Corrosion Protection of Advanced Surface Coatings for Decorative Applications

by

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Abstract

If Australian manufacturing industries are to be sustainable into the 21st century, they will have to compete in a global market. This means they will be challenged by increasing cost pressures arising from dwindling material resources and tighter environmental controls. The latter is being driven by a growing public awareness and concern, leading to ever more stringent legislation. These issues have already impacted significantly on the decorative coating industry, particularly in regard to its management of toxic waste. Over the last ten years, this industry has sought to improve the longevity of its product by offering lifetime guarantees. The approach has been to apply a physical vapour deposition (PVD) coating, with the opportunity of depositing coatings with a range of attractive colours, combined with abrasion and corrosion resistance, to many of its electroplated low cost components such as high pressure die-cast zinc or brass. To be successful in this endeavour it is essential that the PVD coatings be deposited at as low a substrate temperature as possible to avoid microstructural damage of the temperature sensitive substrates for decorative applications. This restriction leads to some fundamental concerns that the integrity of PVD coatings may be comprised and hence, limits their ability to provide the necessary protection for applications in the harsher, longer term environments. Furthermore, when such PVD coated metal substrates are exposed to the environment; they may have their electrochemical behaviour affected by the properties of the coating–substrate interface, and by the microstructure of the coatings. In addition, the presence of defects, such as, pores and pinholes in the coating can affect the corrosion protection performance of the coating.

In view of the above considerations, the aim of the present investigation was to study inherent corrosion properties of TiN coatings and the corrosion protection obtained by depositing TiN coating on substrates used in the decorative coating industry, such as brass and high pressure die-cast zinc. This included a study of the development of micro-structural features of decorative TiN, cathodic arc evaporated (CAE) coatings deposited at the low substrate temperature and its effect on corrosion protection performance, decorative properties (colour and optical reflectivity) and tribological behaviour (abrasive wear). The work is presented in two parts: the first relates to the fundamental corrosion properties of TiN as a PVD coating, while the second relates to
the effect of substrate deposition temperature, reactive gas pressure and multilayer formation on corrosion protection performance, decorative properties (colour and optical reflectivity) and tribological performance.

In the first part of the work, the fundamental corrosion properties of TiN coatings were investigated on inert substrates. The study revealed a very slow rate of corrosion (nAcm⁻²) for TiN which indicated the chemical inertness of TiN in sodium chloride solution. The results of further investigation to evaluate the corrosion behaviour of galvanically-coupled TiN coating with typical substrate materials suggested that galvanic corrosion may not be significant for a TiN-substrate system in sodium chloride solution. In the second part of the work, the effect of substrate deposition temperature on the coating microstructure was evaluated by depositing TiN coatings with no prior substrate heating (referred to as TL); rather, the intention was to rely on the energy of ion bombardment, through the selection of a relatively high substrate bias potential, to achieve a dense microstructure. For comparison purposes, TiN coatings were deposited under the same conditions, however, with substrate heating (referred to as TH). The study revealed that the TL TiN coatings exhibited improved decorative properties, corrosion protection and tribological performance than the TH TiN coatings. With respect to the reactive gas pressure, a significant reduction in the macroparticle content of the coating was obtained with increasing deposition pressure. The findings further revealed that the choice of the deposition pressure for decorative coatings is a key issue, since decorative properties and corrosion performance were directly influenced by the deposition pressure. Specifically, decorative properties and tribological performance were found to improve for the coatings deposited at the higher deposition pressure, whilst corrosion protection performance was improved for the coatings deposited at the lower deposition pressure. Although macroparticles have been considered an unfavourable feature of CAE coatings, the results presented in this investigation demonstrated that their effect on the corrosion protection performance was not significant. Finally, the deposition of TiN/Cr sequential multilayer coatings led to significant improvements in the decorative properties, corrosion protection and tribological performance.

The findings show that advanced surface engineering may well be a potential strategy for improvement of the performance of decorative TiN CAE coatings through the
deposition of multilayers of TiN and Cr. In terms of commercial exploitation, these coatings present a valuable multilayer system in which the tribological performance and corrosion protection performance of PVD TiN, decorative coatings can be enhanced significantly.
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STATEMENT OF ORIGINAL AUTHORSHIP

This thesis contains no material which has been accepted for the award to the Candidate of any other degree or diploma, except where due reference is made in the text of the thesis.

This thesis, to the best of my knowledge, contains no material previously published or written by another person except where due reference is made in the text of the thesis.

Signed _______________________

Jayashri Sham Gopalakrishna.
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CHAPTER 1

Introduction

The present research is a collaborative project between the Swinburne University of Technology and Gainsbourough Hardware Industries (GHI) Pty. Limited, Melbourne, Australia. The primary focus of GHI is to manufacture high quality fittings for door hardware with a variety of attractive finishes which are designed to have both functional and decorative aspects. Critical to the overall performance of these fittings is their resistance to corrosion and abrasive wear. The materials used in the manufacture of these fittings are high pressure die-cast zinc, brass and stainless steel.

Brass substrates are usually protected by electroplated layers which are traditionally of copper, nickel and chromium [1]. The function of the copper layer [2] is to provide good adhesion between the substrate and subsequent layers. The function of the nickel layer [2] is to provide a measure of corrosion protection and create the desired surface texture, commonly a mirror bright reflective surface. This nickel layer is protected from tarnishing by a thin layer of chromium that also provides the desired corrosion resistance. In the case of high pressure die-cast zinc substrates, a thicker copper layer known as an “acid copper” layer is deposited between the copper strike and the nickel layers. The function of the acid copper layer is one of levelling [2], i.e. to completely cover surface defects, such as cracks or pores, and to smooth over any roughness in the surface.

Commercial practice usually dictates the thickness of each layer as follows: Cu, 30-40 µm; Ni, 10-15µm; and Cr, 0.5 -1µm [2]. An example of electroplated Cu-Ni-Cr coating on a high pressure die-cast zinc substrate is shown in Figure 1.1 that presents a cross-sectional Scanning Electron Micrograph (SEM) typical of that observed in this present study. Although this coating shows good structural integrity, a closer look at the surface of each of these coatings shows the defective nature typically observed with such types of coating. An example of the defective nature of electroplated coatings on high pressure die-cast zinc
and brass substrates observed in the present study is shown in Figures 1.2 and 1.3, respectively. The presence of defects is considered to arise from defects such as pores, cracks and pinholes in the substrates [3,4]. It is evident that the electroplated layers have failed to cover the defects. The presence of such defects highlights the importance of the quality and integrity of the electroplated coatings for corrosion protection of the substrate. It is common for electroplaters to attempt to overcome these problems by depositing thick nickel layers or duplex layers. However, Weil et al [5] have shown that such attempts have only limited success.

Figure 1.1 Scanning Electron Micrograph of cross-section of an electroplated high pressure die-cast zinc substrate showing the copper/nickel/chromium layers.

Figure 1.1 Scanning Electron Micrograph of cross-section of an electroplated high pressure die-cast zinc substrate showing the copper/nickel/chromium layers.
Figure 1.2  Scanning Electron Micrographs of an electroplated high pressure die-cast zinc substrate showing surface defects on (a) Copper plating and (b) Nickel plating.
Figure 1.3  Scanning Electron Micrographs of an electroplated brass substrate showing surface defects on (a) Nickel plating, and (b) Chromium plating.
The corrosion of decorative products is a major concern to GHI since a significant amount of annual income goes to the repair or replacement of deteriorated products. Also, global competition is forcing GHI to introduce decorative, corrosion-resistant coatings with a lifetime guarantee.

A potential surface finishing solution for improved corrosion resistance, namely the deposition of hard, thin coatings of transition metal nitrides, carbides or oxides from the vapour state, has emerged over the last 20 years. This technology is referred to as physical vapour deposition (PVD). The objective for decorative coaters using PVD technology is to reactively deposit such hard, thin coatings with the opportunity of depositing coatings with a range of colours, combined with abrasion and corrosion resistance. These thin coatings rely on good substrate preparation in combination with good electroplating practice to enhance corrosion resistance and tribological properties [6,7]. Significant advantages of PVD technology are that it is environmentally friendly and generates relatively smooth surfaces with inherent, compressive residual stresses in the coating. Disadvantages are that the coatings are relatively expensive and suffer a low deposition rate.

Vapour deposition of various transition metal nitrides and carbides are being successfully commercially deposited in a range of colours [Table 1.1] [7,8]. Furthermore, these coatings exhibit a complex mix of all three primary forms of chemical bonding (covalent, ionic and metallic), [9] yielding an interesting range of properties, for example, the covalent/ionic bonding is largely responsible for their excellent mechanical properties with the metallic component imparting high reflectivity and electrical conductivity. Among various transition metal nitrides present, titanium nitride (TiN), with its gold-like appearance, is an ideal commercial candidate as a replacement for gold in decorative applications [7,8].
<table>
<thead>
<tr>
<th>Type</th>
<th>Compound</th>
<th>Colours</th>
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<tbody>
<tr>
<td>Nitrides</td>
<td>TiN</td>
<td>Golden-brown-yellow</td>
</tr>
<tr>
<td></td>
<td>ZrN</td>
<td>Yellow-green</td>
</tr>
<tr>
<td></td>
<td>CrN</td>
<td>Metallic</td>
</tr>
<tr>
<td></td>
<td>TaN</td>
<td>Blue-grey</td>
</tr>
<tr>
<td></td>
<td>(Ti,Al)N</td>
<td>Golden-dark blue</td>
</tr>
<tr>
<td></td>
<td>(Ti,Zr)N</td>
<td>Golden</td>
</tr>
<tr>
<td>Carbides</td>
<td>TiC</td>
<td>Bright grey</td>
</tr>
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<td>TiC/WC</td>
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<td></td>
<td>ZrCₓNᵧ</td>
<td>Silver-golden-violet</td>
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</tbody>
</table>

The nature of PVD technology is such that there are many ways to deposit thin TiN coatings for decorative applications: for example, sputtering, ion plating, electron beam evaporation and cathodic arc deposition [10]. Magnetron sputtering and cathodic arc evaporation (CAE) systems are now widely accepted methods. These techniques are briefly compared from a decorative point of view in this chapter and a comprehensive review is presented in Chapter 2.

Magnetron sputtering is considered to be a particularly good candidate for decorative coatings applications since it is possible to deposit coatings with complex chemical composition, with low ion energy and thus, low deposition temperatures [8,10]. This means that the technique is useful for deposition on temperature sensitive substrates. However,
target poisoning can lead to the removal of a compound film from the target, resulting in loose particles being incorporated in the “as deposited” coating [11-14], which can, in turn, affect the reflectivity of the coating [8, 10]. It is therefore essential that there is full process control on deposition parameters such as deposition rate, nitrogen partial pressure and substrate temperature. Otherwise, as Randhawa [15] demonstrated in his early work, there may be difficulties with colour matching of the PVD coated components for different batches.

In the cathodic arc evaporation process, an arc discharge is initiated on a cathode surface using a mechanical trigger that is momentarily brought into contact with the cathode. The dwelling time of the trigger and consequently the arc discharge at any location on the cathode surface is sufficiently short that no molten pool is generated [16, 17]. The high current density at the arc spot causes the cathode to emit metal plasma containing a high density of metal ions (~ $10^{23}$ m$^{-3}$) as well as electrons, neutral atoms and spherical agglomerates called ‘macroparticles’ [16] which vary in size from tens of micrometers to sub-micrometers. These macroparticles are formed by evaporation of the molten or solid target material [16] and their number and size increase with lower melting point materials, higher cathode currents and higher cathode temperatures. The main advantages of CAE include high ionisation efficiency with a high deposition rate, uniform coating on complex three dimensional parts and ease of control of process parameters [16]. The main limitation, however, is the presence of macroparticles in the “as deposited” coatings and their detrimental affect on visual appearance, corrosion resistance and tribological properties of the coating [16]. Extensive research has been carried out on the reduction of macroparticle content in the “as deposited” coating using various techniques [16-28], with the most successful being the curved plasma duct filter [17,18]. Techniques based on these designs are known collectively as filtered arc deposition (FAD) and have been shown to be successful at depositing high quality PVD coatings with very few macroparticles [18,21]. These techniques rely primarily on plasma filtering which reduces the number of macroparticles by obstructing the line of sight between the cathodic arcs and the substrates. However, the inclusion of plasma filtering techniques has the distinct disadvantage of
introducing complexity into the deposition system, resulting in a reduction in deposition rate which significantly increases the cost of production [17,25].

It has been shown that macroparticles in CAE coatings can be reduced by varying the total pressure of the reactive gas and the arc current [20-23,25]. Interestingly, the influence of the reactive gas pressure is related to the fact that the gas reacts with the cathode surface, covering it with a compound layer. This effect is known as cathode poisoning [16] and results in the reduction of macroparticles.

Although reduction of macroparticles in the cathodic arc process has provided significant advantages for TiN coatings for cutting tool applications, very limited information is available regarding the use of filtration techniques for decorative coating applications [28,29,30].

It should be noted that when such a PVD technique is used on temperature sensitive substrates such as die cast zinc and brass, it is essential that low substrate temperature is used to avoid microstructural damage of these substrates [8,27,28]. This restriction leads to the fundamental concern that the PVD coatings may consist of open columnar grains with intergranular voids [31,32]. The consequence of open columnar structure and its effect on the corrosion protection, tribological performance and decorative properties has not been fully explored in the literature and hence, these aspects needs to be investigated by depositing CAE TiN coatings at low substrate temperature.

It should be further noted that decorative coatings have to accomplish a number of tasks, namely, giving aesthetic appeal and protecting the underlying substrate from wear and corrosion [8,31-33]. When metal substrates are PVD coated to improve their decorative properties, they form a complex system, which when exposed to the environment, may have their electrochemical behaviour affected by the properties of the coating–substrate interface, through the intrinsic electrochemical behaviour of PVD coating and substrate, and also, by the microstructure of the PVD coatings. In addition, it is likely that there will be defects in the coating in the form of pores and pinholes where corrosive electrolyte may
be trapped, thus causing a galvanic interaction between the coating and the underlying metals. Under this scenario, it is necessary to investigate the ‘claimed’ corrosion protection offered by depositing transition metal nitrides on metal substrates used in the decorative coating industry. Furthermore, although a number of studies have dealt with the corrosion behaviour of TiN coatings [28,29,31], the effect of the microstructure formation on corrosion protection performance of low temperature, CAE deposited, TiN coatings on brass and high pressure die-cast zinc substrates for decorative applications has largely been overlooked.

This project has emerged from an identified need of the industrial partner to gain a competitive edge by developing improved wear and corrosion resistant, decorative coatings for application in door furniture and tapware. In view of the above considerations, the present investigation was carried out with the aim of evaluating the intrinsic corrosion behaviour of the TiN coating itself in NaCl solution and also, the corrosion behaviour of galvanically-coupled TiN coating with substrate materials of high pressure die-cast zinc and brass. This work included a study of the microstructure formation of decorative, TiN, CAE coatings deposited at the low substrate temperature and its effect on the corrosion protection performance, decorative properties and some aspects of tribological performance. The brass and high pressure die-cast zinc substrates were employed in the present study with their commercial importance for the decorative industry. In order to consider the suitability of such coatings on decorative components, the coatings were also successfully deposited on back plate, hinge and door handle. The research was focused on two major areas:

- Deposition and characterisation of TiN coating as a function of key deposition parameters such as substrate deposition temperature and reactive gas pressure;
- Investigation of improved corrosion performance through the exploitation of a relatively novel technique of multilayer deposition consisting of TiN and chromium (Cr) layers.

The work as presented is divided into the following seven chapters.
In Chapter 2, a theoretical background for decorative and corrosion studies is presented. Further, an overview of the current state of knowledge regarding TiN coating properties (decorative properties and corrosion protection ability) and their relation to PVD deposition conditions is presented.

Chapter 3 provides the necessary background for the interpretation of the experimental results obtained using various surface analysis techniques. The deposition techniques of partial filtered arc deposition (PFAD) and random cathodic arc evaporation (CAE) used in this thesis are described. Besides this, some of the relevant physical properties of the TiN coatings investigated in this thesis are summarized.

In Chapter 4, results from a fundamental study of the corrosion properties of PVD TiN coatings are presented. In addition, results from galvanic corrosion studies of TiN coatings on active substrates are presented. This chapter also includes the use of a relatively novel technique of a PFAD system for depositing TiN coating on the temperature sensitive substrates of high pressure die-cast zinc and brass.

In Chapter 5, results of the investigation of the effect of deposition temperature on the coating microstructure and morphology are presented. The decorative properties (optical reflectivity and colour), tribological performance and corrosion protection ability are studied.

Chapter 6 is devoted to the improvement in the TiN coatings performance (corrosion resistance and decorative properties). The first part of this chapter deals with the reduction of defects (macroparticles) in CAE TiN coatings by means of nitrogen pressure. In the second part, a relatively novel technique of multilayer coating consisting of sequential TiN and Cr layers is investigated.

Chapter 7 presents a general discussion and finally Chapter 8 presents conclusions for the entire study.
CHAPTER 2

Literature Review

2.1 Decorative coatings

A material can generate different colours by dispersion (prisms), interference (filters), diffraction (grids), scattering (granules) or absorption (atomic, molecular), when white light is incident upon it. For PVD hard coatings the main mechanism associated with the colour of nitrides is free carrier absorption [8] which is discussed briefly in the following section. Following this, the effects of PVD processes and process parameters on the decorative properties of TiN coatings are discussed.

2.1.1 Optical reflectivity and colour

The interaction of visible light with materials [34] can occur in intrinsic or extrinsic mode to produce colour. The extrinsic mode involves roughness or defects in the materials which alter the light direction of different wavelengths, leading to the specific colour. The intrinsic mode refers to the electrons in materials selectively absorbing and emitting light with specific wavelength/colour. The absorption mechanism most relevant to the present study is the free carrier absorption [8,34].

The response of free carriers to light can be described by the Drude model [34,35]. Accordingly, the response is represented in terms of the refractive index, n, and the extinction coefficient, k. The refractive index is the ratio of the light velocity in vacuum and in the medium under consideration. The extinction coefficient is an indication of the exponential damping of electromagnetic wave amplitude during propagation in a medium and depends mainly on the conductivity of the material. Both terms are described together as the complex refractive index, N. The Drude model relates the complex refractive index
with the number of free electrons, $N_e$, the electronic charge, $e$, an effective electron mass, $m_e$, and the angular frequency of the light, $\omega$, and is given by the following equation:

$$N = 1 - \frac{4\pi N_e e^2}{m_e \omega^2} \quad (2.1)$$

The frequency for a zero complex refractive index is defined as the plasma frequency, $\omega_p$, where:

$$\omega_p^2 = \frac{4\pi N_e e^2}{m_e} \quad (2.2)$$

The plasma frequency is the critical frequency separating a highly reflecting and totally transparent region. The colour of a metal is observed from the reflected light and is described by the reflection coefficient or reflectivity, $R$, which is the ratio of reflected energy over the incident energy of the light. With normal incidence of light, reflectivity is expressed as a function of the complex refractive index as:

$$R = \left| \frac{1 - N}{1 + N} \right|^2 \quad (2.3)$$

By replacing the complex refractive index with equation (2.1), the reflectivity can be related to the number of electrons in terms of the plasma frequency and is given by the following equation:

$$R = \frac{\omega^2 / \omega_p^2}{2 + \omega^2 / \omega_p^2} \quad (2.4)$$

The minimum reflectivity region about the plasma frequency is called the plasma edge [34]. The reflectivity of the material increases with an increase in the number of free electrons. For a transition metal nitride with a partially filled d valence electron band, the interaction with electromagnetic radiation produces excitation of the free carrier electrons from their original ground state to unfilled higher energy states. As excited electrons return to lower energy states, photons are emitted that are representative of a specific colour [8,15,34].
The appearance of colour is subjective to the human observer and is classified by means of visual sensation into three independent properties [36]: hue, chroma and brightness. Hue is classified in terms of the primary colours and each hue corresponds to a relative spectral intensity of a particular wavelength. Chroma indicates the strength of colour. Brightness is proportional to the overall intensity of reflected light reaching the eye.

The Commission Internationale de l’Eclairage (CIE), which is an international organization concerned with light and colour, has developed many numerical methods to quantify colour. One such method is L*a*b* colour space which has been used since 1976 to provide more uniform colour difference in relation to visual differences [8,36]. This system describes colour appearance by dividing it into three parameters; L*, a*; and b*, (see Figure 2.1). The colour sphere is composed of three mutually perpendicular axes, L*, a* and b*, which run from the centre of the sphere to the surface. The vertical axis, L*, stands for lightness or brightness; its values range from zero at the south pole through 50 at the centre to 100 at the north pole. Brightness correspondingly varies from pure black at the bottom (zero) to pure white at the top (100). The horizontal axes, a* and b*, are the chromaticity coordinates and their signs and magnitude indicate hues and saturation, respectively. The plus and minus signs of a* are assigned for red and green respectively, and the plus and minus sign of b* represent yellow and blue, respectively. The magnitudes of both a* and b* vary from zero at the centre of the sphere to 100 at the surface, both in the plus and minus directions.
The L*a*b* system indicates colour by accounting for both the reflectivity spectra of materials and the sensitivity of the human eye to detect the visible spectrum. In the present study, the colour evaluation of the TiN coatings was evaluated using L*a*b* system.
2.1.2 PVD systems used for decorative coating applications

Over the last twenty years there has been a significant expansion in the exploitation of PVD technology, mainly in applications demanding high wear resistance, but now the decorative coating industry has realised the potential of PVD technology. PVD systems involving thermal evaporation, magnetron sputtering and cathodic arc evaporation have been successfully employed for decorative applications [10,15]. In the following sections, these three methods are reviewed from the point of view of process parameter control, which is essential for the reproducibility of colours in the case of decorative applications.

The thermal evaporation technique involves depositing thin film coatings in a vacuum by thermal evaporation from either a resistively heated filament or using an electron beam source. A major disadvantage of the evaporation technique is the low energy of the evaporant resulting in poor adhesion and porous coatings. In addition, the desired microstructure and stoichiometry of the deposited film are difficult to control. In order to overcome these difficulties [24] a combination of ion beam deposition and thermal evaporation, ion assisted deposition (IAD), was developed. It is well documented that ion bombardment during film growth results in a dense microstructure [24,32]. However, it should be noted that careful control of the fundamental parameters of IAD, such as ion energy and incident ion flux, are required to obtain a dense microstructure.

From the point of view of exploiting PVD technology for decorative coatings Zega et al. [37], in 1977, thermally evaporated TiN on stainless steel substrates with the intention of generating golden surface hues for watch cases. The golden hue observed from TiN coating is considered [8,15,37] to be due to strong depression of reflectance at the blue end of the spectrum, which corresponds to a minimum reflectivity, known as the plasma edge. Comparison of the reflectance spectra of TiN with Au (see Figure 2.2) shows that they are similar, i.e. high reflectance at the long wavelength end of the visible range (red-green) and low reflectance at the low end of the visible region (yellow-blue region). This work paved the way for the substitution of PVD TiN for gold on watches.
Zega [37] also noted that deposition conditions such as deposition temperature and substrate bias potential affected the colour of PVD TiN coatings. They observed a darker hue of TiN coatings deposited at a high substrate temperature (800°C) and high substrate bias potential compared to those deposited at a low substrate temperature (500°C) and low substrate bias potential, and suggested the difference in colour was due to a difference in the compositions of the TiN coatings (atomic ratio of nitrogen to titanium), however, a detailed explanation was not offered. This work laid the foundation for further research carried out largely by Perry *et al.* [38, 39] who investigated the golden hues displayed by TiN coatings.
Perry et al. [38] used an ionic model to examine the complex dependence of colour on composition and lattice parameters of TiN coatings. According to this model, transition metal nitrides, such as, TiN, are formed by a transfer of charge from the titanium atom to the nitrogen. They found that an increased deposition rate was accompanied by an increase in vacancy concentration. Using an ionic model, they proposed that the corresponding reduction in the free carrier concentration, led to a fall in the yellow chroma of TiN coating. They also demonstrated further the change in the position of the minimum reflectivity, a plasma edge, could be accounted for, in terms of the change in coating colour. They showed that, reduction in the nitrogen decreased the reflectance at the red end of the spectrum, thereby shifting the plasma edge towards a smaller wavelength, increasing reflection in the blue, thereby causing a decrease in the net yellow chroma. Consequently, TiN coating colour appeared more silvery due to the higher contribution from the blue end of the spectrum. It was concluded that the film composition variation resulted in free electron concentration variation which was responsible for causing a shift in the plasma edge, thereby affecting reflectivity and colour of the nitrides. Perry et al. [38] further demonstrated that lattice–defect type were dependent on the deposition rate, which also affected the colour of the coating. For example, they showed that TiN coatings deposited at lower deposition rates in an atmosphere of nitrogen and argon; argon absorption and interstitial titanium and/or nitrogen caused the lattice expansion, resulting in a reduction in the charge per unit volume and hence a shift towards the red end of the spectrum, making the coating colour more golden. In contrast, at higher deposition rates, they found that argon absorption in the coating was minimal and lattice vacancy concentration increased; this led to an increase in the yellow chroma.

In a later study, Perry [39] observed a colour change of TiN coatings during long term storage and explained this was due to a contraction of the expanded lattice towards the equilibrium value over a period of time. According to the ionic model, any contraction of the expanded lattice can lead to a reduction in the yellow chroma. The findings were similar to those reported by Munz et al. [40] who found that a change in coating colour was associated with lattice volume or free carrier concentration changes.
It should be noted that, although the ionic model was successfully employed to elucidate the colour change of TiN coatings with variation in deposition parameters, the influence of microstructure was largely overlooked. Further, poor colour stability of TiN coatings during long term storage was considered as a major drawback of the thermal evaporation method, even though a range of coloured coatings, other than gold, could be prepared using binary or ternary compounds [10]. In addition, these coatings suffer from poor adhesion due to the low ion energy (~ 0.2 eV) used during deposition of the coating.

For decorative coating applications, sputter deposition is considered to be a particularly good candidate [8,10] since low deposition temperatures appropriate for temperature sensitive substrates can be employed. The sputtering method involves bombarding a target surface with high energy ions (usually argon) using a plasma source. These energetic ions generate a constant flux of sputtered atoms from the target that deposit onto the substrate.

Manory [41] reported that the ratio of nitrogen to argon and the percentage of nitrogen in the gas mixture were more significant in determining film colour compared to the nitrogen partial pressure. On the other hand, Meng et al. [42] pointed out that optical properties of TiN coating were closely related with the nitrogen partial pressure. Nosea et al. [43] observed a bright golden hue of the TiN coating deposited only at the lowest pressure of 0.15 Pa and at a substrate temperature of less than 100ºC. However, they pointed out that in their study of sputtered TiN coatings, stable plasma was achieved at the lowest pressure of 0.3 Pa. Furthermore, they also observed the dependence of the coating colour on the argon flow rate. They suggested that with increasing gas flow rate and hence pressure, the collision rate between sputtered atoms and sputtering gas atoms increased monotonically. Due to loss of kinetic energy of sputtered atoms, they observed the formation of a coarse grained columnar microstructure of the coating. In addition, the increment in the mean free time for sputtered atoms arriving at the substrate resulted in the incorporation of residual oxygen in the coating from the deposition chamber and consequently, formation of an oxide of titanium led to a significant reduction in the brightness and hence optical reflectivity of TiN coating. It was pointed out by Mitterer et al. [44] that a smooth surface morphology was essential for the improvement in optical properties of the coating.
Roquiny et al. [45] and Reiners et al. [8] observed a colour change from metallic grey to yellow with increasing nitrogen flow rate in the sputtered TiN coatings and correlated this colour change to the composition change (N/Ti ratio). Roquiny et al. [45] deposited TiN coatings on silicon and glass substrates using magnetron sputtering at a deposition temperature less than 100 °C, with no prior substrate bias potential. The findings were explained in terms of the Drude mode (section 2.1.1.1). According to this model the plasma frequency, \( \omega_p \), is given by the following expression

\[
\omega_p = \sqrt{\frac{4\pi N_e e^2}{m_e}} \quad (2.5)
\]

The plasma frequency divides the visible spectrum into two regions corresponding to propagation (\( \omega > \omega_p \)) and reflection (\( \omega < \omega_p \)) of electromagnetic waves by the material. Plasma energy \( E_p \) is given by,

\[
E_p = \hbar \omega_p \quad (2.6)
\]

where \( \hbar \) is Planks constant,
\( \omega_p \) is the plasma frequency

They observed that, with increasing nitrogen flow rate, the titanium content in the coating decreased and hence the number of free electrons, \( N_e \), decreased. As a result, the plasma energy, \( E_p \), moved towards lower energies and the reflected part of the light spectrum was reduced (\( \omega < \omega_p \)), and consequently, a reduction in reflectivity. Although, they successfully deposited TiN decorative coatings at low deposition temperatures, the effect of the microstructure formation on decorative properties has largely been overlooked.

The development of TiN coating with a fine grained, dense microstructure is acknowledged [14,32] as critical for achieving improved tribological and corrosion performance. Functional TiN coatings, for example, cutting tool coatings, deposited at a high substrate temperature of 500°C typically exhibit a dense structure [10,11]. However, such high temperature of deposition would alter the properties of temperature sensitive substrates
typically used in the decorative coating industry. Researchers [11,15, 44-48] have reported various methods for obtaining a dense microstructure for functional coatings. Primarily these involve bombardment with energetic particles [46] and thus increasing adatom mobility. The bombardment of a growing film with energetic particles has been observed to alter the physical, structural and chemical properties of the coating [46,47].

Mitterer et al. [44] and Bonelli et al. [48] studied the effect of ion bombardment on the surface roughness of TiN coatings by varying the substrate bias voltage. They proposed that with increasing bias voltage, ion bombardment increased, causing re-sputtering. This led to a coarse surface and consequently, reduced optical reflectivity of the coating.

