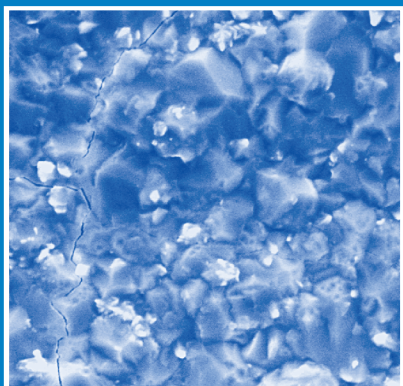


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Surface coatings for protection against wear

B. G. Mellor



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Surface coatings for protection against wear

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This book, as its title indicates, is about surface coatings for protection against wear, wear being defined as progressive damage to a solid surface by the action of relative motion with a contacting substance. As most machinery has moving parts or comes into contact with various materials, wear can be a serious industrial problem. Indeed a survey* of UK industry in 1997 indicated that the cost to UK industry of wear was of the order of £650 million. For industries with wear problems the costs were typically 0.25% of their turnover. There is no reason to suspect that this figure is not true on a worldwide basis. Thus wear is costly and there is a financial incentive to minimise it by design or material changes.

As wear is a surface or near-surface phenomenon, it has long been realised that the wear resistance of a component can be improved by providing a surface of different composition from the bulk material. Metalsmiths have known how to surface harden, by diffusing carbon into surface regions of irons by heating in bone or other carbonaceous material since Roman times while Vikings ‘coated’ or embedded the leading edge of their ploughs with stones to resist abrasion by soil. Nowadays there are many methods to modify the surface properties of a component and this constitutes the field of ‘surface engineering’. The processes used in surface engineering can be broadly classified into three groups.

1. Processes which apply a new material, a coating, to the surface, i.e. lead to the formation of a different phase with a distinct boundary between itself and the substrate.
2. Processes that modify the existing surface by inducing a change in composition of the surface engineered layer. This in general leads to a more diffuse boundary between the substrate and the reaction layer, e.g. as in carburizing.

* Neale, M.J., and Gee, M. (2000) *Guide to Wear Problems and Testing for Industry*, Tribology in Practice Series, Professional Engineering Publishing Limited, London.

3. Processes that modify the existing surface without a change in composition, e.g. transformation hardening.

This book will concentrate on surface coatings, i.e. the first of the above groups. However, the distinction between the first and second groups is sometimes not clear. Some coating processes give rise to a diffuse boundary between the coating and substrate, e.g. in welding surface treatments, while some of the processes which modify the composition of the surface region lead to a reaction layer that has essentially the properties of a coating as defined above, e.g. as in anodising where a layer of alumina is formed or in boronising where layers of borides are produced. Thus the diffuseness of the boundary between the surface region (reaction layer or coating) cannot be used on its own to distinguish between processes in groups one and two. Indeed, as with all classification systems there is some overlap between the three basic surface engineering groups and, where it has been thought useful, surface modification techniques from the second group, especially those that produce a distinct layered structure, are also briefly considered.

The second restriction placed on this book is that the coatings and processes described will be mainly employed to provide wear resistance to components. Coatings used just to provide corrosion resistance, e.g. the overlay welding of stainless steel on to a carbon steel substrate, will not be covered. However, coatings used to provide both wear and corrosion resistance will be treated.

The coating must be able to resist interaction with other parts or with process media while the substrate material must have sufficient strength to be able to support adequately the highly stressed coating, i.e. the properties of both the coating and substrate must be considered in surface engineering. In addition the coating must be sufficiently strongly bonded to the substrate so that service stresses do not cause it to debond or spall. Thus it is necessary to know the stresses developed in wear and the properties of the coating so that the correct coating system can be specified for a given application. Hence wear phenomena and the stresses arising from them must be understood. Equally the properties of coatings and the methods available to measure them must also be appreciated. Thus these two aspects of surface coatings are treated before specific coatings and coating deposition methods are described. Service applications where coatings have proved a success (successful applications) and those where coatings have not lived up to expectations (unsuccessful applications) are highlighted. Reasons for these differences are sought so that the selection of coatings and coating processes for specific applications can be optimised. This leads to a discussion of future trends in surface engineering which will hopefully permit some of the present shortcomings of coatings to be overcome.

The target audience of this book is thus undergraduate students requiring a sound foundation in surface engineering and the practising engineer who needs this surface engineering background to aid the selection of coatings and coating processes.

After this brief introductory preface, the book consists of 11 chapters written by different authors, experts in their field. Wear phenomena and the properties required from a coating as a function of wear phenomena will be addressed in Chapter 1. This will involve a description of the different wear phenomena, namely sliding wear, abrasive wear, erosive wear, fatigue and delamination wear, chemical wear and fretting wear. These wear phenomena are discussed in terms of the surface and subsurface stress fields generated when surfaces contact each other. Examples of both monolithic and coated surfaces are used to illustrate wear mechanisms and stress interactions with surface regions. The properties required from a coating to resist these stresses are considered and the material properties thought to have a major influence on the wear resistance of engineered surfaces discussed. Various parameters such as the thickness of the coating relative to the stress field resulting from the wear process are used to explore the effect of coating parameters such as modulus and thickness on wear performance. The effect on wear resistance of residual stresses present in coatings is explored and the influence of coating properties on stress distributions and thus wear propensity in monolayered and multilayered coatings considered. The rolling contact fatigue resistance of coatings is also treated and the effect of coating parameters highlighted.

Chapter 2 covers coating characterisation and property evaluation relevant to wear resistance, the emphasis being on the mechanical testing of coatings. Such information is required to optimise coating process development, for quality control purposes on the shop floor and as essential inputs in models which are increasingly being used to predict the performance of coatings. After briefly reviewing the techniques available for the measurement of coating thickness, adhesion testing methods are considered in some detail. Among the tests discussed are pull-off tests, mandrel testing, four-point bend testing, both with and without acoustic emission, thermal stress testing, tensile testing, Rockwell indentation and scratch testing. The advantages and disadvantages of each method are reviewed. Instrumented indentation testing of coatings, which permits the determination of properties such as elastic modulus, creep and viscoelasticity as well as hardness, is described and details given of procedures to distinguish the effects of the coating and the substrate in the composite response to indentation. Impact excitation as a method to calculate the modulus is introduced as is the use of laser surface acoustic wave measurements for the determination of thickness, modulus or density of a coating. Methods to measure the residual stress in a coating by coupon bending and X-ray diffraction are also discussed.

Chapter 3 provides an introduction to the various methods available to deposit wear-resistant coatings. Coatings are subclassified as those deposited on to the substrate in either the liquid or the solid state, coatings deposited from a solution of ions, coatings deposited from a vapour and coatings formed by reaction involving the substrate. Processes are allocated to these subgroups, e.g. friction surfacing is a coating deposited in the solid state while thermal spraying, weld hardfacing and laser cladding are deposited in the liquid state. Coatings deposited from the solution of ions are subdivided into electrodeposition and electroless deposition. Physical vapour deposition (PVD) and chemical vapour deposition (CVD) are processes deposited from the vapour. Finally surface engineering processes not normally described as ‘coatings’, e.g. anodising, plasma electrolytic deposition, phosphating, boronising and nitrocarburising, are briefly considered. A comparison of the different processes available is given from the substrate compatibility, component size compatibility and coverage perspectives.

The following six chapters describe in detail wear-resistant coatings produced by various deposition routes. Emphasis is placed on the microstructure property relationship in these coatings which are relevant to their performance as wear-resistant coatings. The first two of these chapters treat wear-resistant coatings produced from the vapour phase, Chapter 4 being on coatings produced by CVD, and Chapter 5 on PVD. The CVD process which is the deposition of a solid coating on a heated surface resulting from chemical reactions at the surface involving the surrounding vapour or gas phase is described and the influence of precursor chemistry, substrate pre-treatments and process operating parameters on film formation and the characteristics of the coating are considered. A discussion of the advantages and limitations of the process, especially the high deposition temperatures needed, leads on to consideration of plasma-assisted or plasma-enhanced CVD which allow lower substrate temperatures to be used. Several CVD coatings that have reached the stage of commercial exploitation in tribological components are then described.

Continuing on the theme of coatings produced from the vapour phase, Chapter 5 describes wear-resistant coatings produced by PVD. This process involves deposition of the coating on an atom-by-atom basis from the vapour phase, the production of the vapour flux being by a physical process (evaporation or sputtering). Once the coating flux encounters the component, it condenses and single atoms are incorporated to form the coating. As the incorporation of adatoms is one of the important stages in determining the coating microstructure and is dependent on the processing conditions, in particular the temperature of the substrate and the energy of the adatom, the properties of the coating thus depend critically on the deposition technology and it is therefore useful to treat materials depos-

ited and deposition processes together. Hence in this chapter the fundamentals of the PVD process are reviewed followed by a description of the commercial deposition technologies available, namely thermionic arc ion plating, thermionically assisted triode ion plating, arc evaporation and unbalanced magnetron sputtering. Ion beam processes are also considered not only as a means of modifying surface properties (ion implantation) but also as a means of assisting deposition in hybrid techniques such as ion-beam-assisted deposition. Typical coating materials, namely hard wear-resistant ceramic layers, soft solid lubricant coatings and multilayer or composite coatings, together with several tribological applications are then covered. Practical advice is given on the design of components with PVD coatings.

The next two chapters treat the formation of coatings from a solution of their ions. The first of these chapters, Chapter 6, considers electroless deposition in detail. The electroless deposition process, as one of several electrochemical methods of metal deposition, is described and the electroless deposition of nickel, copper and cobalt then treated. The electrolyte compositions and operating conditions necessary to produce consistent high-quality coatings are then considered and the role of buffers, stabilisers, complexants, exaltants and other additives highlighted. The influence of the above-mentioned bath additives on deposition rate are presented. The relationship between the corrosion and wear resistance of electroless coatings and coating porosity is then considered and data are given on the corrosion resistance of these coatings. The resistivities, hardnesses, residual stress levels and wear resistances of various electroless coatings both in their as-deposited and as-heat-treated states are described. Finally the wear properties of hybrid coatings consisting of electroless interlayers and PVD TiN are discussed.

Chapter 7 concentrates on electrolytic deposition of single metals and alloys. The fundamentals of the process are described and the corrosion and wear properties of widely used electrodeposited single metals, namely chromium, nickel and zinc, presented. The electrolytic deposition of alloys is then treated followed by a description of the corrosion and wear properties of alloys of cobalt, copper, gold, lead, nickel and zinc. The properties of electrodeposited composite coatings are introduced as novel ways of achieving low wear either by reducing the coefficient of friction with polytetrafluoroethylene additions or by introducing hard particles into the deposit. Finally anodised coatings on light metals are briefly considered.

Following chapters on deposition from a solution of ions the next three chapters deal with the deposition of coatings from the molten or semimolten state. Chapters 8 and 9 cover the thermal spray processes and welding surface treatments respectively, while Chapter 10 considers surface treatments using a laser as the heat source.

Thermal spray and weld surface treatments can produce hard coatings of similar compositions, the main differences being the microstructures of the coating, the natures of the interfacial region between coating and substrate and the coating thicknesses that are normally applied. The development of thermal spray processes is traced in Chapter 8 from the first attempts in the early 1900s to the modern powder spraying systems of high-velocity oxy-fuel and plasma spraying. The relationships between the coating microstructure, the nature of the feedstock, the thermal spraying process and its operating parameters are considered so as to be able to optimise the properties of the resultant coating. The behaviour of several coating systems to different wear phenomena are then presented; these include abrasable coatings where controlled wear is needed as well as coatings that are resistant to abrasion, sliding wear and erosion. Typical successful and unsuccessful applications of these systems are introduced.

Chapter 9 addresses coatings, hardfacings, produced from welding processes. This is an established area and hence standard processes are not described in detail; rather space is dedicated to modern developments such as friction surfacing and pulsed electrode surfacing techniques. The microstructure of the deposit, especially of the interfacial region, where melting of the substrate ensures a metallurgical bond, is stressed as this is a distinguishing feature between hardfacing and thermal spraying. This local melting leads to dilution of the coating material by the substrate which has important metallurgical ramifications, the degree of dilution and its importance depending on the coating process, the deposited material and the substrate. Hardfacing materials, both ferrous and non-ferrous, are dealt with in detail and data are given on the resistance of coatings to various wear phenomena. Where possible, comparative data are given so that the information is useful for coating alloy selection. Hardfacing process selection is considered and related to the hardfacing property requirements, physical characteristics of the component, metallurgical properties of the base and coating material, operator skill and cost. Many examples of successful applications are given. However, factors to take into account to avoid unsuccessful applications are also stressed.

Chapter 10 discusses the use of lasers in surface engineering. Lasers can be used to modify the surface of a component and to add new material to the surface of a component. Typical surface modification processes are laser surface transformation hardening for ferrous alloys and laser surface melting. Laser surface alloying is used to mix additional material with the molten surface of the substrate and laser cladding to melt the coating material and a thin surface layer of the substrate to form a coating. The advantages and limitations of using a laser as the heat source are discussed in this chapter and its niche area established. Applications of laser surface engineering techniques on ferrous alloys, aluminium alloys and titanium alloys are then given.

The final chapter in this book, Chapter 11, is dedicated to future trends in wear-resistant coatings and processes. Trends in both coating materials and coating processes are considered. Among the coating materials discussed are superhard materials with hardness values in excess of 40 GPa. This can be achieved by single compounds such as diamond, diamond-like carbon, cubic boron nitride and carbon nitrides and by means of multiphase coatings such as nanocomposite films. Functionally graded coatings are seen as another coating architecture which offers a method of achieving incompatible functions such as high toughness, high strength and bonding capability without severe internal stress. Developments in smart adaptive coatings, i.e. coatings that respond in a selective way to external stimuli, are another coating architecture highlighted. New processes, especially pulsed plasma processing, pulsed sputtering processes and high-density plasma sources, are described and their advantages in achieving increased control over the structure and properties of coatings stressed. Hybrid processes where different deposition techniques are combined to extend processing capabilities and to overcome the limitations of each individual technique are seen as promising.

The book thus considers wear principles relevant to coatings and the properties of coatings relevant to wear resistance and describes the processes and materials available to achieve wear-resistant coatings.

B.G. Mellor

Understanding surface wear in engineering materials

R.J.K. WOOD

University of Southampton, UK

‘It is better to wear out than to rust out.’ Bishop Richard Cumberland, 1631–1718 (quoted by Horne, *The Duty of Contending for the Faith*).¹

‘I... chose my wife, as she did her wedding gown, not for a fine glossy surface, but such qualities as would wear well.’ Oliver Goldsmith, *Vicar of Wakefield*, 1766, Chapter 1 (*The Oxford Dictionary of Quotations*).²

1.1 Introduction

There are numerous definitions of wear and most take the form of³ ‘the process of losing material from two surfaces that have been rubbed against one another’.

Relative motion between machine component surfaces almost inevitably leads to a change in these surfaces and most likely some form of material loss of at least one of the surfaces. This chapter reviews the different phenomena associated with material removal from engineering surfaces subjected to tribological contacts. These wear phenomena are discussed in relation to modern engineering coating systems and the stress systems that cause wear. The material properties that are thought to be a major influence on the wear resistance of the engineering surfaces are also discussed. The chapter is intended to be an overview and the reader is referenced to significant detailed reviews or research work within the appropriate sections. The chapter will use examples of both monolithic and coated surfaces to illustrate wear mechanisms and stress interactions with such surfaces.

Traditionally wear has been associated with friction, and the wear mechanisms have been classified as adhesion, abrasion, erosion, fatigue and chemical wear. However, as with other researchers, in this chapter to avoid confusion with using the term ‘adhesive wear’, those processes associated with adhesive phenomena have been integrated into a section on sliding

wear. This chapter will start by discussing the surface and subsurface stress distributions (fields) generated when surfaces contact each other. These stresses are linked to how the contact performs (e.g. either elastically or plastically) and are shown to control whether or not wear occurs. If wear occurs, these stresses also determine at what rate and by what mechanism or mechanisms wear proceeds. The chapter will then discuss friction followed by the different classified wear mechanisms and will outline material properties that influence the performance of surfaces subjected to tribological conditions. As this chapter reveals, few robust wear models are available which incorporate the mechanical properties of bulk or coated surfaces; therefore subscale or full-scale experimental testing is still required to gain actual wear performance to inform designers and to predict component life. Those models that do exist are often contradictory in regard to the mechanical properties that are dominant and the sensitivity of wear rates to certain parameters.

1.2 Role of stress distributions in wear

1.2.1 Elastohydrodynamic lubrication and stress distributions

Materials exhibit two types of response to stresses induced by externally applied loads.

1. Surface and subsurface deformation can occur elastically, plastically or in a viscous manner. Many solids exhibit all three processes depending on the stress and temperature. Elastic and plastic deformations are time independent while viscous deformation is time dependent.
2. Fracture of solids creates nascent (new) surfaces which initiate from pre-existing short cracks and void nucleation at or below the surface followed by their propagation, forming long cracks.

Tribological components such as gears, bearings and cams rely on the integrity of their interacting surfaces where loads can often be supported over a small surface area, leading to high surface contact stresses which can influence a much greater region of the materials than that directly in contact. To reduce the wear induced by the contact to a minimum, plastic deformation or fracture within this contact region should be avoided under both stationary and dynamic conditions. Severe wear will result in surface engineered components if extensive plastic deformation or fracture is allowed to occur in the surface coatings or surface treated regions and the substrate material. Therefore, the stress distribution within such components needs to be quantified to inhibit wear.

1.2.2 Contact mechanics

Hertz theory (purely elastic material)

When two curved surfaces are brought into contact, they form either a concentrated point or a more dispersed line contact. With the application of load, elastic deformation takes place over a finite area. A method to determine the size of this region was first described by Heinrich Hertz⁴ in 1881 whilst studying in Berlin. He assumed the following:

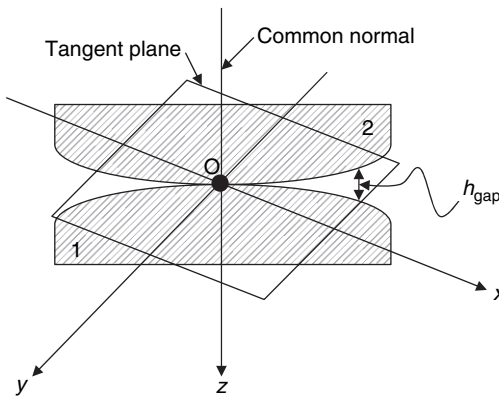
1. The size of the contact area is small compared with the curved surfaces.
2. Both contacting surfaces are smooth and frictionless.
3. The gap h_{gap} between the undeformed surfaces may be approximated by an expression of the form

$$h_{\text{gap}} = Ax^2 + By^2 \quad [1.1]$$

where A and B are constants. Figure 1.1 details the coordinate system used for these contact geometries.

4. The deformation is elastic and can be calculated by treating each body as an elastic half-space (i.e. a flat surface on an infinite elastic solid).

When two cylinders are loaded against each other with a load W' per unit length, a line contact of width $2b$ is produced. When two spheres are loaded together, with load W , a circular contact area of radius a develops. The dimensions and resulting contact stresses acting over the contact surfaces are given by the equations in Table 1.1.



1.1 Rectangular coordinate system (Oxyz) for non-conforming surfaces of two bodies in contact at O. Lower and upper body surfaces are labelled 1 and 2 respectively.

Table 1.1 Hertzian stress equations from the Tribology Group⁵ of the Institution of Mechanical Engineers; online software versions have been reported by the Tribology Laboratory of the University of Florida⁶

	Parallel cylinders: line contact	Spheres: circular point contact
Dimensions of the contact	$b = \left(\frac{4W'R}{\pi E^*} \right)^{1/2}$	$a^3 = \left(\frac{3WR}{4E^*} \right)^{1/2}$
Relative radius R^* of curvature	$\frac{1}{R^*} = \frac{1}{R_1} + \frac{1}{R_2}$	
Reduced modulus E^*	$\frac{1}{E^*} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2}$	
Contact pressure distribution p	$p(x) = p_0 \left(1 - \frac{x^2}{b^2} \right)^{1/2}$	$p(r) = p_0 \left(1 - \frac{r^2}{a^2} \right)^{1/2}$
Mean contact pressure p_m Maximum contact pressure p_0	$p_m = \frac{\pi p_0}{4} = \frac{W'}{2b}$	$p_m = \frac{2p_0}{3} = \frac{W}{\pi a^2}$

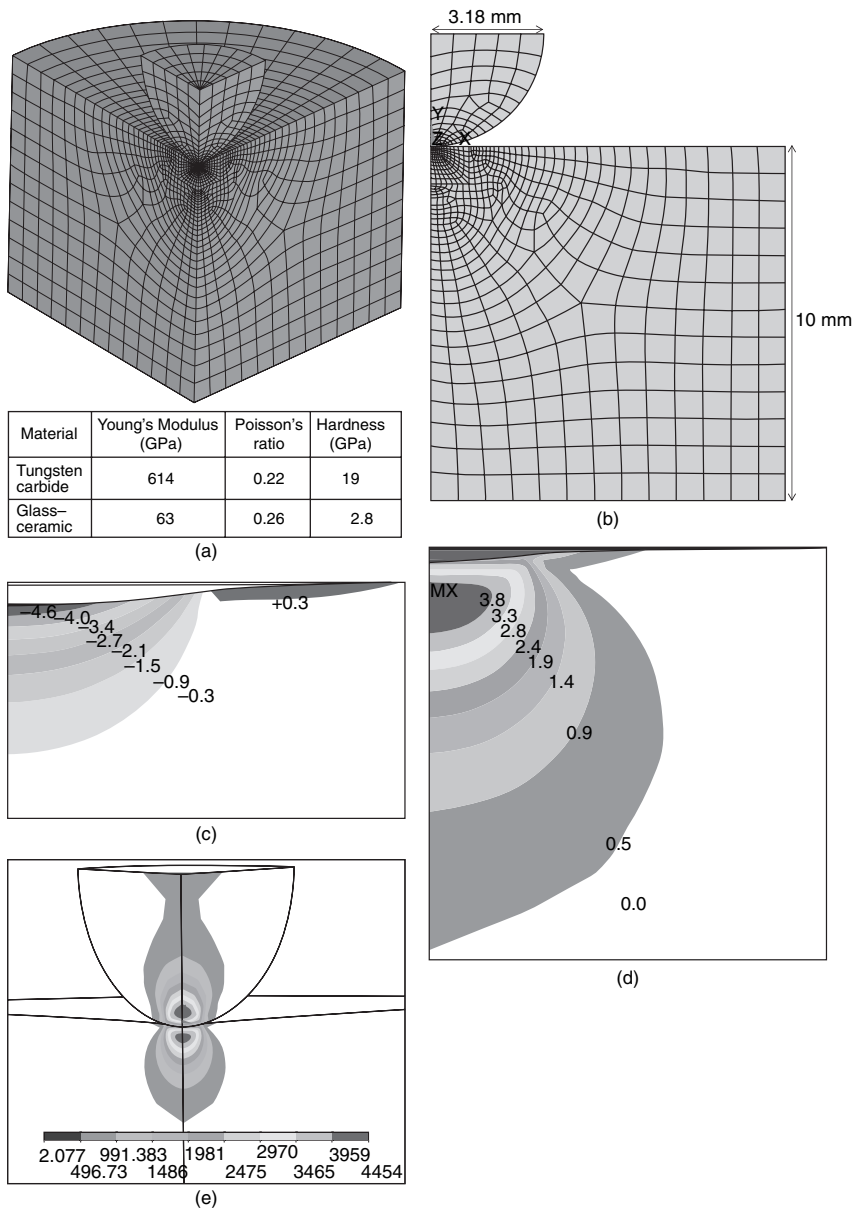
For a concave surface (hemispherical cup or groove) interacting with a sphere, either R_1 or R_2 can be defined as negative. For contact of a sphere or cylinder on to a flat then $R_2 = \infty$.

1.2.3 Normally and tangentially loaded coated contacts

Formulae for stress distributions of various contact geometries are available in textbooks such as those by Johnson,⁷ Suh⁸ and Rabinowicz.⁹

To illustrate typical stress fields developed by contacting surfaces, Fig. 1.2(a) to Fig. 1.2(e) present the finite-element stress analysis of a tungsten carbide (WC) sphere of 6.36 mm diameter loaded against a flat mica-ceramic glass-ceramic. Figure 1.2(a) and Fig. 1.2(b) show the mesh design used while Fig. 1.2(c) and Fig. 1.2(d) show the two-dimensional stress contours for the maximum principal normal stress and shear stress respectively. Figure 1.2(e) shows a three-dimensional plot of von Mises stresses in both sphere and flat plate. These are the important stresses acting. The normal load controls the extent of plastic flow at the asperity-asperity contacts.

For real contacts the surface and subsurface stresses will be influenced by the actual contact zones rather than by the larger apparent contact area and will be dominated by contact between asperities of each mating surface. Alanou *et al.*¹⁰ presented time-dependent stress distributions for contacts and Kweh *et al.*¹¹ have developed a code to simulate surface and subsurface



1.2 (a) Finite-element model mesh of a quarter of the sphere-base arrangements wherein there is a greater concentration of elements around the contact zone. The base material is micaceous glass-ceramic and the sphere is WC. (b) Finite-element model mesh of the sphere-base arrangements. (c) Stress contours (maximum principal normal stresses) in micaceous glass-ceramic indented with a WC sphere ($r = 3.18\text{ mm}$) and a load of 1000 N . Stresses are in GPa. (d) Stress contours (maximum principal shear stress) in a micaceous glass-ceramic indented with a WC sphere ($r = 3.18\text{ mm}$) using a load of 1000 N . Stresses are in GPa. (e) von Mises stress contours in both a glass-ceramic and a WC sphere ($r = 3.18\text{ mm}$) due to a load of 1000 N . Stress contours are in MPa.

stresses between rough contacting surfaces. Contact stresses can be several times the nominal Hertzian maximum pressure, as seen in Fig. 1.3. For example in Forschungsstelle für Zahnräder und Getriebebau (FZG) gear contacts the maximum contact stresses are predicted to be over 6 GPa while calculated maximum Hertzian stresses are only 1.4 GPa. These high stress amplitudes in contacts may well explain the onset of asperity–asperity welding and scuffing (i.e. adhesive failure of such oil-lubricated contacts).

For a static Hertzian point contact between steels ($\nu = 0.3$) subjected to normal loading, the location of the maximum shear stress $\tau_{\max}$ is on the axis of symmetry at a depth below the surface of $0.48a$ while its magnitude is given by

$$\tau_{\max} = 0.31p_0 \quad [1.2]$$

For line contacts, $\tau_{\max}$ is on the axis of symmetry at a depth below the surface of $0.78b$ and its magnitude is given by

$$\tau_{\max} = 0.30p_0 \quad [1.3]$$

Subsurface stress distributions are also related to the surface roughness of the contacting surfaces, as seen in Fig. 1.3. For many contacts the magnitude of the maximum shear stress causes plastic flow or yield and can initiate subsurface cracks, as sometimes found in bearings.

