removed at sufficient high amplitude which is referred to as spallation.[25]

The critical/maximum tensile stress at the interface is calculated by measuring the transient displacement history of the coating’s free surface induced during pulse reflection. This pulse reflection is manifested using an optical interferometer with resolution

![Figure 4. Basic laser spallation setup][25]
of 0.2 ns in single shot mode. The interface strength is determined by the peak value of interface tensile stress at the onset of interface separation.[28]

The laser spallation technique is more convenient as compared to other adhesion methods due to its relatively simple setup. This method enables full quantitative analysis on a wide range of substrates.[35] However, this technique is not suitable for thick and very hard coatings, since the coating would not be completely separated from the substrate due to the formation of interfacial cracks at the interface. Nevertheless, modifications can be made by providing small a coated area within 3 mm diameter so that laser pulse can be directly focused on the specific area and complete separation of the coating area can thus be achieved.[35]

Wang et al. [38] has conducted the parametric study of elastic wave generation by pulsed laser technique. The spalling behavior of thin films deposited onto single crystal Si and fused silica has been reported with the influence of various parameters such as substrate thickness, film/coating thickness, and laser energy. It was found that the maximum interface stress decreases with increasing substrate thickness due to geometric attenuation. However, the interface stress increased to a maximum as film thickness increased. The maximum stress in substrate and coating-substrate interface increased with increasing of laser energy.

3.3. Scratch test

In a scratch test process, a diamond stylus is drawn across the surface of the coated sample at a constant speed with defined normal force over a specified distance. The normal force can either be set to be constant, gradually or incrementally increasing depending on the model of analysis, as shown in Figure 5.

In constant load scratch testing, the normal force is maintained at a constant level while scratching the sample, as shown in Figure 5(a). By increasing the load for each subsequent scratch, a scratch map is generated to determine the critical load corresponding to the specified damage. In progressive load scratch testing, as shown in Figure 5(b), the stylus is drawn along the sample, while the normal force is linearly increased to a maximum predetermined value. The critical load corresponds to the normal force at which the damage is first observed. Incremental load scratch testing consists of incrementally increasing constant load scratch segments and is very useful for coating sample with limited area, as shown in Figure 5(c).

The diamond stylus used in scratch test typically has Rockwell C geometry with an angle of 120° and spherical tip radius of 200 μm. The normal force at coating detachment is known as critical load, \( L_c \), which is defined as the load that corresponds to the failure event. This load corresponds to the practical adhesion strength and damage resistance in coating-substrate system. After completion of the scratch, the scratch track can be microscopically analyzed for specific, well-defined damages such as cracking, deformation, buckling, spallation, or delamination of the coating.

The main advantage of scratch test lies in the relative easy sample preparation. This technique is proven to be an effective adhesion evaluation method for brittle and polymer coatings such as epoxies coating. This single instrument provides valuable information pertaining to surface topography, mechanical properties, mode of delamination, and deformation. The coating hardness and elastic properties are also obtainable due to the capability of stylus to act as an indenter.[35] However, there are several limitations of the scratch test since it is limited to hard brittle coatings and not suitable for softer coatings except under certain testing conditions. In addition, the assessment of adhesion
Figure 5. The three main scratch modes are (a) constant load, (b) progressive load, and (c) incremental load.
strength becomes difficult if coating thinning occurs near to the point of optical transparency without achieving complete coating detachment from substrates.\[35\]

A modified scratch test in the form of multimode scratch testing has been used to evaluate the adhesion of TiN coating deposited onto steel and Ti alloy substrates.\[7\] Progressive loading scratch tests, constant load scratch tests, and multiple scratch tests in the same track and indentation tests were evaluated in this study. The modified scratch test was used not only for identifying coating detachment but also to assess other failure mechanisms such as cracking and cohesive damage. The additional modes of operation enabled the evaluation of chipping fracture mechanisms in scratch track for both metal substrates. The results showed that the chipping fracture was cohesive for TiN coated steel and adhesive for Ti alloy substrate.\[7\]

AE equipment can be utilized to provide secondary data for coating detachment analysis in scratch testing. The sensor in AE equipment offers traceable signals whenever coating detachments occur during a scratch. These signals can be used to compare results from different coating samples and may avoid some subjectivity of observation made by the naked eye.