Although sputtering has the advantage of producing coatings of uniform thickness with low surface roughness, the main disadvantage is that the reaction of the gas with the target material. This, as pointed out by Sproul et al. [12], results in the formation of compound on the target leading to a reduction in the sputtering rate and the target is said to be “poisoned”. Thus, the material deposited from the poisoned state is different from that deposited in a non-poisoned state. This can have an effect on the composition of the coatings and hence colour of the coating [8,15]. Various solutions have been proposed to this problem [11-13], however, they introduce complexity into the deposition system. Considered from the standpoint of reproducibility of colour, such complexities in the deposition system are a major problem and have been largely overlooked for decorative applications. It has been established [12] that careful control of process parameters such as the nitrogen partial pressure, flow ratio of Ar/N₂, total gas pressure and substrate bias is needed to ensure consistency in the colour of sputtered coatings.

Cathodic arc evaporation (CAE) emerged in the 1980s as an alternative technology to evaporation and sputtering for decorative applications [10]. The advantages of the CAE process include [16] high ionisation efficiency (80%) with the potential for high deposition rate. In this deposition process, material is vaporised due to the formation of electric arc spots on the cathode. The arc spots are extremely small, of the order of few micrometers in diameter, and the arc current is in the range of 50 to 150A. As a result, very rapid heating to
a small volume of the cathode surface occurs, followed immediately by flash evaporation. The arc spot then shifts to another location and the process is self generating. The emitted material is highly ionised and energetic. The coatings produced with ionised species with high energies considered [16] as highly adherent and dense in microstructure. Furthermore, in CAE control of total pressure in the chamber is considered complementary from the process control point of view [10, 15], since reactive evaporation and sputtering deposition systems, require control of partial pressure of the reactive gas.

Randhawa [15] demonstrated the advantage of CAE to deposit TiN coatings with a yellow golden hue on stainless steel substrates, in contrast to red and green hue observed in TiN coatings deposited by evaporation and sputtering processes. Coll et al. [49] indicated that in addition to highly ionised metal vapour, the arc also ejects micron-sized particles from the cathode. The size of macroparticles is reported as usually in the range of 0.1 to 100µm. A similar range of macroparticles was observed in the present study (see Figure 2.3(a) and 2.3(b)), when depositing TiN CAE coatings. The incorporation of macroparticles in the coatings can occur at any stage of the deposition and hence their presence can occur within the coating, at the surface or at the substrate-coating interface.

Macroparticles affect the surface morphology by forming pitting defects. It is well documented that the inclusion of macroparticles in the coating has a detrimental effect on the visual appearance, corrosion resistance and tribological properties [23]. Extensive research has been carried out on the reduction of macroparticle content in the as deposited film [16-28] using various chamber configurations. These techniques primarily rely on plasma filtering which consists of obstructing the line of sight plasma trajectory between the cathodic arc source and the substrate. This results in the separation of macroparticles from the plasma flux by means of a physical barrier, while the plasma is manipulated around the curved duct using an electro-magnetic field. In the simplest system the macroparticles can be blocked by placing a shield between the arc source and the substrate [28]. Alternatively, magnetic ducts such as a linear duct filter [49], the ¼ torus filter [21] and the s-filter [17] are extremely effective in blocking the line of sight of macroparticles. The use of such filtering techniques for decorative applications is reported [28, 30, 50].
Mustapha et al. [50] reported an improvement in optical properties of TiN coatings due to a smooth surface morphology with the elimination of macroparticles. However, the inclusion of plasma filtering techniques has the distinct disadvantage [25] of introducing complexity into the deposition system resulting in reduction in deposition rate and hence, significantly increasing the production cost.
Figure 2.3 (a), (b) Scanning Electron Micrograph showing macroparticles in the TiN coating deposited by CAE

It has also been shown that macroparticle content of CAE coatings can be reduced by varying the total pressure of reactive gas and arc current [20,25]. Interestingly, the
influence of the reactive gas pressure is related to the fact that the gas reacts with the cathode surface, covering it with a compound layer known as cathode poisoning [16]. It is argued [22,26] that increasing the melting point of the compound layer results in the reduction of the number and size of macroparticles. This significantly modifies the deposition process since the compound layer has a higher melting point than the pure cathode material, resulting in the emission of few macroparticles from the cathodic arc. In the case of TiN deposition, the compound layer of TiN forming on the surface of the titanium target [22] has a melting point of 2030ºC compared to the pure titanium target of 1660ºC. In practice it is assumed [22] that this increase in melting point results in the reduction of number of Ti macroparticles in the TiN coatings.

There are, however, conflicting views concerning the effect of deposition pressure on the decorative properties of TiN CAE coatings. Randhawa [15] pointed out that the variation in the nitrogen deposition pressure range $5 \times 10^{-3}$ Pa to 10 Pa had little effect on golden hue of TiN CAE coatings. This finding suggests that the CAE can be used over a wide range of operating pressures $5 \times 10^{-3}$ Pa to 10 Pa with a consistent colour of the coating. Niyomsoan et al. [51] studied the effect of variation of deposition pressure on the CAE TiN coatings colour deposited on steel substrates for decorative applications. They observed that the colour variation of TiN CAE was insignificant with the change in coating composition from 0.92 to 1.14 and thus, with the deposition pressure. However, the corresponding deposition pressure range is not revealed in their study. In contrast, Wang et al. [31] observed that the variation in the deposition pressure of $1.33 \times 10^{-3}$ Pa to 13 Pa of CAE TiN coatings deposited on bare brass substrates, had a significant effect on the coating colour and hence, reflectivity. They noticed that the coating deposited at lower deposition pressure displayed a distinct metallic hue with lower optical reflectivity, in contrast, to those deposited at higher deposition pressure with a golden hue and higher optical reflectivity. They attributed improved decorative properties (colour and optical reflectivity) of the coatings deposited at higher deposition pressure to a smoother surface morphology. In order to elucidate the above conflicting findings, further investigation on the effect of cathode poisoning due to high deposition pressure, on the decorative properties of TiN coatings is required.
2.1.3 The microstructure of PVD coatings

The microstructure of the coating is primarily influenced by deposition parameters, and these include substrate temperature, deposition pressure, and the energy of the deposited atoms. Extensive studies over the past 20 years, of the relation between the PVD coating microstructure and key deposition parameters [14,32] was carried out. This work has lead to the development and refinement of several Structure Zone Models (SZM) of film growth. These models correlate the morphology and microstructure of a coating, independently of the material, as a function of adatom mobility. However, these models are specifically applicable for metal coatings. Movchan and Demchishin [52] were the first ones to propose a SZM of film growth in which the coating microstructure was suggested from the ratio of substrate temperature (Ts) to the melting temperature of the depositing material (Tm). This is shown in schematic form in Figure 2.4.

![Structure Zone Model](image)

**Figure 2.4** Structure Zone Model for film growth proposed by Movchan and Demchishin (Ts is the substrate temperature and Tm the coating material melting point [52])

According to this model, microstructure is controlled by shadowing effect (zone1), surface diffusion (zone 2), and bulk diffusion (zone 3) as T/Tm increases. In Zone 1, where T_s/ T_m
< 0.25- 0.3, the microstructure consists of round-topped conical columns because of relatively low atomic mobility which is due to low thermal energy. As the temperature is raised, surface diffusion becomes important in the film growth and the microstructure becomes columnar with smooth topography in region “Zone 2”, with \( T_s/T_m \sim 0.3-0.45 \). If the temperature is raised further, the microstructure takes on the appearance of equiaxed grains. This region is shown as “Zone 3”, with \( T_s/T_m > 0.45 \) where bulk diffusion process is dominant.

In a later study, Thornton [53] refined the model proposed by Mochvan and Demchishin to include the effect of ion bombardment on surface atom mobility. He identified a new microstructural region, “Zone T”, which consisted of fibrous grains. This region was located between zones 1 and 2. Further study by Messier et al. [54] reported similar findings and the corresponding SZM is shown diagrammatically in Figure 2.5. They reported that with an increase in the bombardment energy, the width of the Zone T increased at the expense of Zone 1.

**Figure 2.5** Structure Zone Model for film growth showing the effect of both bombardment and thermal-induced mobility [54]
These models are important in the present investigation, since it is desirable to deposit TiN decorative coatings at low substrate temperature to avoid microstructural damage of the typical substrates used in decorative coating industry (e.g. brass and high pressure die-cast zinc). This restriction, according to the above models should lead to the Zone 1 coating microstructure [53,54] i.e. the coatings consist of an open columnar grain structure with intergranular voids. It is therefore, vital to investigate the effect of microstructure formation of metal nitride (TiN) CAE coatings deposited at low substrate temperature, with no prior substrate heating on the decorative properties, and on the tribological and corrosion protection performance. Studies by Musil et al. [55] and later by Bull [56] demonstrated that a transition of zone 1 to zone T microstructure can be obtained through the energy of ion bombardment, i.e. through the selection of a relatively high substrate bias potential. The insights obtained from the study of the influence of microstructure formation of CAE TiN coatings deposited at low substrate temperature, with no prior substrate heating, but, with the application of high substrate bias potential, on the decorative properties, tribological and corrosion protection performance may well be of considerable importance for decorative coatings industry in order to better design and select such coatings for application in the harsher, longer term environments experienced by door furniture and tapware.
2.2 Corrosion performance of TiN coatings

In the following section, the basic principles of electrochemical corrosion are briefly described. Following this, the effects of PVD processes and process parameters on the corrosion performance of TiN coatings are discussed.

2.2.1 Electrochemical principles of corrosion

The overall corrosion process [57] is defined as “Spontaneous dissolution of the metal by reaction with its environment”. Corrosion of metals is electrochemical in nature. As an illustration, a simple corrosion cell consists of a corroding metal with anodic and cathodic sites immersed in an ionically conducting solution. The reaction occurring at the anode is oxidation (dissolution of the metal M), whereas at the cathode there is reduction of an oxidising agent (for example, O₂, H₂O or Hₐq⁺) in the aqueous environment. This can be represented by the following reactions:

Anode: \[ M (s) \leftrightarrow M^{n+} (aq) + ne (M) \] (2.2.1)

Cathode: \[ Ox(aq) + ne(M) \leftrightarrow R (aq) \] (2.2.2)

Cathodic reaction, usually being oxygen reduction and/or water reduction (hydrogen evolution), is further represented as

\[ O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^- \] in neutral or alkaline solution

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \] in neutral or alkaline solution

The overall cell reaction is the sum of the anodic reaction and the cathodic reaction, as both the reactions occur simultaneously and at identical rates on a metal surface. Corresponding to the above reactions, the corroding metal establishes a mixed potential between the thermodynamic equilibrium potential of the anodic and cathodic reactions [57]. This
potential is known as the corrosion potential or open circuit potential, \( V_{corr} \), where \( V \) indicates that the potential is measured relative to some reference electrode. The metal corrodes at a finite rate when the anodic reaction and the cathodic reaction occur at the same rate in the direction given by equations (2.2.1) and (2.2.2) respectively. The rate at which this steady state situation occurs is called the corrosion rate. The essential electrochemical conditions for corrosion can be stated as:

- \( V_{corr} \) must be more positive than the equilibrium potential for the anodic reaction;
- \( V_{corr} \) must be more negative than the equilibrium potential for the cathodic reaction.

The value of either the anodic or cathodic current at \( V_{corr} \) is called the Corrosion Current, \( I_{corr} \). The corrosion rate, \( R_{corr} \), of the metal in gram s\(^{-1}\) can be determined from \( I_{corr} \) by simple application of Faradays law and is given by the following equation.

\[
R_{corr} = \frac{I_{corr} \times a}{nF} \text{ (gs}^{-1}) \quad (2.2.3)
\]

where \( A \) is the atomic weight, \( F \) is Faradays constant (96,500 coulombs/equivalent), and \( n \) the number of electrons exchanged.

While \( I_{corr} \) cannot be measured directly, it can be estimated using electrochemical techniques [57, 58, 60, 61] in which the corroding metal is part of an electrochemical cell, as described in section 3.6, containing an auxiliary electrode, a reference electrode and the electrolyte concerned. These techniques are

1. Tafel extrapolation (high field approximation),
2. Linear polarisation method (small field approximation)
3. Electrochemical impedance spectroscopy (EIS)

The general electrochemical equation for corrosion rate determination under steady state conditions [59] is as follows

\[
I = I_{corr} \left\{ \exp\left( \frac{V - V_{corr}}{b_c} \right) - \exp\left( \frac{V - V_{corr}}{b_a} \right) \right\} \quad (2.2.4)
\]
where

- $I$ is the total cell current in amps
- $I_{\text{corr}}$ is the corrosion current in amps
- $V$ is the electrode potential
- $V_{\text{corr}}$ is the corrosion potential in volts
- $b_a$ is the anodic Tafel Constant in volts/decade for the anodic reaction
- $b_c$ is the cathodic Tafel Constant in volts/decade for the cathodic reaction

It should be noted that equation 2.2.4, and consequently those simplified forms derived from it (see below) are based on several simplifying assumptions [57,58] and these are listed below:

(i) Both the anodic and cathodic reactions are controlled by the kinetics of the charge transfer reaction at the metal surface, i.e. reactions 2.2.1 and 2.2.2 are proceeding at a rate controlled by the rate of electron transfer at the metal-solution interface;
(ii) IR drop in the electrolyte and in any surface film on the metal is negligible;
(iii) The whole metal surface functions simultaneously as a cathode or anode rather than a combination of separate cathodic and anodic areas;
(iv) There are only two redox reactions occurring on the metal surface;
(v) $V_{\text{corr}}$ does not lie close to the equilibrium potential of either the anodic or cathodic reaction, i.e. $V_{\text{e,a}} << V_{\text{corr}} << V_{\text{e,c}}$.

2.2.1.1 Tafel extrapolation (high field approximation)

From equation 2.2.4, it can be seen that at $V=V_{\text{corr}}$, each exponential term equals one. The external cell current is therefore zero. Near $V_{\text{corr}}$, both exponential terms contribute to the overall current. Finally, as the potential is driven far from $V_{\text{corr}}$, (approximately 50mV deviation from the $V_{\text{corr}}$ value), one exponential term predominates and the other term can be ignored. When this occurs, a plot of log current versus potential becomes a straight line. Tafel behaviour is usually represented in a V-log$_e$I (potential as a function of current) diagram. The Tafel slope, $b$, can be determined from this diagram as the slope of the V-
$V_{\text{corr}}$ vs. log$I$ plot, with $I_{\text{corr}}$ being determined from the intercept with the log$I$ axis, at $V=V_{\text{corr}}$.

With an external potential imposed on the metal depending upon $V>>V_{\text{corr}}$ or $V<<V_{\text{corr}}$, the equation (2.2.4) \cite{57,61} becomes

\begin{equation}
I \approx -I_{\text{corr}} \left( \frac{\exp(V - V_{\text{corr}})}{b_a} \right) = I_a \quad (V>>V_{\text{corr}})
\end{equation}

\begin{equation}
I \approx I_{\text{corr}} \left( \frac{\exp(V - V_{\text{corr}})}{b_c} \right) = I_c \quad (V<<V_{\text{corr}})
\end{equation}

These equations can be solved for $I_{\text{corr}}$, $b_a$, and $b_c$.

2.2.1.2 Linear polarisation method (Small Field Approximation)

By restricting the potential to be very near to $V_{\text{corr}}$, for example ± 10-20 mV, equation 2.2.6 can be further simplified. The current versus voltage curve approximates a straight line near to $V_{\text{corr}}$. The slope of this line has the units of resistance (ohms). The slope is, therefore, called the polarisation resistance, $R_p$. The corrosion current can be estimated from $R_p$ value combined with an estimate of the $b_a$ and $b_c$. These values can be obtained from the Tafel plot.

From equation 2.2.4, differentiation with respect to $V$ and simplifying, the final equation \cite{59} is

\begin{equation}
\frac{dI}{dV}_{V=V_{\text{corr}}} = \frac{b_c b_a}{(b_c + b_a)}
\end{equation}

\begin{equation}
B = \frac{b_c b_a}{(b_c + b_a)}
\end{equation}

Where $B = \frac{b_c b_a}{(b_c + b_a)}$.  

31
Polarisation resistance, \[ R_p = \left( \frac{dV}{dl} \right) \] (2.2.8)

The polarisation conditions used in the LPR technique are relatively mild [60] since determination of \( I_{\text{corr}} \) from I-V data can be determined within ±10 mV of \( V_{\text{corr}} \). Alternatively, \( I_{\text{corr}} \) can be determined repeatedly without significantly altering the working electrode surface.

2.2.1.3 Electrochemical Impedance Spectroscopy (EIS)

An electrochemical impedance spectroscopy (EIS) studies the electrochemical system response by applying an AC potential to a system and measuring the current through it. The response to this potential is an AC current signal, containing the excitation frequency and its harmonics. This current signal can be analysed as a sum of sinusoidal functions (a Fourier series) and does not require assumptions about Tafel constants. EIS analysis of the system response contains information about the electrode/electrolyte interface, its structure and reactions taking place there [58,62]. The response is represented by an electrical equivalent circuit model and the simplest form of such a model is given in Figure 2.6 for a simple electrochemical reaction occurring at a single electrode/electrolyte interface.

The circuit consists of a solution resistance, Rs, a double layer capacitance, C, and polarisation resistance, Rp. Rs is the solution resistance between the reference electrode and the working electrode, C is the capacitance due to an interfacial structure of separated charge which exists between an electrode and its surrounding electrolyte, commonly referred to as the electrical double layer, which behaves like a charged capacitor, and Rp is polarisation resistance, as in section 2.2.2.1.
In EIS a small-amplitude (example 5mV) sinusoidal potential is applied to the working electrode at a number of discrete angular frequencies $\omega$ rads$^{-1}$ where $\omega = 2\pi f$, and $f =$frequency of applied signal in Hz [62]. At each angular frequency the resulting current will exhibit a sinusoidal response which is out of phase with the applied potential signal by a certain amount ($\theta$), i.e.

For $V = V_0 \sin \omega t$
$I = I_0 \sin (\omega t + \theta)$

where $t =$ time in seconds.

The resulting current response has been expressed as a frequency dependent impedance ($Z(\omega)$) such that

$Z(\omega) = V(\omega)/I(\omega)$ (ohm)

or $Z(\omega) = V(\omega)/i(\omega)$ (ohm cm$^{-2}$)

where $i =$ time varying current density.

The frequency dependent impedance $Z(\omega)$ is a complex valued vector quantity with both real and imaginary frequency dependent components, i.e.

$Z(\omega) = Z(\omega)_{(\text{real})} + j Z(\omega)_{(\text{imgl})}$ (2.2.9)

where $Z(\omega)_{(\text{real})} = |Z(\omega)| \cos \theta$
$Z(\omega)_{(\text{imgl})} = |Z(\omega)| \sin \theta$
\[ j = \sqrt{-1} \]

\[ |Z(\omega)| = \sqrt{Z^{2}(\omega)_{\text{real}} + Z^{2}(\omega)_{\text{img}}} \quad (2.2.10) \]

\[ \theta = \tan^{-1}\left(\frac{Z(\omega)_{\text{real}}}{Z(\omega)_{\text{img}}}\right) \quad (2.2.11) \]

The electrochemical impedance \( Z(\omega) \) is a fundamental characteristic of the electrochemical system it describes and is expressed in terms of a magnitude, \( |Z(\omega)| \), and phase, \( \theta \). It is from the resulting \( Z(\omega) \) vs. \( \omega \) response that a knowledge about the electrical properties of the whole electrode-material system can be determined. For example, for the simple circuit shown in Figure 2.6

\[ Z(\omega) = R_{\text{sol}} + \frac{R_{p}}{1 + \omega^{2}R_{p}^{2}C^{2}} - \frac{j\omega C R_{p}^{2}}{1 + \omega^{2}R_{p}^{2}C^{2}} \quad (2.2.12) \]

Hence at very low frequencies (\( \omega \to 0 \))

\[ Z(\omega) \omega \to 0 \approx R_{\text{sol}} + R_{p} \]

while at very high frequencies (\( (\omega \to \infty) \))

\[ Z(\omega) \omega \to \infty \approx R_{\text{sol}} \]

thus polarisation resistance, \( R_{p} \), can be determined by the measured impedance at sufficiently low frequencies [62]. Corrosion rate can be determined using the value of \( R_{p} \) in equation 2.2.7.

In practice, frequency related data \( Z(\omega) \) or \( \theta \) is usually presented or plotted in the form of:

(a) A Bode plot; \( \log |Z(\omega)| \) vs. \( \log(\omega) \)

(b) A Phase angle plot: \( \theta \) vs. \( \log(\omega) \)

(c) A Nyquist plot: \( Z(\omega) \) (imj) vs. \( Z(\omega) \) (real)

All three forms are used in this study.
2.2.2 Corrosion of Coated Systems

Generally, coatings are classified according to their electrical conductivity as follows [59]:

1 **Insulating coatings** These types of coatings will behave as a simple barrier layer toward aggressive species such as water, oxygen and chloride ions. In this situation, the resistance of a coating is an indication of its protective ability.

2 **Passive coatings** A passivating layer forms either as a result of oxidation of the metal to an insoluble surface oxide or as a result of precipitation of some insoluble hydrolysis product of the metal cation. Typically these layers [59] are adherent, non-porous layers. Also, these layers exhibit electronically conducting or semiconducting properties but are usually poor ionic conductors. The passivating layer seals off the metal surface from the solution resulting in a drastic reduction in corrosion rate (e.g. 100-1000 times).

3 **Conducting Coatings (electronically)**

(a) Coatings more corrosive (active) than the substrate material, for example, zinc coatings on iron. In such cases, the coating material will dissolve more readily protecting the substrate; the substrate is said to be cathodically protected.

(b) Coatings noble than the substrate material, for example, tin coatings on iron. Defects in the coating material expose the substrate to electrolyte and we then have the classic case of galvanic corrosion with a large cathode area and small anode area which plays a significant role in this corrosion process [58]. This is because a large cathodic area provides a larger surface area for the reduction reaction, and the anodic dissolution current (rate) must increase to accommodate this. Consequently the rate of the fundamental corrosion reaction of the substrate \((M_\circ \rightarrow M^{n+} + ne (M))\) will be increased in the coupled state relative to that for the freely corroding or uncoupled substrate. As a consequence, the galvanic corrosion or penetration rate increases.
The above two cases of conducting coatings corrosion are shown schematically in Figures 2.7 (a) and (b). In these Figures, H\(^+\) reduction as the cathodic reaction is used for illustrative purposes only.

![Diagram with chemical reactions](image)

(a)      (b)

Figure 2.7  Conducting coatings (a) coating more corrosive than substrate, (b) coating noble than substrate

TiN coatings are electronically conducting and usually more noble than the metallic substrate onto which these are deposited [63] and hence belong to the second type of coatings (as noted above) as far as galvanic corrosion is concerned. Therefore galvanic corrosion may well be a significant theoretical phenomenon in coating failure.
2.2.2.1 The effect of PVD coating on the corrosion behaviour of the underlying substrate

Wang et al. [31] showed that corrosion protection of bare brass substrates was improved by depositing CAE TiN coatings, in artificial human sweat solution. The protective nature of TiN coatings for substrates was also demonstrated by Erdemir et al. [64]. They studied the corrosion protection performance of electron beam evaporated TiN coatings deposited at a relatively higher deposition temperature of 500°C on three different types of substrates, such as, stainless steel, high speed steel and stabilised iron. They observed improved corrosion protection of substrates and suggested the result was due to a fine-grained, dense microstructure of the TiN coating deposited at the relatively high deposition temperature of 500°C.

Alternatively, Elsener et al. [65] and Massiani et al. [66] demonstrated that the corrosion protection behaviour of the coatings is determined by the nature of the substrate i.e. if it is active or passive. Elsener et al. [65] deposited TiN coating on stainless steel (passive) and mild steel (active) substrates and showed that better corrosion protection by TiN coating was achieved on substrates which undergo passivation. Massiani et al. [66] deposited TiN coatings on stainless steel and Armco iron substrates, and obtained the improved protection ability of TiN coatings deposited on stainless steel substrates as compared to Armco iron substrates. They suggested this result was due to the passive nature of the stainless steel substrates.

The above results are not unexpected and can be interpreted by considering galvanic coupling of the coating with the underlying metal substrate. Considering the case of the coatings deposited on the passive substrates, the passive substrates may prevent the corrosion of the substrates in the course of the penetration of electrolyte through coating defects. In principle, the passivating layer on the substrate itself may well be a potential strategy for imparting corrosion protection of the substrate. In contrast, in the case of PVD coatings on the active substrates, it may well be the case of galvanic coupling of less corrosive coating with more active substrate materials. The presence of defects, such as
porosity and pin-holes in the coating can lead to the penetration of electrolyte to the substrate. It can be considered as the classic case of galvanic corrosion with a large cathode area and small anode area. This is because a large cathodic area provides more surface area for the reduction reaction, and the anodic dissolution current (rate) must increase to accommodate this. Consequently the rate of the fundamental corrosion reaction of the substrate \( M_{(s)} \rightarrow M^{n+} + ne \) may well be increased in the coupled state relative to that for the freely corroding or uncoupled substrate, leading to an increased in the galvanic corrosion or penetration rate of the active substrate.

### 2.2.2.2 The effect of coating microstructure and inherent defects

The microstructural features that most probably influence corrosion performance of the coatings are those that extend through the coating. It can be expected that with increasing thickness these defects are reduced, which may beneficially affect the corrosion characteristics of the investigated system. This was confirmed by the Brown et al. [67] in their investigation on the effect of the sputtered TiN coating thickness variation on the corrosion protection performance. They suggested that this was due to a reduction in defect density with increasing thickness. In contrast, Telama et al. [68] reported that an increase in the sputtered TiN coating thickness from 1.7 to 3.5 \( \mu m \), had insignificant effect on the corrosion performance of the coatings, and suggested that this was due to the columnar microstructure of the coating. They found that growing columns failed to cover possible pinholes between the columns, thus allowing access for electrolyte to the substrate, causing dissolution of the substrate and eventually causing localised corrosion attack. Similar findings were reported by Massiani et al. [69]. However, the TiN coating microstructure obtained by depositing at a relatively high substrate temperature of 500ºC by Telama et al. [68] and Massiani et al. [69] is in stark contrast to the “claimed” dense microstructure typically observed [54,55] for such high temperature deposited coatings.

In coatings exhibiting a high density of defects, corrosion failure was found to be associated with these defects [70, 71]. Such a failure mode was observed for thin sputtered
coatings on steel substrates [70]. Park et al. [71] and Tzneva et al. [72] supported these findings in their study of CAE TiN coatings on stainless steel and low carbon steel substrates respectively and observed that the macroparticles in the coating affected corrosion resistance significantly.

While defect density can be reduced by increasing the thickness of the coating, there are some drawbacks, such as increase in stress as well as in processing costs. In order to keep the thickness of the coating low, and at the same time improve corrosion performance by lowering defect density, other alternatives were suggested, and are presented in the following sections.

2.2.2.3 The effect of metallic interfacial layers

When PVD coated metal substrate, is exposed to the environment, electrochemical properties may be affected by the properties of the coating–substrate interface and by the microstructure of PVD coatings. It was demonstrated that the interfacial structure between substrate and coating played a major role in the mechanical and tribological properties of the coating [19], for example, adhesion and hardness. This interfacial structure can be modified prior to coating deposition by various surface modification techniques, for example, metal ion implantation [19], or plasma nitriding, or as an inherent passive layer on typical substrates used, such as stainless steel.

Erdemir et al. [73] deposited TiN coatings on M50 bearing steel by three different deposition systems. In the first system, Ti coating were sputter deposited in an argon atmosphere and then implanted with N\(^+\) ions to a dose of \(4\times10^{17}\) ions/cm\(^2\) with an acceleration voltage of 50 keV. In the second, TiN coatings were sputter deposited. In the last technique, TiN coatings were prepared by reactive evaporation. All the above coating depositions were carried out at a substrate temperature of 500\(^\circ\)C with 1 \(\mu\)m thick TiN coatings. They observed the best corrosion performance was from the evaporated TiN coatings in acid (0.1M H\(_2\)SO\(_4\)) solution and suggested the result was due to its dense microstructure as a consequence of the high deposition temperature.
He and Hon [74] employed the ion implantation technique and the magnetron sputter deposition system for TiN coatings deposition on iron substrates and studied their electrochemical behaviour in H\textsubscript{2}SO\textsubscript{4} solution. The first type of TiN coating was formed using ion implantation of N\textsuperscript{+} (110 keV) onto an iron substrate coated with 80 nm thick titanium layer. These TiN coatings consisted only of a TiN phase and exhibited a smooth surface. A second type of TiN coating was deposited in the same way as the first, however with a titanium interfacial layer of thickness 500 nm. This process yielded a mixed phase on the Ti-Fe interface. In the third type, Ti and TiN coatings were deposited by magnetron sputtering with corresponding thicknesses of 500 nm each and were composed of TiN and Ti\textsubscript{2}N phases. All three types of coating were found to improve the corrosion resistance of the substrate, although to a different extent. The first type of coating (with 80 nm thick Ti layer implanted by N\textsuperscript{+}) demonstrated the best corrosion behaviour. In the second type of coating, consisting of Ti and TiN phases, the corrosion resistance was worse, due to the poor mixing of the Ti-Fe interface which facilitated the dissolution process. In the third type of coating, deposited by magnetron sputtering, large pores were observed at the surface of the coatings. They suggested that penetration of electrolyte through defects in the coating, such as, pores, exposed the substrate, and led to poor corrosion protection performance.