For dynamic (sliding contacts) the stress field is skewed owing to frictional (tangential) forces. The magnitude and location of maximum shear stress are affected by tangential forces with the point of maximum shear moving towards the surface as friction increases and reaches the surface⁸ when μ approaches 0.33. Under such conditions, plastic flow wear mechanisms dominate such as asperity adhesion–shear and fatigue crack propagation. Sliding motion also induces large tensile stresses normally at the trailing edge of the contact on the surface and, for example, for line contacts can be as high as $2\mu p_0$. For point contacts the tensile stress is given by the Hamilton¹³ equation

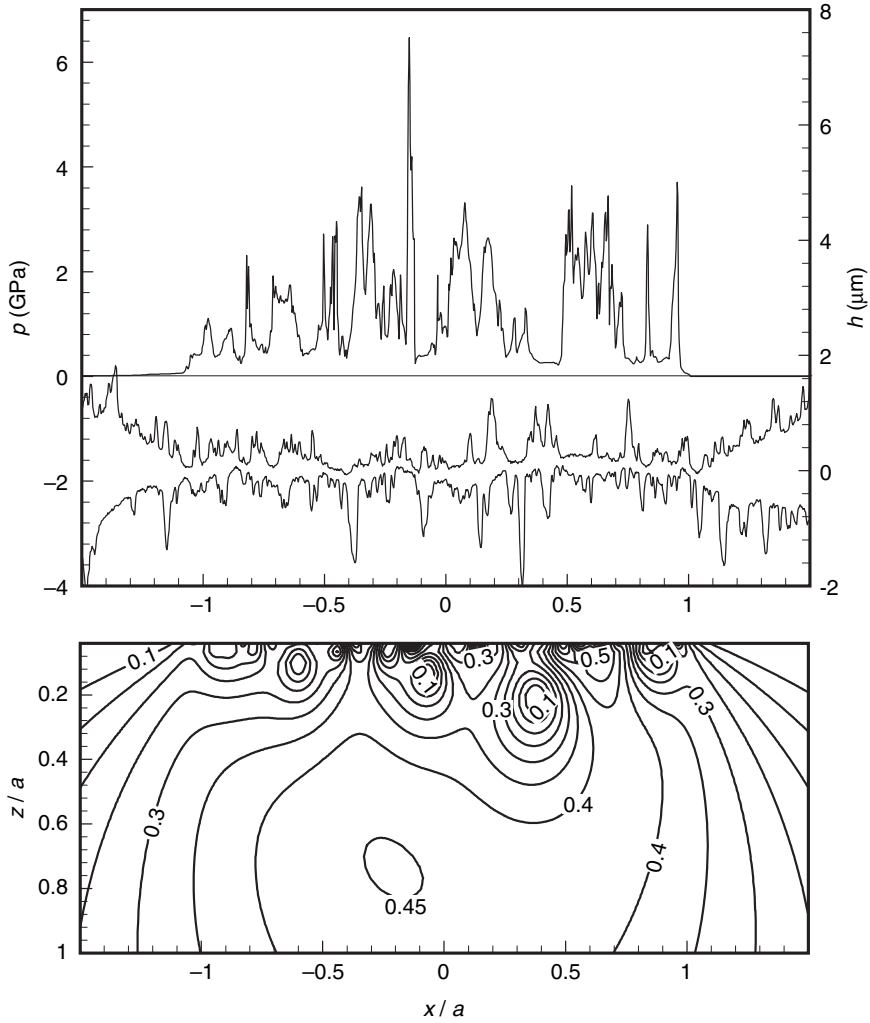
$$\sigma_x = p_0 \left(\frac{\pi\mu(4 + \nu)}{8} + \frac{1 - 2\nu}{3} \right) \quad [1.4]$$

These substantial tensile stresses can contribute to fatigue-based wear mechanisms and can also initiate surface cracks directly.

1.3 Wear in tribocontacts

1.3.1 Friction

Friction is the resistance force encountered when surfaces in contact move relative to each other. A popular way to express this force in



1.3 Pressure at a particular time step in a micro-elastohydrodynamic lubrication solution for gear tooth contact in an FZG test. The corresponding maximum Hertzian pressure is 1.4 GPa. Also shown are contours of τ (GPa) for the subsurface maximum shear stress. The sliding-rolling direction is from right to left. (Reproduced with permission from Snidle.¹²)

terms of a loaded sliding contact is by using the coefficient of friction, μ , defined as the frictional force F divided by the normal load W on the contact:

$$\mu = \frac{F}{W} \quad [1.5]$$

For lubricated contacts in relative motion separated by a fluid film the coefficient of friction is typically very low ($\mu < 0.1$) and can be as low as $\mu = 0.01$ even when the oil film is only a few nanometres thick. These values compare with values of around 1.0 for unlubricated dry sliding. Friction between contacting surfaces in relative motion result primarily from forces acting perpendicular to the applied load. As the fluid film thins, interaction of surface asperities can cause increases in friction. A useful ratio used to help to identify likely surface–surface interactions within lubricated contacts is the lambda ratio, defined as

$$\lambda = \frac{h_{\min}}{(R_{q1}^2 + R_{q2}^2)^{1/2}} \quad [1.6]$$

where the subscripts 1 and 2 of the root-mean-square surface roughness R_q represent the two surfaces within contact. If $\lambda \leq 1$, then surface–surface interactions are likely and increased friction may result although, if a fully formulated lubricant is used, low friction may be maintained owing to coverage of surface asperities by a tribochemically formed composite additive film of nanometer-scale thickness that is wear resistant. These films are self-healing (assuming that sufficient additive concentrations are present in the oil supply) and typically contain organic outer layers with inner glassy structured layers containing dispersed solids. However, the film is unevenly distributed, with its roughness oriented in the direction of sliding. This directional roughness inhibits the entrainment of fluid film in the mixed lubrication regime, increases the proportion of load supported by solid–solid contact and consequently results in the high friction often associated with the use of zinc dialkyl dithiophosphate additives.¹⁴

Bowden and Tabor¹⁵ proposed a model which in its simplest form assumes that frictional forces arise from adhesive forces and deformation forces induced by the abrasive ploughing nature of harder asperities interacting with softer asperities of the counter surface. The adhesive force is linked to the asperity–asperity contact which makes up the real area of contact between surfaces and the junctions between them. The shear strength of these junctions influences the level of friction. Adhesive effects are thought to be due to the summation of interfacial intermolecular interactions which operate at asperity contacts. There are also likely to be some chemical processes activated within the contact, such as oxidation, which can form coherent films and their composition can influence friction levels. The presence of oxide layers and adsorbed films on metal surfaces generally weaken the shear strength of the asperity junctions and thus lower adhesive forces resist motion, resulting in lower friction. For example, a multilayered film can be formed on ferrous surfaces under dry sliding, typically with FeO close to the surface, which is covered by a layer of Fe₃O₄, which in turn is covered

by Fe_2O_3 . The Fe_2O_3 layer is associated with high friction ($\mu = 1.1$) but, if this layer is penetrated exposing the sublayers, then lower friction ($\mu = 0.5$) can result.¹⁶ However, for soft ductile metals, and where the oxide layers or adsorbed films are partially removed, appreciable adhesion between nascent surfaces can result. Adhesion can also be enhanced if similar surfaces are in contact, i.e. stainless steel pairs.

The relative speed of sliding is also important as this can control the contact temperature. This temperature in conjunction with the operating temperature will affect the mechanical properties of the surfaces, the rate of oxidation or absorption and whether phase transformations occur. All these factors influence friction levels. For metal contacts, the rate of strain hardening or production of ductile–brittle transitions can cause large variance in the friction levels. Slowly moving contacts suffer a specific type of adhesive wear called galling, which leads to plucking of material from the surfaces and highly fluctuating friction levels.

Suh and Sin¹⁷ suggested that without significant temperature increases in the sliding contact the mechanical properties of the surfaces in contact dominate the frictional behaviour over the chemical processes. They included the role of wear debris in friction and suggested that friction is the sum of adhesion, asperity deformation and ploughing mechanisms. High values of the coefficient of friction approaching unity are associated with deep penetration by wear debris.

In the case of rolling contacts, the coefficient of friction is normally much smaller. The contact kinematics are different from those in sliding contacts with other effects including microslip, elastic hysteresis, plastic deformation and adhesion within the contact dominating the frictional performance.

The discussion above has focused on metallic surfaces but modern tribological contacts use the whole range of engineering materials including ceramics, lamellar solids and polymers.

Ceramics such as silicon carbide (SiC), silicon nitride (Si_3N_4), alumina (Al_2O_3) and zirconia (ZrO_2), with either ionic or covalent bonding, show limited plastic flow at room temperature; thus asperity contact between ceramics is predominantly elastic. The plastic strains associated with junction growth in all-metal contacts are not normally realised with ceramics but adhesive forces are present, resulting in coefficients of friction between 0.25 and 0.80. These values are similar to those levels generated by oxidised metals sliding in air. Non-oxide ceramics, such as SiC and Si_3N_4 , can form oxides in air within sliding contacts while oxide ceramics will react with water, whether present as moisture or vapour, to form hydrated surface layers on sliding. These effects are termed tribochemical and result in surface films that can reduce interfacial shear strength and thus the coefficient of friction.

Lamellar solids, such as graphite and molybdenum disulphide, under certain conditions show low-friction characteristics owing to weak interplanar bonding, frequently lowering shear strength. These are often considered as solid lubricants together with more expensive options such as silver typically used in bearing surfaces for space applications.

The friction coefficients of diamond-like carbon (DLC) films grown in reactant gases with very high hydrogen-to-carbon ratios (e.g. 10) can be superlow ($\mu = 0.003$). The friction coefficients of films grown in reactant gases with intermediate hydrogen-to-carbon ratios were between 0.003 and 0.65. However, experiments also revealed that the frictional properties of these films were very sensitive to test environments.¹⁸

Contact between polymers or alternatively between polymers and metals are predominantly elastic for smooth surfaces and in this respect are different from metal–metal contacts. Their E/H_V ratios are typically low (about 10), where E is Young's modulus and H_V is the Vickers hardness of the rough surface. The E/H_V ratio together with the surface topography indicate the level of plasticity likely and for metal–metal contacts, where $E/H_V = 100$, more plastic deformation is expected when compared with contacts where polymers are employed. However, polymers used with rough surfaces can suffer plastic deformation. The mechanical properties of these materials are time dependent, and most polymers are viscoelastic and show increased flow stress with increased strain rate. This all leads to a complex relationship between friction levels and sliding speed, temperature and normal load.

As with metal–metal contacts the friction of plastics is thought to be a summation of two effects termed deformation and adhesion. These terms have been discussed in detail by Briscoe and Tabor.¹⁹ Polymer–metal or polymer–hard-material contacts often result in polymer material transfer on to the counterface. The formation of coherent films and their properties directly influence the friction and the subsequent wear levels. Two examples of polymers with these characteristics are high-density polyethylene and polytetrafluoroethylene, which produce low coefficients of friction because of their unbranched linear molecular structure, high level of crystallinity and weak intermolecular bonding.

1.3.2 Wear phenomena

Wear should be avoided in most engineering applications, as in many cases it causes loss of functionality and potentially energy. The exception is in the case of machining where material loss is a requirement. Wear debris can also induce failures or accelerate wear downstream in oil lubrication and hydro-transport systems.

Mechanisms

Wear is almost the inevitable companion of friction.²⁰ However, the inter-relationship between friction and wear within a contact is not well understood. The assumptions that low friction accompanies low wear and that high friction accompanies high wear are not universally valid. For example, low friction can result from the high wear rate of solid lubricants such as silver or graphite.

Material removal from a surface can be categorised into several wear mechanisms. In typical engineering contacts, more than one mechanism can act at the same time,²¹ amplifying the difficulties of selecting a surface for minimum wear performance.

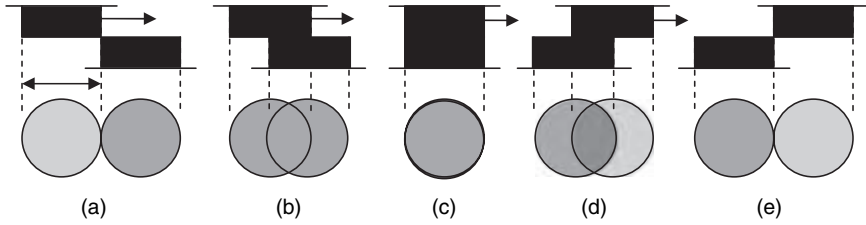
Sliding wear

Adhesion plays an important role in sliding contacts but other processes, such as abrasion, can act instead of and as well as adhesion to generate wear and these will be discussed in the section on abrasive wear. The terms scuffing or scoring and galling are often associated with adhesive wear although scuffing and scoring are limited to lubricated contacts while galling is generally used when severe adhesion occurs between surfaces subjected to dry sliding at low sliding velocities. Both terms relate to localised surface damage and material transfer or transformation associated with local solid-state welding between sliding surfaces. Both of these processes can cause catastrophic failure of engineering systems owing to adhesive seizure of sliding surfaces and the associated high friction or torque.

The main theory for sliding wear of metals is based on the assumption that contact between two surfaces occurs where asperities contact and the local deformation is plastic. The true contact area is therefore given by the summation of individual asperity contact areas and is closely proportional to the normal load. The evolution of a single contact 'patch' for two interacting asperities is schematically illustrated in Fig. 1.4. For the middle case in Fig. 1.4(c), the contact area is at a maximum and circular, of radius a , and the fraction of the normal load, δW , supported by this area is given by

$$\delta W = \sigma_y \pi a^2 \quad [1.7]$$

where σ_y is the yield pressure (approximately its indentation hardness) for the plastically deforming asperity. With the onset of sliding, the load is transferred from this contact to other asperity contacts, which in turn plastically deform. Wear is associated with the detachment of material from the asperity contacts and the volume of each wear debris will relate to the size of the individual asperity contact. Assuming that the debris volume



1.4 Schematic diagram showing the evolution of a single contact area as two asperities move over each other.²²

$\delta V \propto a^3$, where the contact dimension is assumed to be hemispherical of radius a , gives

$$\delta V = \frac{2\pi a^3}{3} \quad [1.8]$$

If it is assumed that a proportion ϕ of the asperity contacts generate wear debris, then the average volume loss of worn material, δQ , per unit sliding distance due to sliding one pair of asperities through a distance $2a$ is

$$\delta Q = \frac{\phi \delta V}{2a} = \frac{\phi \pi a^2}{3} \quad [1.9]$$

The overall wear rate Q (volume loss per unit sliding distance) is the summation of contributions over the entire real contact area:

$$Q = \sum \delta Q = \frac{\phi}{3} \sum \pi a^2 \quad [1.10]$$

The total normal load W can be expressed by

$$W = \sum \delta W = \delta_y \sum \pi a^2 \quad [1.11]$$

Hence

$$Q = \frac{\phi W}{3\sigma_y} \quad [1.12]$$

If $k = \phi/3$ and $P = H_c$, the equation above becomes the well-known Archard²² wear law

$$Q = \frac{kW}{H_c} \quad [1.13]$$

The Archard wear law suggests, for a system with constant k , that the wear rate is directly proportional to load on the contact but inversely propor-

tional to the surface hardness H_c of the wearing material. It can be written

$$\kappa = \frac{V}{WL} = \frac{k}{H_c} \quad [1.14]$$

where κ is the dimensional specific wear rate (typically quoted in units of $\text{mm}^3\text{N}^{-1}\text{m}^{-1}$ or m^2N^{-1}), V the volume loss, W the applied load, L the sliding distance, k the dimensionless wear coefficient and H_c the material surface hardness.

The term k has been defined to include the probability that each asperity contact produces a wear particle. However, it could represent the number of cycles of deformation required by each asperity before a debris particle is ejected.

Although Archard has been widely associated with deriving the relationship in Equation [1.14], Preston²³ had derived a wear equation in 1927 in relation to polishing glass, namely

$$h = \int_{t_1}^{t_2} DpUdt \quad [1.14a]$$

where h is the wear depth developed between times t_1 and t_2 , D is a wear factor, p is the pressure and U is the relative velocity of the workpiece contact point with respect to the tool contact point.

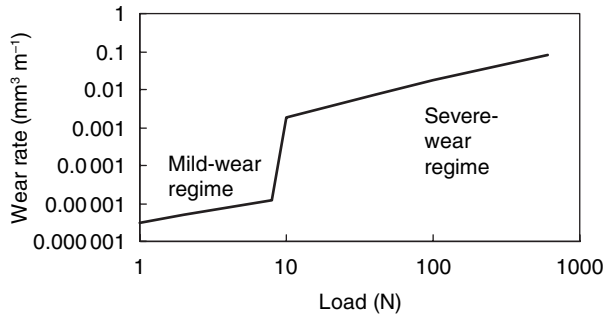
Equation [1.14a], derived by Preston, is often quoted in chemical mechanical polishing, which is now being used increasingly in silicon fabrication processes of microchips. It has the same form as the 1953 Archard wear equation because the product Udt gives the sliding distance and because pressure can be substituted as load/area (W/A); as Ah is the wear volume V , Equation [1.14a] can be rewritten as

$$D = \frac{h}{\int pUdt} = \frac{h}{pL} = \frac{hA}{WL} = \frac{V}{WL} \quad [1.14b]$$

Note that Equations [1.14b] and [1.14] are identical and that $D = \kappa$.

It has been shown experimentally that the loss of material by wear is proportional to sliding distance except for short tests where the non-linear running-in period is significant. However, proportionality between wear rate and normal load is less often found. Abrupt transitions from low to high wear rates and sometimes back again are often found with increasing load. Figure 1.5 shows this type of behaviour. Examples of this behaviour are seen for leaded α - β brass and silver sliding against hard Stellite® (Cobalt-based alloy), lubricated by cetane at 0.7 m s^{-1} at various contact stresses.²⁴

When low wear rates occur at low loads, this regime is called 'mild wear' while the regime of higher wear rate above the transition load is termed



1.5 Schematic diagram of the transition from mild wear to severe wear.

‘severe wear’. Mild wear typically produces fine wear debris ($0.01\text{--}1\text{ }\mu\text{m}$), predominately of oxides, while severe wear produces particles of $20\text{--}200\text{ }\mu\text{m}$ size. Complex material transfer between surfaces is a feature of mild wear due to oxidational processes while severe wear occurs typically by detachment and ejection of transferred material (soft to hard) from the contact.

For unlubricated wear of metals, no single wear mechanism dominates as sliding progresses. Mechanical stresses, temperature and oxidation state within the contact control which wear mechanism dominates.

Lack of predictive equations for the different wear mechanisms as well as friction makes identifying the most important or controlling material property or combination of properties very difficult.

Clearly from the Archard equation (see Equation [1.14]), the hardness H_V (the measure of plastic flow stress) of the material or resistance to indentation is important, predicting that $\kappa \propto 1/H_V$. However, the hardness of a wearing surface is likely to be different from the initial bulk hardness value and assuming that H_V is the only parameter to consider is not advised when predicting wear rates. Composite surfaces further complicate wear prediction as it is often unclear which phase hardness to include, should they be known.

The plasticity index ψ helps to predict the onset of plasticity (plastic flow) at asperities and incorporates the important ratio E/H_V :

$$\psi = \frac{E}{H_V} \left(\frac{\sigma^*}{r} \right)^{1/2} \quad [1.15]$$

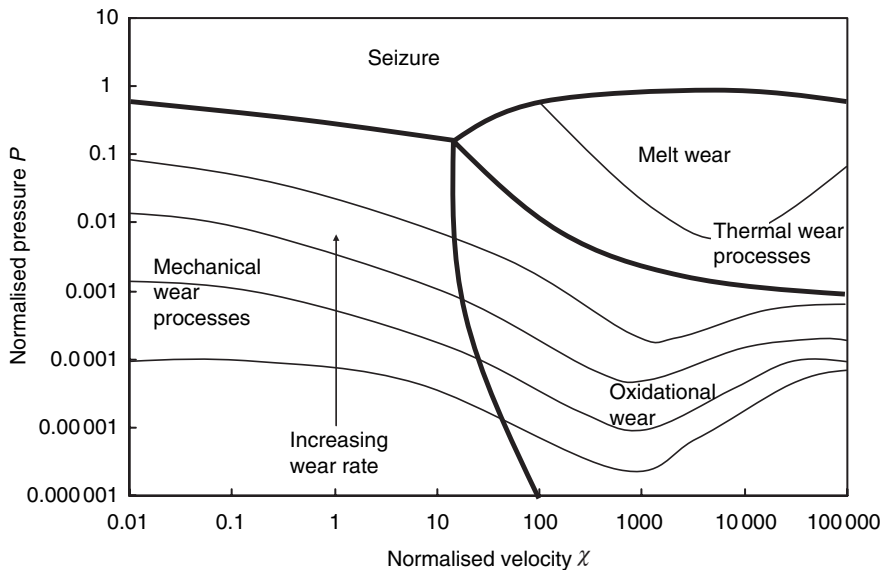
where σ^* is the standard deviation of asperity heights and r is the radius of the spherical asperity tips. For values of ψ below unity the contact is likely to be elastic while, for values above unity, the contact is likely to be plastic. The boundary between elastic and plastic regimes is found when this ratio approaches unity.

Wear maps offer a tool to predict transitions between wear mechanisms and to infer wear rates. Lim and Ashby²⁵ generated a very useful load-speed-based wear map for dry sliding steel in 1987. The map is divided into approximately three regions: seizure (excessive loads at any speed), a mechanically dominated region (lower speeds) and a thermally dominated region (higher speeds). Transitions from mild to severe wear processes are also mapped (Fig. 1.6). The map plots normalised pressure p/H_v against normalised velocity χ where

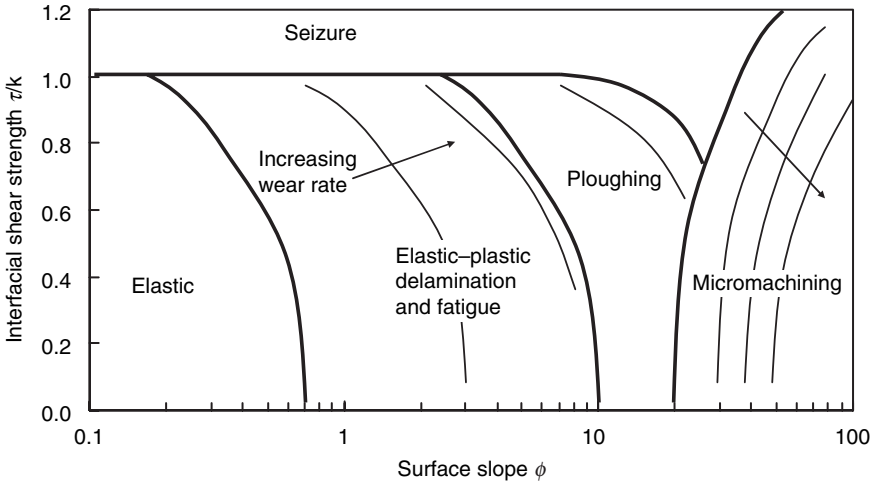
$$\chi = \frac{U}{\beta} \left(\frac{A_{\text{nom}}}{\pi} \right)^{1/2} \quad [1.16]$$

with A_{nom} the nominal contact area, β the thermal diffusivity of the wearing material and U the sliding velocity.

Alternatively, if thermal aspects are considered less important for the contact under consideration, the shear strength at the interface should be considered when mechanical processes dominate. Interfacial shear strength can be plotted against a roughness parameter, typically the average slope of the surface roughness, as in Fig. 1.7 from the paper by Childs.²⁶ This map shows five regions; seizure, elastic, elastic-plastic (delamination and fatigue),



1.6 The main features of a load-speed dry-sliding wear mechanism map for steel based on a pin-on-disc configuration. Thick lines delineate the different wear mechanisms and thin lines are contours of equal wear rate. (From Lim and Ashby.²⁵)



1.7 Wear mechanism map for a rough surface plotted as interfacial shear strength (τ/k) against mean slope ϕ of the rough surface (asperity attack angle). Thick lines delineate different wear mechanisms and thin lines are contours of equal wear rate. (After Childs.²⁶)

ploughing and micromachining. Thus, for smooth surfaces and low ψ (<1) the properties required to minimise wear relate to minimising the fatigue and damage accumulation. Once into the elastic-plastic region, delamination wear can evolve. For rougher surfaces, abrasion or ploughing can occur with significant plastic deformation taking place. Micromachining occurs when plastically deformed material is lost from the contact. Decreasing the interfacial shear stress in this region, by adding say a lubricant, actually increases wear volume removal while, for the other regions, decreasing the interfacial shear stress results in a decrease in wear rate.

For melt wear, flash temperatures $\theta_{\max}$ in the contact are comparable with the melting temperature of the surface and generate liquid metal films in the contact. These act in the same way as a hydrodynamic lubricating film and allow the coefficient of friction to drop but the wear rates are typically high. Material properties that control the flash temperatures (maximum temperature generated within the contact) are given by

$$\theta_{\max} - \theta_0 = \frac{2}{\pi^{1/2}} \frac{\dot{h}a}{\beta} Pe^{-1/2} \quad [1.17]$$

where $\dot{h} = \mu p U$, $Pe (= Ua/2\kappa)$ is the Peclet number, $\beta (= K/\rho c)$ is the thermal diffusivity and a is the Hertzian contact radius or half-width (K is the thermal conductivity, ρ the density of the half-space, c the specific heat, U the sliding velocity, μ the coefficient of friction, θ_0 is the initial temperature and p the contact pressure).

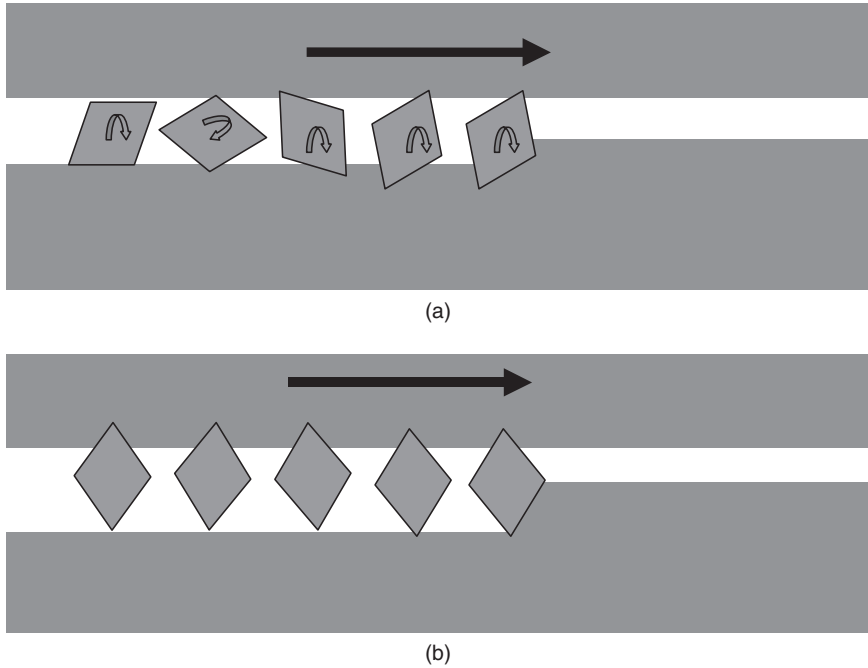
Quinn²⁷ related oxidational wear rates to the kinetics (rates) of the oxidation process and this can be described by an Arrhenius relationship leading to an expression for wear rate W_r given by

$$W_r = \frac{A}{f\rho_{\text{ox}}Ut^{1/2}} C_0 e^{-(Q_0/R\theta_{\text{max}})} \quad [1.18]$$

where Q_0 is the activation energy, R the universal molar gas constant, C_0 the Arrhenius constant, θ_{max} the flash temperature, A the real contact area, f the mass fraction of oxygen in the oxide, ρ_{ox} the mean density of the oxide in the contact zone, U the sliding velocity and t the time over which the equilibrium mild wear is measured.