Figure 6 represents the plot of AE vs. scratch distance obtained from typical scratch test equipment equipped with an AE sensor. Coating detachment is observed when there is a sudden jump in AE signal. $L_{c1}$ represents the first critical points of coating detachment corresponding to a cohesive failure of coating. $L_{c2}$ signifies the second critical points of coating detachment where complete removal of coating starts to occur. The $L_{c2}$ point represents the critical load of coating failure and adhesion strengths.

AE sensor has been utilized in the scratch test of reactively sputtered TiN coatings deposited onto a soft substrate.\[39\] The test was performed using Rockwell C diamond stylus with tip radius of 200 μm and equipped with AE monitoring equipment. Initial testing on TiN coating having a thickness of 1.5 μm showed coating loss with an increase in AE value and had cracked at the critical load. However, for thinner coating of thickness 1.2 μm or less, no observable cracking or coating loss was observed, although there is an increase in AE value at critical loads. These findings suggested that AE emission was able to provide accurate information on the occurrence of coating failure for certain level of coating thickness despite the failure being non-observable. In other study conducted by Bull \[9\], the scratch test analysis using AE sensor was

![Figure 6. Plot of AE and scratch distance produced from the scratch test.](image-url)
performed on TiN coatings deposited onto different substrates from soft nickel to hard cemented carbide in order to identify the failure modes.

On the other hand, Yamamoto and Ichimura [40] have studied the relationship between AE behavior and intrinsic properties of deposited TiN film during scratch test. The mechanical strength of TiN coatings was evaluated by analyzing the AE intensity. AE intensity of the coatings measured during the scratch test was found to be dependent on adhesion of coating-substrate interface and intrinsic properties of deposited TiN films. It was found that the substrate hardness had a minor effect on AE intensity. In contrast, AE intensity had increased with the decrease in toughness and internal stress of coated films. Therefore, the analysis of AE behavior during scratch test can qualitatively evaluate the mechanical strength such as toughness of coating samples.

Another approach in adhesion assessment is to monitor the tangential friction force between the indenter and coating in order to detect the critical load, which has been reported by Valli et al. [10] The friction force monitoring method offers advantages over AE detection in scratch test by enabling the determination of critical load for coating samples with thickness of less than 0.3 μm. Furthermore, the critical load results by monitoring tangential friction force were within the defined band for given substrate condition and test parameters. This method can monitor the force continuously during the scratch test and is particularly suitable for thin coatings with thicknesses of less than 1 μm.

Figure 7 shows the scratch test apparatus used for adhesion assessment, showing the arrangement of the frictional force transducer and the AE detector. Figure 8 shows the comparison between the AE emission and tangential force signals detected from the scratch test on deposited TiN coating. For thin coatings, the coating failure is identified by a change in frictional force instead of AE.

An energy description model has been introduced for adhesion assessment during coating removal by scratch test.[11] The compressively stressed coating in the region ahead of the indenter reduces its stored energy by peeling or spalling from the substrate during the scratch test.

Figure 7. Schematic representation of scratch test apparatus for adhesion assessment by developing the tangential friction force.[10]
at critical load. Thus, a simple energy balance criterion for stored elastic energy in coating ahead of indenter was generated in order to create new surfaces at critical normal load. The adhesion force calculated from basic scratch test exhibited lower magnitude than the estimation based on condensation energy measurement. Table 2 summarizes the calculated work values, $W$, of adhesion for selected material using the formula given in Equation (2).[11]

Table 2. Calculated work ($W$) of adhesion for selected material.[11]