Van Leaven et al. [75] implanted several different elements in TiN coatings in order to modify coating microstructure and improve corrosion resistance. They deposited CAE TiN coatings on tool steel and stainless steel substrates and implanted nitrogen, titanium and gold into these TiN coatings, as well as into the uncoated substrate, up to a concentration of 1×10\textsuperscript{16} ion cm\textsuperscript{-2} at an accelerating voltage of 80 keV. They found that the implanted species failed to improve corrosion behaviour of tool steel and stainless steel substrates for the applied concentration levels, since they introduced defects in the coating. They further observed a change in the corrosion features associated with ion implantation: while the plain steel corroded uniformly in chloride solution, the implanted steel, as well as implanted TiN coated steel, showed localised corrosion.
Van Stappen et al. [76] studied the effect of the titanium interfacial layer on TiN coating surface morphology, crystallographic orientation, hardness and adhesion to the substrate. They observed improved adhesion of the TiN coating by the presence of the titanium interfacial layer and suggested this could be due to the strong chemical bonding between titanium and the oxidised surface of the stainless steel substrate. If nitrogen was then added to the plasma, nitrogen atoms formed stable bonds with the freshly formed titanium layer and this leads to the TiN layer being strongly bonded to the titanium interfacial layer. Massiani et al. [77] demonstrated that the TiN coatings with a titanium interfacial layer showed an improved corrosion performance over a thick TiN coating without a titanium interfacial layer and suggested that this was due to the improved adhesion of the TiN coating. Again, these studies were conducted in acid solution (H₂SO₄).

It was demonstrated that apart from titanium, other metallic interfacial layers also strongly influence the corrosion properties of the coating. Leyland et al. [78] suggested an electroless nickel, particularly incorporated with phosphorous (which enables it to be heat treated to a high hardness), as an alternative interfacial layer material. They observed that significant improvement in terms of corrosion and abrasive wear was achieved by duplex coating systems consisting of plasma-assisted PVD TiN top coating and phosphorous doped electroless nickel (ENi-P) as an interfacial layer on a steel substrate. Helmersson et al. [79] also reported similar findings. They suggested that an electroless nickel interfacial layer can prevent general corrosion attack on the TiN-coated low carbon steel substrates. Again, the above corrosion studies [78,79] were also conducted in acid solution. Chen et al. [80] studied the corrosion protection of TiN coated low carbon steel using electroless Ni-P as an interfacial layer in a more aggressive NaCl solution. They deposited TiN coatings using both CAE and Hollow Cathode Discharge (HCD), methods. They obtained improved corrosion characteristics of the CAE-TiN coated substrates with the Ni-P interfacial layer. They suggested that this was due to the lamellar structure of Ni-P inhibiting the penetration of corrosion species. The findings suggest that the interfacial layer may interrupt the columnar structure and can lead to the improved corrosion protection performance of the coating and thus highlights the role of coating microstructure in the corrosion performance.
Park et al. [71] studied various pre-treatment procedures designed to isolate stainless steel substrates from the environment. These included combinations of plasma oxidising, plasma nitriding and introduction of a chromium interlayer in TiN coatings. They observed that TiN coatings with a metallic chromium interfacial layer exhibited better corrosion performance than conventional single-layer TiN coatings in acid solution and suggested this was due to passivation of the chromium interfacial layer.

All these studies were conducted for coatings deposited at relatively high substrate temperature of 300ºC to 500ºC. For decorative coating applications however, low substrate temperature is essential to avoid microstructural damage of the temperature sensitive substrates used in the decorative industry. Vershinin et al. [28] reported a study of CAE, TiN coatings deposited at a low substrate temperature of 50ºC, appropriate to temperature sensitive substrates. They carried out a comparative study of corrosion protection of the TiN coatings on glass substrates using different PVD techniques such as CAE, magnetron sputtering and evaporation. They observed the best corrosion performance of the CAE deposited TiN coatings, however, failed to elucidate the corrosion improvement of the coating. It may well be that the differences in the coating morphology, microstructure and composition related either to those existing between deposition mechanisms or to the deposition parameters, can contribute in the corrosion protection performance of the coatings. Such a study of the coating morphology, microstructure and composition related to the coatings deposited at low substrate temperature, can provide insights into the mechanisms of corrosion protection performance of the coatings.

2.2.2.4 The effect of multilayer deposition

In an attempt to further improve corrosion performance of PVD coatings; one novel technique is the introduction of multilayered coatings. Basically this involves [81] the vapour deposition of alternating layers of different materials. The driving force behind this innovation is the fact that the multilayer structure interrupts the columnar growth of multilayer coatings; this thereby reduces direct access of the corrosive media to the substrate through the grain boundaries and coating defects [81]. The number of multilayer
sequences may vary from three to several hundred for a total coating thickness of a few microns.

Hubler et al. [82] have investigated thin multilayer TiN/Ti composites as a possible alternative for protection of steels. They deposited coatings with various thicknesses of TiN and titanium interfacial layers by magnetron sputtering. Corrosion tests revealed that multilayered coatings with a total thickness of 0.5 µm were as good as a 3 µm thick, single layer TiN coating. They observed that multilayer coatings had a considerably lower porosity which was ascribed to open structures reaching from the surface to the substrate in TiN layers being interrupted by intermediate titanium interfacial layers. Further they suggested that, oxidation of the titanium interfacial layer in acid solution led to partial closing of micropores and consequently, improved corrosion protection of the underlying substrate material. Liu et al. [83] also reported improved corrosion protection of Ti-TiN multilayer coating compared to single layer TiN coatings in acid solution. Munemasa et al. [84] suggested this was due the reduction in defect density with multilayer coatings deposition and also demonstrated that the higher the number of coating layers, the better the corrosion protection performance of the system. The ability of a coating to provide corrosion protection of the substrate is closely related to its microstructure. To achieve good protection, columnar microstructure with open paths to the substrate has to be avoided. Other studies with Ti/TiN multilayered coatings deposited by magnetron sputtering [85] and Arc Evaporation technique [86] also showed marked improvements in corrosion protection performance of the coatings. Later studies by Herreanen et al. [87] demonstrated improvement in corrosion protection by using thick interfacial layers rather than thin interfacial layers. They demonstrated that coatings with a large number of thin titanium interfacial layers retained the columnar structure of TiN coating and correspondingly failed to provide corrosion protection.
2.3 Concluding Remarks

The decorative coating industry is seeking from PVD technology a finish coating that is able to enhance the appearance of their product and give a life time guarantee through improved corrosion performance and tribological performance. It was therefore determined from the review that there is a need to deposit hard, corrosion resistant, PVD coatings in order to protect the underlying substrate. However, the coating-substrate system commonly suffers corrosion due to defects in the coating structure (pores, pinholes). These defects allow aggressive environments to penetrate the coating and reach the underlying substrate, leading to its dissolution. In addition, PVD coatings applied on consumer parts, such as doorhandles, kitchen and bathroom accessories, are exposed to a range of corrosive environments including water, chemicals and cleaning products and slight abrasive wear due to handling. Furthermore, since TiN coatings are electronically conducting and usually noble than the metallic substrate onto which these are deposited [63], galvanic corrosion may well be a significant theoretical phenomenon in coating failure. The actual rate of galvanic corrosion will depend on the slower reaction of the galvanic couple, which is usually the oxygen reduction on the more noble coating. Hence, the influence of TiN in causing galvanic corrosion of any underlying substrate will depend on the rate of water reduction (hydrogen evolution) or oxygen reduction or both on the TiN. If TiN is a poor electrocatalyst for both of these reactions then galvanic corrosion may not be significant. It is therefore essential to investigate the corrosion protection and tribological performance of decorative, PVD coated-components for their long term application.

The study of coating microstructure is of major significance, since it not only determines decorative properties but also controls the corrosion protection performance and therefore, environmental stability and long term reliability of these coatings. Although a number of studies have dealt with the corrosion protection performance of hard nitride coatings, the corrosion protective ability of low temperature, CAE deposited, TiN coatings on brass and high pressure die-cast zinc substrates for decorative applications has not been fully explored in the literature. Furthermore, since the coating represents a part of the decorative
component, it should be taken into account that the substrate corrosion behaviour in real systems may well be affected by galvanic corrosion.
CHAPTER 3

Experimental Techniques

This chapter includes a description of the PVD systems and various characterisation techniques used. The experimental programme is presented in the flow chart shown in Figure 3.1.

![Flow chart of the experimental programme](image)

**Figure 3.1** Flow chart of the experimental programme
3.1 Substrate preparation prior to TiN coating

TiN coatings were vapour deposited on two types of substrates. The first types were inert substrates, namely, silicon wafer (100) and glass slides used for studying the fundamental corrosion performance of the TiN coatings. The second types were chromium plated brass and high pressure die-cast zinc substrates used for studying the following properties:

(1) decorative (colour and optical reflectivity),
(2) tribological (abrasive wear),
(3) corrosion protection.

The substrates of brass and high pressure die-cast zinc, were employed in the present study with their commercial importance for the decorative industry. In order to assess the suitability of such coatings on decorative components, the coatings were also successfully deposited on back plate, hinge and door handles. The electroplated substrates were provided by the industry partner, GHI, and coatings were made up of copper (approximately 30-40 µm thick), followed by nickel (approximately 15-20 µm thick) and a top layer of chromium (approximately 0.2 to 0.5 µm thick). Prior to TiN coating deposition, these electroplated substrates were first cleaned using an aqueous cleaning line in which they were washed in alkaline soap solution, while at the same time being subjected to ultrasonic and mechanical agitation. This was followed by a rinse in de-ionised water and drying at 110 °C. Silicon wafers were cleaned in HF acid to remove the oxide layer from the surface. Following this, they were cleaned in acetone and de-ionised water. The glass slides were cleaned in an ultrasonic bath of acetone, de-ionised water and dried in air.

3.2 TiN coating deposition

All coatings investigated in the present study were deposited in one of two PVD coating systems. The first was a partially filtered cathodic arc system which consisted of dual cathodic sources. The second PVD system was a DC random cathodic arc coating system with 10 cathodic arc sources. A description of two PVD coatings systems is given in the following sections.
3.2.1 Partially Filtered Cathodic Arc Deposition

In the present study, partial filtration mode was employed as shown in Figure 3.2 with a linear plasma duct (200 mm. diameter) fixed between the cathode and the deposition chamber. The second cathodic arc source was located diametrically opposite to the one shown in Figure 3.2. The plasma flux was focused using focusing coils (90-140 Gauss) fitted to the ducts. A water cooled copper anode was axially located inside each duct. The chamber was fitted with an ion gun that provided a source of nitrogen ions for etching the substrates prior to TiN coating deposition. The ion source was operated with a discharge voltage of 2.0 kV and discharge current of 150 mA. The various processing steps are given in the flow chart (Figure 3.3) and corresponding process parameters are presented in Table 3.1.

![Figure 3.2](image)

Figure 3.2 Schematic representation of the filtered arc deposition system showing partially filtered configuration.
The substrates were positioned on the holder in deposition chamber which was pumped down to a base pressure of $2 \times 10^{-3}$ Pa. The substrates were subjected to a 10 minute nitrogen ion etch using the ion gun, at ambient temperature. Subsequently, a metallic interlayer of titanium (Ti) was deposited prior to TiN coating. It was deposited in an argon atmosphere at a pressure of $7 \times 10^{-3}$ Pa, for 2 minutes using a single arc source with an arc current of 100A. Following Ti interlayer deposition, nitrogen gas was introduced into the coating chamber to a pressure of $7 \times 10^{-3}$ Pa for the deposition of the TiN coating. Again, a single arc source of Titanium was operated at an arc current of 100 A. Reactive deposition was carried out for 20 minutes. Following this, substrates were cooled in an Argon atmosphere for a further 10 minutes in the coating chamber.
Table 3.1  Process parameters adopted during partially filtered arc deposited (PFAD) TiN coatings on chromium plated zinc, chromium plated brass, silicon and glass substrates.

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>PFAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure</td>
<td>$2 \times 10^{-3}$ Pa</td>
</tr>
<tr>
<td>Temperature</td>
<td>Ambient</td>
</tr>
</tbody>
</table>

**Nitrogen ion etch I**

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>PFAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge voltage</td>
<td>2 kV</td>
</tr>
<tr>
<td>Discharge current</td>
<td>150 mA</td>
</tr>
<tr>
<td>Time</td>
<td>10 minutes</td>
</tr>
<tr>
<td>Pressure</td>
<td>0.1 Pa</td>
</tr>
<tr>
<td>Substrate bias</td>
<td>0 V</td>
</tr>
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**Pump down**

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>PFAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>$2 \times 10^{-3}$ Pa</td>
</tr>
</tbody>
</table>

**Metallic interlayer, Ti**

<table>
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<tr>
<th>Process parameter</th>
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<td>Arc current</td>
<td>100 A</td>
</tr>
<tr>
<td>Time</td>
<td>2 minutes</td>
</tr>
<tr>
<td>Pressure</td>
<td>$7 \times 10^{-3}$ Pa</td>
</tr>
<tr>
<td>Substrate bias</td>
<td>$-150$ V</td>
</tr>
</tbody>
</table>

**TiN Coating**

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>PFAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc current</td>
<td>100 A</td>
</tr>
<tr>
<td>Time</td>
<td>20 minutes</td>
</tr>
<tr>
<td>Pressure</td>
<td>$7 \times 10^{-3}$ Pa</td>
</tr>
<tr>
<td>Substrate bias</td>
<td>$-150$ V</td>
</tr>
</tbody>
</table>
3.2.2 Random Cathodic Arc Deposition

The second PVD system used in this study utilized a cathodic arc system consisting of ten vertically mounted cathodic arc sources. However, only a maximum of five were used simultaneously in the present investigation. The arc sources (120 mm diameter) surrounded a substrate holder configured in 3-fold planetary rotation. The average distance between the arc sources and the substrate holder was 180 mm. The stainless steel deposition chamber had a volume of approximately 1.0 m³ (1,200 mm diameter × 920 mm height) that housed 6 spindle attachments which rotated about centrally located heating elements on a diameter of 840 mm. Chamber pressure was controlled using a rotary backed diffusion pump. Once the chamber was loaded with substrates the chamber pressure was reduced to a base pressure of 5×10⁻³ Pa prior to the start of all coating cycles.

The substrates including non-conductive substrates such as glass and silicon wafers fixed to the substrate holder using bar-magnets along with chromium plated brass coupons and were biased to a potential of -200V. All substrates were initially cleaned with metal ion etching for a period of 12 minutes using Ti ions with a substrate bias of –800 V. For the deposition of a single layer TiN coating nitrogen was introduced at 6 × 10⁻¹ Pa with a substrate bias of –200 V.

3.2.2.1 Effect of substrate deposition temperature

The TiN coatings were deposited on chromium plated brass substrates and silicon wafers (100). The deposition process included a high voltage titanium metal ion etch followed by a reactive evaporation of Ti in a nitrogen atmosphere. One set of TiN coatings was deposited at low substrate temperature (without prior substrate heating). The coating is referred to as the TL coating. It was observed that the substrate temperature at the end of coating cycle had reached a temperature of 140°C due to the heat generated from ion bombardment. Further, for comparison purposes, TiN coatings were deposited under the same conditions but, with prior substrate heating to the temperature of 200°C. Both coatings were deposited
under the same conditions of arc current, base pressure, nitrogen pressure and deposition time. The process details are presented in Table 3.2.

Table 3.2  Process parameters adopted during random cathodic arc evaporated TiN coatings deposited at low and high substrate temperature conditions on chromium plated brass and silicon substrates.

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>TL</th>
<th>TH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure</td>
<td>$5 \times 10^{-3}$ Pa</td>
<td>$5 \times 10^{-3}$ Pa</td>
</tr>
<tr>
<td>Temperature</td>
<td>140 ºC</td>
<td>200 ºC</td>
</tr>
<tr>
<td>Metal ion etch I</td>
<td>×1 Ti target</td>
<td>×1 Ti target</td>
</tr>
<tr>
<td>Arc current</td>
<td>80A</td>
<td>80A</td>
</tr>
<tr>
<td>Time</td>
<td>12 minutes</td>
<td>12 minutes</td>
</tr>
<tr>
<td>Pressure</td>
<td>$8 \times 10^{-1}$ Pa</td>
<td>$8 \times 10^{-1}$ Pa</td>
</tr>
<tr>
<td>Substrate bias</td>
<td>−800V</td>
<td>−800V</td>
</tr>
<tr>
<td>TiN Coating</td>
<td>×3 Ti target</td>
<td>×3 Ti target</td>
</tr>
<tr>
<td>Arc current</td>
<td>80 A</td>
<td>80 A</td>
</tr>
<tr>
<td>Time</td>
<td>20 minutes</td>
<td>20 minutes</td>
</tr>
<tr>
<td>Pressure</td>
<td>$6 \times 10^{-1}$ Pa</td>
<td>$6 \times 10^{-1}$ Pa</td>
</tr>
<tr>
<td>Substrate bias</td>
<td>−200 V</td>
<td>−200 V</td>
</tr>
</tbody>
</table>
3.2.2.2 Improvement in the TiN CAE coating performance

3.2.2.2.1 Effect of deposition pressure

The CAE system suffers from the major drawback of the presence of macroparticles. It is well documented that the inclusion of macroparticles in the coating has a detrimental effect [23] on the visual appearance, corrosion resistance and tribological properties. It has been demonstrated that the macroparticle content of CAE coatings can be reduced by varying the total pressure of reactive gas [20-23,25]. Interestingly, the influence of the reactive gas pressure is related to the fact that the gas reacts with the cathode surface, covering it with a compound layer known as cathode poisoning [16]. It is argued [22,26] that increasing the melting point of the compound layer results in the reduction of the number and size of macroparticles. The influence of deposition pressure on the decorative properties, corrosion protection and tribological performance of TiN CAE coatings deposited at low substrate temperature has not been explored fully. In this study, an investigation was carried out on the effect of nitrogen pressure on TiN CAE coatings, in light of the above properties.

TiN coatings were deposited at various nitrogen pressures using the CAE system. Initially, the chamber pressure was measured as a function of nitrogen gas flow rate for depositing TiN coatings using three arcs operating at 100 A arc current and a substrate bias voltage of −200 V. An initial nitrogen gas flow rate of 50 sccm was used to establish a stable chamber pressure that was typically below 0.1 Pa. At this pressure, arcs were initiated. The rate of gas flow was then increased in steps of 10 sccm and the pressure noted for each incremental value of flow rate. Once the chamber pressure reached its critical value (typically between 2 and 3 Pa), the flow rate was decreased in steps of 10 sccm back to original value of 50 sccm. The results are represented graphically in Figure 3.4 and it shows a slight hysteresis effect, not dissimilar to that observed in the case of sputtering deposition [11]. The hysteresis plot can therefore be interpreted along similar lines. At gas flow rate T1 (Figure 6.1) all the reactive gas introduced into the chamber is being used in the evaporation/deposition process. At gas flow rates T2 and T3, there is a sharp rise in pressure with an increase in gas flow rate, indicating that not all the nitrogen is being used.
up in the evaporation/ reactive deposition process. In sputtering, it is well acknowledged that this pressure rise is a consequence of target poisoning, i.e. the surface of the Ti target is covered with a thin layer of TiN which alters the physics of the evaporation process because TiN has a higher melting point (2030°C) than Ti (1660°C). Munz et al. [22] and Harris et al. [25] argued along similar lines for random CAE and they concluded that this effect results in fewer macroparticles. By gas flow rate T4, there is complete cathode surface poisoning and hence the chamber pressure now increases monotonically with increase in gas flow rate. This curve was then used to select a chamber pressures at which to deposit coatings onto chromium plated brass and silicon substrates. Four different pressure/nitrogen flow rates were selected as presented in Table 3.3. These corresponded to;

i. No target poisoning-(T1)
ii. Partial target poisoning -(T2)
iii. Partial target poisoning- (T3)
iv. Complete target poisoning- (T4)

Process details are given in Table 3.4
Figure 3.4 Variation of chamber pressure as a function of nitrogen gas flow rate for the deposition of TiN coatings

Table 3.3 Selection of deposition pressure for TiN coating from the hysteresis curve

<table>
<thead>
<tr>
<th>TiN Coating</th>
<th>Deposition Pressure (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>0.1</td>
</tr>
<tr>
<td>T2</td>
<td>0.4</td>
</tr>
<tr>
<td>T3</td>
<td>0.8</td>
</tr>
<tr>
<td>T4</td>
<td>1.25</td>
</tr>
</tbody>
</table>
Table 3.4   Process parameters adopted during random cathodic arc evaporated TiN coatings under different deposition pressures on chromium plated brass and silicon substrates.

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
<th>T4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure</td>
<td>$5 \times 10^{-3}$ Pa</td>
<td>$5 \times 10^{-3}$ Pa</td>
<td>$5 \times 10^{-3}$ Pa</td>
<td>$5 \times 10^{-3}$ Pa</td>
</tr>
<tr>
<td>Temperature</td>
<td>140ºC</td>
<td>140ºC</td>
<td>140ºC</td>
<td>140ºC</td>
</tr>
<tr>
<td>Metal ion etch I</td>
<td>×1 Ti target</td>
<td>×1 Ti target</td>
<td>×1 Ti target</td>
<td>×1 Ti target</td>
</tr>
<tr>
<td>Arc current</td>
<td>80A</td>
<td>80A</td>
<td>80A</td>
<td>80A</td>
</tr>
<tr>
<td>Time</td>
<td>12 minutes</td>
<td>12 minutes</td>
<td>12 minutes</td>
<td>12 minutes</td>
</tr>
<tr>
<td>Pressure</td>
<td>$8 \times 10^{-1}$ Pa</td>
<td>$8 \times 10^{-1}$ Pa</td>
<td>$8 \times 10^{-1}$ Pa</td>
<td>$8 \times 10^{-1}$ Pa</td>
</tr>
<tr>
<td>Substrate bias</td>
<td>−800V</td>
<td>−800V</td>
<td>−800V</td>
<td>−800V</td>
</tr>
</tbody>
</table>

| Coating TiN       | ×3 Ti target  | ×3 Ti target  | ×3 Ti target  | ×3 Ti target  |
| Arc current       | 80 A          | 80 A          | 80 A          | 80 A          |
| Time              | 20 minutes    | 20 minutes    | 20 minutes    | 20 minutes    |
| Pressure          | $1 \times 10^{-1}$ Pa | $4 \times 10^{-1}$ Pa | $8 \times 10^{-1}$ Pa | $12.5 \times 10^{-1}$ Pa |
| Substrate bias    | −200 V        | −200 V        | −200 V        | −200 V        |
3.2.2.2 Effect of multilayer coatings deposition

It has been widely reported [81, 87] that the tribological and corrosion protection performance has been significantly improved with the multilayer deposition of coatings. Hubler et al. [82] pointed out that a reduced grain size and correspondingly large number of interfaces, enhance the hardness and consequently, an improved tribological performance. An enhanced corrosion protection of the steel substrates was demonstrated by Herreanen et al. [87] with the multilayer deposition of TiN/Ti at a deposition temperature of 450°C. They suggested that this improvement was due to the lower porosity of the multilayer coating compared to a single layer coating, since the open columnar microstructure reaching from the coating surface to the substrate will be interrupted by repeated nucleation at the interfaces between sublayers.

The influence of the microstructure formation with multilayer coating deposition at low substrate temperature for decorative coatings applications, however, has not been explored in the literature. Therefore, in an attempt to further improve the corrosion protection and tribological performance of CAE, TiN, decorative coatings, the novel concept of exploring the potential of multi-layer coatings was investigated in the present study. The coating included two multi-layers of Cr/TiN coating which consisted of an interlayer of Cr and a top layer of TiN. A chromium layer was selected due to its ability [71] to form a passive oxide layer with excellent protective properties.

Multilayer coatings were deposited on chromium plated brass substrates and silicon wafers (100) at a bias of −200V, without prior substrate heating. Multilayering was achieved by interrupting the nitrogen flow rate using the mass flow controllers, the sequence being Cr/TiN/Cr/TiN. The coating is referred to as the TM coating in this study. The multilayer coating performance was compared with the bilayer coating of Ti-TiN referred to as TLB coating deposited under similar conditions to that of the TL coating (Table 3.1). Process details for the deposition of TM and TLB coatings are presented in Table 3.5.
Table 3.5 Process parameters adopted during random cathodic arc evaporated multilayer and bilayer TiN coatings on chromium plated brass and silicon substrates.

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>TM</th>
<th>TLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure</td>
<td>$5 \times 10^{-3}$ Pa</td>
<td>$5 \times 10^{-3}$ Pa</td>
</tr>
<tr>
<td>Temperature</td>
<td>140 ºC</td>
<td>140 ºC</td>
</tr>
<tr>
<td><strong>Metal ion etch</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\times 1$ Cr target</td>
<td>$\times 1$ Ti target</td>
</tr>
<tr>
<td>Arc current</td>
<td>80 A</td>
<td>80 A</td>
</tr>
<tr>
<td>Time</td>
<td>8 minutes</td>
<td>12 minutes</td>
</tr>
<tr>
<td>Pressure</td>
<td>$8 \times 10^{-1}$ Pa</td>
<td>$8 \times 10^{-1}$ Pa</td>
</tr>
<tr>
<td>Substrate bias</td>
<td>$-800$V</td>
<td>$-800$V</td>
</tr>
<tr>
<td><strong>TiN Coating</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\times 3$ Ti target</td>
<td>$\times 3$ Ti target</td>
</tr>
<tr>
<td>Arc current</td>
<td>80 A</td>
<td>80 A</td>
</tr>
<tr>
<td>Time</td>
<td>8 minutes</td>
<td>20 minutes</td>
</tr>
<tr>
<td>Pressure</td>
<td>$6 \times 10^{-1}$ Pa</td>
<td>$6 \times 10^{-1}$ Pa</td>
</tr>
<tr>
<td>Substrate bias</td>
<td>$-200$V</td>
<td>$-200$V</td>
</tr>
<tr>
<td><strong>Metal ion etch</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\times 1$ Cr target</td>
<td></td>
</tr>
<tr>
<td>Arc current</td>
<td>80 A</td>
<td></td>
</tr>
<tr>
<td>Time</td>
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<td></td>
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<tr>
<td>Pressure</td>
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<td></td>
</tr>
<tr>
<td>Substrate bias</td>
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<tr>
<td><strong>TiN Coating</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\times 3$ Ti target</td>
<td></td>
</tr>
<tr>
<td>Arc current</td>
<td>80 A</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>8 minutes</td>
<td></td>
</tr>
<tr>
<td>Substrate bias</td>
<td>$-200$V</td>
<td></td>
</tr>
</tbody>
</table>
3.3 TiN Coating characterisation techniques

The characterisation of the coating is an essential prerequisite for achieving improved tribological, decorative and corrosion protection performance of the decorative PVD coated-component. Specifically, comprehensive knowledge about the chemical composition, microstructure and surface morphology of the coating is of great significance in ensuring the functional properties of the decorative, coated-component. This was achieved using various analytical techniques which are described in the following sections.

3.3.1 Chemical composition (X-Ray Photoelectron spectroscopy (XPS))

In the present investigation, it was considered critical to determine the composition of the coating, i.e. the atomic ratio of nitrogen to titanium (N/Ti ratio) since decorative properties (optical reflectivity and colour) of TiN depend primarily upon its composition [38, 88]. Furthermore, corrosion processes are well acknowledged for their complex nature. Bear and Thomas [89] acknowledged the importance of surface analytical techniques to obtain the insights into these processes and consequently, the solution to corrosion problems. Surface sensitive methods such as X-Ray Photoelectron spectroscopy (XPS) provides information about thin layers (of the order of 5-10 nm) which can have large influence on corrosion and therefore, in this investigation, XPS was employed for determination of the surface composition.

XPS involves ionization of the sample surface by bombarding with X-Ray photons of constant energy [90]. The incident photons interact with atoms in the surface region, causing emission of electrons (referred to as photoelectrons) by the photoelectric effect and the corresponding energies of the emitted photoelectrons are measured. The surface of the specimen is bombarded with low energy X-Rays and typically magnesium or aluminium sources are employed.
Consider an X-ray incident upon a surface with energy, $\hbar \nu$, and then the energy of emitted photoelectrons ($E_k$) is given by the following equation [90]

$$E_k = \hbar \nu - E_b - \phi_s$$  \hspace{1cm} (3.1)

where $\hbar \nu$ is the energy of the photon,

$E_b$ – binding energy of the element,

$\phi_s$ – spectrometer work function.

The resulting XPS spectrum is obtained as a plot of the number of detected photoelectrons as a function of their kinetic energy. The binding energy, $E_b$, is characteristic of the element and chemical state of the specimen, whilst the spectrometer work function is constant for the particular system. Since the incident energy, $\hbar \nu$, is known, elemental and chemical bonding information can be determined by calculating the binding energy of the peak in the XPS spectrum. Further, since the mean free path of the electrons in solids is small, the detected electrons originate from the top few atomic layers, which make XPS a unique tool for chemical surface analysis. Quantitative data can be obtained from the assigned elemental peak areas and the sensitivity factor of the element.

In this investigation, the XPS analysis was carried out on a Kratos XSAM800 pci system using a Mg K$_\alpha$ (1253.6 eV) X-ray source operating at 225 W. The pressure of the analysis chamber was lower than $5 \times 10^{-8}$ Pa. All spectra were acquired in the fixed analyser energy mode. Pass energy of 160 eV was applied to wide scans, while 20 eV was used for narrow region scans. For narrow scans, the step size was 0.1 eV, with an instrument resolution of 0.88 eV for Ag 3d$_{5/2}$ from a standard silver sample at 20 eV pass energy. The binding energies were calibrated with reference to C1s at 284.8 eV for adventitious hydrocarbon contamination. The coating analysis area was 6mm × 4mm with a typical analysis depth of 2-5 nm. The coating samples were briefly sputtered using Argon to remove carbon contamination. The sputtering was stopped when the carbon level reduced to an acceptable level.
3.3.2 Surface roughness, morphology, microstructure and preferred orientation

3.3.2.1 Surface roughness

Surface roughness plays a crucial role in decorative coating applications since it influences coating properties. In particular, the roughness of coatings can have considerable effect on decorative properties [44, 48] through its effect on optical properties, such as, optical reflectivity and colour. It can also have significant effect on the corrosion performance [84]. In the present study, the surface roughness of the TiN coatings surface was measured using a Mahr Perthometer Concept surface profilometer (Stylus: FRW-750, traverse length: 5.60 mm).