Abrasive wear

There are two types of abrasion: two-body or grooving abrasion as shown in Fig. 1.8(a) while three-body or rolling abrasion is illustrated in Fig. 1.8(b).



1.8 (a) Schematic diagram of rolling abrasion due to the motion of entrained solid particles between two sliding surfaces. (b) Schematic diagram of grooving abrasion due to the motion of embedded solid particles in one surface.

Wear rates of rolling abrasion are generally lower than those generated by grooving abrasion. Industrial surveys place abrasion as the most common wear mechanisms with over 50% of wear problems being associated with both types of abrasion.²⁸ In abrasive wear, material is removed or displaced from a surface by hard particles, or sometimes by hard protuberances or asperities, on a counterface or embedded hard particles within a surface, forced against and sliding along the surface. The sources of the hard particles, which can be entrained into the sliding contact, include contaminants from the outside environment, wear debris, oxidation products formed with the tribocontact or other chemical processes.

Depending on the contact conditions, one of these types of abrasion may predominate but, generally, complex contact conditions result in either mixed modes where both types of abrasion produce material loss or the type of abrasion changes with time. Another important factor is the crushing strength or friability of the abrasive particles within the contact. If individual contact stresses exceed the crush strength, significant particle degradation in size and shape results together with increased particle numbers which will directly influence the load per particle and, thus, the type of abrasion and wear rate.

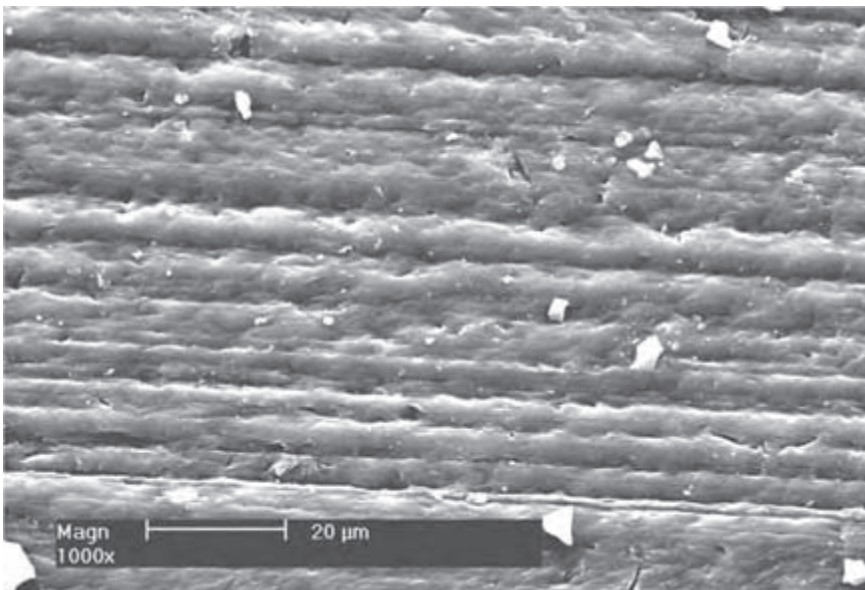
Models for predicting entrainment of particles into the contact have been recently developed by Kusano and Hutchings.²⁹ The first model treats the conditions under which a spherical abrasive particle of size d can be entrained into the gap between a rotating sphere of radius R and a plane surface. These conditions are determined by the coefficients of friction between the particle and the sphere, and the particle and the plane, denoted by μ_s and μ_p respectively. This model predicts that the values of $\mu_s + \mu_p$ and $2\mu_s$ should both exceed $2^{1/2}d/R$ for the particles to be entrained into the contact. If either is less than this value, the particle will slide against the sphere and never enter the contact. The second model describes the mechanisms of abrasive wear in a contact when an idealised rhombus-sectioned prismatic particle is located between two parallel plane surfaces separated by a certain distance, which can represent either the thickness of a fluid film or the spacing due to the presence of other particles. Kusano and Hutchings showed that both the ratio of particle size to the separation of the surfaces and the ratio of the hardnesses of the two surfaces have important influences on the particle motion and hence on the mechanism of the resulting abrasive wear.

Shipway³⁰ has recently presented a mechanical model which predicts the mode of motion of a particle between two surfaces loaded against each other, where the particle supports the load; this is in contrast with the early work of Williams and Hyncica^{31,32} which addressed the problem of particles passing through a lubricated contact where the fluid film itself supported the load. The model shows that particle sliding will tend to be promoted

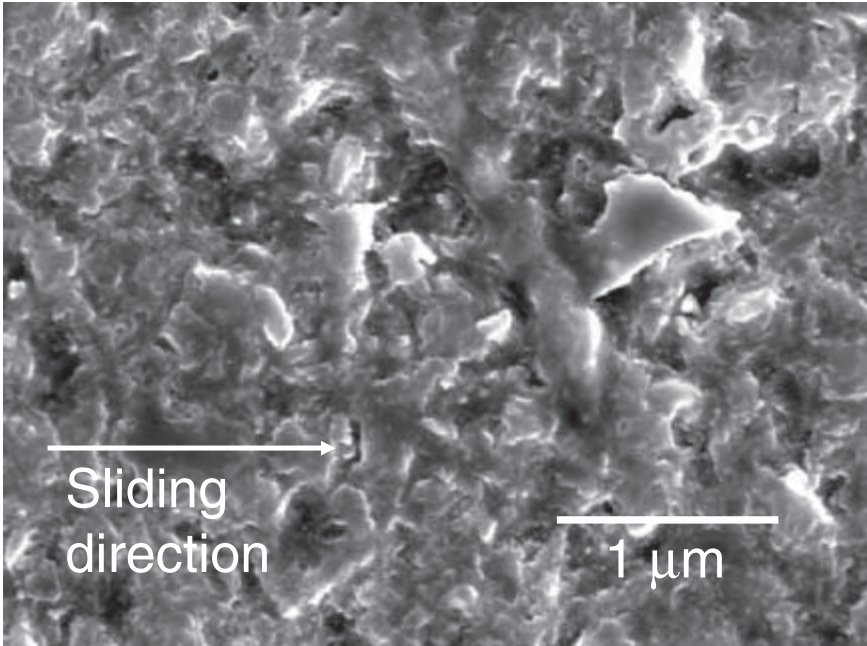
by high loads per particle and by a large hardness differential between the two surfaces as well as by particles with high aspect ratios. The coefficient of friction at the sliding surface also has a strong effect on particle motion within the contact.

Two-body or grooving abrasion typically results from hard asperities of a relatively rough counterface or from embedded hard particles within the counterface which, under load and sliding, cause the softer surface to wear. The penetration of the hard particles or asperities causes plastic flow in the softer wearing surface and the relatively tangential movement of the contacting surfaces results in ploughing, wedge formation and cutting.³³ However, for contacts with a differential hardness between surfaces, wear debris of the harder surface can become embedded into the softer counterface. This results in the protection of the softer surface while promoting wear of the harder. Two-body or grooving abrasion (as the name suggests) results in a surface topography dominated by long grooves parallel to the sliding direction as seen on the surface of the polyamide 11 coating which was hot dipped and air cooled and is shown in Fig. 1.9. Depending on the severity of the contact conditions these grooves can range from light scratches to severe gouges.

Three-body or rolling abrasion can cause multiple-indentation damage on the wearing surface of a boron carbide coating obtained by chemical vapour deposition (CVD) (Fig. 1.10).



1.9 Showing grooving of a polyamide 11 coating.



1.10 Scanning electron micrograph of the surface of a CVD boron carbide (B_4C) coating after being subjected to rolling abrasion (three-body abrasion) by $5\mu m$ SiC abrasive particles.

Micro-abrasion testers are now being deployed to look at abrasion resistance of thin coatings.^{34,35} The advantage of this test is that microscale wear scars are generated, requiring only small samples; running a perforation test allows both the wear rate of the coating and substrate to be quantified.

Recent work by Adachi and Hutchings³⁶ used a model by Williams and Hyncica³² to attempt to predict whether two- or three-body motion will be generated when slurry is entrained into a contact between a rotating spherical ball and a flat plate. The model defines a severity index S_i and its relationship with the hardness ratio of the contacting surfaces. The severity index is derived from assuming a static analysis is applicable and is, therefore, likely to be inappropriate where contact dynamics change the entrainment of solids into the contact. The severity index does, however, help to include contact conditions and the load per particle in the contact:

$$S_i = \frac{W}{Av_s H'} \quad [1.19]$$

with

$$\frac{1}{H'} = \frac{1}{H_b} + \frac{1}{H_s} \quad [1.20a]$$

$$A = \pi(a^2 + 2Rd_p) \quad [1.20b]$$

where a is the elastic Hertzian contact radius calculated by the equation in Table 1.1, R the radius of the sphere, d_p the diameter of the spherical abrasive, H_b the ball hardness, H_s the flat-plate sample hardness and v_s the volume fraction of solids in the slurry.

A similar wear equation to the adhesive Archard wear law (Equation [1.14]) can be derived for abrasion:³⁷

$$Q = \frac{kW}{H_c} \quad [1.21]$$

The hardness H_a of the particle involved in abrasion has a major influence on the rate of wear. If the particle hardness H_a is lower than that of the component surface hardness H_c (i.e. $H_a/H_c < 1$), much less wear will result compared with harder particles where $H_a/H_c > 1$. For cases where H_a is much greater than H_c , the exact value of H_a matters far less as the rate of wear is relatively insensitive to hardness ratios $H_a/H_c > 10$, as reported by Moore.³⁸ This trend can be explained by looking at the contact mechanics of the individual particles and a plane surface. For a spherical particle on a planar surface the maximum contact stress is about 0.8 times the indentation hardness of the particle. Therefore, a spherical abrasive of hardness H_a will cause plastic indentation damage on a surface of hardness H_c if $H_c < 0.8H_a$ or $H_a/H_c > 1.25$. In other words, high levels of wear can be expected when abrasive particles are 1.25 times harder than the surface. The Vickers hardness of sand, a typical abrasive particle, is about 1200 HV and is significantly higher in hardness than most steel alloys, thereby indicating that steels are vulnerable to sand abrasion. Even surfaces containing hard phases (carbides), such as thermally sprayed cermets, will have softer binder phases which are susceptible to abrasion. Ceramics, on the other hand, offer hard and homogeneous surfaces to combat plastic deformation and to inhibit abrasive wear but suffer brittle fracture failures under high stresses owing to their inherently low fracture toughness.

For polymers, it has been shown that the Ratner–Lancaster relationship, which suggests the wear rate is inversely proportional to the energy required for tensile yield ($\kappa \propto 1/\sigma_y \epsilon_y$), correlates better³⁹ with abrasion rates than those found by using Equation [1.21]. The relationship depends on the product of the yield stress σ_y and strain ϵ_y at yield. Such correlations between the wear rate and the Ratner–Lancaster relationship suggest the wear mechanism is dominated by tensile failure.

Erosive wear

Erosion is a process by which discrete small solid particles strike the surface of a material causing damage or material loss to its surface. It accounts for 2% of wear-related failures in UK industry as seen in the most recent survey by Neale and Gee²⁸ in 2000, with this value being considerably higher in certain industries, notably the offshore oil and aerospace industries where valves and missile domes are eroded. Erosion can also be a problem for components such as turbine blades, propulsors, pipelines and fluidized-bed combustion systems. Erosion does have its beneficial applications, notably for cleaning and preparation of surfaces for subsequent coating and painting by grit blasting and cutting through rocks or subsea steel oil structures using abrasive water jets.

There are three categories of erosion depending on the nature of the erodent. They are as follows.

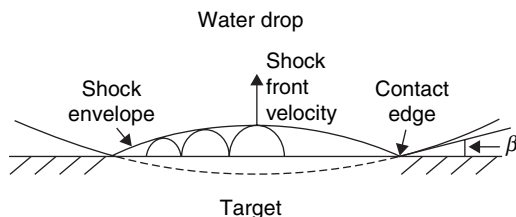
1. Cavitation erosion.
2. Liquid-droplet erosion.
3. Solid-particle erosion.

Cavitation erosion In high-velocity flows where the local pressure falls below the saturated vapour pressure, bubbles or cavities can be generated. When these bubbles collapse near an adjacent solid surface, the pressure pulse associated with shock wave and microjet impingement produced by asymmetric bubble collapse can rapidly damage the surface, leading to cavitation erosion. Such cavity collapses have been studied by Bourne and Field,⁴⁰ who used high-speed photography to view the process. It is a particular problem for liquid circulation equipment (i.e. pumps, valves and pipes) as well as bearings and cylinder linings of high-speed reciprocating engines.

Liquid-droplet erosion In liquid-droplet erosion, the impact of high-velocity liquid droplets on to a solid surface can result in damage to the target material. It is a particular problem in high-speed aircraft, missiles, steam turbine blades and wet gas wells.

In liquid-droplet erosion, the damage resulting from the impact is caused by the propagation of stress waves that are generated in the material. Figure 1.11 shows a schematic diagram⁴¹ of the initial stage of impact.

Immediately after impact, the edge of the liquid–solid contact area moves outwards at a high velocity. The exact value of this velocity is dependent on the impact velocity and the radius of the drop. Initially, it is travelling faster than the shock velocity; this prevents any free outflow from the contact. It is only when the speed of the contact edge falls below that of the shock velocity that the shock in the liquid moves up the free surface of the liquid



1.11 Schematic diagram showing the process of liquid-droplet impact on to a solid surface.

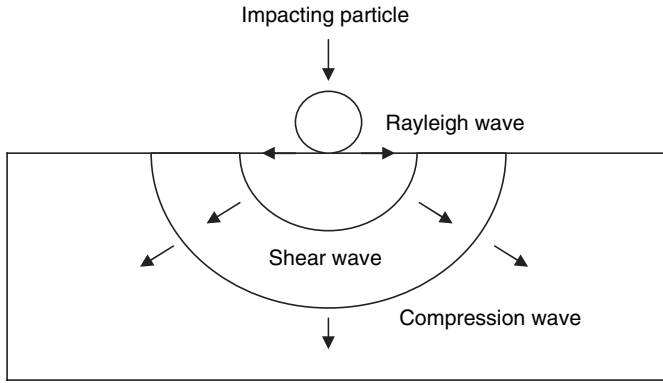
and the high pressures are reduced by jetting (free outflow from the liquid–solid contact) as detailed by Dear and Field.⁴² In the period before jetting takes place the liquid behaves in a compressible manner, giving water hammer pressures of the order of

$$P_{\text{wh}} = \rho_l c_l V \quad [1.22]$$

where P_{wh} is the pressure, ρ_l the density of the liquid, c_l the compression wave velocity for the liquid and V the impact velocity.⁴³

However, the pressures at the expanding contact edge are much higher, reaching a value of $3\rho_l c_l V$ just prior to the shock envelope overtaking the contact edge. The contact edge pressure is less significant because of its short duration of impact. Once this has occurred, stress waves are released into the material. These waves can take three forms: longitudinal, transverse or Rayleigh waves. Figure 1.12 shows these three types of wave propagating into a solid following impact. They have been photographed and reported by Field *et al.*⁴⁴

The classical damage features that are generated by liquid impact on brittle materials consist of rings of discontinuous cracks surrounding the area of impact. The central region of impact is usually largely undamaged. This is because the compressive strength of brittle materials is often greater than that in tension. It is often high enough to resist deformation caused by the high pressures generated by the initial impact. The circumferential cracks are caused by the interaction between Rayleigh surface waves and pre-existing surface flaws larger than a certain critical size in the target material.⁴⁵ They are short because the stress pulse forming them is itself short,⁴⁶ typically less than $1\mu\text{s}$. An additional mechanism by which damage can occur in thin samples is by interaction between Rayleigh waves and reflected bulk waves.⁴⁵ Following impact, compression waves are propagated into the body of the material. When they reach the rear surface, they are reflected back and return to the front surface as tensile waves. At certain



1.12 Schematic diagram of the stress waves produced in a target material following impact by a solid or liquid erodent.

radii from the initial impact zone the position at which the reflected wave returns to the front surface will coincide with the position of the Rayleigh surface wave, resulting in stress reinforcement which generates even higher stresses at these locations. It should be noted that longitudinal waves travel more rapidly than Rayleigh waves. The stress reinforcement can lead to the nucleation of further cracks at the front surface.

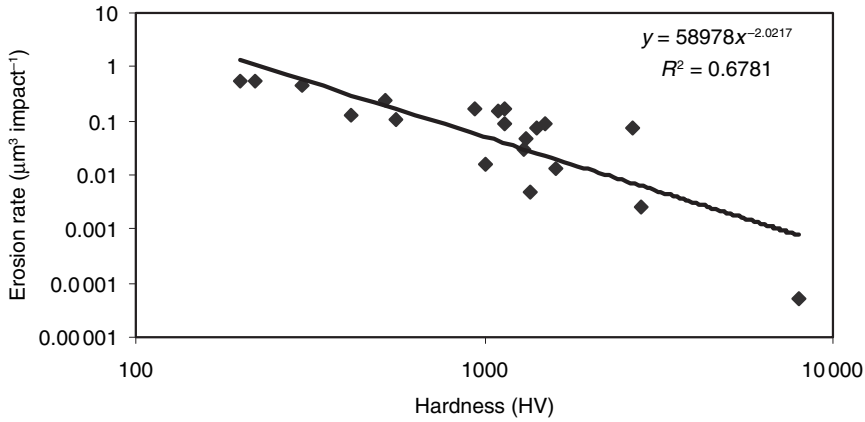
Solid-particle erosion Solid-particle erosion is caused by the impact of particles on solid surfaces. The particles can be entrained in a liquid or gas and can be present either intentionally, as in powder- or mineral-handling facilities, or as contaminants, such as oxide debris from the inside of pipelines or sand from hydrocarbon reservoirs.

Erosion rates are often linked to hardness and, as discussed earlier, assuming that the Archard wear law applies, we predict that the erosion rate is proportional to $1/H_v$ but erosion tests of a wide range of engineering materials and coatings show that the erosion rate is proportional to $1/H_v^2$ (Fig. 1.13).

Erosion rate can be expressed by dividing the erosion volume loss by the number of erodent impacts, N , causing that loss. This unit volume loss per impact, V_u , has units of $\mu\text{m}^3 \text{ impact}^{-1}$. If the erodent particles are assumed to be spherical with an average particle diameter d_p , then

$$E_v = \frac{Qxt}{\rho_e} = N \frac{\pi d_p^3}{6} \quad [1.23]$$

where Q is the mass flow rate, x the fraction of the erodent, t the duration of the test and ρ_e the density of the erodent. Now



1.13 Erosion rate for various engineering surfaces under 16 m s^{-1} jet impingement at 90° with 2.1% w/w sand–water slurry with $200 \mu\text{m}$ sand.

$$V_u = \frac{V_l}{Qxt} \frac{\pi d_p^3}{6} \rho_e \quad [1.24a]$$

In terms of the specific volume loss V_s , where $V_s = V_l/E_v$, then

$$V_u = \frac{V_s \pi d_p^3}{6} \quad [1.24b]$$

Plots of V_u ($\mu\text{m}^3 \text{ impact}^{-1}$) versus kinetic energy of impact, E_k (μJ), can be used to generate an erosion map. These maps, proposed by Moore and Wood,⁴⁷ enable comparisons to be made between materials in a wide range of impact energies independent of particle size (Fig. 1.14). E_k is defined as

$$E_k = \frac{2}{3} \pi R^3 \rho_e V^2 \quad [1.25]$$

where R is particle radius, ρ_e the erodent particle density and V the impact velocity. Care should be taken as experimental evidence shows that erosion rates can be dependent on $V^n d^y$ where n and y are far removed from 2 and 3 assumed in the simple energy approach above.⁴⁸

Factors affecting solid-particle erosion of materials There are a number of factors that affect the behaviour of materials when they are subjected to erosive flows. These can be placed in four categories.

1. The nature of the fluid transporting the particles (liquid or gaseous).
2. The nature of the particles.

3. The flow field.
4. Target parameters.

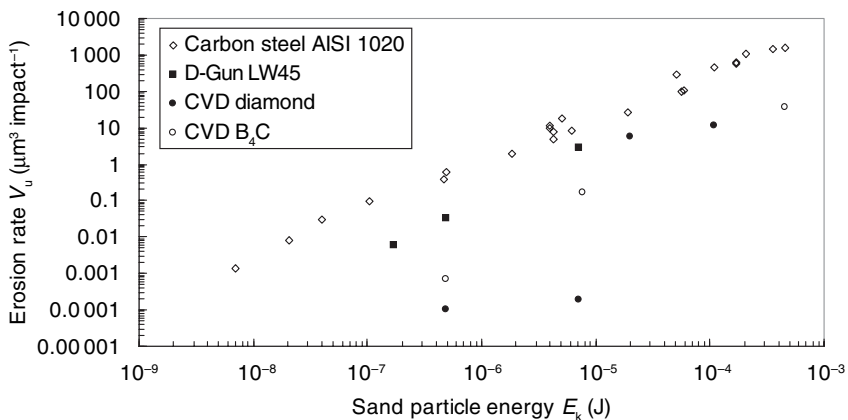
They are summarised in Table 1.2.

Erosion results when solid particles entrained in a fluid stream impinge on to a surface. These solid particles can remove material from the surface and penetrate or destroy any protective passive films, leading to accelerated damage caused by erosion–corrosion. The complexity of erosion prediction has been demonstrated by Meng and Ludema⁴⁹ who quoted 33 independent parameters in a recent review of 22 erosion models and predictive equations. The main parameters of concern for erosion relate to the solid-particle–target interactions and thus the number of particles impinging, the individual particle energies, the particle impingement angles, the particle-to-target-hardness ratios and the shape of the particles. Near-wall particle–particle interactions can also severely influence erosion rates when the volume concentration of solid particles present is high.

Finnie⁵⁰ developed an erosion model based on cutting wear mechanisms of the form

$$V_u = C \frac{M_p V_p^2}{4\sigma} f(\alpha) \quad [1.26]$$

where C is an arbitrary constant denoting the number of particles that cut the surface. Gane and Murray⁵¹ found that a value of $C = 0.5$ gave reasonable predictions. Keating and Nescic⁵² in numerically predicting erosion–corrosion in bends and sudden expansions by two-phase flows



1.14 Erosion rate as a function of particle impingement energy for steel and thermally sprayed WC LW45 as well as CVD coatings of diamond (20 μm thick) and B₄C (15 μm thick).

Table 1.2 Factors affecting the solid-particle erosion of materials

Category	Factor
Nature of the fluid	Viscosity Density Corrosivity (erosion–corrosion synergy) Temperature
Nature of the particles	Size Density Friability Shape Particle-to-target-hardness ratio
Flow field	Particle velocity Particle kinetic energy Particle–particle interactions Impact angle Particle flux Particle impingement efficiency Particle drop-out
Target parameters	Hardness Elastic modulus Fracture toughness Residual stress Surface roughness Surface treatment Size and distribution of microstructural flaws

(liquid–solid) used a modified Finnie approach based on earlier work by Bergevin.⁵³ This approach incorporated the concept of a critical velocity for plastic deformation, V_{cr} . They substituted $(V_p \sin \alpha - V_{cr})$ for the impact velocity in Equation [1.26] to give the following: for small angles ($\alpha \leq 18.5^\circ$)

$$V_u = \frac{M_p(V_p \sin \alpha - V_{cr})}{2\sigma} \left[V_p \cos \alpha - \frac{3}{2}(V_p \sin \alpha - V_{cr}) \right] \quad [1.27]$$

and, for larger angles of impingement,

$$V_u = \frac{M_p(V_p \sin \alpha - V_{cr})^2}{12\sigma} \frac{\cos^2 \alpha}{\sin^2 \alpha} \quad [1.28]$$

Bitter⁵⁴ quoted a value of $V_{cr} = 0.668 \text{ ms}^{-1}$ for steel. Keating and Nesic used this value to predict erosion rates successfully in a sudden expansion and found the original Finnie model to be not so accurate. However, modelling of erosion–corrosion damage in a U-bend used the original Finnie model

as the modified version yielded no erosion due to the low particle velocities involved. Keating and Nesic conclude that their modelling needs more experimental validation before further refinements can be made.

Erosion models typically recognise that two erosion mechanisms act, namely cutting and deformation erosion, with discrete models representing each, and have been successfully used by Forder *et al.*⁵⁵ and Wood and co-workers,^{56–59} to predict erosion of internal components within choke valves and slurry ducts. The cutting erosion model for small impact angles was first proposed by Finnie⁵⁰ and later modified by Hashish.⁴⁸ The deformation model was proposed by Bitter⁵⁴ and is thought applicable at larger impact angles (30–90°). Particle shape and material properties for both particle and target have been included which earlier simpler models have not considered. As the particle impingement angles are predicted to be below 10°, for critical components such as straights and bends,⁵⁷ the contribution to the overall wear rate from deformation mechanisms can be ignored; so the volumetric erosion per impact can be given by the Hashish model only:

$$V_u = \frac{100}{2 \times 29^{1/2}} r_p^3 \left(\frac{V_p}{C_k} \right)^n \sin(2\alpha) (\sin \alpha)^{1/2} \quad [1.29]$$

where $n = 2.54$ and

$$C_k = \left(\frac{3\sigma R_f^{0.6}}{\rho_p} \right)^{1/2} \quad [1.30]$$

Erosion–stress field interactions If coatings are used for erosion resistance, the coating thickness is one of the most important factors. It has been shown, using a finite-element model, such as that by van der Zwaag and Field,⁶⁰ that thick coatings reduce the stresses at the coating–substrate interface. If the coating is of a sufficient thickness, all the stresses can be contained within it. However, in some coating systems the erosion resistance decreases with thicker coatings because of increased residual stresses.