<table>
<thead>
<tr>
<th>Material</th>
<th>Critical load ($\times 10^3$ kPa)</th>
<th>$\sigma_{appl}(x)$</th>
<th>$\sigma_{int}(x)$</th>
<th>$\sigma(x) = \sigma_{appl}(x) + \sigma_{int}(x)$</th>
<th>Adhesion energy $W$ ($J m^{-2}$)</th>
<th>Condensation energy from critical condensation experiments ($J m^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>5</td>
<td>0.79</td>
<td>-0.01</td>
<td>0.78</td>
<td>0.40</td>
<td>0.24</td>
</tr>
<tr>
<td>Au</td>
<td>2</td>
<td>0.58</td>
<td>-0.08</td>
<td>0.50</td>
<td>0.16</td>
<td>-</td>
</tr>
<tr>
<td>Al$^a$</td>
<td>5</td>
<td>0.79</td>
<td>0.07</td>
<td>0.72</td>
<td>0.38</td>
<td>0.72</td>
</tr>
<tr>
<td>Al$^a$</td>
<td>70</td>
<td>1.90</td>
<td>-</td>
<td>-</td>
<td>2.40</td>
<td>-</td>
</tr>
<tr>
<td>Fe$^a$</td>
<td>100</td>
<td>2.10</td>
<td>-0.96</td>
<td>1.14</td>
<td>0.38</td>
<td>-</td>
</tr>
<tr>
<td>Fe$^a$</td>
<td>500</td>
<td>3.60</td>
<td>-</td>
<td>-</td>
<td>3.80</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: Where $\sigma_{int}(x)$ is unavailable, $\sigma_{appl}(x)$ has been used for the calculation of $W$. Values of $\sigma_{appl}(x)$ have been calculated for $f = 0.3$.

$^a$The critical load increases with time [the values quoted are for as-deposited Al and for aging periods of 400 h (for Al) and 200 h (for Fe)].
where $E$ is the coating young’s modulus, $h$ is coating thickness, and $\sigma(x)$ is stress in coating, which is considered to be constant throughout the thickness. The coating stress $\sigma(x)$ is calculated using Equation (3).

$$\sigma(x) = \sigma_{\text{appl}}(x) + \sigma_{\text{int}}(x)$$  \hspace{1cm} (3)

where $\sigma_{\text{appl}}(x)$ and $\sigma_{\text{int}}(x)$ are applied stress and internal stress, respectively. The internal stress $\sigma_{\text{int}}(x)$ was found to be almost constant in all materials, whereas the applied stress $\sigma_{\text{appl}}(x)$ resulted from the sliding indenter. The applied stress would decrease throughout the coating thickness if the value of contact circle radius was higher than the coating thickness.

Extrinsic variables such as frictions, lubrication, surface roughness, and surface preparation influence the results of scratch test and should also be taken into consideration. Nevertheless, this method has been proven to be reliable in determining the adhesion of coating-substrate system.[41] Investigation on the factors affecting scratch test results such as surface roughness and friction between coating and indenter has been conducted on TiN-coated HSS.[41] Frictions were the dominant factor for the decrement of adhesion strength, and the use of thin ion-plated silver overlay increased the critical normal force remarkably by reducing these frictions. The use of lubrication such as oils enhanced the repeatability of testing for hard coatings on high-strength substrates. The surface roughness of the substrate should not exceed 0.25 $\mu$m in order to eliminate the poor surface preparation effect on the scratch test results. Poor surface finish decreased the critical normal force, showing lower adhesion value as compared to polished surfaces.

Table 3 summarizes the critical load of TiN coating deposited onto HSS substrate having different surface roughness.[17] It was found that the critical values of TiN coating were dependent on the roughness of the substrate surface. It is believed that the adhesive properties can vary since the surface roughness is influenced by the efficiency of cleaning operation.

Perry[42] has reported the effect of coating thickness and substrate hardness of TiN and TiC coatings deposited onto steels and cemented carbides. The result has shown that the critical load increases with increasing coating thickness and substrate thickness.

Table 3. Critical loads measured for TiN coating deposited onto HSS substrates having different surface roughness according to surface preparation.[17]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface preparation</th>
<th>Average roughness, Ra ($\mu$m)</th>
<th>Total roughness Rt ($\mu$m)</th>
<th>Critical load (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polishing (600 grit paper)</td>
<td>0.03</td>
<td>0.40</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>Rectification</td>
<td>0.05</td>
<td>1.00</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>Polishing (alumina)</td>
<td>0.07</td>
<td>0.60</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>Shot peening</td>
<td>0.40</td>
<td>4.65</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>Milling</td>
<td>1.75</td>
<td>12.5</td>
<td>27</td>
</tr>
<tr>
<td>6</td>
<td>Shot blasting</td>
<td>7.00</td>
<td>70.0</td>
<td>13</td>
</tr>
</tbody>
</table>
hardness. For hard coatings deposited onto steel, the critical value of TiN coating had increased with the coating thickness up to certain thickness value. For hard coating deposited onto cemented carbide, the critical loads were relatively independent of the coating thickness.