The well acknowledged parameter used for charactering the roughness of PVD coated surfaces, the arithmetic average roughness, \( R_a \) [25, 91], was also used in the present study. It is calculated as the area between the roughness profile and its mean line, or the integral of the absolute value of roughness profile height \( y \) over the evaluation length \( x \), according to the following equation;

\[
R_a = \frac{1}{L} \int_0^L |y(x)| \, dx
\]

3.3.2.2 Scanning Electron Microscope (SEM)

A high resolution Philips XL 30 SEM was used to study the morphology of the TiN coatings. The beam accelerating voltage was set at 20 kV, while the probe current was fixed at 0.120 \( \mu \)A
3.3.2.3 Focussed ion beam milling (FIB)

The relatively new technique of focused ion beam milling (FIB) was employed to study cross-sections of TiN coatings. The cross-sections were used to observe the microstructure and thickness of coatings, as well as coating defects. The advantage of this technique [90] over a conventional mechanical polishing technique is the ease of preparation of a smooth surface cross-section. FIB system operates [90] in a similar fashion to a SEM except, rather than a beam of electrons, FIB system use a finely focused beam of Gallium ions that can be operated at low beam currents for imaging.

As shown in a schematic of the FIB technique in Figure 3.5, a fine beam of highly energetic (30 keV) gallium ions hits the sample surface and sputters a small amount of material, which leaves the surface as either secondary ions (Io) or neutral atoms (Ao) (Figure 3.5). The primary beam also produces secondary electrons (\(e^-\)). As the primary beam raster on the sample surface, the signal from the sputtered ions or secondary electrons is collected to form an image.
Figure 3.5 A schematic of focused ion beam milling technique.

3.3.2.3.1 Sample preparation for FIB Milling

In the present study a FEI XP200 focussed ion beam miller was used to prepare cross sections of TiN coatings and thin film sections (~100 nm) for examination by transmission electron microscopy (TEM). The methods of sample preparation are discussed [109] in the following sections. Prior to loading the samples (TiN coatings on chromium plated brass coupons) into the FIB, the samples were first ultrasonically cleaned in a bath of acetone before being dried with warm air. The samples were then securely fixed to a specimen holder so that they were electrically conductive. The key steps in the FIB milling process are illustrated in Figure 3.6. In the first step the sample is bombarded with Ga\textsuperscript{+} ions and then in the second step a rectangular section is milled. The sample is then tilted through 45° (step 3), so that the cross section of the TiN coating can be observed.
3.3.2.3.2 TEM sample preparation using FIB Milling

TEM samples were prepared from the TiN coated silicon and electroplated brass coupons. Samples were cut using a diamond cut-off wheel and then mechanically thinned using silicon carbide abrasive paper to dimensions of approximately 2500 μm×1000 μm×50 μm. Figure 3.7 shows the preparation of the TEM specimens. First the area of interest was selected by the FIB imaging. Then, a platinum strip was deposited over the area of interest since the strip protects the underlying coating and provides a reference point for identifying the surface of the sample in subsequent TEM imaging. Rectangular trenches are milled on either side of the platinum strip such that a wall is left between the trenches. This area in the middle is thinned until it is electron transparent to a thickness of about 50 to 120 nm. This technique is sometimes referred to as the ‘H type’ or ‘bar H’ technique [109], since the specimen is shaped like the letter ‘H’ when viewed from above. The sample was then
mounted onto a copper support grid (3 mm diameter) using an adhesive, M-Bond 610 epoxy for TEM study (see Figure 3.8).

Figure 3.7  Preparation of sample using FIB technique for TEM study

Figure 3.8  Sample of the TiN coating for TEM study
3.3.2.4 Transmission electron microscopy (TEM)

The microstructure of the TiN coatings was examined using a Philips TEM with CM200 FE gun. The preparation of TEM samples was done using FIB milling as described in the previous section. The microscope was fitted with an EDAX energy dispersive x-ray spectroscopy system which allowed chemical analysis to be conducted from regions as small as 10 nm in diameter. In addition the microscope had a SIS (Soft Imaging System) CCD camera for direct recording of digital images.

3.3.2.5 X-Ray Diffraction (XRD)

The crystal structure of materials including crystal orientation, strain state, grain size, and defect structure can be determined from the XRD technique [92]. This technique is based on the diffraction of X-rays from crystal planes parallel to the surface of the sample which takes place according to Bragg’s Law. A crystal consists of a variety of crystal planes or atomic planes, all of which have a distinct interplanar spacing or d-spacing. The planes of a crystal are described using planar indices or Miller’s indices or simply as h,k,l in parenthesis, (hkl), with the d-spacing of a given plane denoted as \(d_{hkl}\). Bragg’s Law is satisfied when an incident beam of X-rays is reflected because of constructive interference, hence;

\[
n\lambda = 2d_{hkl} \sin \theta_{hkl}
\]

where \(\theta_{hkl}\) is called the Bragg angle and is measured between the incident beam and the particular crystal planes being considered and \(\lambda\) is the wavelength of the incident X-rays. The diffracted X-rays are detected at an angle of 2\(\theta\), typically called the diffraction angle.

Bragg Brentano XRD was used in this work to determine the preferred orientation of TiN thin coatings. XRD analysis was carried out using a Siemens D500 glancing angle X-ray diffractometer. The spectra were obtained using Co K\(\alpha\) X-ray radiation in the 2\(\theta\) ranges; 40° to 80° with a step size of 0.05°.
3.4 Tribological performance (Abrasive wear)

PVD coatings have been successfully employed for functional coating applications, for example, cutting tool applications, due to their excellent hardness and wear resistance. Classically, these coatings are applied at elevated substrate temperature of 250ºC or higher to achieve good adhesion to the substrate [93]. However, with the introduction of the constraint of low temperature deposition for decorative applications, the effect of microstructure formation on tribological performance has largely been overlooked in the literature. In this thesis, the investigation of tribological performance, in particular, abrasive wear, is considered significant, since decorative coatings applied on consumer parts, such as, doorhandles and knobs etc., are exposed to abrasive wear due to handling. The investigation of tribological properties requires sliding contacts under dry friction conditions, since coatings are exposed to mild abrasive situations.

In the present study, tribological performance of the TiN coatings was evaluated using Taber Abrasor (model 513Q) (see Figure 3.9). Wear is produced under dry friction conditions by the sliding action of two weighted, abrading wheels against a rotating coated panel test sample. In the present study, abrasive wear was evaluated as the wear out of the coating (first exposure of the substrate) at a number of abrasion cycles.

Figure 3.9  A photograph of Taber Abrasor (Model 513Q) used for evaluating tribological performance of the TiN coatings
3.5 Decorative properties (colour and optical reflectivity)

Decorative properties of TiN coatings were determined by using a spectrophotometer, (Minolta CM–500 d-series) Figure 3.10. Optical reflectivity was determined from the reflectivity spectrum as the intensity of the radiation reflected by a sample, at each wavelength. From the measured data, colour appearance from agreed conventions of the Commission International de l’Eclairage (CIE) L*-a*-b* system [36] was determined. CIE is a tricolour system that is based on the fact that any colour can be matched by a suitable mix of the three primary colours. The main parameters L*, a*, and b* are as discussed previously (section 2.1.1.1):

Figure 3.10 A photograph of the Minolta CM–500 d-series spectrophotometer for evaluating decorative properties of the TiN coatings.
3.6 Corrosion studies

In this thesis, the aim of the corrosion studies was to investigate the inherent corrosion properties of the TiN coatings and the corrosion protection obtained when these coatings are deposited on the active substrates used in the decorative coating industry, such as brass and high pressure die-cast zinc. A fundamental understanding of such properties is of significant importance, in order to better design and select such coatings for application in the harsher, longer term environments experienced by door furniture and tapware. In addition, corrosion of the substrate beneath the coating is not only critical to the substrate but also affects the adhesion of the coating to the substrate. Consequently, the corrosion products formed under the coating may have a detrimental effect on the visual appearance.

AC and DC electrochemical techniques were employed in this research to investigate the corrosion behaviour of TiN coatings. The coatings were deposited on an inert substrate (silicon and glass), as well as on active substrates (chromium plated high pressure die-cast zinc and chromium plated brass). The description of the electrochemical techniques, along with the electrochemical cell and design of test electrodes employed is presented in the following sections.

3.6.1 Galvanic corrosion studies

This investigation included a study of some of the detailed aspects of the galvanic corrosion phenomenon. One objective was to investigate if the TiN coating is more or less corrosion resistant than the substrate and if the rate of galvanic corrosion is substantial. For this purpose, the investigation included a study of the behaviour of TiN coatings when in galvanic contact with a range of substrates used in the decorative coating industry. Although the galvanic corrosion is dictated by the corrosion potential differences [58] between the materials to be coupled, such studies of electrode potentials may only indicate the driving force for this type of corrosion. The actual rate of the galvanic process can be obtained by measuring the galvanic corrosion current.
3.6.1.1 Galvanic corrosion studies using ZRA

Galvanic corrosion is the accelerated corrosion of a metal or an alloy caused by electrical contact with a more noble, electronically conducting material while exposed to a corrosive electrolyte. Galvanic current flows between two dissimilar metals electrically coupled in the same electrolyte. A simple ammeter placed between anode and cathode does not accurately measure galvanic current occurring under short circuit conditions due to a potential drop with its finite resistance. As a result, anode and cathode potentials will be separated by the ammeter potential drop and the measured galvanic current will be less than the true coupled current. For this reason a zero resistance ammeter (ZRA) [58] is widely used.

Figure 3.11 shows a typical circuit diagram for a ZRA based on a simple operational amplifier. In ZRA, the very high input impedance of the operational amplifier supplies feedback current to maintain a zero potential difference between the two metals (anode and cathode forming a short circuit) of the galvanic couple. The magnitude of the feedback current is identical to that flowing in the galvanic cell. It is effectively the same current that would flow if the two electrodes were joined by a zero resistance wire and hence is termed as ZRA. The circuit illustrated shows one electrode is connected to the non-inverting terminal of the amplifier whilst the other is connected to the inverting terminal. These electrodes are connected by an external feedback resistor, \( R_f \). There is zero potential difference between the cathode and the anode and the current is \( I_g \) (galvanic current) since it represents the galvanic coupling current when the potential difference is zero between the two electrodes, i.e. in the true short circuit condition. Galvanic contact between a bare metal (zinc, nickel or copper) and a TiN coating on a glass substrate was established by short circuiting them through the use of a ZRA. For such a configuration

\[
I_g = -\frac{V_o}{R_f} \quad (3.6.1)
\]

where \( I_g \) is the galvanic current, \( V_o \) is the output voltage of the operational amplifier and \( R_f \) is the feedback resistor.
3.6.1.2 Electrochemical cell and test electrodes

The electrochemical cell (100 ml beaker) consisted of the galvanic couple immersed in an electrolyte of 0.5 M NaCl solution (prepared from AR grade chemicals and de-ionised water). The galvanic couple was connected to a ZRA, constructed in this laboratory. Sodium chloride solution with 0.5M concentration (pH 6), which approximates the chemical composition of perspiration [63], as a relevant electrolyte medium was used in this study since the coatings on door furniture and taps, are frequently exposed to human perspiration. Equal exposed areas (1cm² each) of anode (bare metal (either zinc or copper or nickel or brass foil) and cathode (TiN coatings on inert substrates) were tested with a separating distance of 3 cm between them. Electrode potentials were measured with respect to the Hg/Hg₂Cl₂/0.5M NaCl reference electrode (CE); the potential of this reference system is 86mV relative to the saturated calomel electrode. The electrolyte used in the reference electrode was the same as in test solution to avoid liquid junction potentials.
Test TiN electrodes were prepared from the TiN coating specimen deposited on glass substrates. A wire was attached to the back face of each specimen by using silver loaded conducting epoxy (RS Components, UK) for electrical contact, followed by masking the rest of the sample and the epoxy contact with araldite, as illustrated in the schematic diagram, Figure 3.9. Tests were performed for periods ranging between 3 to 4 days. Measured galvanic currents were monitored as a function of time. The data were processed and stored by a computerized data acquisition system via an analog/digital data acquisition system and associated software (Picolog Technology Ltd., UK, 16 bit). With this DAQ configuration, galvanic currents of four systems could be simultaneously monitored.

All studies were performed in duplicate. The polarity of the electrodes was established by electrode potential measurements before coupling via the ZRA. Cell connections were made using a bare metal (either zinc or copper or nickel or brass foil) as an anode and a TiN coating as a cathode. The specimens were cleaned with distilled water, and acetone prior to their exposure to the test solution. The pH of the test solution was measured at room temperature both before and after each experiment. At the conclusion of each test, the specimen was cleaned with distilled water, and acetone. The cleaned specimen was visually examined to evaluate the extent of damage in both electrodes resulting from galvanic interactions.
3.6.2 Measurement of corrosion potential

The corrosion potential of the TiN samples was measured with respect to a reference electrode in the sample cell, as illustrated in Figure 3.13. The potential measurements were recorded with a data acquisition (DAQ) Picolog, interface and associated software (Pico Technology Ltd, UK). The cell potential measured is called a mixed or corrosion or open circuit potential, which lies between the half cell potentials of the anodic and cathodic reactions occurring on that electrode. These reactions are usually metal dissolution (TiN corrosion in this case) and oxygen reduction and/or water reduction (hydrogen evolution), respectively.

The measurement of variation of corrosion potential or open circuit potential of TiN coated inert substrates (glass and silicon) as a function of test duration (a period of 20 days) was carried out. The study was of considerable significance to determining whether the TiN was active or noble with respect to the substrates used in this study. In addition, measurement of the corrosion potential of TiN coatings on active substrates, such as
electroplated brass and zinc was carried out, since such a study may provide an indication of penetration of electrolyte through defects in the coating with exposure of the substrate.

Figure 3.13 Schematic diagram of electrochemical cell for measurement of corrosion potential of TiN

3.6.2.1 Electrochemical cell and test electrode

The electrochemical cell comprised of TiN electrodes (10 mm ×10 mm area) covered with an epoxy (Figure 3.14), which served as a working electrode (i.e. WE), calomel electrode (Hg/Hg₂Cl₂/0.5M NaCl) as a reference electrodes, and a platinum mesh as a counter electrode was employed in this present study. All studies were performed in duplicate. The electrolyte used was 0.5 M NaCl prepared from AR grade chemicals and deionised water. The potential measurements were recorded as described in section 3.6.2.

The TiN electrodes for measurement of corrosion potential were prepared from TiN coated substrates. A flag type design of TiN coated substrates was adopted, with exposure of a planar face of selected area (Figure 3.14). Electrical contact to the TiN coating was made at the back face of the electrode with the copper wire by using silver loaded, epoxy adhesive (RS Components, UK), and the whole contact in turn was coated with non-conducting
epoxy, Araldite. The electrical contact was further sealed (epoxy) in glass tubing to completely eliminate possible exposure of the contact to electrolyte and to provide stronger physical support to the contact.

![Schematic diagram of the TiN electrodes used for corrosion studies](image)

Figure 3.14  Schematic diagram of the TiN electrodes used for corrosion studies

### 3.6.3 Electrochemical polarisation studies

Electrochemical polarization methods used in the present study included galvanostatic (controlled current) and potentiodynamic (controlled potential). The former technique was employed to determine exchange current densities of water and oxygen reduction reactions on the TiN coating surface. This study was of particular importance since the magnitude of these current densities may determine the rate of galvanic corrosion and hence, the severity of galvanic corrosion between the TiN coating and underlying substrate. The latter technique was employed to study the electrochemistry of the TiN coating itself and also when deposited on the active substrates the electrochemistry of the TiN /substrate system. The two techniques are described below.
3.6.3.1 Galvanostatic technique

Galvanostatic (controlled current) conditions were used to plot steady state polarisation curves. The galvanostatic circuit used consisted of two main parts: potential measurement and the circuit for current control. The potential of the working electrode is measured with respect to a reference electrode with a voltmeter. Within the current control circuit, a constant current is supplied between the working electrode and an inert counter electrode of platinum. The corresponding block diagram is presented in Figure 3.15.

In the present investigation, the galvanostatic condition was achieved using a constant current source constructed in this laboratory (1 µA to 3A). The current was monitored directly with a 0-5A DC ammeter with sensitivity of ±0.1mA. Within the potential measurement circuit, a high impedance ($10^9 \, \Omega$) digital volt meter (DVM) with sensitivity of ±0.1mV was utilized to measure the specimen potential versus that of Hg/HgCl$_2$/0.5MNaCl reference electrode.

Figure 3.15 A circuit block diagram for galvanostatic polarisation
3.6.3.1.1 Electrochemical cell and test electrodes

Galvanostatic studies were conducted in a conventional, 3-electrode cell using a Pt coil counter electrode separated by a glass frit from the working electrode TiN/Si coating and electrolyte. All potentials were measured and reported with respect to the Hg/Hg$_2$Cl$_2$/0.5M NaCl reference electrode (CE). All solutions were made in high purity (Mill-Q) water using AR grade chemicals. The electrolyte used was 0.5M NaCl with pH 6. The flag type design of the TiN coated electrode was adopted for the working electrode as described in section 3.6.2.1.

Galvanostatic experiments were conducted in NaCl solution with varying pH. The electrolyte used was 0.5 M NaCl prepared from AR grade chemicals and high purity (Mill-Q) water. The pH of the solution was varied from 1 to 6 by adding drops of HCl to the chloride solution. In all experiments, current-potential plots were recorded on two silicon based TiN electrodes (area = 0.06 and 0.05 cm$^2$), each set of current-potential data being recorded twice.

3.6.3.2 Potentiodynamic polarisation technique

The potentiodynamic polarisation technique consists of the application of positive and/or negative going potentials with respect to the corrosion potential of the working electrode, with the resulting changes in current being monitored. Further, the potentiodynamic scan rate must be slow enough to ensure linear behaviour. The corresponding circuit block diagram is presented in Figure 3.16. The high input impedance voltmeter was employed to measure the potential of the working electrode with respect to the reference electrode. The current flowing between the counter and working electrodes was measured as a potential drop across a 100 $\Omega$ precision resistor ($\pm$ 0.1%). Polarisation curves (current–potential) for the silicon based, TiN electrodes were recorded using a potentiostat (JB Thomson, UK) with voltage input at a designated scan rate from an AMEL 567 function generator. The potential and current ranges of the potentiostat are $\pm$ 2V and 100$\mu$A to 1A, respectively. In
addition, a X-Y recorder (Rikadenki, RDK, UK) (X axis-potential and Y axis- current) was used for automatic recording of polarization curves.

![Circuit Block Diagram for Potentiostatic Polarisation](image)

Figure 3.16 A circuit block diagram for potentiostatic polarisation.

### 3.6.3.2.1 Electrochemical cell and test electrodes

Potentiodynamic studies were conducted in a conventional three-electrode, water-jacketed cell (temperature controlled at 25°C) using a Pt coil counter electrode separated by a glass frit from the working electrode electrolyte. All potentials were measured and reported with respect to the Hg/Hg$_2$Cl$_2$/0.5M NaCl reference electrode (CE). All solutions were made in high purity (Mil-Q) water using AR grade chemicals. The electrolyte used was 0.5M NaCl. A flag type design of TiN coated electrode with areas of electrodes varying from 0.25 cm$^2$ to 1 cm$^2$, was adopted for the working electrode as described in section 3.6.2.1. Finally, a nitrogen purge for a period of 30 minutes was used to prevent air access to the solution and to remove oxygen from solution if required. In all, current-potential plots of TiN coating on inert substrates (glass and silicon) as well as the active substrates were recorded in duplicates for each substrate using a fresh electrode in each case.
3.6.4 Electrochemical impedance spectroscopy (EIS) studies

With the EIS technique, the impedance of an electrochemical system is studied as a function of the frequency of an applied ac signal. In the present investigation, EIS studies were carried out to further reveal the electrochemistry of the TiN system at various potentials relevant to the potentiodynamic polarisation plots of the TiN system, both in the presence and absence of oxygen. The impedance data was obtained using EG&G Princeton Applied Research potentiostat (PAR 273) and lock in amplifier (model 5210). The impedance measurements in all cases were carried out over a frequency range of 100 kHz to 1 mHz using a sinusoidal voltage of 5 mV amplitude.

3.6.4.1 Electrochemical cell and test electrodes

The same three-electrode cell arrangement that was used in the electrochemical experiments (section 3.6.2.1) was used in the EIS studies. The working electrode was a TiN coated silicon substrate prepared as described in section 3.6.2.2. The exposed surface of the test-coated specimen was 0.06 cm². The counter electrode was platinum mesh with a surface area considerably greater than that of the working electrode. The reference electrode was Hg/Hg₂Cl₂/0.5M NaCl. The volume of the test solution (0.5M NaCl) inside the cell was 150 ml.
CHAPTER 4

Results & Discussion

Characterisation and fundamental corrosion studies of TiN, decorative coatings deposited by the partial filtered arc deposition system

In this chapter results are presented which relate to a fundamental study of the corrosion properties of TiN coatings and their suitability for corrosion protection on typical substrates used in the decorative coating industry, such as die cast zinc and brass. The potential problem of galvanic corrosion due to the deposition of TiN coatings on these substrates is addressed. Furthermore, as presented in Chapter 2, most reported studies regarding the protective ability of TiN coatings were based on the composite performance of TiN coatings on active, metal substrates. Such studies may well complicate the observed electrochemical behaviour of the TiN coating due to defects or poor adhesion, with exposure of the underlying, electrochemically active substrate to the electrolyte. There have been few studies of the electrochemistry of TiN itself and these have been primarily conducted in acid solution [63,94-96]. In this study, the TiN coating is formed on electrochemically inert substrates of silicon or glass and the electrochemistry studied in the more relevant chloride medium.

The TiN coatings were deposited using the relatively novel technique of partial filtered arc deposition (PFAD) system. This filtration mode was selected because of its potential [18] to reduce defects in the form of macroparticles of the arc deposited TiN coatings. This result was verified by carrying out a comparative morphological study with unfiltered or random cathodic arc evaporated (CAE) coating. The TiN coatings were deposited at a lower temperature using the PFAD system, on inert substrates of silicon and glass as well as active substrates of chromium plated brass and chromium plated high pressure die-cast zinc. They were characterised in terms of surface morphology, thickness, roughness, and
optical reflectivity of the coatings. It was observed that the substrate temperature at the end of deposition cycle was 50°C. On the other hand, CAE TiN coatings were also deposited at a temperature of 200°C on chromium plated brass and silicon substrates.

4.1 TiN coating characterisation
4.1.1 Surface morphology and roughness

TiN coatings on silicon substrates were deposited at an arc current of 120 A at a nitrogen pressure of 0.6 Pa with no substrate heating and no substrate bias. A SEM fractograph of a PFAD TiN coated silicon substrate is shown in Figure 4.1. This shows a single layer TiN coating of thickness about 0.8 µm. A deposition rate of 2.4 µm/hr was obtained with the PFAD system under these conditions. The effectiveness of partial filtration is shown in the surface morphology of TiN coating deposited on silicon substrates (Figures 4.2(a) and 4.2(b)). They show a smooth surface with very few macroparticles/pinholes relative to CAE. The lower micrographs (Figures 4.2(c) and 4.2(d)), show the surface of the TiN coating deposited on silicon substrates, using unfiltered or random cathodic arc evaporation (CAE) system. The surface consists of micro sized macroparticles ranging in the size from 1µm to 10 µm. A comparison of the two sets of micrographs shows a substantial reduction in macroparticle content in the TiN coating deposited by the PFAD system.

In general, the defects such as pores, pinholes, pitting type defects, and macroparticles in the unfiltered CAE TiN coatings had a larger concentration than the PFAD TiN coatings. This increase in the size and number of defects therefore, can be anticipated to have a direct influence on the surface roughness of the coatings. An average surface roughness of the TiN coating surface over an area of 500µm × 500µm was measured using a TENCOR P10 surface profilometer in the present study. The average surface roughness, Ra, of 0.08 µm was obtained for the PFAD TiN coatings compared to a Ra of 0.63 µm for the CAE TiN coating. The roughness results clearly correlate to the SEM observations and reinforce the fact that there is a significant reduction in macroparticle content for PFAD TiN coatings.
similar trend in the surface roughness was reported [25] for TiN CAE coatings although these coatings were deposited at much higher substrate temperature of 450ºC.

Figure 4.1  SEM fractographic cross-section of TiN coating deposited by PFAD system, indicating a coating thickness of 0.8 µm.
Figure 4.2  Scanning electron micrographs showing the surface morphology and macroparticle content of the as deposited (a), and (b) TiN-PFAD coating, (c) and (d) random CAE TiN coating

4.1.2 Optical reflectivity

The optical reflectivity of TiN is of a great significance in decorative applications with its gold like appearance. Figure 4.3 shows the optical reflectivity spectra of the TiN coatings deposited using PFAD and CAE. The curve indicates a higher reflectance of the PFAD TiN coating with the maximum reflectance of about 0.79 in the infrared region as compared to 0.73 for the CAE coating. The reflectivity is relatively high at the higher end of the visible region. The reflectivity starts to drop in the blue-green region (500 nm wavelength) and approaches 15 in the violet region (400 nm wavelength). The difference in the optical reflectivity can be ascribed to the smooth morphology of the PFAD coating due to reduced roughness in comparison to CAE TiN coating. The findings are in agreement with the general view [44, 48] that the surface morphology does affect the optical reflectivity.
Figure 4.3  Comparison of optical reflectivity of TiN/Cr/brass coatings deposited using the PFAD and CAE systems of deposition.
4.2 Corrosion performance of TiN PFAD coating

4.2.1 Electrochemical polarisation studies

Figure 4.4 shows the observed variation in open circuit potential or corrosion potential ($V_{\text{corr}}$) with time for three electrode samples (all TiN coatings on glass substrate) in 0.5 M NaCl solution. As indicated there are small differences between the samples, but there is a general trend to more negative potentials with time. The difference in potential values may well be due to small differences in the reference electrodes as three different reference electrodes were used for three working electrodes. A similar trend has been observed previously in sulphate-based electrolytes [63], although over a much shorter time period (1 hour), with potential becoming constant after approximately 25 minutes. It should be noted that corrosion potential is a mixed potential consisting of the cathodic reactions accompanying metal dissolution (TiN corrosion in this case) these usually being oxygen reduction and/or water reduction (hydrogen evolution).

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \text{ in neutral or alkaline solution} \]

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \text{ in neutral or alkaline solution} \]

The equilibrium potential for the hydrogen evolution reaction and oxygen reduction reaction (air atmosphere) in 0.5M NaCl (pH = 6) is $-0.652$V and $0.573$V, respectively vs the Hg/Hg$_2$Cl$_2$/0.5M NaCl reference. Consequently, at the corrosion potentials displayed in Figure 4.4, the supporting cathodic reaction is most likely oxygen reduction, the hydrogen evolution reaction being thermodynamically unfavourable at potentials more positive than the equilibrium potential. As expected in such a situation, the corrosion potential was observed to become more negative as oxygen is removed from solution by nitrogen purging, consistent with a decrease in the rate of oxygen reduction and with decrease in the concentration of dissolved oxygen in solution. This qualitative observation indicates that the rate of oxygen reduction is low on TiN because, at the corrosion potential displayed in Figure 4.4 ($\sim-120$mV), the overpotential for oxygen reduction reaction ($V_{\text{corr}} - V_{\text{eO}_2, \text{H}_2\text{O}/\text{OH}^-}$) is very high($\sim-0.7$V).
Figure 4.4  Variation of corrosion potential of TiN/glass samples with time in 0.5 M NaCl solution

The observed trend towards more negative corrosion potential over a relatively long time period could be due to a slow chemical reaction taking place on the surface. This reaction may include slow dissolution of an oxide film on the surface, with consequent, enhanced corrosion of TiN, or the slow formation of an oxide film or mixed oxynitride film on the surface that is a poor catalyst for the oxygen reduction reaction.

To investigate the possibility of passivation of the TiN coating a potentiodynamic study was carried out. Figure 4.5 shows a typical cyclic voltammogram (potentiodynamic passivation plot) for TiN/Si in 0.5M NaCl in the absence of oxygen commencing at \(-0.85\) V/CE. In this investigation, small area electrodes were employed in order to avoid large current densities. The scan was recorded using X-Y recorder (Rikadenki, RDK, UK) (X axis-potential and Y axis- current). The major electrochemical feature of TiN in sodium chloride solution is the single anodic peak that occurs at a sharply defined potential of
around +50mV on the anodic scan. Hydrogen evolution, as indicated by an increase in the cathodic baseline current, starts to occur around −0.7V. Also, as indicated in the figure, no further anodic current peaks, other than the one shown, or any significant increase in anodic current occurs up to potentials of +1.5 V, indicating that TiN is a poor catalyst for water oxidation (oxygen evolution). The electrochemistry of TiN appears relatively simple, with only one surface reaction occurring over a very wide potential range. This result is consistent with the recognized chemical inertness of TiN in aqueous solution [63]. In order to validate the presence of a TiN surface oxidation reaction, a variation in the anodic peak current (Ip) with the potential scan rate (ν) was recorded and is presented in Figure 4.6.

Figure 4.5 A typical potentiodynamic plot for a TiN/Si sample in 0.5M NaCl, unstirred solution, with an electrode area of 0.25cm² and potential scan rate of 1mVs⁻¹.
Figure 4.6 Dependence of anodic peak current for TiN oxidation on potential scan rate in 0.5 M NaCl, unstirred solution, with an electrode area of 0.06 cm²

The slope of the line in Figure 4.6 is 0.63 which suggests that $I_p \propto \nu^{2/3}$, this variation being characteristic of a surface reaction where the reaction product forms a current inhibiting, surface layer [97]. Further indication of a surface reaction is given by the observation that the anodic current peak is absent if the direction of the potential scan is reversed on the cathodic going scan from a potential insufficient to reduce the passive film, e.g. $-0.1$V. The same anodic peak has been observed to form in sulphuric acid solution, however, in contrast to that formed in this study in chloride solution; the anodic surface film formed in acid is stable, with no subsequent reduction peak being observed on sweeping the potential negative after film formation [63]. The composite voltammogram shown in Figure 4.5 clearly shows that the anodic film is readily reduced in chloride solution as indicated by the reduction peak at $-0.2$V. Again previous XPS [98, 99] and Auger [63] studies on the film formed in sulphate solution indicate that the anodic (oxidation) process corresponds to either the formation of a mixed oxynitride of titanium, or TiO₂ formed on top of the TiN film via an oxynitride intermediate. Capacitance and photoelectrochemical studies of the oxidized surface formed in sulphuric acid [63] suggest that the oxidized surface is semiconducting, this classification being consistent with the observation in Figure 4.5 that the
oxidized surface is not completely current blocking, as the post peak current is considerable and does not drop to zero.