Hedenqvist and Olsson⁶¹ investigated TiN coatings obtained by physical vapour deposition (PVD) on high-speed steel with coating thicknesses of 0.4, 1.3 and 3 μm . The coatings were tested in a centrifugal erosion tester using 62–125 μm Al_2O_3 particles at 20 ms^{-1} ; the impact angle was 90°. The results showed that the critical particle dose required to cause coating removal on the 3 μm coating was as much as 180 times greater than for the 0.4 μm coating, demonstrating the benefits of thicker coatings.

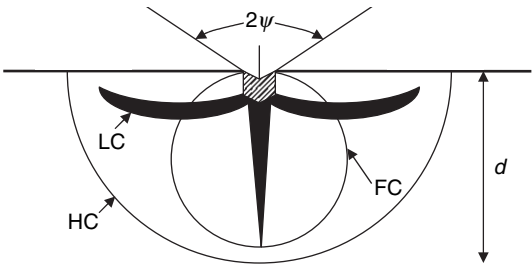
For thin coatings subjected to point loading, when the stress field extends into the substrate, the substrate can be forced to yield plastically. Pajares *et al.*⁶² studied the nature of subsurface damage in plasma-sprayed Al_2O_3 – TiO_2 coatings deposited on a mild steel substrate. Metallographic sections of

indented regions revealed extensive microcracking and plastic deformation in the substrate as well as some delamination at the interface. The thinner coating ($170\mu\text{m}$) exhibited considerably more plastic deformation and delamination than the thicker coating ($425\mu\text{m}$), although the free-standing coating exhibited an even lower incidence of plastic deformation.

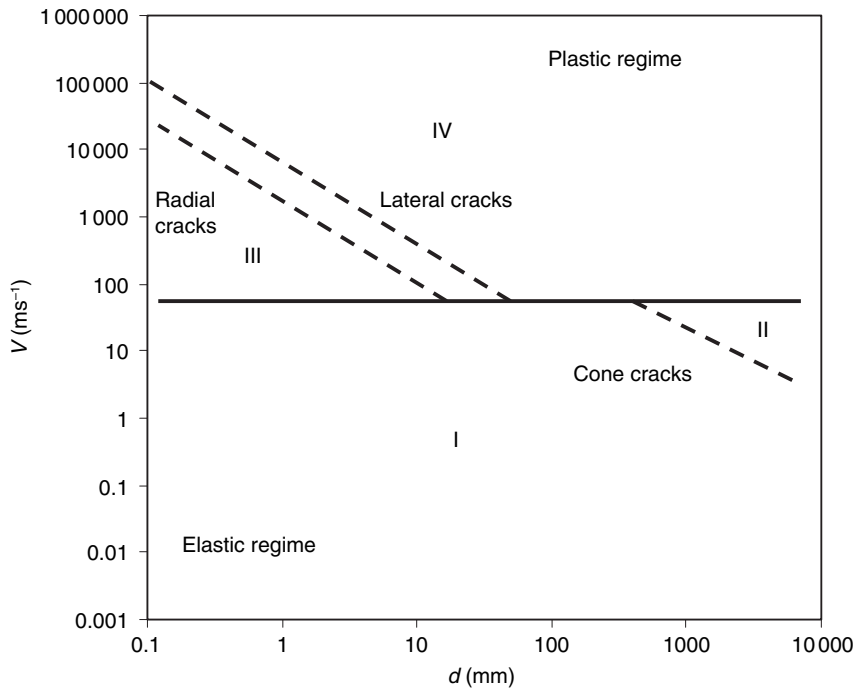
The performance and useful lifetime of coatings can often be related to normalised coating thickness C_T/a_m , which is the ratio of the coating thickness C_T to the Hertzian contact radius a_m . Komvopoulos⁶³ used the finite-element method to study the elastic contact of a substrate coated with a film of greater stiffness. Part of the work involved examining the effect of normalised coating thickness. The results showed that thicker coatings offered better protection to the substrate. Thick coatings resulted in lower and more uniformly distributed strains. When $C_T/a_m > 1$, significantly enhanced resistance against deformation was provided by the coating. Furthermore, thicker coatings also greatly reduce the shear stress at the coating–substrate interface. In contrast, for coatings where $C_T/a_m < 1$, the stresses in the substrate are predicted to be even higher than those present when uncoated. The dominant deformation mechanism was also found to be dependent on the normalised coating thickness; for thin coatings ($C_T/a_m < 0.45$), surface microcrack initiation dominates while, on thicker coatings ($C_T/a_m > 0.45$), interfacial microcrack initiation was the dominant damage mechanism. This can be directly related to the stress fields developed within the contact zone. Such fields are illustrated by shear stress and tensile stress plots such as those given by Fisher-Cripps *et al.*⁶⁴ and derived from finite-element analysis.

Particle impacts can be described by a quasi-static indentation process and have been classified as those which cause dominant elastic deformation at small indentation loads and those that cause dominant plastic deformation at higher loads. Hard spherical particles may generate a variety of damaging crack systems on impact with a brittle target (Fig. 1.15). These crack systems depend on the particle shape, diameter and velocity. Verspui *et al.*⁶⁵ presented equations for the transitions between impact damage regimes and predicted the existence of cone cracks in the plastic regime. These equations can be presented in an erosion map of particle size against impact velocity (Fig. 1.16). Thus, brittle surface cracks may be present in both categories. The following equations give the critical velocities to promote certain failure modes and to show the sensitivity of damage patterns to various mechanical properties of the target surface; the critical velocity for transition from elastic to plastic regions is

$$V_{\text{crit,p}} = \frac{9}{80} 15^{1/2} \pi^2 \frac{H_v^{5/2}}{E^{*2} \rho^{1/2}} \quad [1.31]$$



1.15 Schematic diagram of the side view of the cracks generated in glass by a pointed indenter: HC, half-penny crack; FC, full-penny median crack; LC, lateral crack; d , depth of median crack perpendicular to surface; 2ψ , angle of indenter.



1.16 Theoretical erosion map for borosilicate glass under spherical impact,⁵⁶ plotting impact velocity V against particle diameter d .

the critical velocity for cone cracks is

$$V_{\text{crit,c}} = \frac{9}{80} \left(\frac{15}{\pi} \right)^{1/2} \frac{K_c^{5/3}}{E^{*7/6} \phi_1^{*5/6} \rho^{1/2} R^{5/6}} \quad [1.32]$$

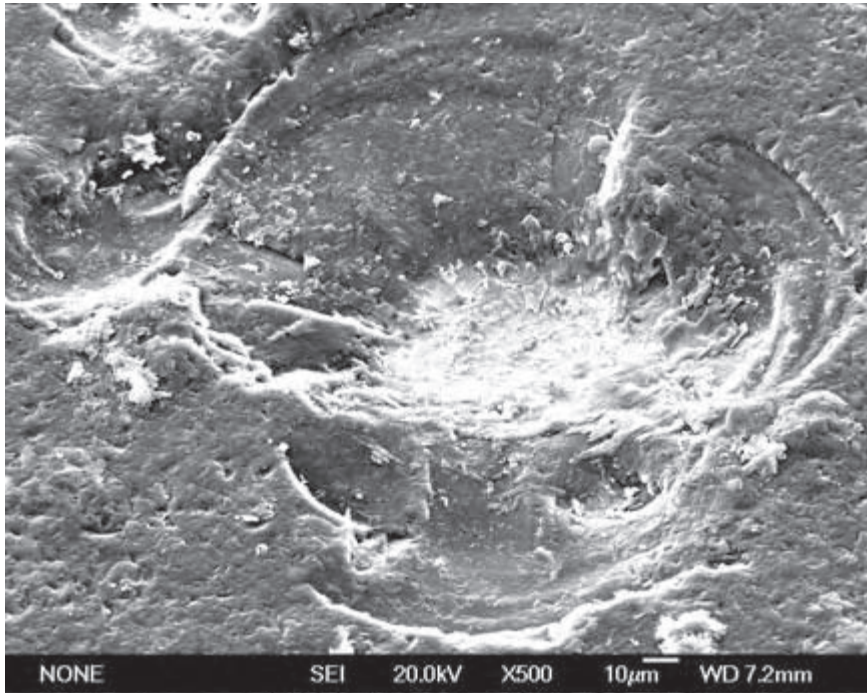
(where $\phi_1 = (1 - \nu)\phi^*$ with ϕ^* a dimensionless material constant), the critical velocity for the plastic regime (radial and median cracks) is

$$V_{\text{crit,r}} = 32 \frac{E^{3/4} K_c^3}{H_V^{13/4} \rho^{1/2} R^{3/2}} \quad [1.33]$$

and the critical velocity for the plastic regime (lateral cracks) is

$$V_{\text{crit,l}} = 105 \frac{E^{3/4} K_c^3}{H_V^{13/4} \rho^{1/2} R^{3/2}} \quad [1.34]$$

Experiments show that these predictions are sensitive to particle size distributions and shape as well as to target property and microstructure anisotropy. Figure 1.17 shows lateral crack damage to a CVD $B_{13}C_2$ coating $15\mu\text{m}$ thick at high solid-particle impact energy. The coating hardness was $6250 H_{V25g}$.

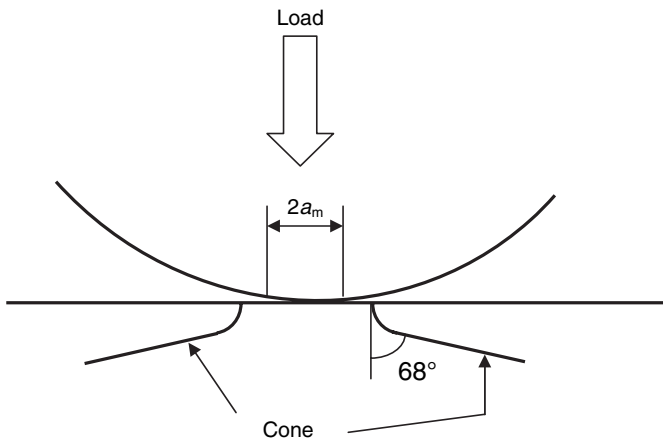


1.17 A 30° tilt scanning electron micrograph of a typical erosion impact site after 150 min by 250–400 μm glass beads impacting at 250ms^{-1} , showing typical lateral c-type cracks propagating outwards from the centre of the impact (SEI, secondary-electron image; WD, wear depth).

In a later paper, Komvopoulos⁶⁶ examined the effect of coating thickness on the contact pressure, subsurface stresses and strains, as well as on the location, size and shape of the plastic zone. It was found that the thickness of the coating influenced the extent of the plastic zone as well as its location. Thinner coatings provided less resistance to plastic deformation. The plastic zone was predicted to initiate at the coating–substrate interface directly beneath the indenter. Increasing the coating thickness reduced the extent of substrate yielding. If the stress field could be completely contained within the coating, plastic deformation of the substrate could be eliminated. The damage patterns induced in bulk ceramics and ceramic coatings by solid-particle erosion and impact have been nicely reviewed in the book edited by Ritter.⁶⁷ Chapter 4 of that book includes computer models of high-energy impact damage to space shuttle tiles amongst other ceramic coating systems.

Erosion performance of coatings under slurry and air–solid impact conditions are given in the literature and examples for high-velocity oxy-fuel (HVOF), CVD and polymer coatings can be found in the papers by Wood and co-workers.^{68–80}

Dynamic Hertzian impact theory To predict certain erosion damage patterns such as the diameter of ring and cone cracks (Fig. 1.18), dynamic Hertzian impact theory can be used for systems where the contact is primarily elastic. The contact radius of a spherical solid particle impacting on a



1.18 Schematic diagram showing the formation of a Hertzian cone crack following indentation of a brittle material with a spherical indenter. a_m is the contact radius.

surface can be calculated using Hertzian contact theory applied to single particle impacts.⁸¹ The maximum load F_m was calculated using

$$F_m = \left(\frac{5\pi\rho_2}{3} \right)^{3/5} \left(\frac{4k}{3E_1} \right)^{-2/5} R^2 V^{6/5} \quad [1.35]$$

The mean pressure P_m is

$$P_m = \frac{1}{\pi} \left(\frac{5\pi\rho_2}{3} \right)^{1/5} \left(\frac{4k}{3E_1} \right)^{-4/5} V^{2/5} \quad [1.36]$$

where ρ_2 is the density of the impacting particle, E_1 the elastic modulus of the target surface, R the particle radius and V the particle velocity. The value of k is obtained using the following equation:

$$k = \frac{9}{16} \left[(1 - \nu_1^2) + (1 - \nu_2^2) \left(\frac{E_1}{E_2} \right) \right] \quad [1.37]$$

where E_1 and E_2 are the elastic moduli of the target surface and the sand particles respectively, and ν_1 and ν_2 are Poissons's ratios of the target surface and the sand particles respectively.

Using equations [1.35] and [1.36], values for F_m and P_m can be calculated. These can then be used to obtain the maximum contact radius a_m , which is calculated using the following equation:

$$a_m = \left(\frac{F_m}{\pi P_m} \right)^{1/2} \quad [1.38]$$

The maximum tensile stress σ_m at the contact circle can also be calculated, using the following formula:

$$\sigma_m = \frac{1}{2} (1 - 2\nu_1) P_m \quad [1.39]$$

The duration t_e of elastic impact was determined using the following formula:

$$t_e = 2.94 \left(\frac{5\pi\rho_2}{4} \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right)^{2/5} V^{-1/5} R \quad [1.40]$$

For a circular point contact, the maximum shear stress τ_m under the contact can be calculated, assuming no relative motion at the interface, using

$$\tau_m = 0.31 \frac{3P_m}{2} \quad [1.41]$$

The depth z at which this occurs, is

$$z = 0.48a_m \quad [1.42]$$

Fatigue and delamination wear

Many practical tribological applications require the loaded component surfaces to withstand repeated loaded contacts. If, in the initial contact, the peak Hertzian contact pressure p_0 exceeds the elastic limit, plastic deformation will occur within the near surface, causing residual stresses in the material. This case will occur, assuming that the Tresca yield criteria applies, when p_0 is between 3.3 and 4.0 times the shear flow stress. These induced residual stresses can restrict the likelihood of yield and sometimes build up to allow the applied load to be carried elastically. This effect is termed elastic shake-down. So, if we consider a hard rough surface sliding repeatedly on a softer component, protective residual stresses may be developed in the near-surface layers of the weaker material, which enable loads sufficiently large to cause plastic deformation during early cycles of loading now to be accommodated purely elastically.⁸²

The effect of strain hardening within the surface layers of the contact regions increases the shear strength of the material, thus reducing the regions of yield. For materials with non-linear strain-hardening characteristics, plastic ratchetting can occur. After thousands to millions of loading cycles, the gross deformation of the surface or near-surface regions accumulates with each cycle, contributing an element of plastic strain.

Metallic wear tracks often reveal severe plastic shearing after repeated sliding with microcracking either parallel or at an angle to the surface.⁸³ The wear debris typically is laminar in form, leading to the introduction of the term delamination wear. However, models of these processes based on propagating shear cracks using elastic fracture mechanics (Hertzian) have largely been unsuccessful because of friction associated with the crack face. As the cracks appear in plastically deformed near-surface layers, this would suggest that they are ductile fractures driven by plastic strain rather than by elastic stress intensity. The plastic strain of the worn surfaces is an accumulation of small increments of plastic strain events and is referred to as ratchetting.

Models by Kapoor *et al.*⁸³ suggest that softer surfaces worn by the asperities of a harder counter-surface have a wear rate W approximately proportional to load, $W \propto L^{1.5}$, and an increasing function of a single non-dimensional parameter termed the plasticity index for repeated sliding. This parameter relates the roughness of the hard surface to the limiting elastic strain of the softer wearing surface. For small values of this parameter the wear rate becomes negligibly small and a shakedown state is obtained in which the deformation of the surface is entirely elastic and ratchetting effectively stops. The hardness of the wearing surface and the coefficient of friction at the interface both influence the wear rate through their influence on the value of the plasticity index for repeated sliding ψ_s :

$$\psi_s \equiv \frac{E^* (\sigma_{\text{rms}} R)^{1/2}}{p_s} \quad [1.43]$$

where ψ_s is the plasticity index in repeated sliding, σ_{rms} the root-mean-square value of the asperity height of the harder surface, R the curvature of the spherical asperity of the harder surface, E^* the reduced modulus of the softer wearing surface and p_s the shakedown pressure (maximum Hertz contact pressure for onset of shakedown in the softer wearing material), which is equal to $(2/\pi)E^*(\delta_s \kappa)^{1/2}$ (δ_s is the compression of the spherical asperity of curvature R).

Surface engineering offers the deposition of a well-bonded hard coating on a softer substrate so that both the elastic and the plastic properties of the coating can differ from those of the underlying material; these differences present further difficulties in formulating and displaying the corresponding shakedown limits. In addition to the values of hardness and stiffness of the coating and those of the substrate, other important system parameters are the thickness of the coating (in comparison with the characteristic dimension of surface roughness), the integrity of the interlayer bonds and the coefficient of friction between the coated component and the counter-surface.

The results of a sequence of studies into these effects can be displayed in the form of non-dimensional shakedown charts or maps which demonstrate to the materials engineer or designer the potential improvement that might accrue from optimal surface engineering.⁸⁴ These can also inform coating or surface treatment selection or help to predict conditions under which certain coating–substrate combinations are inappropriate or will suffer high levels of degradation and wear.

Chemical wear

Chemical or tribochemical wear occurs by detrimental chemical reactions within the contact, induced by the local environment, and in combination with mechanical contact mechanisms. Contact between sliding surfaces can accelerate chemical reactions and material removal. Rubbing contacts result in increased surface temperatures and can induce surface cracks and the generation of nascent surfaces which are highly reactive with their environment. However, the chemical formation of surface films can be advantageous as they can have low friction properties and also promote material transfer to change the contact from base–base material to chemical film–chemical film and thus change the contact conditions.

Oxidation wear is the most common chemical wear process. The presence of thin oxide layers on contacting metal surfaces often inhibits wear and catastrophic failures by seizure. The ability of the surface to reoxidise within

the contact is critical as the rubbing action tends to deoxidise and delaminate the oxide layer. The process of oxidation wear, therefore, is heavily dependent on the kinetics of oxidation.

In order for tribological surfaces and coatings to operate to their design life, the role of tribochemical reactions in the contact must be considered. Some recent research in this field is presented in the section on wear-corrosion to illustrate the diverse applications where coatings are being considered and where tribochemical wear processes predominate.

Fretting wear

Fretting wear is a result of small-amplitude oscillatory motion, usually tangential, between two solid surfaces in contact. This results in oxidised debris and a wear coefficient that increases rapidly with increasing amplitude of the motion. It is a problem for many contacting machine components. One illustration of such fretting damage evolution is the blade and disc contact of turbine engines which are subjected to a wide spectrum of vibrations, gross and partial slip conditions occur in the dovetail contact. Both wear and crack nucleation are generated. In critical situations, cracks can propagate, mainly driven by macroscopic fatigue loading.⁸⁵

Splined couplings are one of the commonest methods of connecting elements in rotating machinery. Their performance is limited not only by torsional fatigue but also by fretting wear arising from angular misalignment. Wear is especially common in mechanical transmissions which have light-weight and flexible casings, such as those in helicopters.⁸⁶

Wear-corrosion

The role of mechanochemical effects in accelerated material removal from hard and brittle surfaces such as engineering ceramics has been studied by Stolarski.⁸⁷ Maximum wear rates were achieved when both mechanical action and chemical reactions take place simultaneously. The mechanical action was found to be governed by the applied load, the amount of relative slip within the contact zone and the size of abrasive particles. Chemical effects, on the other hand, depended mainly on the nature of lubricant additives present and their ability to react with the ceramic surface under contact conditions.

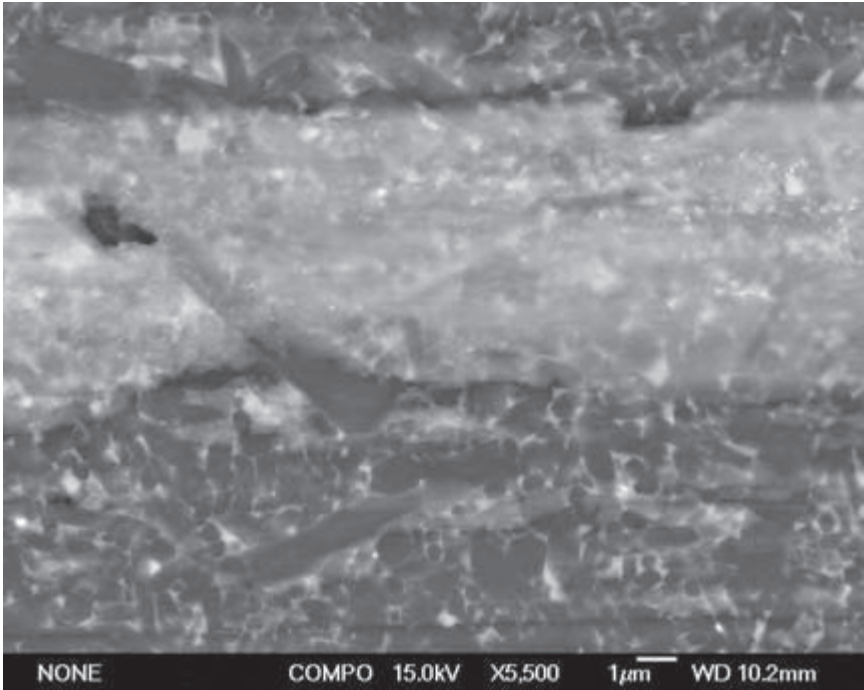
For ceramics, Rainforth⁸⁸ suggested that the micromechanical and microchemical processes which take place during friction are not fully understood. The occurrence of surface plasticity and microfracture on a subgrain size scale has been suggested. Tribochemical wear mechanisms are now considered to be critical to the wear performance of ceramics; so specific experimental evaluation is required to identify the mechanisms and domi-

nant films, prior to optimising surface compositions. For example, for zirconia-toughened ceramics sliding against metal and ceramic counterfaces, the dominant wear mechanism is tribochemical as a result of dissolution of the ceramic surface into a metallic oxide transfer film for the metal counterface, and the formation of an amorphous surface hydrate against a ceramic counterface. In both instances, it is considered that the tribochemical reaction dictates the minimum wear rate achievable and therefore particular attention should be paid to modification of the ceramic composition to optimise the surface chemistry to promote the optimum hydrate properties, such as the resistance to hydration. The water content of the amorphous hydrate films appears critical as suggested by observations that the wear rate of Al_2O_3 and ZrO_2 can increase with water lubrication even if the coefficient of friction is reduced. Other factors to optimise are the adherence of these tribochemical films and their frictional properties as they determine whether the film is beneficial or detrimental to controlling wear rates and friction within the contact. An example of a tribochemical film formed on Si_3N_4 loaded against bearing steel in a high-speed high-load contact is shown in Fig. 1.19.

Instabilities of the tribochemical films and, hence, the resulting wear rates mean that good tribological performance cannot be guaranteed for ceramic couples. Andersson and Blomberg⁸⁹ studied sintered SiC sliding unlubricated on itself. Tribo-oxidation and surface fracture were identified as the dominant deterioration mechanisms. The oxidation products formed were silicon dioxide (SiO_2) and, within narrow operational regimes, silicon monoxide (SiO). Part of the SiO_2 wear debris was compacted under frictional heating to form smooth tribofilms on the mating surfaces, providing protection against excessive wear; the corresponding specific wear rates ranged from 10^{-6} to $10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$. The SiO, when formed, appeared as a loosely attached powder which provided no protection against wear, as indicated by an increase of one order of magnitude in the wear rate. Thus, tribochemical film instability is a concern.

The effects of the environment on the tribochemical effects are also important. The effects of atmospheric humidity on the formation of tribolayers on PVD TiN coatings in contact with various steels and A356 Al-15% SiC have been investigated by Wilson and Alpas.⁹⁰ The TiN coatings suffered rapid wear by tribochemical oxidation and polishing at low sliding speeds and contact loads. This effect was reversed when the contact loads and sliding speeds were raised. Increasing the humidity raised the TiN wear rates and tribochemical wear was seen at low loads and speeds as well as extending into the higher-load and higher-sliding-speed regions.

The tribological properties of self-mated plasma-sprayed Cr_2O_3 coatings have been studied by Wei *et al.*⁹¹ at room temperature using distilled water, water-ethanol, *n*-monohydric alcohols and polyhydric alcohols as lubri-



1.19 Tribochemical layer of SiO_2 formed on the surface of a Si_3N_4 ball after being loaded against a bearing steel surface at 3 GPa contact stress and 7 m s^{-1} sliding velocity and lubricated by aviation oil (WD, wear depth).

cants. Testing indicated that both friction and wear were much higher (approximately twice) in water than in the n -monohydric alcohols. Analysis of the morphology and composition of the worn surfaces indicated that the wear of Cr_2O_3 coating was controlled by the combination of microfracture and tribochemical wear in water and was only controlled by microfracture in ethanol.

Synergy Synergy is defined as ‘the difference between wear–corrosion and the summation of its two parts’ and can be expressed by

$$\Delta E = T - (E + C + \Delta C) \quad [1.44]$$

where T , C and E are typically gravimetric terms relating to wear–corrosion, electrochemical corrosion (*in situ*) and mechanical wear mechanisms respectively. The interactive processes can be broken down into two components ΔE and ΔC , where ΔE is the corrosion-enhanced wear and ΔC is

the wear-enhanced corrosion. Recent literature has defined ΔE as the synergy term and ΔC as the additive term. The following equations relate to erosion–corrosion:

$$T = E + C + \Delta E + \Delta C \quad [1.45a]$$

$$T = E + C' + \Delta E + \Delta C' \quad [1.45b]$$

$$T = E + C'' + \Delta E \quad [1.45c]$$

where E is the pure erosion material loss, C is the static corrosion rate, C' is the solids free-flow corrosion rate, C'' is the corrosion rate under wear–corrosion conditions, ΔC is the enhancement of C due to the presence of erosion and flow, $\Delta C'$ is the enhancement of C' due to the presence of erosion and ΔC is the effect of corrosion on erosion. The synergistic effect S is referred to as ΔE or $\Delta C + \Delta E$ or $C'' + \Delta E$ depending on the literature source and thus readers must take care when extracting synergistic levels for different materials when using multiple sources of literature. ASTM Standard G119-93 is a useful guide for researchers wishing to evaluate synergy.⁹²

Wear can mechanically strip the protective corrosion film, creating fresh reactive corrosion sites and producing⁹³ ΔC , dependent on the rate of repassivation and the integrity of the film formed. Other possible wear-enhanced corrosion mechanisms include the following.

1. Local acidification at wear sites, accelerating corrosion rates and prohibiting film formation.
2. Increased mass transport by high turbulence levels.
3. Lowering the fatigue strength of a metal by corrosion.
4. Surface roughening of the specimen during wear-enhanced mass transfer effects, increasing the corrosion rate.⁹⁴

Corrosion-enhanced wear mechanisms are also possible (ΔE). The ΔE wear rate could arise for the following reasons.