Helmersson et al. [43] investigated the effect of substrate temperature on the adhesion of TiN coatings. The adhesion of coating films increased with increasing substrate temperature from 400 to 500 °C. [43] Other researchers conducted the study on the effect of surface pre-treatment and coating post-treatment to the properties of TiN coatings. [44] Dry micro-abrasive blasting method with SiC abrasive is implemented as a pre-treatment process. Post-treatment is conducted by using drag grinding method. The results show that the grinded surfaces presented better coating adhesion than micro-abrasive-blasted surfaces. [44]

The influence of alternating sequences of heating and deposition on coating adhesion was reported by Schulz et al. [45]. The electron beam was used to apply localized heating on the coating sample using a range of heating rate and final temperatures. The heat treatment process affected the growth and stoichiometry of the coatings. Preheating prior to deposition process might also increase the adhesion of coating.

Several intrinsic parameters play an important role in adhesion assessment such as loading rate, scratching speed, indenter tip radius, and indenter wear, which have been discussed by Steinmann et al. and Randall et al. in their previous works. [17,46] The research evaluated intrinsic parameters such as scratching speed, loading rate, and diamond indenter radius on the measured critical load for scratch tests performed on various combinations of coating-substrate. The measured critical load was found to decrease as scratching speed was increased. In contrast, the critical load was found to increase as the loading rate and indenter radius was increased. However, scratch test was observed to be dependent on loading rate, and variations from the observed trends were possible for certain coating-substrate combinations. [46]

As a conclusion, the scratch adhesion test is a practical method to evaluate the adhesion of coatings. However, care is needed in performing the test in order to obtain accurate and reliable results. Furthermore, it is important to understand the mechanism and mode of coating failures to be able to accurately interpret the adhesion strength analysis of coating-substrate systems.

4. Mechanism of failures in adhesion evaluation test

Understanding the mechanisms and modes of failure is vital in order to interpret the behavior of coating-substrate system under certain loading conditions. Failure of adhesion in coating-substrate system is mainly related to fracture mechanism rather than bonding properties. In thin films, the intrinsic stress may result in adhesive failure even though the chemical bonding may be high.

In the indentation test, the types of coating failures observed were dependent on the amount of loads applied during the test. Four different types of coating failure were observed in TiN-coated high-speed steel. [31] At low normal load of 5–25 N, only circular cracks were found at the rim and inside the indentation. For loads above 60–130 N, radial cracks propagating perpendicular to the rim of circular indentation were created. At loads above 600 N, small cohesive and large adhesive failures outside the indentation were seen.

Different fracture patterns were observed in indentation tests for ceramic coatings at different normal loads. [32] Two types of coating removal mechanisms were chipping
and spalling. The chipping fracture pattern was caused by generation of ring cracks from blunt indenter, whereas the spalling mechanism was a result from the generation of lateral cracks at the interface using sharp indenter.

Figure 9 shows fracture patterns for TiN coatings of different thicknesses, observed during indentation tests. At high coating thickness, no cracks were observed at normal load, \( W \), up to 3000 N. At lower coating thickness, ring cracks were observed at normal load above 1000 N. The results obtained suggest that as coating thickness increases, the resistance of the coating to crack or fail increases. Thus, adhesion of coating would improve as the coating thickness increases. The limitation of this method was that only fracture patterns of the coating at specific indent loads can be determined. The mechanism or fracture patterns of the coating prior to critical loads could not be observed. The static indentation test could be used to evaluate the fracture resistance and coating-substrate adhesion, while dynamic scratch testing is preferable for evaluating the load carrying capacity of the coating-substrate composite.

Brittle coatings behave in a different manner as compared to ductile coating deposited on similar substrates when subjected to loading conditions in scratch testing. Perry [42] has reported in his research work that the mechanisms of brittle and ductile coatings where the brittle films can be removed completely, while ductile films were subjected to gradually thinning.