The presence of an electrochemically formed, “passivation” film offers, by itself, a potential strategy for decreasing the rate of any unwanted galvanic corrosion arising from the coupling of TiN with an active substrate. However unfortunately, as indicated in Figure 4.5, the film is relatively unstable in chloride solution being easily reduced. Comparison of the potentials of the reduction process with those of the corrosion potentials in Figure 4.4 indicates that the passive film is most likely unstable at the corrosion potentials pertaining in 0.5 M NaCl.

4.2.2 Galvanic corrosion studies

The occurrence of galvanic corrosion between an active substrate and the TiN coating was investigated by measurement of galvanic current density using the ZRA technique. The effect of various parameters such as electrolyte stirring and electrode area on the galvanic current was also studied.

All studies were performed in duplicate with fresh TiN–substrate couples each time and the current-time plots presented here are typical of the plots obtained. The uncoupled corrosion potentials of typical substrates such as zinc, copper and nickel in 0.5M NaCl are listed in Table 4.1. Comparison with typical, open circuit potentials for TiN (Figure 4.4) indicate that TiN is noble with respect to Zn, Cu and Ni, hence indicating the potential for galvanic corrosion when TiN is coated onto these substrates. Although such comparative studies of potentials indicate a possible galvanic corrosion problem, they provide no indication of the actual rate of the galvanic process; this parameter can only be obtained by measuring the galvanic corrosion current \( I_g \) itself. The galvanic corrosion current will in turn be determined by the slower of the two primary steps: dissolution of the corroding substrate or the rate of the cathodic reaction, usually water reduction or oxygen reduction, occurring on the more noble surface (TiN in this case). Also, other reactions occurring on the surface of
the corroding metal, that may not be apparent over short time intervals, can influence the actual rate of the galvanic process and therefore its significance in determining the enhanced rate of corrosion of the active material as a result of galvanic coupling with the TiN coating.

It can be seen further from Table 4.1 that coupling the substrate to TiN results in the short circuit potential of the couple being more positive than the open circuit or corrosion potential of the substrate. Consequently the rate of the fundamental corrosion reaction of the substrate \((M_{(s)} \rightarrow M^{n+} + ne (M))\) will be increased in the coupled state relative to that for the freely corroding or uncoupled substrate. Using the data in Table 4.1, the overpotentials \((\eta = V_{sc} - V_{corr})\) for zinc, copper, nickel and brass are 114 mV, 34 mV, 12 mV, and 40mV, respectively. It is therefore expected that galvanic current to be higher for zinc than copper or nickel which is in agreement with the galvanic current variation presented (at least initially) in Figures 4.7 (a) and 4.7(b) in 0.5M NaCl recorded using a zero resistance ammeter. Similarly, the more negative overpotential for oxygen reduction reaction \((V_{sc} - V_c, \text{ where } V_c = 0.573V \text{ at pH 6 for } O_2 + 2H_2O + 4e^- \rightarrow 4OH^-)\) on Zn-TiN (−1.523V) compared to the less negative, overpotential observed for the Cu-TiN (−0.783 V) and Ni-TiN (−0.731 V), indicating a possible higher galvanic current for the Zn couple, consistent with the galvanic current variation presented (at least initially) in Figures 4.7. The observed variation for the Ni-TiN couple was similar to that for Cu-TiN, although the current density magnitude was higher. The final, steady state, galvanic corrosion current density for all three couples is listed in Table 4.1. Both the substrate and TiN/glass electrodes used were 1cm² in geometric area.
Table 4.1  Corrosion potential ($V_{corr}$) of relevant substrates, short circuit potentials ($V_{sc}$) of substrate –TiN/glass couples and final galvanic corrosion current density after 3 days for each couple in 0.5M NaCl

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$V_{corr}$ (mV/CE)</th>
<th>$V_{sc}$ (mV/CE)</th>
<th>$i_g$ ($\mu$A cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>-1064</td>
<td>-950</td>
<td>40.0</td>
</tr>
<tr>
<td>Cu</td>
<td>-246</td>
<td>-210</td>
<td>5.8</td>
</tr>
<tr>
<td>Ni</td>
<td>-170</td>
<td>-158</td>
<td>38.0</td>
</tr>
<tr>
<td>Brass</td>
<td>-279</td>
<td>-245</td>
<td>13</td>
</tr>
</tbody>
</table>

Figure 4.7  Galvanic current variation with time for (a)Cu-TiN/glass couple, in 0.5M NaCl, unstirred solution, with electrode areas of 1cm²
It can be further noticed that in both the copper and nickel cases, the magnitude of the galvanic current is independent of electrolyte stirring, demonstrating that the rate determining step is under charge transfer not mass transport control. In contrast, the galvanic current for the Zn-TiN couple is sensitive to electrolyte agitation or stirring, increasing markedly from 390 to 480 µA cm\(^{-2}\), with increase electrolyte stirring (magnetic stirrer) by a factor of ~ 1.5. Dependence of galvanic corrosion current on solution stirring is typical of a galvanic corrosion process where oxygen diffusion is the rate determining step in the oxygen reduction process [10] because of the relatively low concentration of dissolved oxygen in solution open to the atmosphere, 2.6 \times 10^{-4} M at 25 °C [102]. The independence of the galvanic corrosion current on electrolyte agitation for the copper and nickel substrates can be rationalized in terms of the short circuit potentials given in Table 4.1. The short circuit potential is obtained by short circuiting two electrodes and measuring their potential. At the more positive potentials shown for the Cu and Ni, the overpotential for oxygen reduction is much lower (−0.783 V for Cu and −0.731 V for Ni) than for Zn, hence it is more likely that the rate of oxygen reduction is occurring under charge transfer.
control and typically independent of mass transfer process arising due to stirring. In contrast, the far more negative short circuit potential observed for the TiN-Zn couple (−0.950V) and consequent much larger overpotential for oxygen reduction on TiN (−1.523V), is more likely to result in oxygen reduction being the rate determining step, with consequent enhancement of reaction rate.

The effect of TiN coating area (geometric area) on the galvanic corrosion current density was studied in 0.5 M NaCl solution and is depicted in Table 4.2. The substrates Cu, Ni and Zn were 1 cm² in geometric area. The data showed a significant variation in galvanic current with TiN electrode area for the TiN-Zn couple. The galvanic current of the TiN-Zn system increased approximately 2.5 times with increase in TiN electrode geometric area of approximately 5 times; whereas the TiN electrode area change did not affect galvanic current density for the TiN-Ni and TiN-Cu couples. The effect of the cathode and anode areas on the galvanic corrosion depends on the type of control over the system. It is well documented [58,61] that variation in the cathodic area will change the total amount of corrosion when the galvanic system is under cathodic control, for example, when oxygen reduction reaction is the rate limiting step for the galvanic corrosion. The results obtained in this investigation indicated that the galvanic corrosion of TiN is mainly cathodically controlled for zinc based systems. In contrast the results obtained for TiN-Ni and TiN-Cu systems indicated that the reduction reaction can be under anodic control and a consequence of the galvanic corrosion of TiN will be anodic dissolution of copper or nickel.
Table 4.2  Effect of TiN/glass electrode (cathode) areas on galvanic corrosion current density in 0.5M NaCl

<table>
<thead>
<tr>
<th>Area of cathode (cm²)</th>
<th>( i_g ) (µA/cm²) (TiN-Cu) couple</th>
<th>( i_g ) (µA/cm²) (TiN-Zn) couple</th>
<th>( i_g ) (µA/cm²) (TiN-Ni) couple</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.41</td>
<td>30.98</td>
<td>0.61</td>
</tr>
<tr>
<td>2</td>
<td>1.42</td>
<td>46.97</td>
<td>0.63</td>
</tr>
<tr>
<td>3</td>
<td>1.44</td>
<td>52.09</td>
<td>0.64</td>
</tr>
<tr>
<td>4</td>
<td>1.47</td>
<td>65.30</td>
<td>0.72</td>
</tr>
<tr>
<td>5</td>
<td>1.50</td>
<td>76.81</td>
<td>0.74</td>
</tr>
</tbody>
</table>

The initial, galvanic corrosion currents shown in Figure 4.7(b) for the Zn-TiN couple indicate the potentially greater severity of galvanic corrosion for zinc, as predicted previously from the short circuit and open circuit potentials for each metal. However, the sudden and sharp decline in galvanic corrosion current to less than 40 µA cm\(^{-2}\) for the zinc substrate after 60 hours illustrates the necessity of recording galvanic corrosion current over long periods of time before reaching conclusions about the severity or significance of galvanic corrosion. This change is typical of the passivation of the zinc surface [103] and does correspond to the observed formation of a white film on the zinc surface. While Pourbaix [103] does not show zinc passivating at pH 6 (passivates between pH 8-10.5 in pure water), the occurrence of oxygen reduction on the TiN may well increase the solution pH, from initial pH of 6, at the zinc surface and hence allow passivation at lower bulk pH. Galvanic corrosion of the underlying substrate will arise where the overlay TiN coating is porous or contains defects, which is usually the case. Thick layers of passivating products formed on the underlying substrate surface at the base of pores, as in the case of zinc, will tend to block pores at the pore base, thus assisting to protect the more active substrate.

While TiN is more noble with respect to Zn, Cu and Ni, as indicated by the various corrosion potentials (Table 4.1 and Figure 4.4), the actual rate of galvanic corrosion will
depend on the slower reaction of the galvanic couple, which is usually the oxygen reduction on the more noble coating. Hence the influence of TiN in causing galvanic corrosion of any underlying substrate will depend on the rate of water reduction (hydrogen evolution) or oxygen reduction or both on the TiN. If TiN is a poor electrocatalyst for both of these reactions then galvanic corrosion will not be significant. For this purpose, galvanostatic (controlled current) conditions were used to plot steady state polarisation curves for the water and oxygen reduction reactions on TiN. From this study exchange current densities were determined for these reactions. In all, current-potential plots were recorded on two, silicon based, TiN electrodes (area = 0.06 and 0.05 cm²), each set of current-potential data being recorded twice.

To study water reduction alone oxygen was first removed from solution via purging with high purity nitrogen. A typical, steady state current-potential plot for water reduction or hydrogen evolution in 0.5M NaCl solution is shown in Figure 4.8(a), the working electrode area being 0.06cm². A clearly defined Tafel region is apparent at potentials more negative than –1600mV. The exchange current density \( i_0 \) for the hydrogen evolution reaction is determined by extrapolation of the Tafel region back to the equilibrium potential for the hydrogen evolution (water reduction) reaction at the pH of the solution concerned. The exchange current density for water reduction or hydrogen evolution was also determined at several pH values in 0.5M NaCl, the pH being varied by the addition of HCl to the sodium chloride solution.

Table 4.3 lists the average exchange current density values observed for water reduction or the hydrogen evolution reaction on TiN at each pH. Thus in 0.5 M NaCl solution, the exchange current density for water reduction on TiN is around \( 10^{-2} \) \( \mu \)A cm\(^{-2} \) which, when compared with that of Pt and Hg in 1M H\(_2\)SO\(_4\), \( 10^{-2.9} \) and \( 10^{-6.3} \) \( \mu \)A cm\(^{-2} \) respectively [104], indicates the reaction rate to be neither very fast or very slow.

A typical, steady state, current-potential plot for oxygen reduction is shown in Figure 4.8(b) and was carried out under oxygen purge. In deriving such a plot the raw current data will contain, at the more negative potentials, a contribution from water reduction. Thus, on the
assumption that the two partial currents are additive, that due to oxygen reduction is obtained by subtraction of the water reduction component from the total current. As anticipated for oxygen reduction a distinct, limiting current is observed at potentials above –900mV, indicating that oxygen reduction is occurring under mass transport control. The current observed at potentials negative of the limiting current region is due to water reduction. The approximate exchange current density values indicate that the rate of oxygen reduction on TiN is extremely slow which is also evidenced by the very high overpotential (≈−0.7 V) required for oxygen reduction on TiN.

Table 4.3 also displays approximate corrosion current densities for TiN corrosion in 0.5M NaCl solution and in sodium chloride solution at more acidic pH values. These values have been determined by extrapolation of the oxygen reduction current –potential data (Figure 4.8) back to the corrosion potential as measured in the various media. The approximate values of current densities indicate a very slow rate of corrosion (nA cm⁻²) for TiN in sodium chloride solution which is also evidenced by the very high overpotential required for oxygen reduction on TiN. It should be noted that values of exchange current density for oxygen reduction are approximate only since currents for oxygen reduction at each potential were not corrected for the mass transport component.
Figure 4.8  Steady state polarization plot for (a) water reduction (nitrogen purge), (b) oxygen reduction (oxygen purge) on TiN/Si in 0.5M NaCl, unstrirred solution with nitrogen purge, with electrode area of 0.06 cm$^2$. 

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Table 4.3  Variation of exchange current density for water reduction and oxygen reduction and variation in corrosion current density for titanium nitride (TiN/Si) with solution pH in sodium chloride solution

<table>
<thead>
<tr>
<th>pH</th>
<th>Exchange current density for water reduction (µA cm(^{-2}))</th>
<th>Exchange current density for oxygen reduction (pO(_2) = 1atm) (pA cm(^{-2}))</th>
<th>Corrosion current density for TiN (nA cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>43 (± 2)</td>
<td>0.69 (± 0.1)</td>
<td>39 (± 1)</td>
</tr>
<tr>
<td>2.3</td>
<td>0.89 (± 0.05)</td>
<td>349 (± 48)</td>
<td>636(± 3)</td>
</tr>
<tr>
<td>3.2</td>
<td>0.08 (± 0.02)</td>
<td>1285 (± 35)</td>
<td>433(± 7)</td>
</tr>
<tr>
<td>6.0</td>
<td>0.0090 (± 0.0001)</td>
<td>665 (± 15)</td>
<td>107 (± 2)</td>
</tr>
</tbody>
</table>
4.2.3 EIS studies

The cyclic, potentiodynamic passivation plot shown in Figure 4.5 indicates a relatively simple electrochemistry for TiN. To further elucidate the electrochemistry of the TiN system preliminary EIS studies were performed in sodium chloride solution at various DC potentials relevant to the voltammogram shown in Figure 4.5, both in the presence and absence of oxygen. For each impedance study the electrode potential was held at the relevant DC potential for 5 minutes before application of the 5mV rms sinusoidal AC potential. Figure 4.9(a) shows typical Bode plots observed at potentials around the corrosion potential in the absence of oxygen (−0.180V/CE), and at potentials sufficiently negative to cause water reduction, namely −0.900, −1.200 and −1.400V. The Bode plot always shows at least two, frequency dependent components as confirmed more clearly by the accompanying phase angle plots (Fig.4.9). The lower frequency impedance component is due to the accompanying cathodic reaction, as indicated by the decrease in impedance as the DC potential becomes more negative. Around the corrosion potential this second impedance term is largely capacitive (Figure. 4.9(a)) and would correspond to perhaps the double layer capacitance at the TiN surface with little charge leakage due to any faradaic corrosion reaction. Water reduction is not thermodynamically possible at the corrosion potential and in the absence of oxygen, it cannot be speculated what may constitute charge leakage across the double layer.

The higher frequency impedance component shown in Figures 4.9(a) and 4.9(b) is a much lower resistance term. This impedance component is most likely due to a relatively low resistance film on the TiN surface. As noted previously [63], XPS analysis shows the presence of oxygen (or oxide) on the surface of TiN. Although there is a decrease in resistance of this film at more negative potentials, for example, from ~ 40 ohm cm² at −0.180V/CE to ~27 ohm cm² at −1.400V/CE, this high frequency component is still present even at the more negative potentials, indicating that the film is not easily reduced. Similarly, the resistance (real impedance) of this film is not increased at the DC potential of +0.4V, which is sufficient to form the additional “passive” film on the titanium nitride surface as shown in Figure 4.5. Nor does any additional impedance component occur in the
AC response when the electrode is held at a potential of +0.4V. These results are consistent with the information contained in Figure 4.5, where the post passive current is still relatively large, indicating that the “passive” film is not electrically insulating.
Figure 4.9  AC impedance response (a) Bode plot, (b) Phase angle plot at various DC potentials observed for TiN/Si in 0.5M NaCl solution in the absence of oxygen with an electrode area of 0.06 cm$^2$

(a = $-0.180$ V/CE, b = $-0.900$ V/CE, c = $-1.200$ V/CE, d = $-1.400$ V/CE).
Figures 4.10(a) and 4.10(b) show the AC response (Nyquist and phase diagrams) of the TiN/Si system at –0.270V and –0.650V in a 0.5M NaCl solution saturated with oxygen (pO2=1 atm) under both non-stirred and stirred electrolyte conditions. Again at a potential near the corrosion potential the AC response is similar to that observed in the absence of oxygen, with both a low impedance, high frequency component and a high impedance, lower frequency component with an essentially capacitive character. At the resolution of the Nyquist plot shown in Figure 4.10(b) only the high impedance component is apparent (plot ‘a’) with a real impedance value in excess of 4 x 10^5 ohm cm². Electrolyte stirring has no influence on the AC response at –0.270 V/CE. At the DC potential of –0.650 V there is a marked decrease in the impedance of the lower frequency component (plot ‘b’, Figure 4.10(b)) as expected if this component represents the impedance response of the cathodic reaction (oxygen reduction). In addition there is a further decrease in the low frequency impedance at –0.65 V/CE with electrolyte stirring (plot ‘c’, Figure 4.10(b)), indicating a mass transport contribution to the kinetics of the cathodic reaction as expected for oxygen reduction. There is also an additional, inductive component in the low frequency AC response (negative phase angle and negative imaginary impedance, Figures 4.10(a) and 4.10(b)). Inductive phenomena are usually ascribed to relaxation of electroactive, adsorbed species [105]. Oxygen reduction would be expected to proceed by a mechanism involving adsorbed oxygen species [106]. It can be concluded again therefore that, as in the absence of oxygen, the higher impedance, low frequency component of the AC response is due to the cathodic reaction of the corrosion couple.
Figure 4.10  AC impedance response (a) Phase plot, (b) Nyquist plot at various DC potentials observed for TiN/Si in 0.5M NaCl solution, saturated with oxygen (pO2 = 1atm), with electrode area of 0.06 cm² a = -0.270 V/CE, b = -0.650 V/CE (without stirring), c = -0.650 V/CE (with electrolyte stirring).
4.3 Summary

The advantage of the PFAD system for deposition of decorative coatings demonstrated a smooth surface morphology. The comparative study of optical reflectivity with conventional random cathodic arc evaporated coatings also demonstrated higher reflectivity of PFAD TiN coating due to the reduction of defects (macroparticles).

Fundamental corrosion studies of TiN decorative coatings deposited by the PFAD system on inert substrates were carried out. The potential galvanic corrosion problem arising from electrolyte penetration to the underlying substrate due to the deposition of a noble coating of TiN on active (corrosive) substrates was addressed. The presence of an electrochemically formed, “passivation” film on the TiN coating surface may well be a potential strategy for decreasing the rate of any unwanted galvanic corrosion arising from the coupling of TiN with an active substrate. However unfortunately, it was revealed that the passivating film is relatively unstable in chloride solution, being easily reduced. The study therefore, suggests that the corrosion protection of typical substrates by a TiN coating will be purely as a physical barrier to moisture and oxygen. While TiN is more noble with respect to Zn, Cu and Ni, the actual rate of galvanic corrosion may well be determined by the slower of the two primary steps: dissolution of the corroding substrate or the rate of the cathodic reaction, usually water reduction or oxygen reduction or both, occurring on the more noble surface. The results obtained in this investigation indicated that the galvanic corrosion is under cathodic control for zinc base systems. Further it was demonstrated that rate of oxygen reduction on TiN is extremely low, indicating that TiN is a poor electrocatalyst for the reactions and hence, suggests that galvanic corrosion may not be significant for a TiN-substrate system in NaCl solution. Further study revealed a very slow rate of corrosion (nAcm\(^{-2}\)) for TiN, which suggested that TiN is chemically inert in NaCl solution.
CHAPTER 5

Results & Discussion

Effect of substrate deposition temperature on decorative properties, tribological and corrosion protection performance of CAE TiN coatings

In chapter 4 an investigation to study electrochemical behaviour of TiN coatings was carried out, which could be reasonably expected to not to be dependent upon the method of deposition onto an inert substrate. It was further established that the use of PFAD for depositing TiN coatings led to a reduction in the defect content and an improvement in the decorative properties. However, it was acknowledged that the complexity associated with the cathodic arc source and the low deposition rate of a PFAD system can be commercially unattractive. The unfiltered or random cathodic arc evaporation (CAE) technique has been the technique most widely exploited for deposition of decorative PVD coatings. The studies reported in chapter 4 were carried out before realising the drawback of a PFAD system and therefore the CAE technique was investigated in this chapter.

The formation of microstructure at a low substrate temperature and its effect on the corrosion protection, tribological performance and decorative properties has not been fully explored in the literature. Therefore, these aspects were investigated in the present study by depositing CAE TiN coatings with no prior substrate heating. Rather, the intention was to rely on the energy of ion bombardment, through the selection of a relatively high substrate bias potential, to achieve a dense microstructure [93,106]. TiN coatings were deposited with a substrate bias of −200V and the effect on decorative properties, tribological properties and corrosion protection was investigated. Results are presented in terms of microstructure and defect content.
One set of TiN coatings was deposited on chromium plated brass substrates and silicon wafers (100) without prior substrate heating. These coatings are referred to as the TL coatings. The process included a high voltage Ti metal etch followed by a reactive evaporation of Ti at a nitrogen pressure of 0.6 Pa. It was noted that the substrate temperature at the end of the deposition cycle was 140°C due to ion bombardment. Further, for comparison purposes, TiN was deposited under the same conditions but with prior substrate heating to the temperature of 200°C, referred to as the TH coatings.

5.1 Characterisation of TiN coatings

5.1.1 Surface morphology, roughness and microstructure

The surface morphology of the TL and TH TiN coatings deposited on chromium plated brass substrates was initially examined using cross-sectional FIB. The corresponding micrographs of the TL and TH coatings are presented in Figures 5.1(a) and 5.1(b) respectively. The TL coating (Figure 5.1 (a)) shows a relatively smooth surface. This probably is a consequence of two factors, one being the limited adatom mobility at low substrate temperature [93] and secondly, the ion bombardment due to substrate bias creating a self sputtering effect [106]. These factors may well contribute and produce a fine grain structure, which explains the fine scale micro-roughness. In contrast the TH coating (Figure 5.1 (b)) is evidently rougher with rough surface features. The micro-roughness appears to be ‘etched’ which explains that it is a consequence of sputtering etching at the higher deposition temperate of what is a coarse grain structure.

The increase in the surface roughness was further verified by carrying out a profile study using a Mahr Perthometer Concept surface profilometer and the electrochemical technique of potentiodynamic polarisation test on the coating. The average surface roughness, Ra, values over an area of 500µm × 500µm were 0.18µm and 0.63µm for the TL (TiN/Si) and TH (TiN/Si) coatings, respectively. Using the potentiodynamic polarisation technique, the charge associated with the anodic peak was taken as an indication of the surface area of the TiN coatings. A potentiodynamic polarisation study of the TL (TiN/Si) and TH (TiN/Si)
coatings (each with geometric surface area of 0.25 cm²) were carried out in 0.5 M NaCl deaerated solution in the absence of oxygen. A charge of 67 µC/cm² and 519 µC/cm² was obtained for the TL and TH coating respectively. The higher charge for the TH coating indicates a greater surface area and hence, a greater surface roughness. The findings obtained by the use of the above techniques are in agreement with the general view [107] that the coating surface roughness increases with the substrate temperature. The higher surface roughness obtained for the TH coating compared to the TL coating can be interpreted by considering the significant increase in the number of defects (pores, pinholes, macroparticles and pitting defects) which are evident in SEM micrographs of the coating surfaces (see Figure 5.2 (a) and 5.2 (b)). Measurement of macroparticle density was carried out by recording six micrographs of two samples each at 1500X and counting (average number of macroparticles over unit area) and thus, recording the average value. The measurement also indicated a higher density of the TH coating (5·4×10⁴ mm⁻²) than the TL coating (3·4×10⁴ mm⁻²).

The microstructure of TiN coatings on a silicon substrate was studied using cross-sectional transmission electron microscope (X-TEM). The corresponding bright field images for the TL and TH coatings are presented in Figures 5.3(a) and 5.3(b), respectively. The thickness of the TL and TH coatings are approximately 400 nm and 340 nm respectively. In Figure 5.3 (a), the different regions are marked as (I) epoxy glue, (II) Ti interlayer, (III) TiN coating and (IV) silicon substrate. It is evident that the TL coating shows an open columnar grain structure in which some of the grains extended to the surface of the coating. Such a microstructure of TiN coatings deposited at low temperature has been observed previously [7]. On the basis of simulation studies, Torre [108] suggested that this type of structure is a consequence of the substrate rotation during the coating deposition process. The substrates will receive vapour flux at an angle due to the rotation of substrates and hence the columnar grain grows in the direction of impinging atoms. Figure 5.3(a) further shows a sharp interface with a light patch approximately 50 nm thick and this was identified as a titanium interfacial layer using selective area diffraction (SAD). The origin of this interfacial layer is assumed to be a consequence of the high voltage titanium ion etch of the substrate, prior to reactive deposition of TiN.
In contrast, the TH coating (see Figure 5.3 (b)), did exhibit a less clear columnar structure. This observation may be explained by the well accepted fact [33, 93] that the microstructure of PVD thin coatings is related to the mobility of the adatoms. The different sources of adatom energy are thermal and energetic particle bombardment. Both these sources assist in enhancing the surface mobility of the adatoms. The relatively dense microstructure of the TH coating therefore, can be due to the fact that it was deposited at a high initial substrate temperature of 200ºC. A further interesting observation was that the TH coating did not show a titanium interfacial layer, not withstanding the fact that it had a similar high voltage titanium metal ion etch of the substrate as part of the TiN coating deposition cycle. Cairney et al. [109] suggested the absence of the interfacial layer can be due to the nm thick titanium interfacial layer immediately nitrided on exposure to the reactive nitrogen gas, at the relatively high deposition temperature of 450ºC. In the present investigation, the Ti coating (an interfacial layer) is only few nm thick and is subjected to an intense ion bombardment from the plasma, therefore nitriding at 200ºC can not be ruled out.
Figure 5.1 FIB micrographs of the TiN/Cr/brass coatings showing the morphology of (a) TL and (b) TH, TiN coatings.
Figure 5.2 SEM micrographs of the TiN/Cr-brass coatings showing the morphology of (a) TL and (b) TH, TiN coatings.
Figure 5.3 Cross-sectional TEM micrographs showing the microstructure of the CAE deposited (a) TL (TiN/Si) and (b) TH (TiN/Si) coatings.
5.1.2 Preferred orientation

Knowledge of preferred orientation of PVD coatings is important since it is acknowledged [55, 92] to influence mechanical properties, such as, stress, hardness etc., and also tribological properties. In the present investigation, the preferred orientation of the TiN coatings was studied using the Bragg-Brentano diffraction method. Scans were performed on the TiN coatings deposited on chromium plated brass substrates, as well as on the uncoated chromium plated brass substrate, over the range of $2\theta = 40^\circ$ to $80^\circ$. The results of XRD studies indicated that the TiN coatings were composed of a NaCl type single-phase structure. No metallic phases (e.g. from macroparticles) were detected. Peak positions correlated well with the TiN powder diffraction file (DF 38-1420). It should be noted that peaks observed in the pattern at $2\theta = 50.85^\circ$, $52.15^\circ$, $59.45^\circ$ and $61.35^\circ$ correspond to the electroplated copper and nickel substrates. The peak observed at $2\theta = 58^\circ$ in both the samples was unidentified peak and was not related to any other peak heights. The TL coating (Figure 5.4(a)) deposited at low substrate temperature is characterised by a (111) orientation, which changes to a (200) orientation for the TH coating deposited at high substrate temperature (Figure 5.4(b)). This shows that the preferred orientation of the TiN coatings depends upon the substrate temperature. Similar findings [93] have been reported previously. Knuyt et al. [110] suggested that the classically observed coating evolution trend towards the smallest surface energy results in preferred orientation of the coating. Pelleg et al. [112] later proposed the total energy minimisation principle in which the preferred orientation of the coating is governed by a thermodynamic constraint of minimising overall total energy of the coating system. Consequently, the growing films not only have a driving force to lower the surface energy, but also have another driving force to minimize the strain energy. The competing planes [111] in the TiN coating are (200) with the lowest surface energy and (111) with the lowest strain energy. Accordingly the preferred orientation is determined by the completion between the strain and the surface energies. The surface energy does not vary with the film thickness while the strain energy increases with it. The increasing rate of the strain energy, which is dependent on the plane (hkl), is larger on the (200) plane than on the (111) plane. Therefore, at small film thicknesses, the surface energy term is significant and (200) orientation with a minimum
surface energy is preferred. At a large film thickness the strain energy difference between
different lattice planes becomes dominant and the (111) preferred orientation is observed.
Accordingly, at small coating thicknesses, it is highly likely that the surface energy controls
growth, whereas at large film thicknesses, the strain energy predominates. The preferred
orientation is then established from a critical competition between the surface energy and
the strain energy. The observed (200) orientation for the TH coating deposited at the high
substrate temperature in the present study therefore, can be attributed to the control of
surface energy, whereas (111) orientation for the TL coating deposited at the low substrate
temperature can be attributed to the control of strain energy. Based on these observations, it
can be inferred that the critical thickness of the transition is 400nm.
Figure 5.4  X-ray diffraction pattern of the CAE deposited (a) TL and (b) TH TiN coatings on chromium plated brass substrate. (* unidentified peak)
5.1.3 Chemical composition

The composition of the TiN/Cr/brass coatings was determined using the XPS technique. Figure 5.5(a) shows typical survey scan spectra of the TL TiN coating with the Ti2p, N1s, O1s, and C1s peaks. The peak at 284.8 eV corresponds to adventitious hydrocarbon species [90]. Figures 5.5(b), 5.5(c) and 5.5(d) show typical high resolution region scan spectra for Ti-2p, N1s and O1s respectively for the TL coating. The Ti-2p spectrum shown in Figure 5.5(b) reveals binding energies of Ti (2p$_{3/2}$), 455 eV; and Ti (2p$_{1/2}$), 461 eV. These binding energies are comparable with those reported in the literature [113]. The broad feature between 458.5 eV and 455 eV was observed only for the TL coating and can be attributed to titanium oxynitride [113,114]. The N-1s spectra shown in Figure 5.5(c) at 397 eV could be constructed as an envelope consisting of two peaks of 397.5 eV and 396.3 eV which in turn can be assigned to titanium nitride [115] and titanium oxynitride [115], respectively. The O-1s spectra shown in Figure 5.5(d), binding energy of 530.8 eV, and has been attributed to the binding energy of 531.4 eV for titanium oxynitride [115].