5. The removal of work hardened surfaces by corrosion processes which expose the underlying base metal to erosion mechanisms.⁹⁵
6. Preferential corrosive attack at grain boundaries, resulting in grain loosening and eventual removal.⁹⁶
7. The increase in the number of stress concentration defects resulting from micropitting.
8. Detachment of plastically deformed flakes on the metal surface due to stress corrosion cracking.

Most of the above mechanisms, if dominant, would be expected to lead to positive synergy. However, in some instances, negative synergy can occur. Possible mechanisms which reduce wear rates ($-\Delta E$) are as follows.

9. Increased work hardening due to corrosion mechanisms.
10. Shot peening⁹⁷ by high-velocity sand particle impacts.
11. The presence of a soft or loosely adherent corrosion film.
12. Blunting of the crack tips by lateral dissolution retarding the speed of crack propagation.

The reduction in corrosion rates ($-\Delta C$) could result from rapid corrosion film growth, scaling or the formation of a passive film, reducing corrosion rates dramatically.

Examples of experimental attempts to quantify synergy for erosion–corrosion of coatings by aqueous slurries have been given by Wood and co-workers.^{98–101}

1.4 Stress fields for coated systems

1.4.1 Residual stresses (thermal and intrinsic)

Residual stresses in coatings are internal stresses that originate from the manner of growth of the coating and the method of coating growth. For uncoated materials these stresses may result from microstructural changes within plastic regions within the contact region induced by manufacture or repeated (cyclic) contact loading. Residual stress can arise from the mismatch in properties between coating and substrate as well as coating microstructure. In many cases the difference in the thermal expansion coefficients is the dominant influence on the nature and magnitude of the residual stress. The level of stresses varies and is very system specific but, for example, for ceramic coatings on metal substrates the residual stresses are typically in the range¹⁰² 1–3 GPa. These residual stresses can be either tensile or compressive depending on the nature of the coating and substrate.

Whether the residual stresses are tensile or compressive can also influence the mode of deformation of the coating. Coatings with a residual tensile stress have an increased tendency to surface cracking, while those containing large residual compressive stresses are susceptible to delamination and spalling.¹⁰³ Delamination processes can also be assisted by the presence of small flaws in the coating.¹⁰⁴ Excessive levels of residual stress will lead to complete removal of the coating from the substrate. Such coatings will, therefore, offer poor protection to substrates exposed to solid-particle erosion, abrasion or adhesion mechanisms. For example, studies of thin hard coatings such as TiN less than 30 μm thick found that compressive residual stresses reduce the tensile stresses induced in the coating during sliding. However, the tendency for spalling and delamination of coatings increased with increased compressive stress or increasing coating thickness.¹⁰⁵

There are typically two sources of residual stress in coated systems: thermal stresses and intrinsic stresses. The total residual stress σ_t is the sum of the two:

$$\sigma_t = \sigma_{th} + \sigma_{in} \quad [1.46]$$

where σ_{th} is the thermal stress and σ_{in} the intrinsic stress.

The thermal stress σ_{th} is a consequence of the mismatch between the thermal expansion coefficients of the coating and the substrate. It is usually compressive in nature owing to the greater contraction of most substrates on cooling to room temperature following deposition. It is possible to estimate the thermal stresses σ_{th} using

$$\sigma_{th} = E_f(\alpha_f - \alpha_s)\Delta T \quad [1.47]$$

where E_f is the biaxial elastic modulus of the coating, α_f and α_s are the thermal expansion coefficients of the coating and substrate respectively and ΔT is the temperature difference, which is typically the difference between the deposition temperature and room temperature.

The intrinsic stress σ_{in} in the coating is usually tensile because of a number of microstructural influences during the deposition process. The first source of these stresses lies in the differences between the lattice parameters of the coating and the substrate. The second source is due to the microstructure of the coating and the presence of impurities and structural defects in the coating. These include grain boundaries and structural defects such as dislocations, twins, stacking faults and vacancies. Systems with higher grain boundary densities result in a higher intrinsic stress. Intrinsic stresses are typically in the range 0.1–3.0 GPa.

Wheeler¹⁰⁶ reported that, for erosion-resistant CVD diamond coatings between 10 and 120 μm thick grown on tungsten substrates, compressive residual stresses between 0.84 and 1.3 GPa are present. Calculations based on equation [1.47] estimate that thermal stresses should be about 3.7 GPa; thus tensile intrinsic stresses of the order of 2.4–2.9 GPa are inferred.

Thornton and Hoffman¹⁰⁷ suggested that the internal stresses depend on the ratio of deposition temperature to melting point temperature of the material, T/T_m . For low T/T_m , intrinsic stresses dominate while, at high T/T_m ratios, thermal stresses dominate.

Thermally sprayed molybdenum coatings are widely used to combat degradation of components and structures due to mechanical wear. However, the behaviour and durability of these coatings are extremely dependent on their properties and on the spraying conditions. The adherence of flame-sprayed molybdenum on steel substrates and the internal stress distribution at the interface of the structure obtained are critical to their tribological performance. The use of a Ni–Al bond coat 0.2 mm thick

inhibits the dissipation of the fracture energy and microcracks through the layer during delamination. The influence of an 80% Ni–20% Al bond coat and/or a post-annealing at 850 °C for 1 h in a vacuum were found beneficial to the adherence.¹⁰⁸ The annealing reduced the microhardness and residual stress gradients, leading to higher energy dissipation, while in addition the bond coat acted as a barrier to iron and molybdenum reactions which can lead to the formation of brittle intermediate phases.

In many cases, high compressive stresses are an unwanted side effect of PVD coatings, because they are known to reduce the adhesive strength of the coating on the substrate. However, in some applications a main focus of the PVD coatings consists in bringing the surface of a substrate into a compressive state. A surface in a compressive state is more likely to withstand thermal and mechanical alternating stresses within the surface and has a higher resistance against forming cracks. Arc ion plating is a PVD process, which is known to cause high compressive stresses in coatings owing to its high ionisation rate and the applied bias voltage to the substrate. Therefore, processes such as arc ion plating can be used to bring the surface of a substrate into a compressive state.¹⁰⁹

Costa and Camargo¹¹⁰ have worked on SiC films deposited by radio frequency (RF) magnetron sputtering on to WC and silicon substrates. Microhardness and residual stress measurements of the films 5 μm thick revealed that, at high deposition rates (up to 40 nm min⁻¹) and high power (400 W), relatively low compressive residual stresses (less than 2 GPa) and high hardness (30 GPa) are obtained, although a superhard material (greater than or equal to 40 GPa) could be achieved at lower RF power (100 W). Wear rates of the coated pieces were found to be reduced to less than half of those of the uncoated pieces.

1.4.2 Influence of coating properties on stress distributions

Monolayered coatings

The situation is made more complex than outlined above owing to the anisotropy in the mechanical properties σ_y , E and ν within coated or surface-treated materials, particularly with depth from the surface. Selection of a coating system, as pointed out by Godet *et al.*,¹¹¹ for tribological applications must therefore be based on knowing the coating factors such as deposition method and parameters, composition, thickness, hardness (indentation and scratch) and coating-to-substrate adhesion. Selection would also be based on experience (if available) where the coating has performed well and relevant tribological data are available. Correct surface selection also requires knowledge of thermal and stress distributions generated by the contact for both the coating and the substrate. Thus, the properties required for both the coating and the substrate are Young's modulus, Poisson's ratio, coeffi-

cient of thermal expansion, thermal conductivity, density and specific heat. The temperature and stress limits for both materials must also be known together with any residual stress levels present.

The ratio of the coating to substrate stiffness can govern substrate failure. For coatings where $0.5 < c_t/a_0 < 1.5$, the substrate is subjected to higher stresses when covered by stiff coatings, $E_c/E_s > 1$. This is in contrast with thick coatings, $c_t/a_0 > 1.5$, which protect the substrate as the highly stressed zones are within the coating.

Leroy *et al.*¹¹² in 1989 looked at thermomechanically induced cracking of thin hard coatings under sliding heavy loads using moving heat source modelling. They derived temperature and thermoelastic stress fields to aid the understanding of coating system performance and their optimisation for such duties. Leroy and Villechaise,¹¹³ a year later in 1990, listed the most important stresses to consider in coating design as the maximum von Mises stress, the maximum interfacial shear stress, the lateral tensile stress and the normal compressive stress. They also concluded that there is no ideal coating thickness to minimise all these stresses.

Multilayered coatings

Multilayer coatings offer several mechanisms for higher strength.

1. Deflection and/or termination of cross-sectional cracks at layer interfaces.
2. Stress relaxation by plastic deformation in a softer layer.
3. Increased hardness by dislocation motion termination on layer interfaces, dislocation reflection into layers of lower elastic modulus or dislocation termination in a coherent field of compressive–tensile strains induced by layer lattice mismatches on interfaces.

Voevodin *et al.*¹¹⁴ have modelled and experimented on multilayer Ti/TiN coatings. A single pair of Ti/TiN coatings $3\mu\text{m}$ thick resulted in maximum shear stresses below the coating–substrate interface, leading to plastic deformation in this region causing adhesive and cohesive failure. A five-pair Ti/TiN coating had maximum shear stresses at the coating–substrate interface while with a ten-pair multilayer coating the stress was moved into the coating volume, reducing the normal and shear stresses in the substrate by 40% and 22% respectively.

Nanolayer composite coatings enable creation of stable structures with a combination of properties conventionally considered incompatible with each other, such as high hardness and high toughness. Coatings, typically $1\text{--}4\mu\text{m}$ thick, can be deposited at a total pressure ranging from 0.9 to 3 Pa, at a relatively low substrate temperature not exceeding 200°C . Sobota *et al.*¹¹⁵ deposited nanostructured multilayer coatings of the C–N/MN_x type,

where M could be Ti, Nb or Zr. Various substrates such as highly polished WC, steel and silicon were used. They studied the tribological properties of C–N/MN_x nanostructured multilayers and found that C–N/ZrN_x outperformed C–N/NbN_x with lower friction and higher wear resistance at temperatures up to 400 °C. This performance was due to transfer layers on the steel counter-surface.

Layers that are truly a nanometre thick have been studied by Lee *et al.*¹¹⁶ who presented two examples. The first example is the synthesis and optimisation of nitrogenated carbon (CN_x) nanolayers 1 nm thick as protective overcoats in extremely-high-density hard-disk systems. The second example is the development of multilayer coatings for wear protection at elevated temperatures. These studies demonstrate that atomically smooth CN_x overcoats 1 nm thick can be deposited. In addition, they show that superhard coatings based on TiB₂/TiC multilayers with high thermal stability, low internal stress and high wear resistance can be synthesised by proper choice of nanolayer thickness and process conditions.

Gorishnyy *et al.*¹¹⁷ developed an approach for the design of multilayer coatings with enhanced toughness to fracture and improved adhesion for wear-resistant applications. Finite-element analysis was utilised to investigate the distribution of stress in monolayer, bilayer and multilayer films under combined normal and tangential loads. The influence of film architecture and substrate material on the mechanical stress within the films was studied. The metallic layers were found to have significantly lower $\sigma_{(xx)}$ stress levels than the ceramic layers, while both $\sigma_{(yy)}$ and $\tau_{(xy)}$ stress levels within the layers were largely independent of the layer material.

Residual stress in the films was determined from X-ray measurements. When used in multilayer architectures, CrN films had high compressive stress on both steel and aluminium substrates, while chromium films had a lower compressive stress on steel substrates and tensile stress on aluminium substrates. Coating adhesion was measured by a scratch test and wear rates were measured using a pin-on-disc testing apparatus for the aluminium and steel substrates. The strongest correlations were found between the σ_{xx} stress at the film–substrate interface and coating adhesion and wear resistance.

The stresses at the interface between ceramic layers and metallic substrates were found to be very high, resulting in an overall reduction in performance of monolayer Cr₂N and multilayer CrN/Cr₂N films. The highest adhesion and the lowest wear rates were observed in the films that consisted of alternating CrN layers separated by thin chromium layers. Increasing the thickness of the chromium layers degrades the performance of the films owing to a decrease in the overall stiffness of the coating.

In summary, PVD multilayer coatings offer coatings with multifunctional character, lower residual stresses, good adherence to metallic substrates,

improved hardness to toughness ratio and low friction coefficients for a composite exposed to complex wear conditions. Holleck and Schier¹¹⁸ presented results concerning multilayer coatings mainly based on TiC/TiN. Improved toughness due to fine-grained microstructure, crack deflection, reduced stress concentrations, lower stress and strain fields and reduced residual stresses were reported.

1.4.3 Linking stress distributions to coating delamination and cracking

A good review of the consequences of stress within thin films has been given in Chapter 4 of the book by Freud and Suresh.¹¹⁹ Stress distributions and edge effects on delamination and fracture were discussed as well as interfacial delamination and crack growth associated with fracture criteria. Spontaneous delamination of a strained coating from its substrate was also examined.

An example of delamination is given by PVD (Ti, Zr)N- and TiCN-coated cermet tools which suffer severe and early delamination when machining austenitic steel owing to adhesive and cohesive coating failure, linked to the thermal conductivity of the coated cermets.¹²⁰

Oliveira and Bower¹²¹ have looked at modelling the influence of microcracks in the coating, substrate and interface as well as residual stress in the coating. They used linear elastic fracture mechanics to predict loads required from an elastic cylindrical indenter to initiate fracture. Fracture was found to initiate from flaws in the coating (assumed to be a brittle elastic layer) rather than at the coating–substrate interface. Damage patterns were strongly influenced by the mismatches in elastic properties between the coating and substrate.

1.4.4 Surfaces under slide–roll motion

Rolling contact fatigue

Rolling contact fatigue (RCF) can be defined as the crack propagation and subsequent pitting (delamination) in the near-surface layers of contacting surfaces subjected to alternating Hertzian stresses induced by rolling or a combined rolling and sliding within a tribocontact. It is thought that cracks propagate under mode II loading (shear).¹²² It can, therefore, cause the failure of components subjected to rolling–sliding contacts such as rolling element bearings, gears and camshafts and is an increasing problem in high-speed, mixed and heavy-haul railways.¹²³

For hydrodynamically lubricated line and point contacts, with no asperity interactions between surfaces, high stresses can be generated. For pure

rolling the maximum Hertzian stress p_0 can exceed the yield stress of the material. The maximum shear stress is $0.30p_0$ at a depth of $0.78b$ for line contacts, and $0.31p_0$ at $0.48a$ for point contacts. Localised plastic deformation can occur at these depths if the stress exceeds about $1.67\sigma_y$. When these stresses act on inclusions, which may be present at these depths, cracks can be propagated under applied cyclic stresses, leading to pitting of the surface. When asperity contact occurs, local stress fields are established in the near-surface region and are superimposed on to the macrostress field described in Section 1.2.2, making pit propagation under these contact conditions difficult to understand or predict.

For rolling–sliding contacts a frictional traction occurs in the bulk film and at the asperities, which induces tensile stresses at the surface. For a line contact the maximum tensile stress of $2\mu p_0$ (where μ is the coefficient of friction) occurs at the trailing edge and is a potential source to induce surface cracking. Subsurface shear-driven cracks can also be generated as discussed in the previous paragraph, except that the magnitude of stress increases and the location of maximum shear stress moves upwards towards the surface as friction levels increase. This results in different subsurface stress fields. All these factors contribute to making fatigue life prediction difficult.

For point contacts and using equation [1.4] the tensile stress for frictionless contacts can be calculated for typical bearing steels as $0.133p_0$ which again may be a potential source to induce surface cracking.

Recent work has shown that hot, isostatically pressed Si_3N_4 is emerging as an extremely promising material for fabricating high-performance all-ceramic or hybrid steel–ceramic rolling contact bearings. Compared with conventional steel bearings, Si_3N_4 bearings have been shown to offer significant benefits in terms of rolling contact fatigue life, and the lower density of the material greatly reduces the dynamic loading at ball–raceway contacts in very-high-speed applications such as machine tool spindles and gas turbine engines.¹²⁴ Their wear resistance whilst lubricated by aviation oils is also superior to VIMVAR M50 bearing steels.¹²⁵ Hybrid or fully ceramic options are candidates for particularly demanding applications such as aircraft gas turbine mainshaft ball bearings, cruise missile turbine shaft bearings, target drone engine bearings and rocket propellant pump bearings.

Test rigs Roller-type testing machines with either two or three rollers are commonly used to evaluate the RCF performance of surfaces and coatings to simulate rolling–sliding line contact configurations associated with gear and cam–tappet applications. In addition to the roller-type machines, pure rolling conditions can be generated by using a modified four-ball machine¹²⁶ or a ball-on-rod machine.¹²⁷ These machines are capable of simulating the kinematics of rolling bearings and can provide point contact configuration.

The choice of test machine can, however, have an influence on the RCF performance,¹²⁸ thereby iterating the need for full-scale component testing.

Effect of lubrication The effects of chemical additives on the fatigue life are not well understood and may well relate to complex corrosive and tribochemically induced anti-wear film formation scenarios developed in tribocontacts. Readers are referred to the book by Sethuramiah¹²⁹ for a more detailed review of related work.

Rolling contact fatigue of coatings

Full understanding of the RCF of coated components has yet to be realised but some important findings are highlighted below.

Thermal spray coatings The RCF resistance of coatings is highly dependent on coating quality. For example, the process of thermal spraying can result in coatings with discontinuities such as pores, thermal-stress-induced cracks, oxide lamellae or incompletely molten particles. These discontinuities in the coating microstructure and composition are highly dependent on the spray processes and parameters. Very different RCF performances have been recorded for coatings deposited by different types of spray system.¹³⁰

The coating thickness has been shown to be an important parameter in the RCF resistance of thermally sprayed coatings.¹³⁰ Investigations indicate that increasing coating thickness is beneficial in improving the RCF life of thermal spray coatings, with coatings greater than 200 μm thick displaying superior RCF performance over thinner coatings. This is attributed to the location of shear stresses in relation to the coating–substrate interface, changing the delamination mechanism from adhesive (interfacial) to cohesive driven.

Coatings obtained by physical vapour deposition For PVD coatings, it has been indicated that the optimum thickness of TiN and DLC coatings to resist RCF was found to be in the region of 0.75 μm . On increasing coating thickness past this level, early failures occurred under RCF conditions (typically with the three-ball-on-rod test geometry at 3–5 GPa contact stress and for between 0.4 and 100×10^6 cycles) owing to microstructural defects associated with intercolumnar regions. Two types of failure have been detected in PVD coatings under RCF, namely subsurface-initiated RCF and near-surface-initiated RCF. It has also been shown that PVD TiN coatings fail adhesively while CrN coatings fail cohesively. In analysing the effect of residual stresses on PVD coatings, in general a compressive residual stress enhanced the RCF performance of PVD coatings. However, the thickness

and the composition of the coating have effects on the extent to which the residual stresses enhance the RCF performance of the coating.¹³⁰

Coatings obtained by chemical vapour deposition With CVD coatings, an optimum range for the level of compressive residual stress (less than 180 MPa) within the coating has been found for SiC coatings 250 μm thick at which the RCF performance was enhanced at 5.5 GPa contact stress. If the compressive residual stress levels are above 180 MPa, then debonding between the coating layers is likely.

1.5 Conclusions

This chapter has introduced the stress fields induced by contacting surfaces and the contact conditions that invoke wear processes and the subsequent degradation of contacting surfaces in relative motion. It has also introduced the origins of friction and classified the different wear phenomena associated with a tribocontact. It has discussed how coatings can be used to control contact stresses and therefore wear processes and rates. It highlights the need to understand subsurface stress fields induced by tribocontacts particularly for coated surfaces to limit substrate deformation (yield) and subsequent coating failure. Several wear equations are presented to help to highlight the mechanical properties that are thought important in controlling the different wear processes and thus inform material or surface selection for maximum wear resistance. Examples from recent research have been used, wherever possible, to illustrate these points and to highlight current active areas of interest in the subject, such as tribocorrosion. It also contains references to material for further reading within this subject area. It is intended to provide a foundation in the role of stresses in wear phenomena and surface performance within tribocontacts to undergraduate students and researchers and also to encourage readers to develop a better understanding of contact degradation and how to develop better surface treatments and coatings to improve surface performance.

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1.7 Appendix: Nomenclature

a	Hertzian point contact radius or half-width (m)
A	real contact area (m^2)
A_{nom}	nominal contact area (m^2)
b	Hertzian line contact width (m)
c	specific heat capacity ($\text{kJ kg}^{-1} \text{K}^{-1}$)
c_l	compression wave velocity for the liquid (ms^{-1})
C	pure corrosion (mg or mgs^{-1})
C_k	cutting characteristic velocity (ms^{-1})
C_T	coating thickness (m)
C_0	Arrhenius constant
d_p	particle diameter (m)
D	Preston wear coefficient
E	Young's modulus (Pa)
E	pure wear or erosion (mg or mgs^{-1})
E^*	reduced modulus of the softer wearing surface (Pa)
E_k	kinetic energy of impacting particle (J)
E_v	dimensionless volumetric erosion rate
f	mass fraction of oxygen in the oxide
F	frictional force (N)
F_m	maximum load (N)
h	wear depth (m)
$\dot{h}$	steady rate of thermal energy input per unit area ($\text{Nm}^{-1} \text{s}^{-1}$)
h_{gap}	gap between the undeformed surfaces (m)
h_{min}	minimum film thickness (m)
H_c	hardness of the wearing surface (Pa)
H_v	Vickers hardness
k	dimensionless Archard wear law coefficient
k	shear strength of the weaker material
K	thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
M_p	particle mass (kg)

n	velocity ratio exponent (= 2.54 for carbon steel ⁴⁷)
N	number of erodent impacts
p	contact pressure (Pa)
p_s	shakedown pressure (maximum Hertz contact pressure for onset of shakedown in the softer wearing material) = $(2/\pi)E^*(\delta_s\kappa)^{1/2}$
p_0	mean contact pressure (Pa)
P_m	mean pressure (Pa)
P_{wh}	water hammer pressure (Pa)
Pe	peclet number = $Ua/2\beta$
Q	volume loss per unit sliding distance ($\text{m}^3 \text{m}^{-1}$)
Q_0	activation energy (J)
r_p	particle radius (m)
R	universal molar gas constant = $8.31451 \text{ JK}^{-1} \text{mol}^{-1}$
R	component radius (m)
R^*	relative radius (m)
R_f	roundness factor for particle (= 0–1)
R_q	root-mean-square surface roughness (μm)
S	synergy
S_i	severity index
t	time over which the equilibrium mild wear is measured (s)
t_e	elastic contact time (s)
T	total wear or erosion loss (mg or mgs^{-1})
U	sliding velocity (ms^{-1})
v_s	volume fraction of abrasives
V	flow velocity assumed to be the impact velocity (ms^{-1})
V_{cr}	critical particle impact velocity for plastic flow (ms^{-1})
V_p	particle impact velocity (ms^{-1})
V_s	specific volume erosion loss (m^3)
V_u	erosion rate ($\mu\text{m}^3 \text{impact}^{-1}$)
W	applied load (N)
W'	load per unit length (Nm^{-1})
W_r	wear rate (Quinn)
x	fraction of erodent by weight

1.7.1 Greek letters

α	angle of impingement (deg)
β	thermal diffusivity = $K/\rho c$
δ_s	compression of the spherical asperity of curvature R
δV	debris volume (m^3)
δW	fraction of the normal load (N)
ΔC	wear-enhanced corrosion (mg or mgs^{-1})
ΔE	corrosion-enhanced wear (mg or mgs^{-1})

ε_y	strain at yield
$\theta_{\max}$	flash temperature
κ	specific wear rate ($\text{m}^3 \text{N}^{-1} \text{m}^{-1}$)
λ	ratio of the minimum film thickness to the surface roughness
μ	coefficient of friction
ν	Poisson's ratio
ρ	density of the half-space (kg m^{-3})
ρ_l	density of the liquid (kg m^{-3})
ρ_{ox}	mean density of the oxide in the contact zone (kg m^{-3})
ρ_p	density of the particle (kg m^{-3})
σ	dynamic plastic flow stress for target (Pa)
σ^*	standard deviation of surface asperities (m)
σ_{rms}	root-mean-square asperity height of the harder surface (m)
σ_y	yield stress (Pa)
$\tau_{\max}$	maximum shear stress (Pa)
φ	proportion of asperity contacts that generate debris
χ	normalised velocity (ms^{-1})
ψ	plasticity index
ψ_s	plasticity index in repeated sliding

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2.1 Introduction

There are several reasons why the mechanical testing of coatings may be required. As performance requirements steadily increase, new advanced coatings are continually being developed. During the development of new coatings, it is highly beneficial for any new materials to be characterised, as it is too slow and expensive to take a 'suck it and see' attitude to development. Indeed, it is extremely useful when any coated system is optimised to have reliable data to feed into the development process.

The type and number of mechanical test methods required to specify a coating depend strongly on the type and range of applications envisaged. It is sometimes the case that a coating may be being developed as a general-purpose solution or at least for a more generic set of applications. In this case, it is important that a comparably generic set of measurements be carried out to determine a range of parameters able to indicate the likely performance of the coating in different circumstances. An extreme case of this approach is the growing drive to use modelling to predict the performance of coatings and to provide a virtual route to directed or 'fast' prototyping. These models usually require fundamental materials properties such as Young's modulus, Poisson's ratio, yield strength (hardness), thickness, adhesion and fracture properties. This places high demands on the type and accuracy of the coating test methods employed. Test methods occupy a continuum between those that are highly performance based and application specific to those that are further removed from in-service performance but more readily analysed to generate fundamental materials property values. In some circumstances, the only tests available provide a composite result and considerable effort is required before fundamental property data of the required accuracy are obtained.

Increasingly, surface engineers are realising that performance and cost benefits are available if a holistic approach, of matching the substrate and coating properties to optimise overall component performance, is taken. Here the specific application is usually known, and the mechanical properties that relate to good performance are understood; so a more specific set of measurements are required for the optimisation process.

Application-specific performance tests are most at home on the shop floor where there is an increasing demand for simple but rapid and reliable quality control. Here the coating selection has already been made and the demand is for test methods that are simple to conduct, are empirical in nature but can be related to the typical (or actual) application of the coating being manufactured. An example of this is the ‘hole-drilling’ test for the quality control of coated drill bits. Here a randomly selected drill bit from a batch is used to drill holes into a block of an appropriate material until failure or seizure occurs. The number of holes drilled is a direct measure of the performance of the coated drill. Similarly, scratch tests are also often used in a quality control role.

Measurement of the properties of coatings is an active area of research. Many measurement methods are already available for the measurement of these properties and new methods are being developed all the time. This chapter does not attempt to be an exhaustive survey; rather it attempts to address a number of the key coating parameters of interest and to provide a framework for discussion of the issues affecting the most important measurement methods available in each case.