The failure of TiN films coated on various substrates from soft nickel to hard cemented carbide has been summarized by Bull [9] according to the behavior of the coating-substrate system. Brittle failure modes in scratch testing were categorized into gross spallation, spallation ahead of the indenter, recovery spallation behind indenter, hertzian cracking, and tensile cracking. Spallation was common failure mode where the coating is detached to minimize the amount of elastic energy stored by large
compressive stresses ahead of the moving stylus during scratch test. Gross spallation occurred when the adhesion was poor or with the increment of residual stress level in the coating. Hertzian ring cracks were formed when tensile radial stresses at the edge of diamond contact generate ring cracks that are propagated from the surface through the coating into the substrate. On the other hand, tensile cracks were formed at the rear of the diamond contact. These cracks can intersect one another and may form crack network along the edge of crack track.[9]

Ductile failure modes in scratch testing can be classified into spallation, buckling, conformal cracking, and tensile cracking. Spallation and buckling modes are similar to brittle spallation failure mode except for the magnitude of failure that are smaller and confined within the scratch track. Conformal cracks could be seen when there was through-thickness cracking at the front and sides of the indenter due to partial ring cracks, which occurred ahead of the indenter and pushed into the scratch track. Tensile cracking appeared at the rear of diamond contact due to tensile stress generated on sliding as can be observed for brittle materials.

Figure 10 presents the diagrammatic sketch and scanning electron microscope (SEM) images of brittle and ductile failure modes in scratch testing. For ductile failure, the area of uncovered substrate was small and within the scratch track. In contrast, the
area for brittle failure mode was more extensive and often would extend beyond the limit of the scratch track.

Table 4 summarizes the failure modes of thin film deposited onto different brittle and ductile substrates depending on the applied stresses, whether compressive or tensile. For brittle substrates, interface failure occurred for both tensile and compressive stresses if adhesion was poor and possibility of interfacial cracking formation for tensile stress. For ductile substrates, interface failure again can occur for both tensile and compressive stresses also provided that interfacial adhesion was poor. However, if interfacial adhesion was good, failure tended to occur within the coating.

The failure mechanism can also be categorized into hard and soft coating-substrate systems instead of brittle and ductile coating-substrate system. Soft system commonly exhibits viscoplastic deformation, whereas hard system exhibits brittle fracture in the substrate. The failure mechanism of interfacial delamination was occurred for medium and hard materials during scratch test. Table 5 illustrates the variation of failure modes in scratch test as a function of the hardness of coating-substrate system.

Failure modes of thin TiN coating on HSS substrate were studied by Hedenqvist et al. based on scratch tests with various coating thickness and substrate hardness. Four groups of coating damage and detachment mechanisms were recognized as deformation, crack, chipping, and flaking. The scratch mechanisms were observed below and above the critical normal force. Initially, no visible surface damage was observed at critical normal force due to elastic deformation of the coating-substrate system. As the normal force is increased, the plastic deformation extends through the coating into the substrate. Transverse surface cracks are often observed due to the generation of tensile stresses behind the moving diamond tips which resulted in internal transverse cracking. The increase in the normal force would lead to the increase of internal transverse cracks and external transverse cracking. Beyond the critical normal force, chip formation and flaking would start to occur. Discontinuous chip removal mechanism would expose the underlaying substrate materials, and the detached chips would consist of heavily deformed coating-substrate materials. Flaking predominantly occurred outside the scratch track due to high frictional force values.

Major damage mechanism during scratch test of TiN-coated HSS substrate was reported by Stebut et al. in their previous study. A tensile-type cracking nucleation might form behind the trailing edge of the diamond indenter. This tensile-type crack pattern consisted of partial ring crack prior to spalling and envelope cracks parallel to the sliding direction. However, no conformal cracking generated ahead of the indenter.

<table>
<thead>
<tr>
<th>Stress</th>
<th>Film</th>
<th>Substrate</th>
<th>Interface bonding</th>
<th>Decohesion mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile</td>
<td>Brittle</td>
<td>Ductile</td>
<td>Good</td>
<td>Film cracking (no decohesion)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Poor</td>
<td>Film cracking (interface decohesion)</td>
</tr>
<tr>
<td>Compressive</td>
<td>Brittle</td>
<td>Ductile</td>
<td>Good</td>
<td>Buckling propagation in film</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Poor</td>
<td>Buckling propagation at interface</td>
</tr>
<tr>
<td>Tensile</td>
<td>Brittle</td>
<td>Brittle</td>
<td>Good</td>
<td>Film cracking and interface decohesion</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Poor</td>
<td>Edge decohesion at interface</td>
</tr>
<tr>
<td>Compressive</td>
<td>Brittle</td>
<td>Brittle</td>
<td>Good</td>
<td>Substrate splitting</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Poor</td>
<td>Buckling propagation at interface</td>
</tr>
</tbody>
</table>