Table 5.1 summarises the chemical composition of the both the TL and TH coatings, obtained from the experimental data. Calculations were based on the integrated area under the assigned elemental peaks and the sensitivity factor for that element [90]. The nitrogen to titanium (N/Ti) ratios for the TL coating and TH coating were determined to be 0.67 and 1.29, respectively. The difference in the composition can be explained by considering the effect of substrate bias potential and the differences in the temperature dependent sticking coefficients for the titanium and nitrogen atoms. It should be recalled that the deposition process for both, the TL and the TH coating was carried out at a substrate bias potential of −200V. Basically, for arc evaporation, the energy of the ion impinging on the growing film is proportional to substrate bias potential. Consequently, for TiN coating deposition the mobility of the ionized species, of titanium and nitrogen will be enhanced. In addition, the ions impinging on the growing arc evaporated coatings will result in the preferential sputtering of the atoms. Under these circumstances, the atoms with the lower temperature sticking coefficient will be sputtered preferentially [107], which is the case for titanium atoms. These different effects can justify the increase in N/Ti composition of the coating
with an increase in substrate temperature. Further from Table 5.1, it is evident that O/Ti ratio is slightly higher for the TL coating compared to the TH coating, indicating the slightly higher amount of oxygen in the TL coating which can be attributed to the coating microstructure as proposed by Martin et al. [30]. They suggested and as did Ernsberger et al. [107] that PVD coating with an open columnar microstructure may absorb relatively large amount of oxygen when exposed to air. This suggestion is supported by the present findings of large amount of oxygen as detected by XPS.

**Figure 5.5** XPS spectrum of (a) a typical survey scan of TL TiN coating on chromium plated brass substrate.
Figure 5.5  XPS spectrum of (b) a typical titanium peak and (c) a typical nitrogen peak.
Figure 5.5  XPS spectrum of (d) a typical oxygen peak.

Table 5.1  Composition of the TL and TH TiN coatings on chromium plated brass substrates

<table>
<thead>
<tr>
<th>Sample</th>
<th>N/Ti ratio</th>
<th>O/Ti ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>(TiN/Cr/brass coating)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TL</td>
<td>0.67</td>
<td>0.42</td>
</tr>
<tr>
<td>TH</td>
<td>1.29</td>
<td>0.34</td>
</tr>
</tbody>
</table>
5.2 Decorative properties (colour and optical reflectivity)

Variation in colour for the TL (TiN/Cr/brass) and TH (TiN/Cr/brass) coatings were measured using a spectrophotometer (Minolta CM-500 d-series). The coating colour was expressed using the CIE L*a*b* system, and the corresponding results are presented in Table 5.2. Parameters a* and b* are: a* is the redness in the positive direction, and greenness in the negative direction; b* is the yellowness in the positive direction, and the blueness in the negative direction. It is evident that with increasing deposition temperature, brightness (L*) decreases slightly whereas the yellowness b* increases, and the colour contribution from red/green increases in the positive a* direction (less green and more red). This is consistent with the low substrate temperature TiN coatings appearing bright yellow.

The optical reflectivity spectra of TL and TH coatings in the visible range (400 to 700 nm) are presented in Figure 5.6. The TL-TiN coatings display higher reflectivity than those of the TH-TiN coatings over the entire wavelength range. The spectra further show a maximum reflectance of about 75% and 73% for the TL and TH coatings, respectively, indicating a higher optical reflectivity for the TL coating. Interestingly, both these coatings are also characterized by a minimum reflectivity, independent of coatings deposition temperature. An absorption peak corresponding to minima appears near 420nm for the TL coating and near 440 nm for the TH coating.

The results of colour variation and reflectivity with substrate temperature can be explained in the light of both the Drude model and the ionic model [45, 38] which propose a mixed character of bonding. According to the Drude model, the reflectivity is determined by the interaction of free electrons with visible light. This is directly influenced by the chemical composition (atomic ratio of nitrogen to titanium). Specifically, a higher N/Ti ratio results in less Ti free electrons since, according to the ionic model; a transition nitride is formed by transfer of electrons from the transition metal to nitrogen. With the lower number of available free electrons, therefore, the reflectivity decreases. As a result, the minima of the reflectivity curve shifts to a lower wavelength side for the TH coating. Due to a high
contribution of blue color in the reflected light, the TH coating appeared yellow, but with a different hue.

A further understanding of reflectivity and colour can be gained by considering the microstructure and morphology differences. The observed coarse grained microstructure of the TH coating, deposited at higher substrate temperature may lead to a slight reduction in the reflectivity. Consequently, the overall visible appearance remained yellow but with decreasing brightness for increasing roughness of the coating surface. These findings are in agreement with the general view [44,48] that the coating loses brightness with increasing surface roughness.

Table 5.2  L*a*b* values of the TL and TH TiN coating deposited by CAE on chromium plated brass substrates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>TL-</td>
<td>75.5</td>
<td>5.59</td>
<td>38.36</td>
</tr>
<tr>
<td>TH</td>
<td>73.1</td>
<td>6.98</td>
<td>39.35</td>
</tr>
</tbody>
</table>
Figure 5.6 Optical reflectivity of the TH (TiN/Cr/brass) and TL (TiN/Cr/brass) coating deposited by CAE at a substrate bias potential of –200 V.

5.3 Tribological performance (Abrasive wear)

A simple laboratory test was carried out using the Tabor abrasive wear tester for assessing wear performance of the TiN coatings. The wear out of the TL coating (first exposure of the substrate) was at 1000 cycles compared to 600 cycles for the TH coating. This observation indicates a higher wear resistance of the TL coating compared to the TH coating. The number of recommended wear cycles for PVD decorative coatings is 1000 cycles [10]. The result suggests that the TL coatings may well exhibit the greater durability than the TH coatings when used in decorative applications.

The Taber test is basically abrasion wear and therefore, starts with sliding action of weighted abrading wheels against a rotating coating surface. The tribological mechanism in sliding contacts is discussed by Holmberg and Mathews [116]. They proposed that the tribological mechanisms can be analysed by four main parameters: the coating hardness, the coating thickness, the surface roughness and the debris in the contact. Based on these
parameters, hardness combined with thickness in addition to smoother surface may well exhibit better tribological properties- which are the case for the TL coatings. The results of XRD study [section 5.1.2] suggested a higher strain in the TL coating compared to the TH coating. Typically higher strain is related to increase in the hardness [93] of the coating and consequently, higher wear resistance. It is possible that a titanium interfacial layer in the case of the TL coating can be a supporting factor in the delay of complete wear of the coating. The findings also support the general view [117] that thin coatings wear out considerably compared to thick coatings. Furthermore, the Taber wear test consisted of rotation of the PVD coated disk. This process may extract macroparticles out of the coatings and consequently, the crater- like defects left behind may act as potential sites for wear out of the coating. The depth of the wear out of the coating therefore may increase with the number of macroparticles, and consequently, decrease the wear resistance- which is the case for the TH coating.
5.4 Corrosion studies

5.4.1 Corrosion potential measurements

In this section, the results of corrosion potential measurements are presented for the TiN coatings deposited on chromium plated brass substrates. The variation of corrosion potential for the TH and TL electrodes was recorded in 0.5M NaCl solution over a period of 20 days and is presented in Figure 5.7. As noted previously (Chapter 4), a similar trend in corrosion potential towards more negative potential is observed and is consistent with the view of a slow development of oxide film on the chemically active surface of TiN coating [section 4.2]. Initial potential values displayed by both electrodes are similar to previously reported values for TiN coatings on an inert (silicon) substrate [Section 4.6], also supporting the assumption that TiN coatings act as a barrier to the corrosive electrolyte (NaCl in this case).

Figure 5.7 shows further that after an initial period of approximately 5 days of immersion, the corrosion potential stabilises around –90mV and –140 mV for the TL and TH electrodes, respectively. With further exposure, a sudden change of approximately –350 mV was observed for the TH electrode compared to the TL electrode (approximately –110 mV). This sudden change in the corrosion potential after ~11 days is consistent with penetration of the electrolyte through the coating to the chromium plated brass substrate. This interpretation is supported by the finding that the corrosion potential for the chromium plated brass measured under similar conditions was found to be about –500 mV. It is interesting to note that within this measurement period, the corrosion potential of the TL electrode remained around –200 mV and did not drop to the potential of Ti interfacial layer (approximately –60 mV) or to that of chromium plated brass. After 20 days of immersion in the electrolyte, no peeling of the coating or corrosion of the substrate was observed for the TL and TH electrodes. The findings revealed the sensitivity of the corrosion potential measurement technique with the coating failure being indicated well before apparent signs of visible corrosion. Thus it can provide a simple method of monitoring coating failure.
compared to the conventional salt spray test at least when the corrosion potential of the coating and substrate are significantly different.

![Graph showing corrosion potential variation with time for TiN/Cr/brass (TL and TH) coatings in 0.5 M NaCl, unstirred solution.](image)

**Figure 5.7** Variation of corrosion potential with time for TiN/Cr/brass (TL and TH) coatings in 0.5 M NaCl, unstirred solution.

The results of the corrosion potential measurement can be explained by considering a mathematical derivation by Stern [119] which demonstrates that $V_{\text{corr}}$ depends on the relative areas on which the anodic and cathodic reactions occur. It was proposed that the corrosion potential of a corroding metal becomes more negative or less negative depending upon whether the anodic reaction is confined to a larger or smaller area on the metal surface. The corresponding equation is given by [119]

$$V_{\text{corr}} = V_{\text{corr}(0.5)} - \left( \frac{1}{b_a + b_c} \right)^{-1} \log \left( \frac{f_a}{f_c} \right) \quad [5.1]$$
where $V_{\text{corr}(0.5)}$ is corrosion potential when anodic and cathodic areas are equal, $b_a$ and $b_c$ are Tafel constants, $f_a = \text{anodic area fraction}$ and, $f_c = \text{cathodic area fraction}$ such that $f_a + f_c = 1$

Accordingly, Figure 5.8(a) and 5.8(b) shows models depicting both the TL and TH TiN coatings being exposed to the electrolyte, respectively. Further, it shows that TiN coating surface with area $A$, comprising regions which act as sites for the cathodic reaction with area fraction, $f_c$, and sites for the anodic reaction with area fraction, $f_a$.

**Figure 5.8 Schematic models showing the (a) TL and (b) TH TiN coatings on chrome electroplated substrate exposed to the electrolyte solution**

It was demonstrated earlier that TiN coatings are cathodic to the electroplated substrates (Chapter 4). It was further envisaged that the coatings can provide significant corrosion protection when they are free of defects (pinholes or cracks). In the absence of such defects in the coating the anodic and cathodic reactions due to the slow corrosion of the TiN coating (Chapter 4) will both occur on the TiN coating. However, with exposure of the defective TiN-substrate system to the electrolyte and subsequent penetration of the electrolyte to the substrate, the anodic corrosion reaction ($M (s) \rightarrow M^{n+} (aq) + ne (M)$) will occur preferentially on the more active substrate with the cathodic reaction occurring on the TiN coating, i.e. $f_a < f_c$ or anodic area $<<$ cathodic area, $(f_a/f_c<1)$. The greater the number of
defects, or the increasing penetration with time of more existing defects, or the lifting of the coating with time due to corrosion of substrate under the coating at the base of defects, the larger the ratio $f_a/f_c$. That is $f_a/f_c$ increases with time and, according to equation 5.1 $V_{corr}$ becomes more negative with time as observed.

Thus the observed variation in corrosion potential with time suggests that TH coatings contain more defects allowing penetration of electrolyte to the active substrate than TL coatings or some other feature of the TL coating inhibiting access of electrolyte to the active substrate. The higher negative corrosion potential displayed by TH coatings compared to TL coatings therefore can be attributed to the apparent higher surface roughness due to the higher number of defects and consequently, the higher surface area. In addition, a titanium interfacial layer between the coating and the substrate for the TL coating, as presented in schematic diagram (Figure 5.8), may also be the supporting factor in further inhibiting access of the electrolyte to the active substrate and thus, maintaining its potential well below the potential of the underlying substrate.

5.4.2 Potentiodynamic polarisation study

Investigation of the corrosion protection offered by the TL and TH TiN coatings on chromium plated brass coupons, (each with surface area of 0.25 cm$^2$) in 0.5 M NaCl de-aerated solution was evaluated using the potentiodynamic technique whereby the potential is scanned positive from $V_{corr}$ at 1mVs$^{-1}$. Initially all coatings were immersed in 0.5 M NaCl solution for a period of half an hour to achieve an approximately steady state potential.

Figure 5.9 shows typical potentiodynamic polarisation curves (E-I plots) for the TL and TH TiN coatings and also, substrate materials, namely, uncoated brass and chromium plated brass. This investigation did not include a pitting study.
On the positive going scans for the TL and TH coatings, the anodic current increases as the potential rises. Further, at more positive potentials, current increases rapidly. As observed in the earlier work of TiN coatings deposited on silicon substrate (Chapter 4, Figure 4.5), the potentiodynamic polarisation study indicated that an anodic peak formation at $\sim-50$ mV on TiN occurred with no further oxidation or electrochemical activity up to $+1.5$ V. The rising part of the potentiodynamic scan in Figure 5.8 therefore may be due to the water oxidation (i.e. oxygen evolution) or corrosion of the substrate, i.e. substrate dissolution. The possibility of the water oxidation was ruled out since the equilibrium potential for oxygen evolution reaction in 0.5M NaCl solution is 0.573V vs. the Hg/HgCl$_2$/0.5MNaCl reference. This reaction is therefore thermodynamically unfavorable at the potentials observed in Figure 5.8 which are less than 0.5V. The observed rapid increase in the current density and corrosion of the substrate is, therefore, consistent with penetration of electrolyte through the coating and corrosion of the underlying substrate rather than any breakdown of the coating. This was also indicated by the islands of black corrosion product, possibly CuO, within the intact coating that was visible on the electrode surface after potentiodynamic testing. Furthermore the current density values displayed by TiN coatings on the brass (active) substrate are three orders of magnitude higher in comparison to currents observed on TiN coatings on the silicon (inert) substrate (Figure 4.5).

Figure 5.10 shows potentiodynamic polarisation curves obtained for each of two deposited TL (TiN/Cr/brass) and TH (TiN/Cr/brass) coatings which display a similar trend to that shown in Figure 5.9. This further confirms that the electrochemical behaviour is similar for the TL and TH coatings. All these coatings exhibit a rapid increase in the current density beyond a certain potential. Anodic current density values at potentials of 0 mV, 100 mV, 200 mV and 300 mV, obtained from data in Figures 5.9 and 5.10, are listed in Table 5.3. Both the coatings TL and TH illustrate that current density values at each potential are lower than those of brass and chrome plated brass substrate materials. The results highlight the beneficial protective effect of TiN coating deposited on these substrate materials. The findings are in agreement with Wang et al. [31] who observed the similar trend in the current density for the TiN coatings deposited on bare brass substrates, although their
coatings were deposited at a relatively higher substrate temperature of 250°C. Figure 5.10 shows further that anodic current densities for the TL coating are much lower at any potential, compared to the TH coating, suggesting more defects (pores, pinholes) and therefore exposure of substrate to electrolyte for TH coatings.

Figure 5.9 Typical potentiodynamic polarisation curves for brass, Cr/brass, TL (TiN/Cr/brass) and TH (TiN/Cr/brass) coatings in 0.5 M NaCl, unstirred solution, (electrode area of 0.25 cm², potential scan rate =1mVs⁻¹, t= 25° C)
Figure 5.10 Potentiodynamic polarisation curves for two TiN/Cr/brass (TL and TH) coatings in 0.5 M NaCl, unstirred solution, (electrode area of 0.25 cm², potential scan rate =1mVs⁻¹, t= 25° C).

Table 5.3 Anodic current density values obtained from the potentiodynamic polarisation curves at various potentials

<table>
<thead>
<tr>
<th>Sample</th>
<th>(i) (0 mV/CE) (µA/cm²)</th>
<th>(i) (100 mV/CE) (µA/cm²)</th>
<th>(i) (200 mV/CE) (µA/cm²)</th>
<th>(i) (300 mV/CE) (µA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brass</td>
<td>50</td>
<td>1450</td>
<td>2000</td>
<td>4120</td>
</tr>
<tr>
<td>Cr/brass</td>
<td>580</td>
<td>900</td>
<td>1660</td>
<td>3080</td>
</tr>
<tr>
<td>TH1</td>
<td>63</td>
<td>150</td>
<td>450</td>
<td>998</td>
</tr>
<tr>
<td>TH2</td>
<td>79</td>
<td>190</td>
<td>480</td>
<td>1189</td>
</tr>
<tr>
<td>TL1</td>
<td>20</td>
<td>75</td>
<td>180</td>
<td>650</td>
</tr>
<tr>
<td>TL2</td>
<td>45</td>
<td>100</td>
<td>278</td>
<td>750</td>
</tr>
</tbody>
</table>
For different anodic current density values, corresponding potential values for TiN-coated samples obtained from the data in Figure 5.10 are graphically presented in Figure 5.11. This shows that at any potential the current, and therefore corrosion rate of substrate, is less for TL compared to TH coatings. The findings can be rationalized by using equation 2.2.4, which shows that current is exponentially dependent on electrode potential. Even for an electrochemical reaction proceeding under mass transfer control, i.e. when the rate determining step involves rate of transfer of reactant to, or product away, from the electrode, the relationship between current or current density and applied potential is an exponential one, except when the current corresponds to the limiting value (I_L) which is independent of electrode potential [61]. More specifically, since electrochemical reactions, including corrosion occurs on the surface of a material or electrode; corrosion rate is more correctly measured as current density, i Am^-2 or mAcm^-2, etc. Similarly equations 2.2.4 and its various derivations 2.2.5, 2.2.6 and 2.2.7 can be written in terms of current density, i, example,

\[
i = i_{\text{corr}} \left\{ \exp\left(-\frac{V - V_{\text{corr}}}{b_c}\right) - \exp\left(-\frac{V - V_{\text{corr}}}{b_a}\right) \right\} (5.4.1)
\]

where \(i = I/A\), ‘A’ being the actual area of material exposed to the electrolyte, which may, for a rough material, be much greater than the geometric area.

While the results in Figures 5.9, 5.10, 5.11 and Table 5.3 are in terms of current density, the area used to convert experimental currents, I, to current density, i, is the geometrical area (0.25 cm^2) of the TiN coating electrodes. However, if the currents recorded were from (penetration) substrate corrosion, as suggested, due to electrolyte penetration through defects in the coating, then the effective electrode area is that of the exposed substrate which geometrically will be much lower than the initial electrode area (0.25 cm^2). Similarly the greater the substrate area exposed, the smaller will be the current density at any experimentally recorded current value and the smaller will be the externally applied potential required to generate that current (and vice versa). Consequently, the results in Figures 5.8, 5.9, 5.10 and Table 5.3 indicate that the area of substrate exposed to electrolyte as a result of electrolyte penetration through defects, etc. in the TiN coating is least for TL.
coatings. Thus while TH coatings offer some protection of the underlying substrate, smaller corrosion current at any potential than for brass or chrome plated brass; they are not as effective as that provided by TL coatings under the conditions prevailing during the recording of the potentiodynamic polarisation plots.

Furthermore, the higher oxygen content of the TL coating compared to the TH coating as revealed in composition studies (section 5.1.4), can be attributed to Ti passivation and this passivated layer between the coating and the substrate for the TL coating, is suggested to act as a further barrier to electrolyte penetration and thus may assist further against the substrate corrosion. The findings also reinforce the general view [63] that an interfacial layer between the substrate and the coating contributes in the corrosion protection of the substrate.

![Graph showing variation of anodic current density with potential for the TL (TiN/Cr/brass) and TH (TiN/Cr/brass) coatings.](image)

**Figure 5.11** Variation of anodic current density with potential for the TL (TiN/Cr/brass) and TH (TiN/Cr/brass) coatings.
5.5 Summary

The corrosion performance, decorative and tribological performance were investigated for TiN coatings deposited under two conditions; the first without prior substrate heating (referred to as TL, low temperature deposition of 140°C) and the second with prior substrate heating (referred to as TH, high temperature deposition of 200°C). In both cases, a high voltage titanium metal ion etch of the substrate followed by a reactive evaporation of titanium in nitrogen atmosphere was carried out.

It was demonstrated that various factors influence the protection ability of TiN coatings. These include microstructure, metallic interfacial layer and surface morphology. Microstructure studies using X-TEM indicated a fine grained columnar structure for TiN coating deposited at the low substrate temperature (TL) with a titanium interfacial layer, in contrast to the coarse-grained structure of the TiN coating deposited at a high substrate temperature (TH) without a titanium interfacial layer, although both coatings had a similar titanium metal ion etch as a coating deposition process. The absence of the interfacial layer for the TH coating is suggested as due to self-sputtering at the high temperature deposition process. The TL coatings had a smoother surface morphology than the TH coatings. A surface profile study using a Mahr Perthometer Concept surface profilometer and the electrochemical technique of potentiodynamic polarisation test on the coating, demonstrated higher surface roughness for the TH coating compared to the TL coating, supporting surface morphology observations.

Investigation of the corrosion protection offered by the TL and TH coatings using electrochemical techniques of corrosion potential measurement and potentiodynamic polarisation, indicated the better corrosion protection ability of the TL coatings compared to the TH coatings. The observed variation in corrosion potential with time indicated that the TH coatings contained more defects than the TL TiN coatings, thereby allowing easier penetration of electrolyte to the active substrate. Furthermore, the corrosion potential variations were found to be consistent with a mathematical derivation by Stern [119] which shows that corrosion potential is a function of the relative areas on the metal surface on
which the anodic and cathodic reactions occur. Further, potentiodynamic polarisation studies suggested that the area of substrate exposed to electrolyte as a result of electrolyte penetration through defects in the TiN coating is least for TL coatings compared to TH coatings and consequently demonstrates better protection ability. In addition, improved decorative properties and tribological performance of the TiN coatings deposited at the low substrate temperature compared to those deposited at the high substrate temperature were observed.
CHAPTER 6

Results & Discussion

Improvement in the performance of CAE TiN coatings

This chapter is divided into two parts. In the first part, results of an investigation into the effect of nitrogen pressure on decorative properties, tribological performance and corrosion protection performance of TiN coatings deposited on chromium plated brass and silicon substrates using random CAE are reported. In the second part, results of an investigation into the effect of multilayer deposition on decorative properties, tribological performance and corrosion protection performance are presented. The above coatings were deposited at a low substrate temperature, that is, with no prior substrate heating.

Part I - Effect of deposition pressure on decorative properties, tribological and corrosion protection performance of CAE TiN coatings

6.1 Selection of deposition pressure

In the random CAE system selected for this study, the chamber pressure during reactive deposition was recorded as a function of the nitrogen gas flow rate. The system was operated with three arc cathodes operating at 80A and a substrate bias voltage of –200 V. Arcs were initiated after a stable chamber pressure was achieved at about 0.1 Pa with a nitrogen gas flow rate of 60 sccm. The gas flow rate was then increased in steps of 10 sccm and the chamber pressure recorded. Once the chamber pressure reached its limiting value (typically between 2 and 3 Pa), the flow rate was decreased in steps of 10 sccm back to the
original value of 60 sccm. The pressure/flow rate response is shown graphically in Figure 3.4, as described before (section 3.2.2.1). The deposition pressures, at which the TiN coatings were to be deposited, were selected from the hysteresis plot. These corresponded to nil, partial and complete cathode poisoning conditions and are presented in Table 6.1-same as before (section 3.2.2.1).

Table 6.1 Selection of deposition pressure for TiN coating from the hysteresis plot.

<table>
<thead>
<tr>
<th>TiN Coating</th>
<th>Deposition Pressure (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>0.1</td>
</tr>
<tr>
<td>T2</td>
<td>0.4</td>
</tr>
<tr>
<td>T3</td>
<td>0.8</td>
</tr>
<tr>
<td>T4</td>
<td>1.25</td>
</tr>
</tbody>
</table>

6.2 Characterisation of TiN coating

6.2.1 Surface morphology and roughness

The morphology of TiN coatings on chromium plated brass coupons deposited at the various nitrogen gas pressures was examined using SEM. From the micrographs presented in Figure 6.1, it is evident that the macroparticle content decreases with increasing nitrogen pressure. Measurement of macroparticle density (average number of macroparticles over unit area) indicated a reduction from $8 \times 10^4$ mm$^{-2}$ to $2.7 \times 10^4$ mm$^{-2}$ as the deposition pressure increased from $P_{N_2} = 0.1$Pa to 1.25Pa (Figure 6.32). This trend is in agreement with previously reported research [21,25,26] and can be satisfactorily explained by the formation of TiN on the Ti cathode surface due to cathode poisoning. Macroparticle density
also has an effect on surface roughness as described before (section 4.1.1). The results of a profile study using a Mahr Perhometer Concept surface profilometer are presented in Table 6.2 and plotted as a function of the nitrogen pressure in Figure 6.43, which show a reduction in the surface roughness with increasing deposition pressure. The surface roughness of the TiN coatings decreased from 0.27µm to 0.15µm as the nitrogen pressure increased from 0.1Pa to 1.25Pa.

The thickness of the deposited TiN coatings was determined from fractographic cross-sectional SEM and is presented in Figure 6.54. The TiN coatings deposited at the lowest pressure (PN2 =0.1Pa) and the highest nitrogen pressure (1.25Pa) showed a thickness variation from 1.2µm to 0.3µm. This difference can be accounted for in terms of the cathode poisoning effect. Gruss et al. [120] reported similar findings and associated a reduction in the coating thickness to an increase in deposition pressure. They suggested that at the higher deposition pressure, the formation of TiN compound on the cathode surface causes a change in the erosion rate of the cathode and thus affects the deposition rate.
Figure 6.1 SEM micrographs of CAE TiN/Cr/Brass coatings showing the variation in the macroparticle content with deposition pressure of (a) 0.1 Pa, (b) 0.4 Pa, (c) 0.8 Pa, and (d) 1.25 Pa.
Figure 6.2 Macroparticle density (average number of macroparticles per unit area) as a function of deposition pressure for CAE TiN/Cr/brass coatings.

Figure. 6.3 Arithmetic average surface roughness of CAE TiN/Cr/brass coatings as a function of deposition pressure using a Mahr Perthometer Concept surface profilometer.
Figure 6.4 Fractographic cross-sectional SEM micrographs of the CAE deposited TiN/Si coatings showing the thickness at the deposition pressure, PN₂, of (a) 0.1 Pa and (b) 1.25 Pa.
### Table 6.2 Effect of chamber pressure on the macroparticle density, surface roughness and thickness of CAE deposited TiN coatings

<table>
<thead>
<tr>
<th>Chamber pressure (Pa)</th>
<th>Macroparticle density (number mm$^{-2}$) ($\times 10^4$)</th>
<th>Surface roughness (Ra (µm))</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>8.4</td>
<td>0.27</td>
<td>1.2</td>
</tr>
<tr>
<td>0.4</td>
<td>5.01</td>
<td>0.23</td>
<td>0.6</td>
</tr>
<tr>
<td>0.8</td>
<td>3.2</td>
<td>0.17</td>
<td>0.4</td>
</tr>
<tr>
<td>1.25</td>
<td>2.71</td>
<td>0.15</td>
<td>0.3</td>
</tr>
</tbody>
</table>

#### 6.2.2 Chemical Composition

The effect of deposition pressure on the chemical composition of the TiN coatings was determined using XPS and results are presented in Table 6.3. It is evident that the N/Ti ratio increases with increasing chamber pressure. The change in the composition can be explained by considering the reactions occurring at the cathode surface. At 0.1 Pa, the coating is effectively metal rich which is consistent with the observation in the previous section that minimal cathode poisoning takes place at lower pressure. At 0.4 Pa and 0.8 Pa, the N/Ti ratio rises from 0.56 to 0.69 which is consistent with the fact that partial cathode poisoning is taking place. With a further increase in pressure to 1.25 Pa, the cathode is fully poisoned and the N/Ti ratio appears to plateau at 0.73.