2.2 Thickness

Thickness is one of the most basic physical parameters of a coating. Table 2.1 lists a number of different techniques commonly used. These can be separated into two basic groups. In the first group the thickness is determined from a direct measurement of the distance between two points. In the second, the result is inferred from measurement of a thickness-dependant physical property.

The most direct (and simplest to understand) methods are the displacement measurement techniques. Cross-sectional microscopy, particularly when combined with freeze fracture to avoid smearing or disturbing the coating–substrate interface position, gives a direct measurement of thickness. This technique can give good results, but in some cases there are practical difficulties in obtaining cross-sections where the coating is not deformed or damaged.

Profilometry can be used to measure the step height between a coated and uncoated area of a sample. Best results are obtained if the step is abrupt and if surface roughness does not make it too difficult to define the surface

Table 2.1 Thickness measurement methods

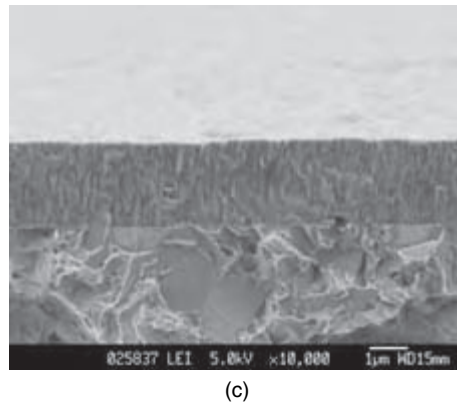
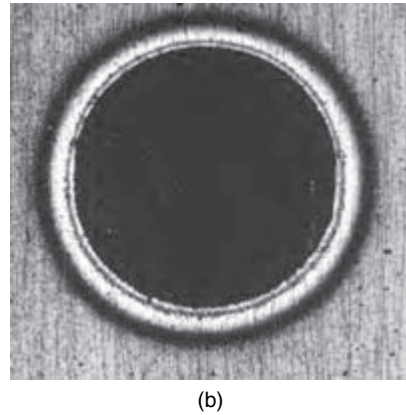
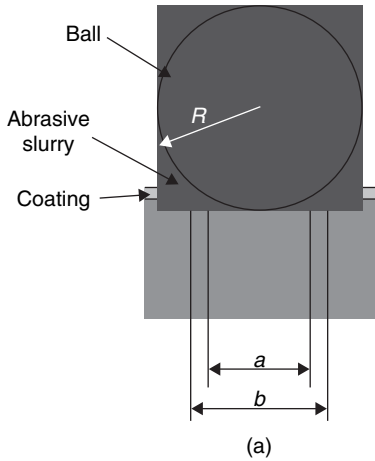
Direct dimensional measurement	Dimple grinding Profilometry of steps Sectioning and microscopy
Physical principles	X-ray fluorescence Resistivity Eddy current Optical (transparent coatings)

planes at the top and bottom of the step. Care must also be taken that any mask used to create a step artificially does not disturb the local deposition conditions significantly, leading to an unrepresentative step height.

An alternative to creating a step by masking is dimple grinding. Here a ball is used to grind a spherical depression through the coating (Fig. 2.1). The thickness of a coating can be calculated from measurements of the diameters of the craters in the coating and substrate. This technique can be easily adapted for the measurement of the thickness of the different layers in a multilayered coating as long as the individual layers are easily distinguished and of sufficient thickness to be resolved by the microscope used to view and measure the crater diameters. An important advantage of the dimple grinding method is that specific regions of interest can be easily selected for thickness measurement. The method is only very locally destructive and, unlike masking techniques, does not interfere with the coating process. Coating thickness can also be readily mapped over a range of positions.

Perhaps surprisingly, quite good results are also obtained by gravimetric methods. This technique neatly spans both groups in Table 2.1. Here, measurements are made of the sample dimensions and the weight of the sample with and without the coating. These measurements are then combined with knowledge (or more usually an assumption) of the coating density to derive an average coating thickness. This method is prone to errors when used to predict the thickness at a specific region on a sample undergoing non-uniform coating deposition. It is also often dangerously naïve to assume that a coating is fully dense. In some cases, specific density measurements may be possible, but success depends on the relative volume and density of the coating and substrate. Density may also be measured by other techniques such as surface acoustic wave spectroscopy (see Section 2.7).

Physically based thickness measurement techniques use a range of physical phenomena to infer thickness measurements. In all cases the calculation of coating thickness from the test results depends on an independent measurement or calibration of the thickness dependence of the specific physical property being measured. A number of methods are commonly used. Two-



2.1 Simple methods for thickness measurement: (a) schematic diagram of cap grinding; (b) crater produced by cap grinding in a multilayer coating enabling measurement of thickness of layers and evaluation of structure; (c) cross-section of TiN coating on tool steel by freeze fracture.

or four-point resistivity or resistance measurements can be used in the case of conductive layers on insulating substrates. Four-point probes are preferable as this avoids errors and uncertainties due to contact resistance. Electromagnetic methods exist, which rely on a calibration of magnetic field strength or capacitance with distance. In its simplest form this requires a substrate that is ferromagnetic or can be made to generate magnetic fields via induction of eddy currents or, for capacitance methods, is a conductor. Usually a calibration of the electromagnetic sensor response on an uncoated portion of the substrate is required. X-ray fluorescence relies on calibration

of the X-ray absorption of the material to be measured. Surface acoustic wave measurement (described in detail later) uses the variation in the speed of sound in materials as a function of density and elastic properties to derive a thickness estimate for a coating. For transparent coatings, optical techniques can be used to measure thickness, but here the refractive index of the coating needs to be known.

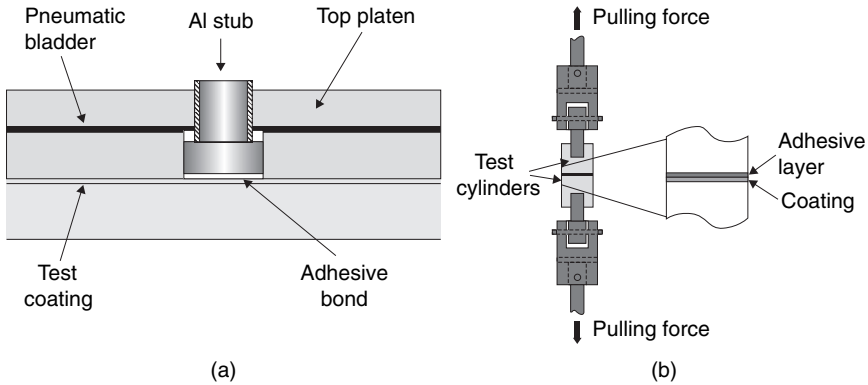
2.3 Fracture and adhesion testing

There are a phenomenal number of different methods in existence, all purporting to test the adhesion of coatings. There is even a regular conference series devoted to the subject. Over 300 different methods or variants of methods were listed in one conference volume.¹ Most of these are, however, highly performance based and very few actually measure the coating adhesion in terms of an interfacial strength or toughness. A range of common test methods is given in Table 2.2.

The simplest test method in concept is the straightforward pull-off test. This test uses a stud, fixed with adhesive on to the coating, which is pulled off using a force-recording mechanical testing system (Fig. 2.2). The difficulty with this test is that the maximum strength that can be measured is the maximum strength of adhesive that can be obtained. High-performance adhesives typically have a tensile strength of less than 100 MPa. Achieving this level of stress in a practical test requires careful techniques to promote adhesion to the coating and for maintaining the force direction perpendicular to the sample. Even slight angular deviations from the perpendicular can result in a premature ‘peeling-mode’ failure. For advanced coatings obtained by physical vapour deposition (PVD) and chemical vapour deposition (CVD) the adhesion strength of the coating to the substrate exceeds

Table 2.2 Adhesion test methods

Substrate deformation	Mandrel bend test
	Four-point bend test
	Tensile test
Coating deformation	Indentation in cross-section
	Rockwell adhesion test
	Nano-impact test
	Scratch test
Coating pull-off	Pressure-sensitive tape test
	Peel test
	Push-off test
	ASTM pull-off test
	ASTM tensile adhesion test

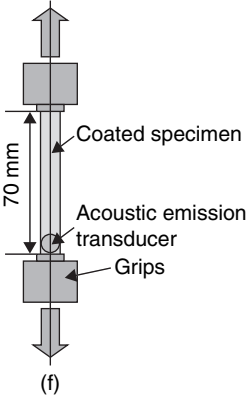
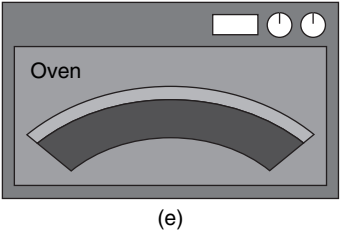
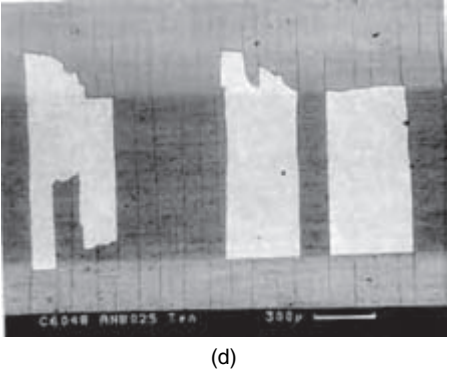
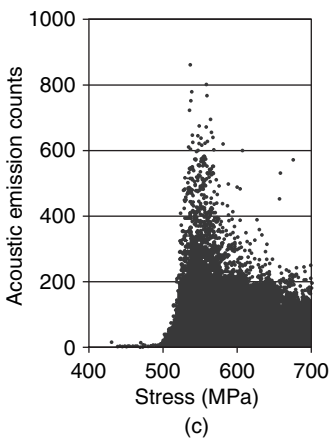
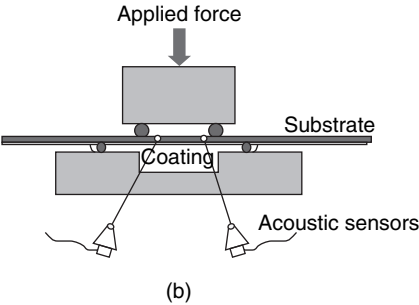
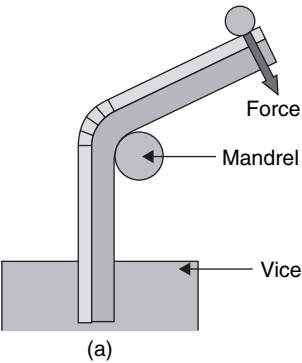


2.2 Conventional adhesion test method: (a) ASTM D4541 pull-off test; (b) ASTM C633 tensile test.

the strength of organic adhesives. Pull-off tests were designed in particular for thick coatings such as oxide scales or thermally sprayed coatings where the strengths of the coating and the interface are generally lower than the typical adhesion strength of PVD and CVD thin coatings. In cases where peeling is the failure mode of interest, the geometry of the test may be adjusted to promote this failure mode. In this case, failure may need to be initiated prior to performing an off-axis pull, so that only the peeling mode is measured.

There are a number of test methods that apply a stress to the coating–substrate interface by means of a deformation to the entire substrate/coating composite structure (Fig. 2.3). In mandrel testing, a coated test sample is bent over a cylindrical mandrel to a preset angle. If cracking or spalling of the coating occurs before this preset angle, the coating is defined to have failed by either cohesive or adhesive failure. This test is a classic example of a very simple pass–fail quality control test that does not give any quantitative information (apart from the pass–fail knowledge).

The four-point bend test is in many ways an instrumented version of the mandrel test. Here a coated sample is tested in a four-point configuration (Fig. 2.3(b)). The sample is oriented so that the coating is put into tension. As a force is applied and the tensile stress in the coating increased, a point is reached where fracture of the coating occurs. Typically, this results in a through-thickness crack in the coating, which runs transverse to the direction of stressing (Fig. 2.3(c) and Fig. 2.3(d)). Observation of crack formation as a function of applied stress is achieved in a number of ways. The simplest way is to stress or strain the sample to preset levels and to examine it *ex situ* by optical or electron microscopy. This is a slow process and introduces uncertainties if the sample has to be remounted and strained further to



2.3 Different adhesion test methods involving deformation of the substrate–coating composite: (a) mandrel test; (b) four-point bend test; (c) acoustic emission output from the bend test; (d) coating cracked and spilled in four-point bend adhesion test; (e) thermal stressing test; (f) tensile test.

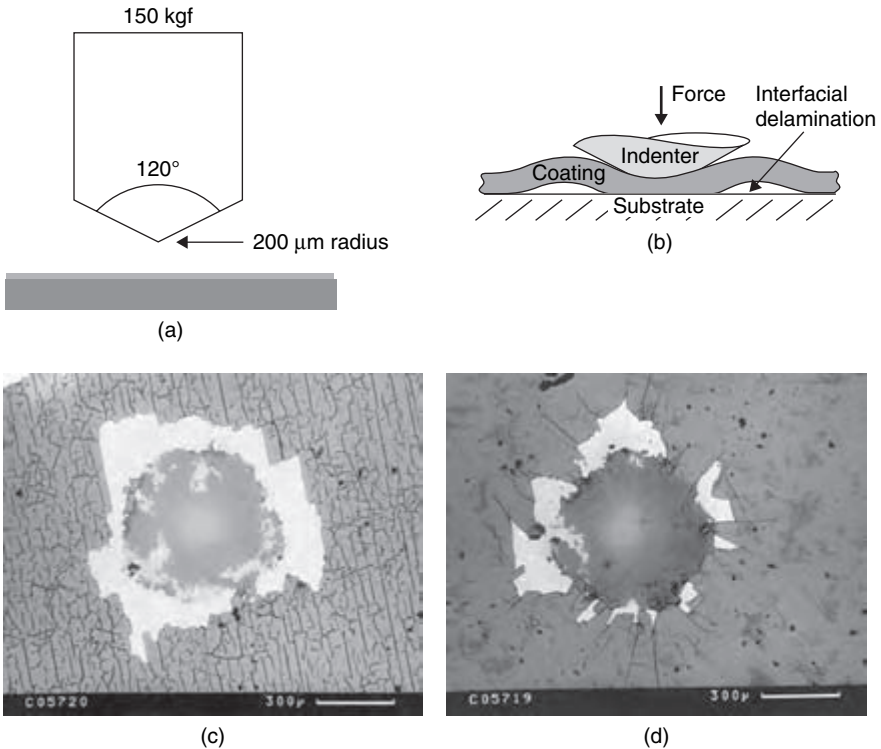
generate fracture. Recent developments have allowed *in-situ* observation of cracking by optical microscopy and even more sophisticated systems use acoustic emission detectors to detect the point at which cracking first occurs. The use of two sensors and time-of-flight windowing to exclude extraneous acoustic signals, e.g. from creaking rollers, can significantly improve the signal to noise ratio. The tensile stress at which cracking first occurs is a measure of the fracture strength of the coating and this generally coincides with the point at which the acoustic emission counts increase markedly.

As the load is increased, more cracks form and the crack spacing reduces until portions of the coating spall off (Fig. 2.3(d)). The strain at which this occurs is a measure of the adhesion strength of the coating to the substrate. Mathematical analysis can be used to derive values for the cohesive and adhesive strength of the coating. This test works best for coatings that fail by brittle fracture, have a well-defined interface and have a coating fracture toughness that is less than the coating–substrate interfacial toughness. This is not always the case. When the coating is ductile, it deforms plastically and does not fracture, although it might delaminate and spall off. For extremely highly adherent coatings (with respect to the coating fracture toughness), failure may begin with idealised perpendicular cracks but progress to other cracking directions in preference to interfacial failure.

In some cases, beam bending can be generated very simply, e.g. by putting a coated sample into a furnace and increasing the temperature (Fig. 2.3(e)). If there is a thermal expansion coefficient mismatch between the coating and the substrate, stresses are generated, which act to bend the sample. If the temperature continues to increase, the stress in the coating correspondingly increases until it is sufficient to cause fracture. The critical temperature at which fracture occurs may be easily identified by acoustic emission monitoring during a sustained temperature ramp. The corresponding stress generated in the coating can be calculated if the physical properties of the coating and substrate are known. It should be noted that this technique is not appropriate if it is known that the physical properties of the materials change significantly with temperature.

Tensile testing can also be carried out, also with acoustic emission and microscopy, for fracture and adhesion testing of coatings (Fig. 2.3(f)).

Rockwell indentation may be used to evaluate coating adhesion. Often called the ‘Mercedes test’, a Rockwell indenter is pressed into the coated sample. The stresses generated around the indentation can cause coating fracture and delamination. The degree of delamination can be used as a measure of the adhesion of the coating to the substrate. If the coating spalls everywhere, it has delaminated; the spalled area can be quantified to yield an adhesion interface toughness value.² Figure 2.4(c) and Fig. 2.4(d) show two different M–Cr–Al–Y coatings with significantly different amounts of adhesion, resulting in different areas of spallation of the coating. The

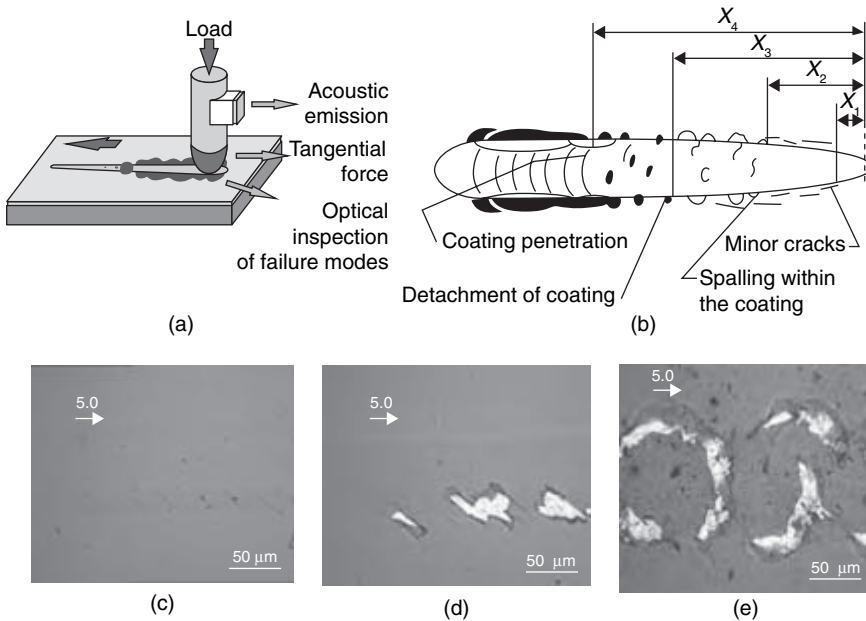


2.4 Indentation test for adhesion measurement: (a) schematic diagram of the indentation test; (b) schematic diagram of the delamination mechanism; (c) M-Cr-Al-Y coating with an interfacial energy of $\Gamma_c = 680 \text{ J m}^{-2}$; (d) M-Cr-Al-Y coating with an interfacial energy $\Gamma_c = 1470 \text{ J m}^{-2}$.

analysis is dependent on spallation occurring and requires a substantial amount of coating and substrate property information to enable the calculation of the strain energy released.

2.4 Scratch testing

Scratch testing was originally introduced as a damage tolerance test and then as an adhesion test for PVD coatings such as TiN in the early 1970s. Figure 2.5(a) shows the principle of the test. A diamond indenter, normally a Rockwell indenter with a 0.2 mm radius, is moved across the surface of the coated sample under an increasing load. The tangential force and the acoustic emission are often monitored during a test. As the scratch proceeds and the load increases, different failure modes are seen in the coating (Fig. 2.5(b)). These different failure modes are illustrated by results from



2.5 Scratch testing: (a) schematic diagram of the scratch test system; (b) schematic diagram of failure events that can occur; (c)–(e) examples of scratch events on carbon film BCR-692 scratch reference material showing (c) Lc1 15 N cracking, (d) Lc2 20 N edge chipping and (e) Lc3 30 N cross-track chipping.

scratches made on the BCR-692 scratch reference coating that was developed in an EU-funded collaborative project.³ In Fig. 2.5(c), initial cracking has started at a load of 15 N (defined as Lc1), edge chipping at 20 N (Lc2) and more complex whole scratch damage at 30 N (Lc3).

With low adhesion coatings, delamination occurs simply along the coating–substrate interface at a well-defined load, and an adhesion strength can be calculated fairly readily, but many modern coatings are much more adherent so that failure is much more complex; indeed adhesive failure sometimes does not occur in the scratch test with these coatings.

If friction and acoustic emission signals are monitored during a scratch test, they can give an indication of failure events, as these parameters usually increase dramatically when failure occurs.

Although many test parameters in scratch testing have an effect on the results that are obtained, by far the most important are the geometry and condition of the indenter used. The European scratch test standard EN 1071-3 requires the use of a Rockwell C stylus, which is defined in ISO 6508 part 2 as a sphero-conical diamond indenter with a radius of $200 \pm 10 \mu\text{m}$.

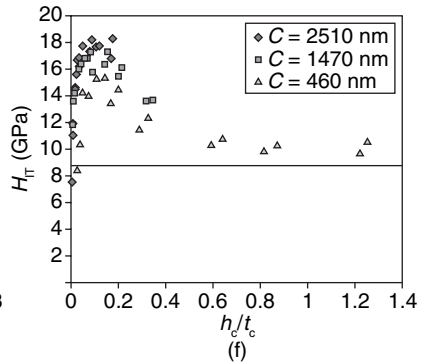
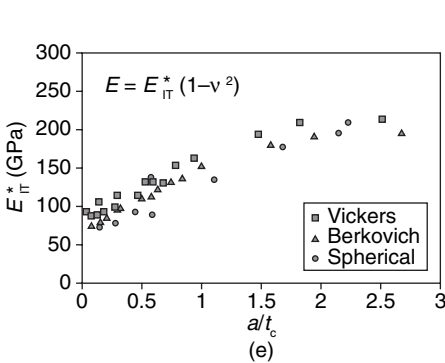
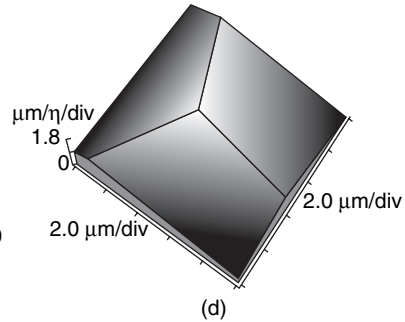
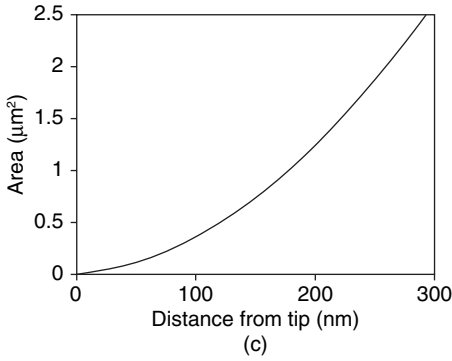
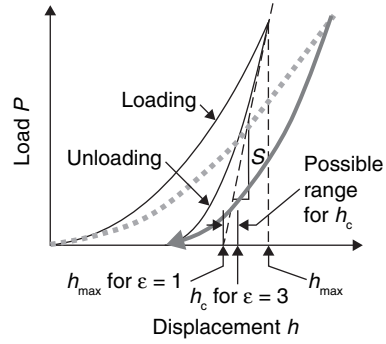
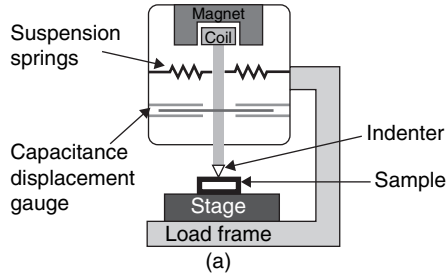
In practice it has been found that there is considerable variation in the radius of the scratch styli supplied and few meet the requirements of the standard.³ It is also important to check the indenters for damage periodically, as this will dramatically affect results.

Recently, a scratch reference materials BCR-692 has been developed in an EU-funded project. Certified reference materials are powerful tools. They can be used to check the performance of scratch test indenters and systems over time and provide a mechanism for comparison of results between different organisations.^{4,5}

2.5 Instrumented indentation testing

Instrumented indentation testing is one of the very few techniques that can measure both the elastic and the plastic properties of very small volumes of materials and so is one of the most useful test methods for determining the mechanical properties of coatings. Conventional indentation testing, in the form of the traditional Vickers, Knoop, Brinell and Rockwell tests, has been used successfully to characterise bulk materials for over a century. For many years, progressively lower force and displacement microhardness testing was quite successfully used to measure the properties of thicker coatings and surface treatments. However, as coating thickness progressively decreased, it became difficult to make indentations large enough for optical measurement without introducing a marked effect from the substrate. Since the advent of its commercial availability in the 1980s, instrumented indentation has produced a tremendous increase in capability, allowing for the measurement of other properties such as modulus, creep and viscoelasticity as well as hardness.

The principle of a typical system is shown in Fig. 2.6(a). The indenter is mounted on an indenter shaft, which is suspended by flexure elements and is pressed against the test sample by a loading actuator (commonly an electromagnetic, electrostatic or piezoelectric system). Most commonly, a parallel-plate capacitor is used to measure the displacement of the shaft (and therefore the indenter) into the sample. By instrumenting the indentation displacement, indents no longer have to be inspected to determine their size and can therefore be much smaller. The method requires, however, detailed knowledge of the indenter shape as a function of depth to enable calculation of the indentation area of contact from measurements of indentation depth. Typically, triangular pyramidal ‘Berkovich’ geometry indenters are used. These were originally designed to have the same surface area–depth relationship as Vickers indenters, but with the added advantage that a three-sided shape is guaranteed to meet at a single point, whereas a four-sided Vickers indenter almost always meets in a ridge-shaped line of conjunction. In recent times, the ‘modified Berkovich’ geometry has become



2.6 Instrumented indentation: (a) schematic diagram of the test system; (b) schematic load-displacement curve; (c) area-distance from the tip curve for the indenter; (d) indenter imaged by AFM; (e) variation in E_{IT}^* with the ratio of the radius of indentation to the coating thickness for a gold coating on nickel three different indenters; (f) variation in H_{IT} with the ratio of the indentation contact depth to the coating thickness for DLC on steel (coating hardness = 18 GPa).

popular, which is designed to have the same relationship of the cross-sectional area to depth as a Vickers indenter.⁶

In a typical quasi-static indentation cycle, force is progressively applied and the indenter is steadily pressed into the sample. As a result, the sample deforms elastically and plastically under the indenter until a maximum force is reached. The force may be held for a while before being progressively removed, the sample relaxing elastically as the indenter is removed from the surface. The key feature is that the applied force and measured displacement are recorded either continuously or at frequent time points throughout this cycle. The immediate output from instrumented indentation is therefore the force–displacement curve (Fig. 2.6(b)). This in itself can be extremely instructive, e.g. the ratio of the areas under the loading and unloading curves is an immediate indicator of the balance between elastic and plastic deformation of the material under test. ISO 14577 provides a number of analyses of the force–displacement curve to provide measurement of sample hardness and modulus. The simplest measurement uses the maximum depth $h_{\max}$ that the indenter was pushed into the material as a measurement of total elastoplastic deformation, previously referred to in the literature as the universal hardness but now defined as the Martens hardness. The simplicity of this measurement is marred somewhat by its complex combination of both the elastic and the plastic properties of the material under test. This makes it of limited use as a materials property measurement. More physically meaningful is the measurement of indentation hardness H_{IT} . This is a measurement of the mean indentation pressure under load. Indentation into anything other than a perfectly plastic material results in a local bowing of the test surface, which means that the total indentation displacement is an overestimate of the depth of indenter actually in contact with the testpiece. The actual contact depth h_c may be estimated from the gradient of the unloading curve and a correction for the complex elastic recovery of the surface as the indenter is removed. As the unloading curve represents the elastic recovery of the surface as the indenter is removed, the plane-strain modulus for the sample may also be calculated from a calculation of the contact area and a determination of the slope S of the unloading curve at the maximum load. The plane-strain modulus is converted to the indentation modulus value after multiplication by a factor of one minus the square of Poisson's ratio. The measured indentation plane-strain modulus is remarkably unaffected by elastic anisotropy, presumably owing to the three-dimensional nature of the stress distribution generated in the material. Generally the value obtained by indentation is close to the elastic modulus of a polycrystalline material with randomly oriented grains. The expected value for an elastically anisotropic material may be calculated as the Voigt-Reuss-Hill average of the anisotropic elastic constants.