Table 4. Failure modes of thin film deposited onto brittle and ductile substrates in relation with stresses.
leading edge was observed for hard coatings on hard substrates in other research findings, which has been discussed by Bull [9]. Thus, spalling failure mechanism was not observed due to non-existence of conformal cracking as the major spalling initiator. The study of coating failure mechanism was conducted by Larsson et al. [31] using the scratch and indentation tests for deposited TiN on HSS substrate. Six different coating failure mechanisms were identified during scratch test and shown in Figure 11, which were as follows:

(1) Cracks parallel with the scratch channel.
(2) Semi-circular cracks within the scratch channel.
(3) External transverse cracks.
(4) Cohesive chipping.
(5) Adhesive spalling.
(6) Complete breakthrough of coating within scratch channel.

Meanwhile, four different types of coating failures were identified during indentation test such as:

(1) Circular crack within the indentation.
(2) Radial cracks outside the indentation.

<table>
<thead>
<tr>
<th>Coating hardness</th>
<th>Substrate hardness</th>
<th>Soft</th>
<th>Medium</th>
<th>Hard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft</td>
<td>Plastic deformation</td>
<td>Coating thinning</td>
<td>Coating thinning</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Extrusion</td>
<td>Scrape off</td>
<td>Scrape off</td>
<td></td>
</tr>
<tr>
<td>Medium</td>
<td>Plastic deformation</td>
<td>Delamination</td>
<td>Delamination</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Extrusion</td>
<td>–</td>
<td>Fracture</td>
<td></td>
</tr>
<tr>
<td>Hard</td>
<td>Plastic deformation</td>
<td>Delamination</td>
<td>Delamination</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Extrusion</td>
<td>Fracture</td>
<td>Fracture</td>
<td></td>
</tr>
</tbody>
</table>

Figure 11. Schematic illustration of coating failures observed during scratch test (1) parallel crack; (2) semi-circular cracks; (3) external transverse cracks; (4) coating chipping; (5) coating spalling; and (6) coating breakthrough.
(3) Cohesive chipping.
(4) Adhesive spalling.

Parallel cracking had developed due to the deflection of the coating into the physically deformed underlying substrate material. External transverse cracking was initiated during or after unloading as a result of high residual stresses generated in the coating. The cohesive and adhesive failures occurred behind the diamond stylus during unloading.

5. Improvement of TiN adhesion strength

TiN coatings provide good wear resistance and enhance the lifespan of cutting tools. It is important that the coating adheres well to the substrate. Current developments in TiN coating technology for tool applications concentrate on coating synthesis using low-temperature processes, although the resulting coating may have poor adhesion strength. Another focus of TiN coating improvements emphasizes on achieving excellent adhesion strengths between the coatings and substrates. These adhesion strengths are influenced by method of processing, composition, and structure of coatings. The influence of these parameters on the resulting adhesion strength will be discussed in the following paragraphs.

Comparison between CVD and PVD methods to deposit TiN shows that the coating deposited using CVD tends to have better adhesion than the coatings from PVD, most likely due to the higher deposition temperature in the CVD. However, PVD methods are preferable in tool applications since the process is environmentally friendly, promotes greater productivity and feasibility for deposition of multiple coatings. Hybrid processes in the form of plasma-enhanced CVD (PECVD) or plasma-assisted CVD (PACVD) attempts to combine the benefits of CVD and PVD. Results have shown that these hybrid process can produce high coating adhesion at low operating temperatures.[2]

Wang et al. reported the effects of Al inclusion on microstructure and properties of (Ti, Al)N coating deposited onto HSS substrate.[50] The coating composition was varied in order to enhance the adhesion strength and properties of the TiN coating. Analysis of the interface microstructure in coating-substrate system showed the presence of a transition layer between (Ti, Al)N and HSS substrate. This transition layer was composed of α-Ti phase in initial layers of deposition and had transformed into a Fe–Ti phase as the earlier phase diffuses into the substrate as the temperature increased. These transition phases are believed to enhance the adhesion of coating-substrate system and improve the adhesion abrasion of substrate with (Ti, Al)N coating. Al atoms are believed to have the ability to fit into TiN crystal structure as the radius was at substitutional or interstitial sites to exhibit denser coating structure.