Table 6.3 shows the oxygen content of the TiN coatings as determined by XPS. It is evident that the oxygen content decreases with increasing deposition pressure. This is in contrast to the observed nitrogen content of the coatings which increased with increasing deposition pressure. The findings are consistent with Niyomsoan [51], who showed that when the amount of oxygen increases in TiN coatings, the amount of nitrogen has the tendency to decrease in the coatings. The oxygen content was approximately 45% at the lowest pressure of 0.1 Pa, reducing to approximately 10% at the highest pressure of 1.25
Pa. It is possible, that this decrease can be related to the microstructure of the coating. Harris et al. [122] suggested that the low adatom mobility at lower deposition pressure results in the formation of an open columnar microstructure. Exposure of the PVD coating to the atmosphere following the deposition cycle results in oxide formation and also in oxygen diffusion in the coating. Interestingly, Harris et al. also [126] suggested that macroparticles provide a path for oxygen diffusion in the coating. This is illustrated in a cross-sectional FIB image of a macroparticle on a TiN coating (Figure 6.6). A path for oxygen diffusion is evident between the macroparticle and the coating. It can be inferred from the results in the present investigation, that the higher number of macroparticles in the coatings deposited at the lower deposition pressure can affect oxygen uptake of the TiN coating. Accordingly, TH coatings (Chapter 5, section 5.1.1) with their higher macroparticle density (5.4×10^4 mm^-2) would be expected to show higher oxygen content. However, composition analysis revealed that the oxygen content in the TH coatings is less than the TL coatings (see section 5.2.2). The oxygen content within the coating may well be correlated to the coating microstructure rather than macroparticle content of the coating.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N (atomic %)</th>
<th>Ti (atomic %)</th>
<th>O (atomic %)</th>
<th>N/Ti ratio</th>
<th>O/Ti ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1 (0.1 PA)</td>
<td>18</td>
<td>37</td>
<td>45</td>
<td>0.49</td>
<td>1.21</td>
</tr>
<tr>
<td>T2 (0.4 Pa)</td>
<td>23</td>
<td>41</td>
<td>36</td>
<td>0.56</td>
<td>0.88</td>
</tr>
<tr>
<td>T3 (0.8 Pa)</td>
<td>34</td>
<td>49</td>
<td>17</td>
<td>0.69</td>
<td>0.35</td>
</tr>
<tr>
<td>T4 (1.25 Pa)</td>
<td>38</td>
<td>52</td>
<td>10</td>
<td>0.73</td>
<td>0.19</td>
</tr>
</tbody>
</table>
Figure 6.5  A cross-sectional FIB micrograph of the CAE deposited TiN/Cr/Brass coating showing a titanium macroparticle and the resultant path for oxygen diffusion in the coating.
6.2.3 Preferred orientation

The structure of T1, T2, T3 and T4 (TiN/Cr brass) coatings deposited at different nitrogen pressure was studied using the Bragg-Brentano diffraction method. All the coatings showed a TiN fcc structure. It is evident from Figure 6.6 that the intensity of the (111) orientation increases and that of (200) decreases with increasing nitrogen pressure. This has also been observed by Carson et al.[123] and Gorkhovsky et al.[124] for arc evaporated TiN coatings. Carson et al.[123] suggested that a reduction in the intensity of the (111) peak for the coating deposited at lower deposition pressure can be due to oxygen incorporation into the crystal structure and this incorporation arises by substitution onto nitrogen lattice sites. Gorkhovsky et al. [124] reported that an increase in nitrogen deposition pressure can significantly increase the number of nitrogen reactive species bombarding the growing film, which can also affect strain in the coatings. In the present study, since all the TiN coatings were deposited at low substrate temperature, the observed (111) orientation is consistent with the total energy minimisation principle proposed by Pelleg et al. [112], and discussed in section 5.1.3. Furthermore, although it is reported that TiN coatings containing low nitrogen (below 35 atomic %) are characterised by having different phases of TiN [123], XRD data in the present study revealed that the TiN coatings deposited contained only the TiN phase and no others.
Figure 6.6 XRD pattern of CAE deposited TiN/Cr/brass coatings at different nitrogen pressure of (a) 0.1 Pa (T1), (b) 0.4 Pa (T2) (* unidentified peak).
Figure 6.6  XRD pattern of CAE deposited TiN/Cr/brass coatings at different nitrogen pressure of (c) 0.8 Pa (T3) and (d) 1.25 Pa (T4)
6.3 Decorative properties (colour and optical reflectivity)

The colour of TiN coatings varies widely in the reported literature [7,33] from grey, pale yellow, golden yellow to red brown. This colour range depends primarily on the atomic ratio of N/Ti. The results of colorimetric measurements using spectrophotometer (Minolta CM-500 d-series), based on the CIE L*a*b* system for T1, T2, T3 and T4 (TiN/Cr/brass) coatings are presented in Figure 6.87. It is evident that, the redness (a*), yellowness (b*) and brightness (L*) increase slightly with increasing deposition pressure. Furthermore, the T3 (P_{N2} of 0.8 Pa) and T4 (P_{N2} of 1.25 Pa) TiN coatings displayed a golden hue, with almost identical chromatic values of a*, approximately, 4, b* approximately, 36 and brightness L* approximately, 77. With a further decrease in deposition pressure, a change in colour to pale yellow was observed and correspondingly decrease in brightness, L* and also, the colour components, a* and b*.

The optical reflectivity of the TiN (TiN/Cr/brass) coatings in the visible range are presented in Figure 6.98. It is evident that the reflectivity curves show two regions, an absorbing region and a reflecting region, which are clearly distinguished at a critical wavelength, as also observed previously (section 5.2). The reflectivity of the TiN coatings increases with increasing deposition pressure over the complete visible range. The data further show that a smooth absorption edge is present with a reflectivity minimum at about 420 nm for the T3 and T4 TiN coatings. The edge becomes broader and moves towards lower wavelength at lower deposition pressure corresponding to change in hue. The reflectance minima for the T1 and T2 TiN coatings are approximately 410 nm and 400 nm, respectively.

The present observations indicate that colour and reflectivity are affected by the deposition pressure as this affects the composition and morphology of the coating. The coating deposited at the lowest pressure of 0.1 Pa revealed a pale yellow hue due to a slight presence of blue. There is considerable evidence [31, 51] that the deposition pressure affects the colour of the coating. The findings are in good agreement with the work of Niyomsoan et al. [51], who observed a variation in hue from pale yellow to a golden yellow of the TiN coating with an increase in deposition pressure. Wang et al. [31] studied the
effect of nitrogen pressure in relation to the production of CAE decorative coatings on brass. They found that the reflectivity of the coating increased with increasing deposition pressure due to a reduction in the surface roughness of the coating. Another explanation for a reduction in the reflectivity of the coating deposited at the low depositing pressure was proposed by Nosea et al. [43]. In their study of sputtered TiN coatings, they observed that oxygen was incorporated into the sputter deposited TiN coating due to its open columnar structure, and consequently, oxidation of the coating decreased the reflectivity of the coating. In the present study, the observed lower reflectivity at lower deposition pressure can be interpreted by considering the surface morphology as well as changes in the chemical composition of the coating due to microstructure of the coating. Interestingly, both the TiN coatings deposited at pressures of 0.8 Pa to 1.25 Pa indicated a similar golden hue. It is suggested that this is due to the strong depression of the reflectance at the blue end of the spectrum. The findings suggest that for decorative applications, a wide range of pressures for depositing TiN coatings can be employed with negligible colour change.
Figure 6.7  L*a*b* values for CAE deposited TiN/Cr/brass coatings as a function of deposition pressure.

Figure 6.8  Variation in the optical reflectivity of CAE deposited TiN/Cr/brass coating deposited at various deposition pressures.
6.4 Tribological performance (Abrasive wear)

The wear out of the TiN coatings was assessed using the Taber abrasion test. The first exposure of the substrate was at 200 cycles for the T1 (TiN coating deposited at 0.1 Pa), 400 cycles for the T2 (TiN coating deposited at 0.4 Pa), 1100 for the T3 (TiN coating deposited at 0.8 Pa) and to 1300 cycles for the T4 (TiN coating deposited at 1.25 Pa), respectively. This observation indicated a higher wear resistance of the T4 coating, compared to all the remaining coatings. It should be recalled that the T4 coating showed the lowest coating thickness (section 6.2.1).

The above findings clearly seem to disagree with the general view [117] that thick coatings are more abrasion resistant than thin coatings. Holmberg and Mathews [116] suggested that the coating microstructure and the hardness arising from the coating microstructure, can have a significant effect on the tribological performance of the coatings. Patsalas et al. [46] have carried out hardness studies of sputtered TiN coatings deposited as a function of deposition temperature and bias voltage. They observed a significant reduction in the hardness value for TiN coatings and attributed this to oxidation of TiNₓ coatings. The hardness of the resulting composite TiNₓ/TiO₂ coatings was reduced due to the lower hardness of TiO₂ (well below 15 GPa). In the present study, composition of the TiN coatings revealed increasing oxygen amount at lower deposition pressure (section 6.2.2), and effectively therefore decreased wear resistance.

In addition to above view, the wear out which may also be related to the macroparticles, as proposed before (section 5.3) must also be considered. The observed large number of macroparticles in the T1 coating deposited at the lowest deposition pressure may well be the major factor in increasing the effective depth of the wear out of the coating, leading to the lower wear resistance.
6.5 Corrosion studies

6.5.1 Corrosion potential measurement

The variation of the corrosion potential of the TiN coatings on chromium plated brass coupons in 0.5 M NaCl solution was recorded over a period of 20 days in duplicate and is presented in Figure 6.9. All coatings showed an initial trend towards more negative potentials similar to that observed earlier (Figure 5.5). This is again consistent with the mathematical derivation by Stren [119] and discussed in section 5.4.1. After an initial period of 3 days, the potential stabilised for the T1, T2 and T3 electrodes and was around –265 mV, –355 mV and –375 mV, respectively. In contrast, T4 showed a significant and relatively rapid change in the potential value to –500 mV. With further exposure, a similar change was also observed for the T3 electrode, but at a later stage, with the corrosion potential around –500 mV. The change in corrosion potential values displayed by T3 and T4 electrodes therefore, suggests penetration of electrolyte through the coating to the chromium plated brass substrate, and was discussed before (section 5.4.1).

The corrosion potential values displayed by the T1 and T2 electrodes were significantly lower and were around –200 mV during the period of measurement. Although it was revealed that the coatings deposited at lower pressures (T1 and T2) had larger macroparticle densities compared to those deposited at higher pressure (T3 and T4), the results of corrosion potential variation with time indicates that only T3 and T4 electrodes allowed penetration of electrolyte to the active substrate. The results therefore, suggest that some additional features of the (T1 and T2) coating may be significant in preventing the electrolyte access to the active substrate. It may be that with the thick coatings (T1 and T2), the effective penetration path of electrolyte to the substrate is increased or may be that the defects in the coatings which extend through the coatings are reduced with the coatings thickness. Furthermore, it is assumed that a titanium interfacial layer between the substrate and the coating is present in all these coatings since they were deposited at lower substrate temperature as revealed by microstructural TEM studies (section 5.1). Unfortunately, with time constraints, TEM studies on all TiN coatings could not be carried out in the present
thesis. The composition analysis (section 6.2.2) showed the higher amounts of oxygen in the coatings deposited at lower deposition pressure (T1 and T2 coatings) compared to those deposited at higher pressure (T3 and T4 coatings). It may be inferred from the results that with the higher amount of oxygen in the coatings, and consequently, oxidation of a titanium interfacial layer, may protect the substrate from further corrosion. The results indicate that although, the defect density of the coatings deposited at the lower pressure is higher than those deposited at the higher pressure, the oxygen content in the coating can have a significant role in offering a better corrosion protection. After 20 days of immersion in the electrolyte, no peeling of the coating or corrosion of the substrate was observed for the T1, T2, T3 and T4 electrodes.

![Figure 6.9 Corrosion potential variations with time of TiN/Cr/brass coatings deposited at different nitrogen pressure in 0.5 M NaCl, unstirred solution](image-url)
6.5.2 Potentiodynamic polarisation study

The corrosion protection performance of the TiN coatings on chromium plated brass substrates was assessed out using potentiodynamic polarisation tests. The voltage scan was carried out from –1000mV to +2000mV at a scan rate of 1mV/sec in 0.5 M NaCl deaerated solution. Figure 6.10 shows typical polarisation curves for the T1, T2, T3 and T4 electrodes. The polarisation curves for uncoated brass and chromium plated brass are also included for purposes of comparison. It is evident from the figure that after initial low current density, there is a rapid increase in the current density as a result of corrosion of the underlying substrate as before and is discussed in section 5.6. A comparison of the anodic current density values, i, for coatings deposited under different nitrogen pressure shows the lower current density for coatings deposited at the lower deposition pressure. Therefore these coatings characterised significantly improved corrosion performance.

For different anodic current density values corresponding potential values for TiN coated samples obtained from the data in Figure 6.10, are graphically presented in Figure 6.12. The results indicate that for any potential the current, and therefore corrosion rate of the substrate, is in the order of T4<T3<T2<T1. Similarly, as before (section 5.4.2), the smaller current density at any experimentally recorded current as a result of the greater surface area exposed will require the smaller externally applied potential to generate that current. The results in Figures 6.10, 6.11 and 6.12 also suggest that the area of substrate exposed to electrolyte as a result of electrolyte penetration through defects, in the T1 and T2 coatings is less compared to the T3 and T4 coatings, not withstanding the fact that the T1 and T2 coatings revealed the higher macroparticle density. Thus, although macroparticles have been considered unfavourable features of CAE coatings, the results presented in this investigation, demonstrated that their effect on the corrosion protection performance was not significant.
Figure 6.10 Potentiodynamic plot for TiN/Cr/brass coatings deposited at various nitrogen pressures in 0.5 M NaCl, unstirred solution.

Figure 6.11 Variation of potential with anodic current density for the T1, T2, T3 and T4 (TiN on chromium plated brass substrates) coatings.
The above results indicate that thick coatings formed at the lower deposition pressures offer better corrosion protection compared to thin coatings deposited at the higher deposition pressures. The findings are in agreement with the general view [67] that with increasing thickness of the coating, the defects in the coating are reduced, which may beneficially affect the corrosion characteristics of the investigated system. It is possible that the high oxygen content of the coatings deposited at the lower pressure compared to those deposited at the higher deposition pressure as well as the presence of a titanium interfacial layer may provide a protective TiO$_2$ interfacial layer. Carson et al. [123] observed an improvement in the corrosion performance of sputter deposited TiN coatings with the higher amounts of oxygen and suggested the improvement in the corrosion protection of the substrate could be due to oxynitride (TiO$_x$N$_y$).
Part II- Effect of multilayer coatings deposition on decorative properties, tribological and corrosion protection performance of CAE coatings

6.6 Deposition of multilayer coating

TiN/Cr multilayer coatings were deposited on chromium plated brass substrates and silicon wafer (100) at a bias of −200V, without prior heating. Multilayer deposition was achieved by interrupting the nitrogen gas flow rate using the Mass Flow Controllers (MFC); the sequence being Cr/TiN/Cr/TiN. The coating is referred to as the TM coating. The performance of the multilayer coating was compared with a bilayer coating of Ti-TiN referred to as the TLB coating, deposited under the same conditions as the TL coating (described in chapter 5).

The choice of the deposition pressure for depositing the TM coating was a significant aspect of this research. This was due to the fact that the results (in Part I of this chapter), revealed that decorative properties and corrosion performance were directly influenced by the deposition pressure. Specifically, decorative properties were found to improve for the coatings deposited at the higher deposition pressure, while corrosion performance was improved for the coatings deposited at the lower deposition pressure. In an attempt to identify the mechanisms of corrosion protection due to the low temperature deposition of multilayer coatings, it was considered essential to have moderate amount of oxygen in the coating. In the present investigation, therefore, multilayer coatings were deposited at a pressure of 0.6 Pa (see Figure 6.1 and Table 6.3). The results of an investigation into the critical role of microstructure and surface morphology in determining decorative properties, corrosion protection and tribological performance of TiN multilayer coating are reported in this section.
6.7 Characterisation of multilayer coatings

6.7.1 Surface morphology, roughness and microstructure

The surface morphology of the coatings was examined using SEM. Corresponding results for the TM (TM/Cr/brass) and TLB (TiN/Cr/brass) are presented in Figures 6.12 (a) and 6.12 (b), respectively. It is evident that the defect content of the TM coating is lower compared to the TLB coating. Measurement of the macroparticle density (number of macroparticles/unit area) revealed the lower density for the TM coating; \(3 \times 10^4 \text{ mm}^{-2}\), than the TLB coating; \(3.4 \times 10^4 \text{ mm}^{-2}\). The findings were further substantiated by a profile study using a Mahr Perthometer concept surface profilometer. The results of the surface roughness measurement showed the rms roughness, \(Ra\), 0.13 \(\mu m\) for the TM (TM/Si) coating compared to 0.18 \(\mu m\) for the TLB (TiN/Si) coating. Harris et al. [25] investigated the effect of different metallic interfacial layers on the macroparticle content and demonstrated that a significant reduction in the macroparticle content with a chromium interfacial layer could be achieved as compared to a titanium interfacial layer and hence, improved surface roughness of the coating. The difference in the macroparticle content due to different metallic interfacial layers was suggested as due to the higher vapour pressure and higher melting point of chromium. The liquid and solid chromium both exhibit an extraordinarily higher vapour pressure \((13 \text{ mbar at } 200^\circ\text{C})\) than titanium \((6 \times 10^{-1} \text{ mbar at } 200^\circ\text{C})\), and also the higher melting point of chromium \((1857^\circ\text{C})\) than titanium \((1660^\circ\text{C})\). Munz et al. [127] demonstrated that chromium with high vapour pressure undergoes sublimation under sufficiently high vacuum and consequently, reducing the emission of macroparticles from the chromium cathode.

The microstructure of the TiN coatings was studied using cross-sectional TEM (X-TEM). The corresponding bright field image for the TM coating is presented in Figure 6.13. It is evident that the interruption of the nitrogen flow has been successful in generating a multilayered structure. It can be further seen that the microstructure consists of fine columnar grains (layer 5) which are interrupted at an amorphous layer (layer 3).
The total thickness of the coating was estimated at around ~350 nm with individual layer thicknesses of 100 nm ~layer 2, 25 nm ~layer 3, 25 nm~ layer 4 and 200 nm ~layer 5. The microstructure of the TLB coating is as described in chapter 5 (section 5.1.1). It should be noted therefore that the coating thickness of the multilayer coating was less than the bilayer coating (400 nm, see Figure 5.1a). The difference in thickness can be related to the variation in the deposition rate for chromium and TiN.

Layers 1, 2 and 3 were identified as Cr electroplated layer, Cr PVD layer and TiN layer, respectively, using selective area diffraction (SAD). The microstructure shows a sharp interface between the layers of 1 and 2. Figure 6.14 (a) and 6.14 (b) shows condensed beam bright field images from layers 2 and 3, respectively. The lines radiating from the spot show that layer 2 (Cr) is crystalline, while the absence of such lines for layer 3 (TiN) is an indication of an amorphous structure. Although such a structure for the TiN coating has not been previously reported, it is suggested that the titanium cathode usually is covered with oxide layer and since titanium metal etching was not carried out in the present investigation, the formation of amorphous titanium nitride takes place. In addition, the possible presence of titanium oxynitride can not be ruled out in the present study.

Further, SAD patterns from layers 4 and 5 are presented in Figures 6.15 (a) and 6.15 (b), respectively. There is no difference between the SAD pattern of the layer 4 and 5, indicating that no phases apart from that seen in layer 5 are present, however the rings in layer 4 are slightly greater in diameter. This indicates that the structure is the same as that observed in layer 5, but the lattice parameter is slightly smaller (4.14 nm). The lattice parameters of CrN and TiN are 4.24 and 4.14 nm, respectively. Layers 4 and 5 therefore, were identified as CrN and TiN, respectively. The surprising result here was the apparent absence of the chromium layer which was deposited rather than CrN. Formation of CrN with fcc structure can be explained by considering the relatively high pressure of 0.6 Pa used for depositing the coating and the effectiveness of the vacuum pumps to maintain this pressure, it will take few minutes to completely remove nitrogen from the chamber during deposition of chromium layer. Such time lag is responsible for the introduction of the CrN phase.
Figure 6.12 SEM micrographs of the CAE deposited (a) TLB (TiN/Si) and (b) TM (TM/Si) coating showing the reduction in the number of macroparticles with the deposition of multilayer coating
Figure 6.13 Cross-sectional Transmission Electron Microscope image of the CAE TiN/Cr multilayer coating showing the microstructure of layer 1: electroplated chromium coating (substrate), layer 2: PVD chromium coating, layer 3: TiN coating, layer 4: CrN coating, and layer 5: the top coating of TiN.
Figure 6.14  Condensed beam bright filed images from (a) Cr coating (layer 2), and (b) TiN coating (layer 3).
Figure 6.15 Selective area diffraction pattern from (a) CrN coating (layer 4) and (b) TiN top coating (layer 5).
6.7.2 Preferred orientation

The structure of the multilayer TiN coating on chromium plated brass substrates was studied using the Bragg-Bretano diffraction method. Scans were performed over $2\theta = 40^\circ$ to $80^\circ$ for all samples. Figures 6.16(a) and 6.16(b) shows XRD patterns for the TM and TLB coatings, respectively. It is evident that both the TM and the TLB coatings show a pronounced preference for (111) orientation. Since both these coatings were deposited at low substrate temperature, the observed (111) orientation is consistent with the total energy minimisation principle proposed by Pelleg et al. [112], and is described in section 5.1.3.
Figure 6.16  Xray diffraction pattern of (a) TM coating and (b) TLB coating
(* unidentified peak)
6.8 Decorative properties (colour and optical reflectivity)

The visual impression of the TM coating (TM/Cr/brass) presented the golden-yellow hue. This was confirmed by measurements using a spectrophotometer (Minolta CM 500-d-series), based on the CIE-L*a*b* system (Table 6.4) giving L* as 77.6, a* as 5.59, and b* as 39.73. The corresponding measurements for the TLB coating (TiN/Cr/brass) revealed slightly lower values of L*(75.5), and b* (38.36). The optical reflectivity (Figure 6.18) also indicates higher reflectivity of the TM coating than the TLB coating. The difference in the brightness and hence, reflectivity can be related to the smooth surface morphology of the TM coating due to the lower macroparticle content. For both, the TM and TLB coatings, the reflectivity minima occurred at a wavelength of 430 nm with the reflectance value of 16.6% which is in agreement with widely reported value [51], and is also related [38] to the depression of the blue.

Table 6.4 Colour (L*a*b*) values of TiN TM and TLB coatings on chromium plated brass substrates at a bias of −200V and at a low substrate temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>TLB</td>
<td>75.5</td>
<td>5.59</td>
<td>38.36</td>
</tr>
<tr>
<td>TM</td>
<td>77.6</td>
<td>5.63</td>
<td>39.73</td>
</tr>
</tbody>
</table>
Figure 6.17 Spectral reflectivity of TiN coating deposited by CAE with multilayer coating TM and bi-layer (TLB), without substrate heating at bias of -200 V onto chromium plated brass substrate

6.9 Tribological performance (Abrasive wear)

The wear performance of the TiN coatings on chromium plated brass substrates was evaluated using a Taber abrasion test. The wear out of the TM coating was at 1400 cycles as compared to 1000 cycles for the TLB bilayer coating. This observation indicated a higher wear resistance of the TM coating than the TLB coating and can be due to hardness of the coating increasing with the multilayer coating deposition [130]. Hooleck et al. [130] suggested that the boundaries between individual layers of the multilayer coating can create a number of interfaces. These interfaces obstruct crack propagation through them, thereby enhancing hardness of the coatings.
6.10 Corrosion studies

6.10.1 Corrosion potential measurement

The variation of corrosion potential with time for the TM and TLB coatings on chromium plated brass coupons in 0.5M NaCl solution over a period of 20 days is presented in Figure 6.18. The data were recorded for two samples each. Initially the potential evolution of the TM coating presented similar behaviour to the TiN coating on an inert substrate of silicon in 0.5 NaCl solution (Figure 4.4). This indicated a noble behaviour of the TiN coating with respect to the substrate. After 2-3 days of immersion, the corrosion potential for the TM and TLB electrodes stabilises around –60mV and –90mV, respectively.

An interesting observation is that with further exposure, the free corrosion potential of the TLB coating becomes more negative than the TM coating, suggesting possibly some electrolyte penetration or oxide formation or dissolution of the coating surface. The observed trend towards more negative corrosion potential is similar to that observed earlier for the TiN coating deposited on an inert substrate of silicon in 0.5M NaCl solution (Figure 4.4). Furthermore, as revealed in section 5.4.1, the greater the number of defects, or the increasing penetration with time of more existing defects, or the lifting of the coating with time due to corrosion of substrate under the coating at the base of defects, the larger the ratio of anodic area fraction/ cathodic area fraction, \( f_a/f_c \). That is, \( f_a/f_c \) increases with time and, according to equation 5.1, \( V_{corr} \) becomes more negative with time as observed. The higher negative corrosion potential displayed by TLB coatings, compared to TM coatings, therefore can be attributed to the higher number of defects and thus, to the higher surface area as before (section 5.4.1). These findings are in agreement with Munemasa et al. [84] who demonstrated that defect density of the coatings decreased with multilayer deposition of coatings. In the present investigation, it was further observed that neither sample exhibited a corrosion potential similar to that of the substrate (~–500 mV), indicating no substantial breaching of the coating with the electrolyte penetration of substrate over the 20 day period. Furthermore, after 20 days of immersion in the electrolyte, no peeling of the coating or corrosion of the substrate was observed for the TM and TLB coatings.
corrosion potential variation for two samples in each case (TLB and TM), showed a similar pattern, indicating consistent behaviour of the coatings examined.

![Figure 6.18 Corrosion potential variations with time for the TiN on chromium plated brass coupons in 0.5 M NaCl, unstirred solution](image)

6.10.2 Potentiodynamic polarisation study

Potentiodynamic polarisation curves for the TM (TM/Cr/brass) and TLB (TiN/Cr/brass) coatings (each with a surface area of 0.25 cm²), in 0.5 M NaCl de-aerated solution, are presented in Figure 6.19. The polarisation curves for uncoated brass and chromium plated brass are also shown for purposes of comparison. The results suggest that the higher the number of layers, the better the corrosion protection performance of the system. Lakatos et al. [131] reported that the corrosion performance of the coatings improved with the multilayer coatings deposition. It is evident from the figure that after initial low values, there is a rapid increase in the current density. This increase may well be ascribed to penetration of the electrolyte and consequently, to the corrosion of the substrate, and is discussed before in section 5.4.2.
Figure 6.19  Typical potentiodynamic polarisation plots for the brass, chromium plated brass, TLB and TM TiN coatings on chromium plated brass coupons in 0.5 M NaCl, unstirred solution, electrode area 0.25 cm².

For different anodic current density values the corresponding potential values for TiN coated samples obtained from the data in Figure 6.19, are graphically presented in Figure 6.20. This shows that for any potential the current, and therefore corrosion rate of the substrate, is less for the TM coating compared to the TLB coating. The findings can be explained in light of the microstructure of the coating. Microstructure examination of the TM coating (Figure 6.12) revealed that the columnar microstructure of the coating was interrupted with an amorphous TiN interfacial layer. This may act as an effective barrier between the coating and the environment (0.5M NaCl solution in the present case). Furthermore, the smaller current density at any experimentally recorded current value as a result of the larger surface area exposed may well require the smaller externally applied potential to generate that current (and vice versa). The results in Figures 6.18, 6.19 and 6.20 indicate that the area of substrate exposed to electrolyte as a result of electrolyte penetration through defects, in the TM coatings is less compared to the TLB coatings.
The results suggest that a significant improvement in the corrosion protection can be achieved by depositing multilayer coatings. Furthermore, although the total thickness of the TM coating is less than the TLB coating thickness (350 nm as opposed to 400 nm), the results demonstrated a better corrosion performance of the TM coating. The findings also reinforce the reported view [131] that thick sublayers in the multilayer coating assist in preventing the columnar structure. Visual inspection of the electrodes following the potentiodynamic test revealed the presence of sparsely scattered islands of black corrosion product, possibly CuO, within the intact coating, indicating that the coating failure was due to corrosion of the underlying substrate in both TLB and TM cases, as before in section 5.4.2.

![Figure 6.20 Variation of anodic current density with potential for the TLB and TM, (TiN on chromium plated brass substrate) coatings.](image-url)
6.11 Summary

In the first part of the investigation, the effect of deposition pressure on the corrosion performance and decorative properties, as well as tribological properties of TiN coating deposited by the cathodic arc evaporation (CAE) technique, was investigated. In the second part of the investigation, the effect of multilayered structure of the type Cr/TiN/Cr/TiN was investigated. The main conclusions are given below.

With respect to the reactive gas pressure, a significant reduction in the macroparticles content of the coating was obtained with increasing deposition pressure. The findings are in agreement with the view that cathode poisoning reduces the emission of macroparticles from the arc spot in random CAE. Reflectivity measurements and colour measurements indicated higher reflectivity, with a golden hue of the coatings deposited at higher deposition pressure. The improvement in the decorative properties was recognised to be due to a smooth surface morphology. The TiN coatings displayed a similar set of values for reflectivity and colour measurements for the coatings deposited at pressures of 0.8 Pa and 1.2 Pa. The findings also highlighted a wide range of choices of TiN coating deposition pressure with negligible colour change for decorative applications. Corrosion studies revealed a better performance of TiN coating deposited at the lower pressure and was due to the higher thickness as well as the higher amount of oxygen in the coating.

The findings also revealed that the choice of the deposition pressure for decorative coatings is a key issue, since decorative properties and corrosion performance were directly influenced by the deposition pressure. Specifically, decorative properties were found to improve for the coatings deposited at the higher deposition pressure, while corrosion protection performance was improved for the coatings deposited at the lower deposition pressure. Furthermore, although macroparticles have been considered unfavourable features of CAE coatings, the results presented in this investigation demonstrated that their effect on the corrosion protection performance was not significant.
A significant improvement in the corrosion protection performance of the multilayer coating was recognised, due to an amorphous TiN interfacial layer interrupting the columnar structure of the coating. Surface morphology examination revealed a smooth surface morphology with reduced macroparticle content in the TM coating. Improvement in the decorative properties and tribological properties of the TM coating in comparison with the TLB coating was observed.
CHAPTER 7

General Discussion

The decorative coating market under consideration in this investigation was in the area of door furniture and tapware. The objective for decorative coaters using PVD technology is to reactively deposit such hard, thin coatings on economically viable substrates, with the opportunity of depositing coatings with a range of colours, combined with abrasion and corrosion resistance. Furthermore these PVD coatings, are required to be deposited at as low a substrate temperature as possible to avoid microstructural damage of the temperature sensitive substrates. To succeed in these economically significant markets, investigation is required to identify the mechanisms of corrosion protection relevant to PVD coatings, in order to better design and select such coatings for application in the harsher, longer term environments experienced by door furniture and tapware.