It is an indicator of the continued rapid development of instrumentation in this field that typical indentation depths have followed a reduction similar to Moore's law. For example, in the 1990s, typical instrumented indentation depths were of the order of $1\text{ }\mu\text{m}$. Now indentations are regularly 100 nm or less and depths of the order of 10 nm are not uncommon. Interestingly, higher-force instruments are also now available, capable of applying forces up to 1500 N at least. Indeed at the National Physical Laboratory, many of the UK hardness scales are defined by an instrumented indenter that is programmed to simulate conventional hardness-testing cycles.

There are many parameters that affect the results of instrumented indentation experiments. The relative dominance of force and displacement uncertainties is material dependent. Hard materials require high forces and result in low indentation depths. This makes an accurate determination of the compliance of the test system essential; well-validated procedures have been established for this. Instrument compliance leads to an apparent additional displacement of the test material on top of the real displacement, resulting in the displaced loading (dashed) and unloading (thicker solid) curves in Fig. 2.6(b). For small-displacement experiments in particular, it is important that the instrument is in an environment with good temperature control and low levels of vibration. Another crucial input parameter to this test method is the shape of the indenter. For very small indentations the indenter tip shape is never a perfect pyramid. Typically the radius of a Berkovich indenter tip is $100\text{--}200\text{ nm}$ and sharper tips have a tendency to wear rapidly to a radius of this order. At very shallow indentation depths a Berkovich indenter is therefore really a spherical indenter. At larger depths, failure to take account of the truncation of the tip, can still result in very significant errors. Determination of the real tip shape has traditionally relied upon an iterative procedure for estimating the tip shape from a series of indentations into a material such as fused silica. Recent work has improved these methods by including multiple reference materials, but the preferred practice now is to measure the tip shape directly with a metrological atomic force microscope as this typically gives more than 2000 area measurements per micrometre of indentation depth.⁷ Figure 2.6(d) shows an atomic force microscopy (AFM) image of an indenter, and Fig. 2.6(c) shows a typical area versus indentation depth curve that has been derived from AFM data. The high data density permits the use of more suitable mathematical functions, such as a *B-spline* series, to define the variations in the tip geometry, e.g. as it changes from a spherical cap to a pyramid.

Care needs to be taken when measuring the hardness and modulus of coatings by instrumented indentation testing, as each indentation is a composite response of both the coating and the substrate. (Note that for modulus

measurement there is, in principle, no 'safe depth' at which a coating-only value may be obtained, since the coating and substrate are effectively responding as two springs in series.) However, procedures have now been developed⁸ that enable the 'coating-only' properties to be extracted effectively and reliably from a composite response and these procedures are contained in a fourth part of ISO 14577 that has recently been published as a draft international standard.⁹ These procedures include a normalisation procedure that allows measurements from coatings of different thicknesses made by different indenter geometries to be directly compared and plotted on the same graph. Indenter geometry differences are handled by using the real indenter area functions to calculate the ratio of effective indentation radius to coating thickness and so to define a dimensionless relative indentation size.

Figure 2.6(e) shows results for the plane-strain indentation modulus of gold on nickel for a number of different experiments. It can be seen that, as the ratio of indentation radius to coating thickness is reduced, the composite modulus response reduces. The intercept value of modulus represents the plane-strain modulus for the coating. A similar plot of hardness as a function of the ratio of indentation depth to coating thickness for three different thickness diamond-like carbon (DLC) coatings is shown in Fig. 2.6(f). For two of the coatings, there is a common plateau in the composite hardness response which represents the hardness of the DLC coating. In the case of the thinnest coating, there is a maximum in the hardness response, but this is much lower than that obtained for the two thicker coatings. This can be explained by considering the depth at which the maximum in the von Mises stress distribution under the indenter occurs. This depth is related only to the indentation size and the indenter tip radius. For equally sized indentations, this stress maximum moves deeper into the substrate if the coating thickness is reduced. Thus, for the thinnest coating, the substrate has begun to yield before the coating has reached its yield point.

This new method is clearly an improvement on the old rules of thumb for coating-only hardness measurement (e.g. buckles less than 10% rule) as it can take account of the fact that, for normal radii of indenter tips, indentation at shallow depths is essentially elastic and it is only when the mean indentation pressure reaches that required to create a fully developed plastic zone in the coating that a plateau hardness value is reached. The position and extent of such plateaux will depend on the ratio of coating to substrate yield strengths and the new procedure is able to adapt directly to that. In this example of DLC on hardened tool steel, the plateau is achieved between 8% and 15% of the coating thickness and indentations at much lower relative depths would in fact yield an incorrect coating hardness result.

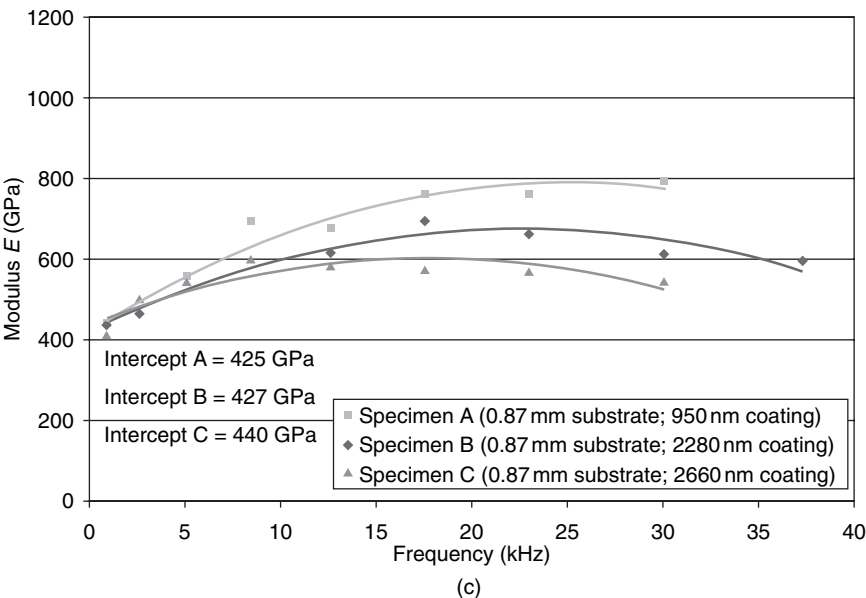
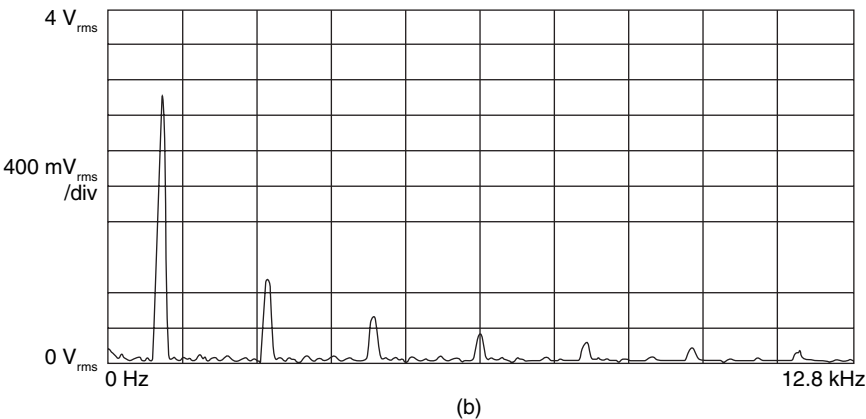
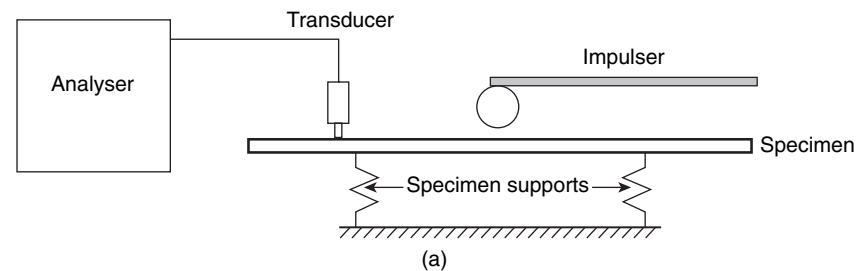
2.6 Impact excitation

As musicians and wheel tappers know, the resonant frequency of a material is related to its elastic properties, density and dimensions. Tapping carefully supported beam-shaped samples can therefore be used to measure the elastic properties of bulk materials and, by careful extension, of coatings.¹⁰ In this method, the sample is placed on supports spaced so that the points of contact are positioned at the nodes of resonance of the beam (Fig. 2.7(a)). The sample is then tapped, and an acoustic transducer and analyser used to measure the resonance spectrum of the vibrations of the sample (Fig. 2.7(b)). These resonant frequencies can be used to calculate the modulus of the sample. If the same sample is then coated and remeasured, the ratio of resonant frequency with the coating to that without the coating, combined with a careful thickness and added mass measurement for the coating, can be used to calculate the coating modulus. The calculation relies on the Euler–Bernoulli flat-plate theorems that assume an absence of shear mode vibrations. This is not the case for finite-thickness samples of finite extent and so a plot of modulus as a function of harmonic frequency is a curve rather than a flat line. However, when the curves are extrapolated back to the modulus axis, a consistent value of modulus is achieved for the coating. Figure 2.7(c) shows the results of this analysis where curves are generated for coatings of different thickness. It should be noted that the test method directly generates a value for Young’s modulus of the materials tested. Thus, if combined with measurements by instrumented indentation, which generates a plane-strain modulus, a value for Poisson’s ratio of the coating may be obtained.¹¹

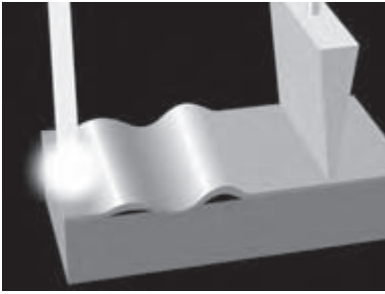
The impact excitation technique relies on careful measurement of the size of the sample, the thickness of the coating, and the elastic properties of the underlying substrate material. However, the technique is simple to carry out and indeed can be easily extended to elevated temperature measurement by the use of a furnace.

2.7 Surface acoustic wave spectroscopy

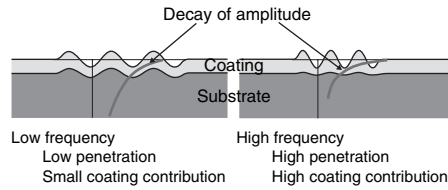
Surface acoustic wave spectroscopy is a relatively recent technique that can be used to measure several properties non-destructively, potentially with a high spatial resolution.¹² The principle is shown in Fig. 2.8. A very-short-duration high-intensity laser pulse is used to generate a broad spectrum of thermoelastic shock waves in the sample to be tested. A transducer is used to pick up the surface acoustic waves at a preset distance from the laser probe position. By accurately varying the distance between pulse and detector, the time of flight and so the velocity of the surface acoustic waves can be determined very accurately. A Fourier transform of the acoustic signal



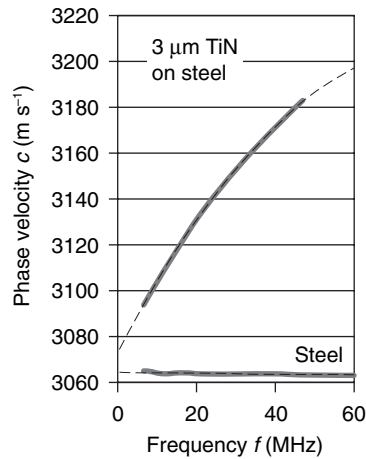
2.7 Impact excitation for the measurement of coating modulus:
(a) schematic test set-up; (b) resonance spectra for a typical impact excitation experiment; (c) typical results.



(a)



(b)



(c)

2.8 Laser surface acoustic wave measurements: (a) schematic diagram of the test; (b) effects of low- and high-frequency acoustic waves; (c) dispersion curves for 3 μm TiN on steel and uncoated steel.

is used to determine the dispersion of the velocities of the different frequencies of surface acoustic wave arriving at the detector. Low-frequency (long-wavelength) waves have a deeper penetration depth beneath the surface than high-frequency waves. The low-frequency waves therefore ‘sample’ more of the substrate than the high-frequency waves.

The effect of this is that, for a homogeneous monolithic material, all frequencies experience the same material properties, travel at the same velocity and result in a dispersion ‘curve’ that is flat (zero gradient). In contrast, a coated sample shows a marked dependence of wave velocity on frequency. Classical acoustic theory can exactly simulate the shape of the dispersion curve if supplied with the thickness, modulus and density of the coating and the properties of the substrate. Depending on the curvature of the dispersion

curve obtained, at least one of these parameters can generally be derived from a fit of the theory to the experiment, given an input of the others.

The measurements are very quick and simple to carry out and can yield high-quality data, particularly when combined with accurate input data or with test methods that can provide such input data. The dispersion curve measured is most sensitive to the density and thickness of the coating. It is less sensitive to the input value for the modulus of the coating and relatively insensitive to the value of Poisson's ratio used. The technique can therefore be readily combined with instrumented indentation and a thickness measurement to determine the density of a coating with an uncertainty of only a few per cent.¹³ Conversely, if the coating density may be assumed with confidence, the thickness of a coating can be measured, non-destructively, with a precision of the order of 1%, which is comparable with the performance of a good high-resolution scanning electron microscope.¹⁴

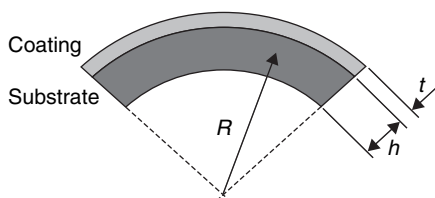
2.8 Residual stress measurement

Residual stresses in coatings can be measured most simply by means of a coupon-bending experiment (Fig. 2.9). An uncoated 'witness' coupon is placed alongside normal substrates in a processing run. After processing, the coupon is coated along with the normal components. The coupon is relatively thin so that, if any residual stress occurs in the coating, the coupon bends under the influence of the residual stress. This bending can be measured by simple microscopy when the residual stress is high, or very precisely by laser profilometry. The residual stress may be derived from simple relationships such as the Stoney¹⁵ formula

$$\sigma = \frac{Eh^2}{6Rt(1 - \nu)}$$

where σ is the residual stress, E is the modulus of the substrate, h is the substrate thickness, R is the measured radius of curvature, t is the coating thickness and ν is Poisson's ratio of the substrate.

This provides a cheap and cost-effective method for the measurement of residual stress, but the Stoney formula only applies for coating systems



2.9 Schematic diagram of the method for measurement of residual stress by coupon bending.

where the coating is very thin relative to the substrate thickness. When this is not true, a more complex analysis is necessary. Residual stresses can also be measured using the ' $\sin^2\phi$ ' X-ray diffraction method.

2.9 Conclusions

A wide variety of test methods now exists for the measurement of the mechanical properties of coatings. These test methods occupy a continuum between those that are highly performance based and application specific to those that are further removed from in-service performance but more readily analysed to generate fundamental materials property values. A particularly effective process for carrying out measurements is to combine a number of different test methods carefully to obtain information that could not in fact be measured by separate methods, and where the use of multiple methods gives a self-validating set of measurements.

Many test methods are, however, still quite complex to carry out, and care needs to be taken both with the selection of the best test for the job and also with the procedure that is used to carry out the measurement. There remains room to improve the current test procedures and to develop new test procedures that are more cost effective to carry out and can be used more easily by engineers, so providing a better compromise between simplicity and generation of materials property information.

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3.1 Introduction

Surface engineering involves the enhancement of certain properties of the surface of a component independently from those of its bulk. The enhancements required can be in areas as diverse as aesthetics, optical properties, wear and corrosion resistance. The processes by which a component can be surface engineered are no less wide ranging but may be divided into three basic groups.

1. The first group consists of processes which modify the existing surface in some way without a change in composition, such as shot peening, transformation hardening and surface remelting.
2. The second group consists of processes which modify the existing surface in some way, with a change in composition of the surface engineered layer being a critical feature of the process. Processes in this group may result in modification of the existing crystal structure by formation of a solid solution or by lattice disruption (processes such as ion implantation) or may result in changes to the transformation behaviour (processes such as carburising of steels which leads to a change in hardenability). However, they may also directly result in the formation of new phases, distinct from those of the substrate, by reaction between elements from the substrate and those introduced by the process. In some instances, the surface engineered layer is composed of these new phases in the form of precipitates within a matrix (such as the formation of aluminium or vanadium nitrides following nitriding of a suitable steel) whereas, in other cases, the new phases form a distinct layer. This reaction layer may well have all the properties that one would normally associate with a coating (a different phase with a distinct boundary between the layer itself and the substrate), but these processes are not commonly referred to as coating processes since the new surface phase is not directly applied

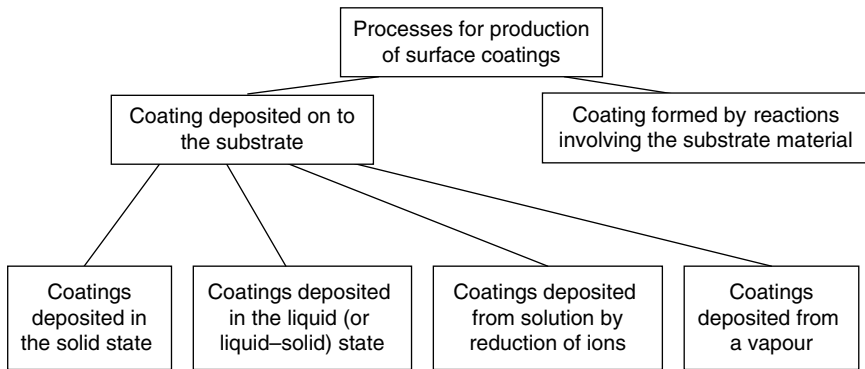
to the substrate. The boundary between the substrate and the reaction layer is normally more diffuse than would be observed in between a true coating and a substrate; moreover, the bond strength is normally higher. Anodising (where an alumina layer is formed on an aluminium-based substrate) and boronising (where layers of borides may be formed on iron-, titanium- or cobalt-based alloys) are examples of such processes.

3. The third group consists of processes which apply a new material to the surface, generally referred to as coating processes. Weld hardfacing, electroplating and chemical vapour deposition (CVD) are examples of processes in this group.

As this book seeks to address *surface coatings for protection against wear*, this chapter will concentrate on surface engineering processes from the third group where a coating is applied to a substrate. However, some of the processes in the second group (where layers of a phase distinct from the substrate, with a well-defined interface, are formed) will also be referred to. The scope of the chapter is further restricted to processes primarily employed to provide enhanced wear resistance of components. Furthermore, not all processes will be specifically addressed, but instead a framework under which coating processes can be classified and their basic processes understood will be presented. Finally the processes will be compared in terms of restrictions of their application associated with both material type and component geometry.

3.2 Basic classification of processes employed for coating

Coatings typical of different processes are distinct from each other in a host of ways, such as thickness, hardness, ductility and residual stress state. Whilst all these attributes are important and are indeed the types of parameter upon which coating selection is made, classification on the basis of these properties provides no generic understanding of the coating methods themselves. Understanding of the coating processes results from an examination of the mechanism by which the coating is built up. Figure 3.1 illustrates a scheme under which coating processes may be categorised. As indicated in the introduction, coatings which are deposited directly are distinguished from those which are the product of a reaction which involves atoms from the substrate. The processes which involve direct deposition of coatings are then further divided into four main groups depending upon the underlying mechanism of coating formation. The following sections examine these groupings in detail.



3.1 Processes for the production of surface coatings: basic classification of coating types.

3.3 Processes: coatings deposited on to the substrate

3.3.1 Coatings deposited in the solid state

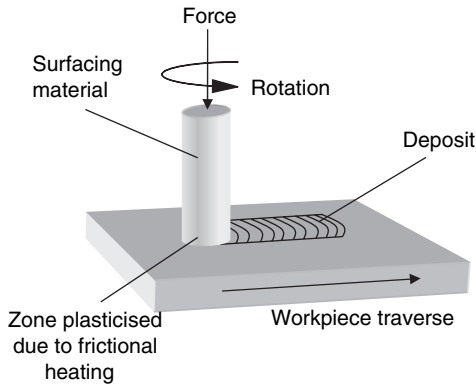
There are a number of processes where substrates are coated or clad with a material which remains in the solid state. These include the following.

1. Explosive welding where a substrate and cladding layer are brought together progressively at a collision front by the action of an explosive force and consequently form a strong bond.
2. Cold-gas dynamic spraying where particles are accelerated to very high velocities in a gas stream (with little or no external heating) and bond with a substrate upon impact.
3. Friction surfacing where a rod is rotated under pressure against a substrate and traversed across it, whereupon material from the rod is deposited as a coating.

All these processes depend upon the disruption of oxides on the surface of the coating and substrate materials and the formation of a metallic bond. Of these three related processes, only friction surfacing is currently widely employed for the deposition of wear-resistant coatings, where, for example, mild steel substrates have been surfaced with tool steel.

Friction surfacing

The process of friction surfacing is shown schematically in Fig. 3.2. Resulting coatings are relatively flat and are commonly deposited to a thickness



3.2 Schematic diagram of the friction-surfacing process.

between 0.5 and 3 mm depending upon operating parameters and materials. The coverage of the coating depends upon the relative movement of the substrate and depositing rod and can be controlled by traditional machine tool technology. Friction surfacing differs from the other two processes in that significant heating is observed. The rod reaches high temperatures whilst being deformed and is thus akin to a forging process. Friction surfacing has been employed to produce wear-resistant coatings in applications such as machine knives.

Cold-gas dynamic spraying

Cold-gas dynamic spraying (otherwise known as cold spraying or kinetic metallization) involves the deposition of coatings from a particulate feed-stock. Particles are accelerated to very high velocities (of the order of 600 m s^{-1} depending upon the powder type) in a supersonic gas stream which is created by the use of a de Laval (converging-diverging nozzle). The particles deform rapidly upon impact with the substrate and a coating can be built up. Helium or nitrogen are commonly employed as the driving gas for the process. Helium has a much higher speed of sound than nitrogen and is thus able to deliver higher particle velocities. However, helium is expensive. Gas heating (temperatures up to about 500°C are common) provides an increase in the speed of sound of either gas and thus allows higher impact velocities to be achieved. This technology is in its infancy and whilst it has been adopted in certain applications, to the author's present knowledge, it is not currently being applied to deposit wear-resistant coatings. However, the ability to coat lightweight materials such as aluminium or titanium with

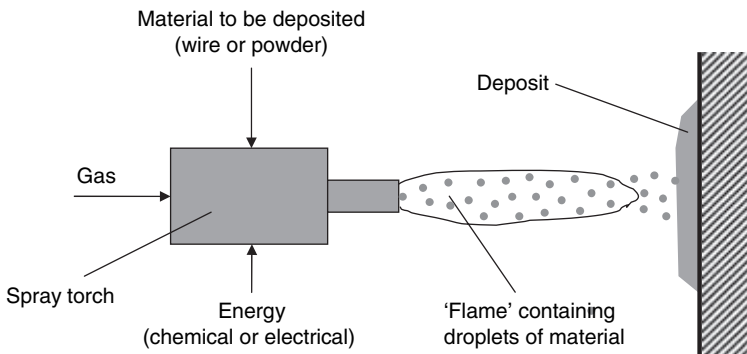
more wear-resistant surfaces for use in sectors such as transportation may be a major driver for the expansion of this technology.

3.3.2 Coatings deposited in the liquid state

Coatings are often applied in the liquid state (or a mixed liquid–solid state), whereupon the solid coating is formed either by solidification from the melt or by evaporation of a solvent or carrier (normally aqueous or organic). Solvent- or carrier-based systems are commonly employed for organic coatings but are also relevant to sol–gel coating which is currently being reported as a means to deposit wear-resistant coatings. However, most wear-resistant coatings in this category are applied in the molten or semimolten state.

Thermal spraying

The thermal spray process involves the heating of a source material (in the form of powder or wire) to form molten (or partially molten) droplets which are then accelerated towards a substrate and, upon impact, splat and solidify (Fig. 3.3). As such, thermal spraying is a line-of-sight process which places certain restrictions on its application. The thermal energy to melt the material is normally derived from combustion of a fuel or from an electrical discharge (arc or plasma). Thermal spraying can be employed to deposit coatings of metals, polymers, ceramics or any combination thereof. There are a wide variety of thermal spray methods available, each with its own unique characteristics. The most significant parameters in a thermal spray system are the thermal and velocity histories experienced by the particle, together with the atmosphere through which the material is sprayed. Other



3.3 Generic schematic diagram of the thermal spraying process.

things being equal, a low particle velocity will lead to a long residence time in the heat source and thus to high particle temperatures. If spraying is being conducted in air, this will also often lead to high oxide levels in the coating. Low particle velocities also tend to lead to the formation of a more porous coating. Thermal spray processes which employ a powder feedstock with a wide particle size distribution are difficult to optimize (as the thermal and velocity histories of a particle depend upon its size) but powders with tight size distributions are expensive and so a compromise must be made.