Adhesion of TiN film was also reported to improve with the presence of pure Ti intermediate layer in between the coating and substrate. The effects of intermediate layer in coating structure on adhesion strength were investigated and discussed by Helmersson et al. [43] The use of 0.1 μm Ti intermediate layer increased the adhesion of TiN film deposited at temperatures below 400 °C. Above 400 °C, thin titanium carbide (TiC) layer was formed in Ti–Fe interface which resulted in reduction of adhesion.

In contrast, the reduction of coating adhesion strength was found for 0.3 μm Ti interlayer deposited in between TiN film and HSS substrate.[10] The difference in both
observations indicated the presence of an optimum thickness value for the intermediate layer.

Gerth and Wiklund have conducted the study on the improvement of TiN adhesion strength by analyzing certain metallic coatings such as W, Mo, Nb, Cr, Ti, Ag, and Al for the interlayer in between coatings and polished HSS substrate.[51] The results showed that interlayer metallic Mo and Nb coatings offered the best adhesion followed by more the conventionally used Ti and Cr interlayer.[51] The presence of pure Ti interlayer improved the adhesion strength due to better bonding with substrates and TiN coating. It was suggested that Ti interlayer acted as graded interface which prevented abrupt changes in composition at the sharp interface between coating and metal substrate.

There is a possibility of adhesion strength enhancement by using multi-compositional gradient coatings such as TiO$_2$/Ti/TiN, ZrO$_2$/Zr/ZrN, and TiO$_2$/Ti/Zr/ZrN, which had been studied in previous research work by Kusano et al. [12] The results showed that the adhesion strength of TiN coating deposited at room temperature increased with the presence of TiO$_2$/Ti layer as shown in Figure 12. TiO$_2$/Ti/TiN and TiO$_2$/TiN multiple coatings exhibited good adhesion strengths at substrate temperature of 300 and 400 °C with TiO$_2$/Ti/TiN coating showed superior adhesion compared to TiN coating at 400 °C substrate temperature. The improved adhesion strength may be the result of compositional change in interface transition region gradient and is expected to enhance both chemical and mechanical bonding of TiN coatings.

Adding a functionally graded layer [52] or a bonding layer [53] in between the coating and the substrate are two important ways to improve coating adhesion. The functions of this interlayer include facilitating good bonding, relaxation, and modification of the stress distribution, providing a supporting layer, imparting better chemical stability to substrate and increasing the hardening depth.[54]

![Figure 12. Adhesion strength of TiO$_2$, TiN, TiO$_2$/TiN, TiO$_2$/Ti/TiN, and TiO$_2$–Ti–TiN coatings deposited at room temperature, 300 and 400 °C.[12]](image)
7. Conclusion

PVD method is more preferred as compared to CVD technique for depositing TiN coating in tooling application although generally TiN coatings deposited by CVD exhibits greater adhesion strength than PVD. This is due to the ability of PVD process to fabricate multiple coatings, have greater productivity and significantly lower production cost as compared to CVD processes. Furthermore, PVD processes are environmentally friendlier as compared to CVD.

The scratch adhesion test is a practical method to study adhesion strength of coating-substrate systems despite other adhesion evaluation techniques such as indentation test and laser spallation test. Substrate hardness, coating thickness, surface roughness, deposition temperature, and substrate pre-treatment are among the extrinsic factors that influence the critical loads and consequently adhesion strengths of TiN coatings. The influence of intrinsic factors which is related to scratch adhesion test such as lubrication, loading rate, scratching speed, indenter tip radius, and indenter wear need to be considered and might well affecting the value of critical loads.

Factors such as method of processing (either CVD or PVD), modification in composition of coatings, and introduction of new intermediate layer or multilayer in coatings–substrate system structure should be considered to enhance the adhesion strengths for TiN coatings. TiN adhesion strength is improved by introducing a metallic interlayer such as pure Ti sandwiched in between TiN film and substrate. Recommendations for future studies include adhesion strength enhancement for TiN coating by using multi-compositional coating such as TiO₂/Ti/TiN and the introduction of TiO₂ layer as the intermediate layer to form Ti multiple coatings.

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References