The major aim of the present investigation was to study the inherent corrosion properties of the PVD TiN coatings and the corrosion protection obtained by depositing TiN coatings on substrates used in the decorative coating industry, such as brass and high pressure die-cast zinc. This study included the investigation of the development of microstructure formation of decorative, TiN, CAE coatings deposited at the low substrate temperature and its effect on decorative properties, corrosion protection and tribological performance. This investigation was carried out as a function of the critical process parameters, such as, substrate deposition temperature, reactive gas pressure and multilayer formation. The major findings are discussed in this chapter.
7.1 Partial Filtered Arc Deposition (PPFAD)TiN coatings

In the first part of this investigation, TiN coatings were deposited using the relatively novel technique of partial filtered arc deposition (PFAD). Results were presented which related to a fundamental study of the corrosion properties of TiN coatings and their suitability for corrosion protection on typical substrates used in the decorative coating industry, namely, high pressure die-cast zinc and brass. Most reported electrochemical studies to assess the protective ability of TiN coatings have involved deposition of TiN coatings on active, metal substrates. This however, may well complicate the observed electrochemical behaviour, due to coating defects or poor adhesion, with exposure of the underlying, electrochemically active substrate to the electrolyte. There have been few studies of the electrochemistry of TiN itself and these have been primarily conducted in acid solution (63,94-96). In the present study PFAD TiN coatings were deposited on the electrochemically inert substrates of silicon or glass and the electrochemistry studied in the more relevant chloride medium. Various electrochemical techniques were employed to obtain a comprehensive understanding of TiN coatings’ corrosion performance.

While TiN was found to be more noble with respect to substrates of zinc, copper and nickel, the actual rate of galvanic corrosion may well be determined by the slower of the two primary steps: dissolution of the corroding substrate or the rate of the cathodic reaction, usually water reduction or oxygen reduction or both, occurring on the more noble surface. Galvanic studies indicated that galvanic current is area dependent and electrolyte stirring dependent; supporting the reaction under cathodic control for the zinc based systems. In contrast for the nickel based and copper based systems, galvanic current is area independent and electrolyte stirring independent; suggesting the reaction is under anodic control. The rate of oxygen reduction was as measured by exchange current densities ($i_0$) at equilibrium potential, on TiN was extremely low, indicating that TiN is a poor electrocatalyst for the oxygen reduction reactions and hence suggesting that galvanic corrosion may not be significant for a TiN-substrate system in NaCl. The partially passivating, protective film formed on the TiN coating surface however, was found to be unstable in 0.5M NaCl in contrast to that reported in sulphuric acid [63]. The study therefore, suggested that the
corrosion protection of the typical substrates by a TiN coating will be purely as a physical barrier to moisture and oxygen. Further study revealed a very slow rate of corrosion (\(\text{nAcm}^{-2}\)) for TiN consistent with the chemical inertness of TiN in sodium chloride solution.

The coatings were characterised in terms of decorative properties. The effectiveness of the partial filtration mode for reducing the number of macroparticles in the coating was demonstrated using surface morphology studies and the findings are in agreement with earlier investigations by Munz et al. [22] and Harris et al. [25]. It was observed in the present study that decorative properties of TiN coatings were improved by depositing with the PFAD system. This result was attributed to smoother surface morphology.

### 7.2 Random Cathodic Arc Evaporation (CAE) coatings

#### 7.2.1 Effect of substrate deposition temperature

It was established in this investigation that the use of PFAD for depositing TiN coatings led to a reduction in the macroparticle content and an improvement in the decorative properties. However, the complexity associated with the cathodic arc source and the low deposition rate of PFAD systems, makes such a system commercially unattractive. The unfiltered or random cathodic arc evaporation (CAE) technique is probably the most widely exploited method for the deposition of PVD decorative coatings. However, it is essential that, when this technique is used on temperature sensitive substrates such as high pressure die-cast zinc and brass, the PVD coatings be deposited at as low a substrate temperature as possible to avoid microstructural damage of these substrates. This restriction leads to some fundamental concerns that the PVD coatings may consist of open columnar grains with intergranular voids [24, 32]. The consequence of microstructure formation of decorative, TiN coatings deposited at the low substrate temperature and its effect on decorative properties, corrosion protection and tribological performance has not been fully explored in the literature and hence, these aspects were investigated in the present study by depositing CAE TiN coatings with no prior substrate heating. It is widely acknowledged [93,106] that through the selection of a relatively high substrate bias potential, a dense microstructure of
the PVD coating can be obtained. In the present study, the TiN coatings were deposited with a relatively higher substrate bias of \(-200\) V (referred to as the TL coating, low temperature deposition of \(140^\circ\)C) and results were discussed in terms of microstructure, morphology and composition of the coatings. For comparison purposes, TiN coatings were deposited under the same conditions, but, with prior substrate heating (referred to as the TH coating, high temperature deposition of \(200^\circ\)C). In both cases, a high voltage titanium metal etch followed by a reactive evaporation of titanium in nitrogen atmosphere was carried out.

Microstructure studies using X-TEM of the TiN coating deposited at the low substrate temperature (TL) revealed a columnar microstructure with some of the grains extended to the surface of the coating. On the basis of simulation studies, Torre et al. [108] suggested this type of structure is a consequence of the substrate rotation during the coating deposition process. The substrates will receive vapour flux at an angle due to the rotation of substrates and hence the columnar grain grows in the direction of impinging atoms. Furthermore, a titanium interfacial layer between the coating and substrate was suggested as a result of the high voltage titanium ion etch prior to TiN coating deposition.

In contrast, TiN coating deposited at the high substrate temperature (TH) did exhibit a less clear columnar structure. This observation was explained by the well accepted fact that the microstructure of PVD thin coatings deposited at higher substrate temperature is related to the greater mobility of adatoms [93]. The different sources of adatom energy are thermal and energetic particle bombardment. Both these sources assist in enhancing the surface mobility of the adatoms. The relatively dense microstructure of the TH coating was attributed to a high deposition temperature of \(200^\circ\)C. Further it was observed that the TH coating did not show a titanium interfacial layer, not withstanding the fact that it had a similar titanium metal ion etch as part of the TiN coating deposition cycle. An explanation for the absence of the titanium interfacial layer was advanced by Cairney et al. [109]. In their experiment, they deposited a titanium interlayer for a few minutes prior to deposition of TiN coating. They were unable to detect any titanium interfacial layer using X-TEM and suggested that nitriding of the nm thick titanium interfacial layer occurred on exposure to
the reactive nitrogen gas, at the relatively high deposition temperature of 450°C. Nitriding cannot be ruled out in the present study.

Investigation of the corrosion protection offered by the TL and TH coatings, using well established, electrochemical techniques, such as, corrosion potential measurement and potentiodynamic polarisation in 0.5M NaCl, indicated the better corrosion protection ability of the TL coatings compared to the TH coatings. The observed variation in corrosion potential with time indicated that TH coatings consisted of more defects than TL coatings, thereby allowing penetration of electrolyte to the active substrate. This was consistent with the higher surface roughness of the TH coatings compared to the TL coatings. Furthermore the variation of corrosion potential with time was found to be consistent with a mathematical derivation by Stern [119] which shows that corrosion potential is a function of the relative areas on the metal surface on which the anodic and cathodic reactions occur. After 20 days of immersion in the electrolyte, no peeling of the coating or corrosion of the substrate was observed for the TL and TH electrodes. The findings revealed the sensitivity of the corrosion potential measurement technique with the coating failure being indicated well before apparent signs of visible corrosion. Thus it can provide a simple method of monitoring coating failure compared to the conventional salt spray test at least when the corrosion potential of the coating and substrate are significantly different.

With the potentiodynamic polarisation technique, current values with increasing applied potential are recorded. It was revealed that the anodic current density values for both, the TL and TH coatings were lower compared to the substrates of brass and chromium plated brass materials, and thus, displayed the beneficial protective quality of the TiN coatings deposited on these substrate materials. These findings are in agreement with Wang et al. [31], however, they deposited TiN decorative coatings at a much higher substrate temperature of 250ºC. Potentiodynamic polarisation studies further indicated that the area of substrate exposed to the electrolyte as a result of electrolyte penetration through defects, in the TiN coating was least for TL coatings compared to TH coatings. Thus it is proposed that while TH coatings could offer some protection of the underlying substrate; this may not be as effective as that provided by TL coatings under the conditions prevailing during
the recording of the potentiodynamic polarisation plots. The findings are consistent with the association of defect density with the corrosion failure [84]. The coating defects in the form of pinholes and pores accelerate its corrosion. Consequently, with the TH exhibiting a higher surface roughness, this could provide a higher surface area for electrolyte access to the substrate. Furthermore, the presence of a titanium interfacial layer between the coating and the substrate for the TL coating is suggested in further delay of substrate corrosion for the TL coating as displayed at any potential, the current, and therefore corrosion rate of substrate, was less for TL compared to TH coatings. Consequently, the higher oxygen content of the TL coating compared to the TH coating was attributed to Ti passivation. This passivated layer is suggested to act as a barrier to assist against the further substrate corrosion.

Variation in colour for the TL and TH coatings were recorded using spectrophotometer (Minolta CM-500 d-series) and the coating colour was expressed using the CIE L*a*b* system. It was observed that with increasing deposition temperature, brightness/brilliance (L*) decreased slightly whereas the yellowness b* increased. This is consistent with the findings of Wang et al. [31] who demonstrated that low substrate temperature deposited TiN coatings appeared bright yellow. The optical reflectivity of the TL and TH coatings in the visible range showed a slightly higher reflectance for the TL coating with the maximum reflectance of about 75% in the infrared region compared to 73% for the TH coating. The results of colour variation and reflectivity with substrate temperature can be explained in the light of the Drude model and the ionic model [45, 38]. Both models proposed mixed character of bonding. According to the Drude model, the reflectivity is determined by the interaction of free electrons with visible light. This is directly influenced by the chemical composition (atomic ratio of nitrogen to titanium). Specifically, higher N/Ti ratio results in less titanium free electrons since, according to the ionic model, a transition metal nitride is formed by transfer of electrons from the transition metal to nitrogen. The reflectivity therefore, decreases with the lower number of available free electrons. As a result, the minima of the reflectivity curve shifts to the lower wavelength side. Due to a high contribution of blue colour in the reflected light, the TH coating appeared yellow, but with a different hue. A further understanding of reflectivity and colour was interpreted by
considering the microstructure and morphology differences. The coarse grained structure of the TH TiN coating deposited at higher substrate temperature is suggested to reduce the optical reflectivity. These findings are in agreement with the general view that the coating loses brilliance with increasing surface roughness [44,48].

The tribological performance, in particular, the abrasive wear, was evaluated using the Tabor abrasive wear tester and the results indicated a higher wear resistance of the TL coating compared to the TH coating. The findings were in agreement with the general view that coatings with the higher strain, and hence higher hardness, exhibit higher wear resistance.

### 7.2.2 Effect of deposition pressure

It is well known that coatings deposited using random CAE invariably suffer from the major problem of surface defects in the form of macroparticles. Hence, it was considered an important part of this investigation to study the effect of macroparticles on decorative properties, corrosion and tribological performance in the random CAE TiN coatings deposited at low substrate temperature. It is widely acknowledged that one of the most influential process parameters regarding macroparticle content is the pressure of the reactive gas [16, 20-23]. It is argued [22, 26] that increasing deposition pressure results in the cathode poisoning effect and consequently, in the reduction of the number and size of macroparticles. An investigation into the effect of deposition pressure on decorative properties, corrosion protection and tribological performance was carried out and corresponding results were reported in Chapter 6.

An initial investigations were carried out to determine the functional relationship between the deposition pressure and nitrogen gas flow rate. The resulting hysteresis effect was not dissimilar to that observed in the case of sputtering deposition systems [12,25] and the hysteresis plot, therefore, was interpreted along similar lines. At low flow rates, the chamber pressure showed very small changes since the majority of the reactive gas
participated in reacting with evaporating titanium ions. The chamber pressure started to increase only when the flow rate of nitrogen gas was sufficient to produce excess nitrogen. This excess nitrogen resulted in the formation of a TiN compound layer on the cathode surface. The latter resulted in a reduction in the evaporation rate from the arc spot which caused a rapid rise in the chamber pressure with further increase in the gas flow rate.

Using the hysteresis plot, a number of TiN coatings were deposited at different nitrogen pressures of 0.1Pa, 0.4Pa, 0.8Pa and 1.25Pa, respectively. These four coatings were identified as T1 to T4 in order of increasing deposition pressure and were characterised using various techniques to examine surface morphology, thickness and composition. SEM studies revealed a significant reduction in the macroparticle content with increasing deposition pressure. The findings obtained are in agreement with the view that cathode poisoning reduces the emission of macroparticles from the arc spot [22,25]. Further examination of coating cross-sections revealed that the coating thickness decreased with increasing gas pressure. Tzaneva et al. [72] suggested that the thickness difference could be due to the cathode poisoning effect at the high deposition pressure. At high deposition pressure, the formation of TiN compounds on the cathode could result in the change of erosion rate of the cathode and consequently, affecting the deposition rate.

Composition analysis of the coatings highlighted increasing N/Ti ratio with chamber pressure. This change was explained by considering the reactions occurring at the cathode/substrate interfaces. At 0.1 Pa, the N/Ti ratio was effectively metal rich which is consistent with the theory that minimal cathode poisoning takes place at lower pressure[20,25], and consequently, a metal rich film. At 0.4 Pa and 0.8 Pa, the N/Ti ratio increased to 0.56 then to 0.67 which was consistent with the fact that partial cathode poisoning is taking place. With a further increase in pressure to 1.25 Pa, the cathode was fully poisoned and the N/Ti ratio appeared to plateau at 0.73. The results of composition analysis further revealed that the amount of oxygen in the coating decreased with an increase in deposition pressure. The oxygen amount was approximately 45% at the lowest pressure of 0.1 Pa, reducing to approximately 10% at the highest pressure of 1.2 Pa. It is suggested that the result was due to the formation of an oxide layer on the surface as well as
on grain boundaries after the deposited coatings were exposed to the atmospheric conditions. In addition, the higher oxygen content in the coatings deposited at the lower deposition pressures was attributed to the microstructure of the coating. That is, the low adatom mobility at lower deposition pressures could result into an open columnar microstructure of the coating [22] and hence in the oxygen diffusion within the coating through grain boundaries.

The results of examination of decorative properties indicated that colour and reflectivity were affected by the deposition pressure. The coating deposited at the lower pressure revealed a pale yellow hue due to a slight presence of blue. The colour of both, TiN coatings deposited at the higher pressures of 0.8 Pa to 1.25 Pa indicated similar golden hue. This can be due to the strong depression of the reflectance at the blue end of the spectrum. The findings highlighted that for decorative applications, a wide range of pressure for deposition of TiN coatings could be employed with negligible colour change. The findings suggest that this may well be an advantage for decorative applications as there is a wide range of choice of TiN coating deposition pressure (0.8 Pa to 1.25 Pa) with negligible colour change. The reflectivity of the coatings deposited at the lower deposition pressure was found to be lower than those deposited at the higher deposition pressure. It is proposed that the result was due to the higher amounts of oxygen in the coatings deposited at the lower pressure as well as rough surface morphology. The findings are in general agreement [43] that the oxygen amount in the coatings and surface roughness reduces reflectivity.

The investigation of tribological performance of the TiN coatings showed that the wear resistance of the coating deposited at the higher deposition pressures was significantly higher than those deposited at the lower deposition pressures. It is suggested that the result was due to the higher amounts of oxygen in the coatings as a result of an open columnar structure formation of the coatings deposited at the lower pressure as well as lower defect content in the coating. Logothetidis et al. [125] demonstrated that the oxidation of TiNx coatings reduced hardness.
Investigation of the corrosion protection offered by the TiN coatings deposited at different nitrogen pressures on chromium plated brass substrates, was carried out using, electrochemical techniques of corrosion potential measurement and potentiodynamic polarisation in 0.5M NaCl. The variation of the corrosion potential with time, for the T1, T2, T3 and T4 coatings showed an initial trend towards more negative potential similar to that observed previously (chapter 4). With further exposure, the coatings deposited at higher deposition pressure (T3 and T4) showed a significant and relatively rapid change in the potential value to −500 mV. This change was ascribed to the penetration of electrolyte through the coating and coming into contact with the chromium plating layer. In contrast the corrosion potential values displayed by the coatings deposited at lower deposition pressure (T1 and T2) were significantly lower and were around −200 mV during the period of measurement. Although it was revealed that the coatings deposited at the lower pressures (T1 and T2) consisted of the larger number of macroparticles compared to those coatings deposited at the higher pressure (T3 and T4), the results of corrosion potential variation with time indicated that the T3 and T4 coatings allowed penetration of electrolyte to the active substrate. It is suggested that the result was due to the different thickness of the coatings and the oxygen amount in the coatings. Furthermore, it is proposed that a titanium interfacial layer between the substrate and the coating was present in all these coatings since they were deposited at lower substrate temperature as revealed by microstructural TEM studies (section 5.1). Unfortunately, with time constraints, TEM studies on all TiN coatings were not been carried out in the present thesis. This interfacial layer is suggested to further provide a barrier against the substrate corrosion.

The results of the potentiodynamic polarisation study also demonstrated that a thick coating at the lower deposition pressure offered better corrosion protection than thin coatings deposited at the higher deposition pressures. The findings are in agreement with the view [67] that thick coatings protect the substrate from corrosion. Furthermore, the results indicated that although, the defect density of the coatings deposited at the lower pressure was higher than that deposited at higher pressure, the oxygen content in the coating played a significant part in offering a better corrosion protection. Thus, although macroparticles have been considered an unfavourable feature of CAE coatings, the results presented in this
investigation demonstrated that their effect on the corrosion protection performance was not significant.

The findings also revealed that the choice of the deposition pressure for decorative coatings is a key issue, since decorative properties and corrosion performance were directly influenced by the deposition pressure. Specifically, decorative properties were found to improve for the coatings deposited at the higher deposition pressure, while corrosion protection performance was improved for the coatings deposited at the lower deposition pressure.

7.2.3 Effect of multilayer coating deposition

The deposition of CAE multilayer coatings, Cr/TiN/CrN/TiN on chromium plated brass substrates and silicon at a bias potential of −200V, with no prior substrate heating, was achieved by interrupting the nitrogen gas flow rate through the Mass Flow Controllers (MFC); the sequence being Cr/TiN/Cr/TiN. The performance of the multilayer coating (TM) was compared with a bilayer coating of Ti-TiN referred to as the TLB coating, deposited under the same conditions as the TL coating (as before in Chapter 5).

The choice of deposition pressure for depositing the TM coating was the main aspect of this research, since it was demonstrated earlier (Chapter 6) that decorative properties and corrosion performance were found to be directly influenced by deposition pressure. In order to acquire insights into the much discussed relationship between the multilayer coatings and the corrosion performance, multilayer coating was deposited at a pressure of 0.6 Pa. This pressure corresponded to a moderate amount of oxygen incorporation. The critical role of microstructure and surface morphology in determining the corrosion protection performance and decorative properties of TiN multilayer coatings was then investigated.

Measurement of the macroparticle density (number of macroparticles/unit area) revealed a slightly lower density for the TM coating; $3 \times 10^4 \text{ mm}^{-2}$, than the TLB coating; $3.4 \times 10^4 \text{ mm}^{-2}$. 

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The findings were substantiated by a profile study using a Mahr Perthenometer concept surface profilometer. The results of the surface roughness measurement showed the rms roughness, $Ra$, 0.13 $\mu m$ for the TM (TM/Si) coating compared to 0.18 $\mu m$ for the TLB (TiN/Si) coating. The findings were in agreement with the work of Harris et al. [25] and Munz et al. [22], who argued that a significant reduction in the macroparticle content with a chromium interfacial layer could be achieved as compared to a titanium interfacial layer and hence, improved surface roughness of the coatings. This, they attributed to the higher vapour pressure and higher melting point of chromium, resulting in a significant reduction in the emission of macroparticles from the chromium cathode.

A microstructural examination of the TM coating demonstrated an interrupted columnar structure and was identified due to the presence of a nanocrystalline amorphous structure of an interfacial layer. Furthermore, a surprising result was the apparent absence of a bcc chromium interfacial layer, rather, fcc CrN phase was detected. This was explained by considering the relatively high deposition pressure of 0.6 Pa used in the present study and the relative ineffectiveness of the vacuum pumps to maintain this pressure. This could require few minutes to completely remove nitrogen from the chamber during deposition of the chromium layer. Such a time lag was suggested to introduce the CrN phase.

The improvement in the decorative properties of the TM coating was attributed to the smooth surface morphology with reduced macroparticle content. The wear out of the TM coating (first exposure of the substrate) was at 1400 cycles as compared to 1000 cycles for the TLB bilayer coating. The improved wear performance of the TM coating compared to the TLB coating was in agreement with the general view [130] that hardness of PVD coatings increases significantly with the multilayer deposition of the coatings.

The investigation of the corrosion protection performance was carried out using corrosion potential measurement and potentiodynamic polarisation technique. The corrosion potential evolution of the TM and TLB coatings on chromium plated brass coupons in 0.5 M NaCl solution showed that the free corrosion potential of the TLB coating was more negative than the TM coating, suggesting possibly some electrolyte penetration or oxide formation.
or dissolution of the coating surface. The observed trend was similar to that observed earlier on TiN coating deposited on inert substrates of glass in 0.5M NaCl solution (Figure 4.4). Furthermore, it was observed that neither sample exhibited a corrosion potential similar to that of the substrate (~−500 mV), indicating no substantial breaching of the coating with the electrolyte penetration of substrate over the 20 days period. Alternatively, as before (section 5.4.1) the greater the number of defects, or the increasing penetration with time of more existing defects, or the lifting of the coating with time due to corrosion of substrate under the coating at the base of defects, the larger the ratio \( f_a/f_c \). That is \( f_a/f_c \) increases with time and, according to equation 5.1 \( V_{corr} \) became more negative with time as observed. Furthermore the higher negative corrosion potential displayed by TLB coatings compared to TM coatings therefore was attributed to the higher surface area and thus, to the higher surface roughness with the higher number of defects as before (section 5.4.1). These findings are also in agreement with Munemasa et al. [84] who demonstrated that by depositing multilayer coatings, defect density decreased.

The results of the potentiodynamic polarisation study for TM and TLB TiN coatings suggested that the corrosion resistance of the coatings improved with the number of layers. Furthermore, although the total thickness of the TM coating was less than the TLB coating thickness (350 nm as opposed to 400 nm), the results demonstrated a better corrosion performance of the TM coating. This may well be due to the columnar structure with open paths to the substrate interrupted with an amorphous TiN interfacial layer (see Figure 6.13). The findings also reinforce the reported view [131] that thick sublayers in the multilayer coating could assist in preventing the columnar structure. This fact was supported by the interesting observation that at any potential value the current, and therefore corrosion rate of substrate, was less for the TM coating compared to the TLB coatings. Visual inspection of the electrodes following the potentiodynamic test revealed the coating failure was due to corrosion of the underlying substrate in both TL and TM cases.

The relatively novel technique of multilayer coating of Cr/TiN/CrN/TiN was demonstrated. This coating demonstrated superior corrosion protection ability combined with improved decorative properties and tribological performance.
CHAPTER 8

Conclusions

The major aim of this thesis was a fundamental study of the corrosion behaviour of TiN coatings and the corrosion protection obtained by depositing TiN coatings on substrates used in the decorative coating industry, such as brass and high pressure die-cast zinc. The investigation integrated a study of the development of microstructure of decorative, TiN, cathodic arc evaporated (CAE) coatings deposited at the low substrate temperature and its effect on corrosion performance, decorative properties (colour and optical reflectivity) and some aspects of tribological performance. The results of the investigation were presented in two parts: the first related to a fundamental corrosion behaviour of TiN as a PVD coating, while the second related to the effect of substrate deposition temperature, reactive gas pressure and multilayer deposition on the corrosion protection performance, decorative properties (colour and optical reflectivity) and some aspects of tribological performance.

In the first part of the investigation, a fundamental study of the corrosion behaviour of TiN coatings was investigated by depositing TiN onto inert substrates. The findings demonstrated that a passivation film was formed on the coating surface in sodium chloride solution. This could decrease the rate of galvanic corrosion arising from the coupling of TiN with an active substrate. However, it was revealed that the passivating film was relatively unstable in chloride solution, being easily reduced. It was therefore, concluded that the corrosion protection of typical substrates, such as, high pressure die-cast zinc and brass, by a TiN coating will be purely as a physical barrier to moisture and oxygen. While TiN was found to be more noble with respect to substrates of zinc, copper and nickel, the actual rate of galvanic corrosion may well be determined by the slower of the two primary steps: dissolution of the corroding substrate or the rate of the cathodic reaction, usually water reduction or oxygen reduction or both, occurring on the more noble surface. Galvanic studies indicated that galvanic current is area dependent and electrolyte stirring
dependent; supporting the reaction under cathodic control for the zinc based systems. In contrast for the nickel based and copper based systems, galvanic current is area independent and electrolyte stirring independent; suggesting the reaction is under anodic control. The rate of oxygen reduction was as measured by exchange current densities ($i_0$) at equilibrium potential, on TiN was extremely low, indicating that TiN is a poor electrocatalyst for the oxygen reduction reactions and hence suggesting that galvanic corrosion may not be significant for a TiN-substrate system in NaCl. Further investigation demonstrated very slow rates of corrosion (nA/cm$^2$) for TiN consistent with the chemical inertness of TiN in sodium chloride solution.

In the second part of the investigation, the effect of substrate deposition temperature on the corrosion protection performance, decorative properties and tribological performance was evaluated by depositing TiN coatings with no prior substrate heating (referred to as TL); rather, the intention was to rely on the energy of ion bombardment, through the selection of a relatively high substrate bias potential, to achieve a dense microstructure. Similar studies were conducted on the high temperature coatings deposited with the same substrate bias potential, but, with substrate heating (referred to as TH). Tribological studies indicated a higher wear resistance of the TL coatings than the TH coatings. The results were in agreement with the general view that coatings with the higher strain, and hence higher hardness, exhibit higher wear resistance. Furthermore, improved decorative properties of the TiN coatings deposited at a low substrate temperature than those deposited at a high substrate temperature were observed.

Investigation of the corrosion protection offered by the TL and TH coatings using the electrochemical techniques of corrosion potential measurement and potentiodynamic polarisation, indicated the better corrosion protection ability of the TL coatings compared to the TH coatings. Corrosion potential measurement studies concluded that the TH coatings consisted of more defects than the TL coatings, thereby allowing penetration of electrolyte to the active substrate. The findings revealed the sensitivity of the corrosion potential measurement technique with the coating failure being indicated well before apparent signs of corrosion. Thus it may well be a simple method of monitoring coating
failure compared to the traditional salt spray test, at least when the corrosion potential of the coating and substrate are significantly different.

The microstructural examination also revealed that the TH coatings contained more defects than the TL coatings. It was concluded further from the microstructural examination that a titanium interfacial layer between the substrate and the coating was present only in the case of the TL coating. This can be critical in providing titanium passivation and hence improved corrosion performance for the TL coatings. The absence of an interfacial titanium layer for the TH coating was attributed to nitriding of the titanium interfacial layer due to ion bombardment from the plasma.

With respect to the reactive gas pressure, a significant reduction in the macroparticle content of the coating was obtained with increasing deposition pressure. This result was attributed to the cathode poisoning effect. Examination of the decorative properties indicated higher reflectivity, with a golden hue of the coatings deposited at higher deposition pressure and was attributed to a smooth surface morphology. Further investigation revealed that the TiN coating displayed a similar set of values for reflectivity and colour measurements for the coating deposited at pressure of 0.8 Pa and 1.2 Pa. It was concluded from the results that for decorative applications a wide range of pressures for depositing TiN coatings can be employed with negligible colour change. The improvement in tribological performance for coatings deposited at the higher deposition pressures was recognised as being due to the lower amount of oxygen content, and the lower defect content in the coating.

Corrosion studies revealed the better corrosion performance of TiN coatings deposited at the lower pressure, notwithstanding the fact that these coatings comprised of the higher number of macroparticles compared to the coatings deposited at the higher deposition pressure. This improvement was attributed to the reduction in the defect content of the coating with increasing coating thickness. In addition, the higher oxygen content of the coatings was recognised in providing a barrier against substrate corrosion by titanium passivation as well as oxide formation on grain boundaries in TiN coatings. Thus, although
Macroparticles have been considered an unfavourable feature of CAE coatings, the results presented in this investigation indicated that their effect on the corrosion protection performance was not significant.

The findings also revealed that the choice of the deposition pressure for decorative coatings is a key issue, since decorative properties, corrosion and tribological performance were directly influenced by the deposition pressure. Specifically, decorative properties and tribological performance were found to improve for the coatings deposited at the higher deposition pressure, while corrosion protection performance was improved for the coatings deposited at the lower deposition pressure.

Finally, the deposition of multilayer coatings, Cr/TiN/CrN/TiN, demonstrated a significant improvement in the corrosion performance, although the total thickness of the multilayer coating (referred to as TM) was less the bilayer coating (referred to as TLB) thickness (350 nm as opposed to 400 nm). This result was attributed to the columnar microstructure of the TM coating being interrupted with an amorphous TiN interfacial layer. It was concluded from the microstructural studies that the improvement in the decorative properties of the TM coating was due to the reduced macroparticles content. The multilayer coatings also exhibited improved tribological properties. The results were in agreement with the general view that with the multilayer coating deposition, hardness increases and consequently, improved tribological performance.

The above research emphasised the critical importance of microstructure and metallic interfacial layer, as well as the reactive gas pressure, in improving the corrosion and tribology of TiN decorative coatings. In addition, the findings indicated that deposition of multilayered Cr/TiN/CrN/TiN coatings at low substrate temperature can be a potential strategy for corrosion protection and tribological performance improvement of TiN decorative coatings. This is an important outcome for commercial exploitation.
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