In thermal spraying, the torch or gun is usually rastered over the component to form a coherent coating. The thickness of coatings deposited by thermal spraying is normally limited by the development of thermal stresses in the coating; as the coating thickness increases, the strain energy which would be released upon debonding of the coating from the substrate increases to a point where debonding occurs spontaneously. As such, thermally sprayed coatings are normally between 100 and 500 μm thick. Bonding to the substrate is not thought to be of a substantially metallurgical character (substrate melting is not observed in thermal spraying). Instead, the surfaces of components are grit blasted before thermal spraying to provide a mechanical key to facilitate bonding. A disadvantage of grit blasting is the retention of blast grit at the interface which may act as a source of fatigue failure.

High-velocity oxy-fuel spraying now has the largest share of the thermal spraying market. In these systems, fuel (commonly hydrogen, propylene or kerosene) is burnt in an internal combustion chamber; the hot flame exits the chamber through a nozzle at high pressure and expands supersonically. Subtleties in the design of such a system have meant that a wide variety of systems are available commercially. Differences centre around the fuel type (gaseous or liquid fuel, with the former generally resulting in a lower-velocity flame), nozzle design (e.g. the use of a de Laval nozzle) and the position of powder injection into the flame (injection into the combustion chamber where the gases have low velocity results in high heat transfer to the particles whereas injection into the nozzle where the gas velocities are higher results in less heat transfer).

Weld hardfacing

Coating material can be applied to a surface by a process akin to welding, known as weld hardfacing. The coating can be formed on the surface of a component by any normal fusion welding method (such as manual metal arc and plasma-transferred arc). Weld hardfacing is often employed where significant wear can be tolerated before further refurbishment of the surface. Depending upon the welding method employed, the coating material is fed into the fusion zone either as a consumable electrode or as a filler rod. In

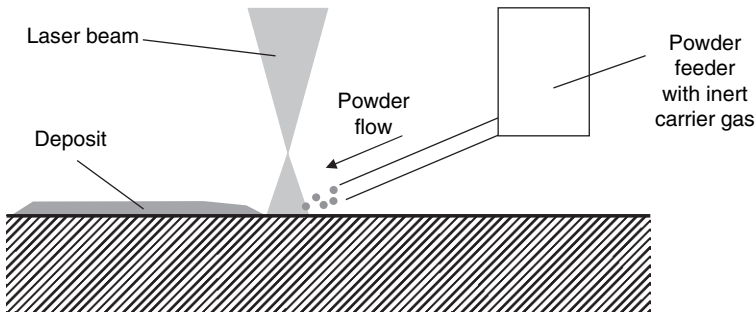
hardfacing processes, the surface of the substrate to be coated is also melted and thus a strong metallurgical bond is formed between the coating and substrate. Weld hardfacing allows the deposition of a coating from 1 to 50 mm thick, generally of metallic materials (such as manganese steels, iron–chromium alloys or tool steels) or cermets; ceramics and polymers are unsuitable for deposition by this process.

Weld hardfacing is often employed to deposit materials to resist abrasive wear; e.g. it is commonly used for refurbishment of earth- and rock-engaging equipment (such as mechanical digger teeth and plough shares) where it has the advantage that processing can be achieved on site using portable welding equipment. In contrast, weld hardfacing of components requiring higher precision is often performed with automatic welding procedures before being machined or ground to a final finish.

As in all welding processes, there exists a dilution zone between the deposited material and the substrate. The high levels of dilution result from the stirring of the weld pool by the electromagnetic, Marangoni and convective forces. Such dilution can affect the properties of the deposited layer. The degree of dilution of the deposit varies with the welding method employed but can be as high as 30%. As in a conventional welding process, the substrate will exhibit a heat-affected zone, and thus care needs to be exercised where thermally activated changes in the substrate properties may occur (such as the formation of martensite in steels with high hardenability or the uncontrolled ageing of tool or age-hardenable steels). As a result of thermal stresses (due to thermal gradients and different coefficients of thermal expansion) and the low ductility of some deposits, deposit cracking can also be a problem in some situations. Problems with the heat-affected zone in the substrate and cracking in the deposit can be ameliorated to some extent by component pre-heating and controlled cooling, but these can affect the formation of the hard wear-resistant martensitic structure required in some hardfacing alloys.

Laser cladding

The problems associated with dilution of the coating in weld hardfacing lead to the development of laser cladding. In this method, a powder from which the coating is to be formed is melted by a laser. Traditionally, CO₂, neodymium-doped yttrium aluminium garnet (Nd: YAG) and excimer lasers have been employed although more recently high-powered diode lasers have been used. Owing to the rapid rate of heat input, the time over which the stirring processes operate is restricted and thus the dilution itself can be restricted to very low levels. Powders can be placed directly on the surface to be clad (normally with a binder) and the laser scanned over this, or powder can be blown into the region to be clad with an inert carrier gas



3.4 Schematic diagram of the blown-powder laser-cladding process.

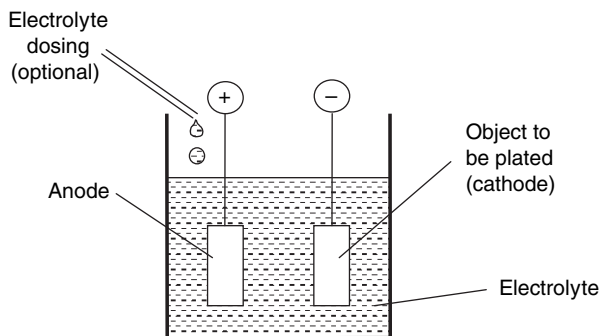
(Fig. 3.4). Laser-clad coatings are typically between 0.5 and 3 mm in thickness and exhibit the high bond strengths associated with fusion bonding with the substrate. In addition to their use in cladding, lasers are commonly employed for remelting of coatings deposited by other techniques such as thermal spraying.

3.3.3 Coatings deposited from solution by reduction of ions

Coatings can be deposited by the reduction of metallic (or complex) ions, normally in an aqueous solution, to form metal atoms. If this reaction can be promoted at a surface, the metal atoms build up to form a coating. The reduction of ions is achieved by two main methods.

Electrodeposition

Coatings of many metals (both single metals and alloy systems) can be formed by electrodeposition. The surface of interest, which must be electrically conductive, is made the cathode (negatively charged) in a low-voltage electrochemical cell and, as current is passed, a coating can be built up (Fig. 3.5). Coating thicknesses achievable are dependent upon the material being plated, but typically range from 5 to 250 μm (although, in some materials, much higher thicknesses can be achieved). Substrates are thoroughly cleaned and may be etched before the deposition process begins. In alloy systems, the rate of deposition of the relevant cations is controlled by the proportions of the cations in the bath and by the use of complexants, which normally serve to restrict the rate at which one of the species deposits. In plating of some single-metal coatings, the anode is made of the material which is being plated to maintain the bath chemistry. However, this is not



3.5 Schematic diagram of an electroplating bath.

always the case; lead is normally used as the anode in chromium plating and inert anodes are commonly used in alloy plating systems. In these cases, bath chemistry is maintained by dosing of the bath.

The deposition of metallic ions from solution is always in competition with reduction of hydrogen ions (from the water) to hydrogen. If the potential at which the metal is deposited is significantly more negative than that for the reduction of hydrogen at the surface, then metal deposition and hydrogen evolution will occur simultaneously. In some systems, hydrogen evolution can be very significant; e.g. an efficiency of just 20% is commonly observed in the plating of chromium.

One of the concerns during electroplating is the throwing power of the bath (throwing power is the ability to produce a uniform coating on a component with complex geometry). Although various agents can be added to the bath to improve the throwing power, the problem of non-uniformity in coating thickness remains.

Electroless deposition

In electroless deposition, the bath contains not only the cations of interest but also an agent to reduce the cations to form the metal. The reaction between the reducing agent and the cations is not spontaneous and a surface is required to catalyse the reaction. The component to be plated (or the already-plated material) acts as the catalytic surface and thus the coating is initiated and grows. Since the local rate of deposition is controlled simply by the chemistry of the bath and the surface, then production of a uniform coating is relatively straightforward. Coating thicknesses achievable are dependent upon the material being plated, but typically range from 5 to 50 μm .

Features common to electrodeposited and electroless deposited coatings

In both types of ion reduction process, coatings are normally deposited from solutions at no more than 90 °C and such low temperatures rarely have any effect on the substrate. The main concern in plating of high-strength steel components (tensile strength greater than 1000 MPa) is the absorption of atomic hydrogen into the substrate and the resulting hydrogen embrittlement. High-strength steels are heat treated at 190–230 °C following plating (the time of treatment depending upon the strength of the steel) to minimise risk of damage by hydrogen embrittlement.

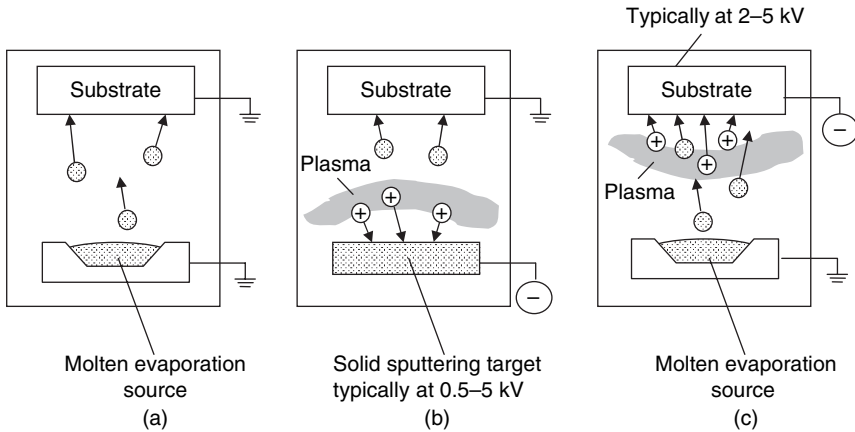
In both process types, second phases (including hard phases such as diamond and silicon carbide as well as solid lubricant phases such as polytetrafluoroethylene) can be incorporated into the deposits simply by suspending solids (normally 1–5 µm in size) in the bath. The agitation of the bath needs to be carefully controlled to give a uniform distribution of the second phase in the coating. In electroless coatings, up to 50% by volume of particles can be incorporated into a coating, but more commonly the volume fractions employed are between 15 and 30%.

3.3.4 Coatings deposited from a vapour

Physical vapour deposition

There are a number of processes which come under the heading of physical vapour deposition (PVD). In all these processes, species are produced in the vapour phase, from which a coating, typically between 1 and 20 µm in thickness, is formed on a substrate. The vapour consists of atoms or ions of a target material (generally solid or liquid) which have been removed from the target by either evaporation or sputtering (collisions with other atoms).

Films may be deposited by condensation of a vapour (Fig. 3.6(a)). Techniques for evaporation of a source material include resistive heating (commonly used for evaporation temperatures below about 1800 °C) and the use of high-energy electron beams (commonly used for evaporation temperatures above about 1800 °C). Films of compounds can be formed by reactive evaporation either where the elemental constituents of the film are separately evaporated and deposit together or where the deposited material reacts with a gas present in the surrounding atmosphere. Most reactive evaporation is of the latter type, an example being the evaporation of titanium in a nitrogen-containing atmosphere to generate films of titanium nitride. It is common to activate the gaseous species (by use of a plasma or some other means) to increase its reactivity and to allow deposition of films at lower gas pressures. It is relatively straightforward to produce a graded structure in such a system; for instance, in forming a titanium nitride film,



3.6 Schematic diagram of generic PVD processes: (a) evaporation; (b) sputtering; (c) ion plating.

the availability of nitrogen can be restricted at the beginning of the process to form a titanium interlayer with the substrate. Evaporated films tend to have relatively poor adhesion to the substrate since the velocity of the depositing atoms results only from their thermal energy (of the order of 0.2–0.3 eV).

In a sputtering process, the target material (the material from which the film is to be made) is made the cathode in an argon glow discharge (plasma) (Fig. 3.6(b)). Argon atoms are ionised in the plasma and accelerated towards the target, arriving with energies in the range 100–1000 eV; collision with the target may result in ejection of a target atom with high energy, known as sputtering. Plasmas are commonly formed from radio-frequency sources; the deposition rate can be significantly increased by the use of magnetron sputtering where magnetic fields are employed to confine the plasma to the near-target region. Again, the sputtering process can be combined with a reactive gas to allow reactive sputtering of compound films. The kinetic energy of sputtered atoms (of the order of 10–40 eV) is much higher than that of evaporated atoms and thus higher adhesion strength between the film and the substrate results. A simple sputtering process will result in a deposition rate of 0.5–5 $\mu\text{m h}^{-1}$ but this can be increased to over 100 $\mu\text{m h}^{-1}$ by the use of magnetrons. Sputtered films are commonly used as wear-resistant coatings in applications such as cooking knives and metal-cutting tools.

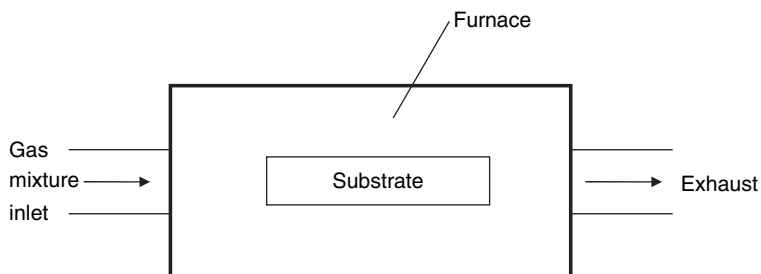
Ion plating is the third distinct group of PVD processes. In this process, the workpiece potential is dropped to between –2 and –5 kV, allowing it to

become the cathode in a low-pressure argon glow discharge formed between it and the earthed components of the system (Fig. 3.6(c)). As such, the workpiece is bombarded by the argon ions. Coating material is evaporated into the glow discharge (by resistance or electron beam heating or by multi-arc evaporation) and is deposited on to the workpiece. Adhesion of the coating is improved by the continual bombardment by argon ions, which results in enhanced diffusion and impingement mixing. Similarly to the other PVD processes, compound films can be formed by partial or total replacement of the argon with a gas capable of reacting with the evaporant in the desired way.

Chemical vapour deposition

CVD is the deposition of a solid coating on a heated surface resulting from chemical reactions at the surface involving the surrounding vapour or gas phase (Fig. 3.7). Typical CVD reactions include thermal decomposition, carburisation and nitridation and these processes normally operate at temperatures in excess of 850 °C. Whilst cemented carbides (commonly coated by CVD for cutting tools) are not significantly affected by the processing temperature, steels require additional heat treatment following coating to optimise their properties. Significant differences between the thermal expansion coefficients of the coatings and substrates result in high stresses on cooling to room temperature; consequently, coating thicknesses are normally limited to around 15 µm. CVD processes can result in high deposition rates (around 1–40 µm h⁻¹), dependent for each process upon the temperature and pressure of operation. Many of the reactants (or precursors) and by-products are extremely hazardous which necessitates use of a closed-loop system and careful disposal.

CVD is now commonly combined with a radio-frequency glow discharge plasma (commonly known as either plasma-assisted or plasma-enhanced



3.7 Schematic diagram of the process of CVD.

chemical vapour deposition) which allows the process to be operated at temperatures typically 400–600 °C lower than their non-assisted counterparts. The use of plasma methods also provides the advantage of being able to sputter clean the component surface prior to film deposition, resulting in significantly improved bonding.

Hard coatings, such as nitrides, carbides, borides and oxides, as well as structures such as diamond and diamond-like carbon can all be deposited by CVD methods and are commonly employed for wear resistance in a variety of industries, from paper processing to metal forming. Major advances in cutting tool technology have been made by the use of CVD coatings; for instance, coatings of TiC are employed on WC-based hard metals and TiN and Ti(C, N) coatings are widely employed on high-speed steel tools. Coatings are commonly made up of multiple layers where a number of properties need to be enhanced or to provide improvements in adhesion to the substrate.

3.4 Processes: coatings formed by reactions involving the substrate

3.4.1 Anodising

Anodising refers to the formation of an oxide layer by a process where the component to be coated forms the anode in an electrochemical cell. The coating is formed by reaction between the substrate and the electrolyte. Anodising is commonly applied to certain alloys based upon aluminium, titanium, magnesium and zinc. An anodised layer can provide a number of benefits (such as increased paint adhesion, corrosion resistance or wear resistance).

Aluminium alloys are attractive materials for use in reciprocating machinery owing to their high strength-to-weight ratio. However, aluminium alloys have poor wear resistance and tend to gall. To provide wear resistance, an anodised coating layer between 25 and 150 µm can be formed and is distinguished from other anodised coatings by being referred to as ‘hard anodised’. A hard-anodised surface on an aluminium alloy would normally have a Vickers hardness in the range 350–650 kgf mm⁻². The hard-anodising bath employs an aqueous sulphuric acid electrolyte (10–20 wt% acid) at temperatures normally between 0 and 10 °C and current densities between 2 and 4 A dm⁻². These conditions tend to minimise the dissolution of the alumina in the acid solution and result in a less porous structure than results from conventional anodising. A hard-anodised surface tends to be rough and is usually ground or lapped to the finish required by the application.

Titanium alloys are also useful structural materials because of their low density but, in situations where motion between mating surfaces occurs,

galling again may result. To alleviate this problem to some extent, titanium can be anodised in either caustic electrolyte or dilute acids (based on phosphoric acid). The anodised layers are of the order of only micrometres thick and, as such, only benefit components subject to moderate mechanical stresses.

3.4.2 Plasma electrolytic deposition

Plasma electrolytic deposition involves the formation of arc plasma discharges in an aqueous solution, which ionise gaseous media from the solution and promote reaction with the substrate material. Whilst plasma electrolysis has been employed to nitride or carburise steels, plasma-enhanced oxidation has been employed to form coating layers on materials such as alloys of aluminium, titanium and magnesium. Whilst the technology itself is not new, it has only recently been developed into a commercial process for the production of wear-resistant surfaces. The process is commonly operated with an alkaline bath at potentials above the breakdown voltage of the oxide film that is growing (typically in the region of 120–350 V), and growth continues through plasma thermochemical interactions. As is the case with an anodised surface, the formation of the coating depends upon reactions involving the substrate material and, as such, bond strengths tend to be relatively high. The nature of the coating depends upon the alloying elements within the substrate; for instance, when treating aluminium alloys, it is more tolerant of elements such as copper and silicon than the anodising process. In aluminium alloys, dense wear-resistant layers (up to 0.5 mm thick) have been reported with hardnesses of greater than 2000 kgf mm⁻². To modify or enhance the properties of the coatings further, fine particles of materials such as hard carbides or dry lubricants can be introduced into the electrolytes, which are then integrated into the coating.

Since this is a relatively new technology, the best sources of information are still in the form of journal publications. A review in this area by Yerokhin *et al.* (1999) is recommended for further information.

3.4.3 Phosphating

Phosphating (or phosphate coating) describes a process whereby an insoluble adherent phosphate coating is formed on a surface (normally of iron, steel, galvanised steel or aluminium) by a reaction between an aqueous solution of phosphoric acid (together with a heavy-metal primary phosphate) and the surface itself. Phosphate coatings are commonly employed to provide wear resistance in situations where sliding motion is present. They are normally used in conjunction with oils or greases but can provide some level of lubrication in their own right.

Heavy manganese phosphate coatings can be used to prevent galling. The workpiece surface is seeded with manganese phosphate by dipping into an agitated aqueous suspension of fine crystals of the same; the component is then transferred to the phosphating bath where the seed crystals act as nuclei for the formation of a fine compact coating. Such a phosphating treatment would be operated typically between 95 and 100 °C for a period of between 10 and 15 min and would result in a coating thickness of between 4 and 8 µm.

3.4.4 Boronising

Boronising, also known as boriding, is a thermochemical treatment involving diffusion of boron into the surface of a component from the surrounding environment which results in the formation of a distinct compound layer of a metal boride. Since it is dependent upon the reaction between the boron and the component, its application is generally limited to steels, titanium-based alloys and cobalt-based hard metals. In steels, boronising is carried out in the austenite regime (normally in the region 800–1000 °C) for several hours, resulting in the formation of layers commonly between 50 and 150 µm thick. The surface reaction layer thus formed consists of two separate phases, namely a layer of Fe₂B adjacent to the substrate and an outer layer of FeB. The proportions of the two phases are dependent upon the composition of the boronising environment and the alloy content of the steel (higher alloy content favours FeB formation). Care is taken to reduce the proportion of FeB in the boride layer since this always exists in tension; as such, high-alloy and stainless steels are unsuitable for boronising. The hardness of the boronised layer is dependent upon the exact composition of the steel but is commonly in the range 1600–1900 kgf mm⁻² (as measured on the Vickers scale). This is significantly higher than many commonly occurring abrasives and, as such, boronising has been employed in situations requiring abrasive wear resistance.

A variety of methods are employed to produce the boron-rich environment for the boronising process such as pack boronising, paste boronising, salt bath boronising and gas boronising. In pack boronising (the most commonly employed method), the source of boron is B₄C which is mixed with an activator and an inert diluent to make up the pack powder.

3.4.5 Nitrocarburising

Nitrocarburising is a relatively low-cost surface treatment commonly employed to low-carbon and low-alloy steels to confer antiscuffing properties. It is another thermochemical treatment which results in the formation of a compound layer on the surface of the component. The process involves

the diffusion of nitrogen and carbon from the surrounding environment into the surface of the steel in the ferrite regime (the process is usually operated around 570°C), whereupon a layer of ϵ -iron carbonitride approximately 20 μm thick is formed. Nitrocarburising can be carried out in a molten salt bath (traditionally using cyanide-based treatments although other less environmentally hazardous alternatives have been developed) or in a gaseous atmosphere, normally consisting of a hydrocarbon and ammonia. The iron carbonitride layer usually exhibits microporosity which can be exploited by introduction of an organic sealant or a lubricant to further enhance the properties of the component.

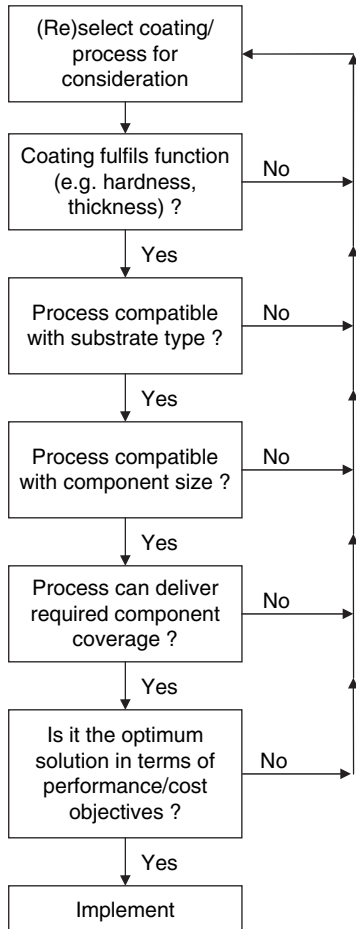
3.5 Comparison of the methods

Selection of a coating process is a complex procedure and is based primarily upon the capability required of the component and economic constraints. Modern design processes consider surface engineering at the outset and thus the technical and economic feasibility of coating methods, together with the compatibility of the process with the substrate, can be adequately weighed. However, coating of a component is still often employed as a means of improving its properties in a situation where it has already been found to fail at a rate that is unacceptable.

When selecting a coating, its function is the primary concern. Its function may depend upon true material properties (such as hardness and fracture toughness) together with properties specifically related to the coating (such as thickness, surface roughness, residual stress state and bond strength). Assuming that the required properties can be realised in a given coating (such features are not specifically considered in detail in this chapter), the selection of process then turns to technical feasibility and economic profitability. In light of this, there are number of features associated with the process and the process–workpiece compatibility which need to be considered. This section seeks to outline the areas which must be considered when selecting a process and to highlight differences between processes in these areas. Figure 3.8 illustrates diagrammatically the areas under consideration in this section.

3.5.1 Process–substrate compatibility

For many processes, there are restrictions on substrate type. For processes where the coating is formed by a reaction between an applied species and the substrate, there are obvious limitations associated with the reaction itself. For example, boronising can only be used with a limited range of material types where hard boride layers form (such as iron-based substrates). Some of the process restrictions are somewhat less obvious. For example, in the case of hard anodising of aluminium alloys, there are a



3.8 Decision flow chart addressing coating selection with respect to component-coating compatibility.

number of factors associated with the substrate which must be taken into account.

1. Hard anodising is difficult on aluminium alloys that contain more than 5% copper or 7% silicon.
2. For heat-treatable aluminium alloys, significant differences exist in the requirements for anodising conditions depending upon the prior heat treatment.
3. Attachments or inserts of metals other than the base aluminium alloy must be masked off (both electrically and chemically) prior to anodising to prevent excessive pitting (commonly referred to as burning) and corrosion.

Other restrictions imposed by the substrate type in the choice of process are associated, firstly, with the successful operation of the process depending upon certain features of the substrate or, secondly, with unacceptable changes in the substrate as a result on the coating process. For example, electroplating processes require a substrate which is electrically conducting; to electroplate a non-conductor, a conductive coating is normally applied by an electroless method (although not all surfaces are amenable to electroless plating) which then allows electroplating to proceed. Also, the temperature at which many processes are conducted may cause changes in the substrate. For example, standard CVD processes are operated at temperatures in excess of 850°C and, as such, will modify the properties of many steel substrates, including tool steels, because of phase transformation or precipitation which could lead to dimensional changes (loss of tolerance) or property changes (especially hardness).

3.5.2 Process–component size compatibility

Certain components are difficult to coat with a given process owing to constraints associated with size. It must be stressed that these are normally difficulties and not inherent restrictions and can thus often be overcome technically if a financial case can be made. Both very large and very small components can be difficult to coat depending upon the process type. The sizes quoted below are included simply to give an indication of the range in question; specialist coaters are already working well outside these ranges and new techniques will allow the ranges to be pushed even further.

Very large components are easiest to coat by processes that do not require the component to be sealed in a chamber or immersed in a bath. As such, thermal spraying or weld hardfacing can be utilised readily on large structures without disassembly and are often used in these contexts for repair in industries such as those involving mineral handling where wear is unavoidable. Components up to around 3m in their largest dimension are regularly coated by processes where they are required to be either immersed in a bath (such as electroplating or electroless plating) or placed in a vacuum chamber (such as PVD or CVD).

Small components are difficult to coat simply because they need to be held in some way during the coating process. Small parts being coated by a CVD process may be placed loosely on trays whereas parts being coated by thermal spraying are normally clamped individually; the two methods will involve very different times (and thus costs) for set-up of the processing. Components down to around 5–10mm are readily coated by processes such as thermal spraying, PVD and CVD processes and electroplating.

3.5.3 Coverage

Components often have complex geometries; the area where a surface coating is required may exist in a recess or in an internal bore and process selection may be restricted by such requirements. Processes with the severest restrictions are referred to as 'line of sight' and the coating can only be formed efficiently on surfaces which can be directly exposed to the source of material. Thermal spraying and PVD processes fall into this group. Electrolytic processes (such as anodising and electroplating) can provide better coverage (with suitable agitation of the electrolyte) but tend to form thicker coatings on surfaces facing the counter-electrode and on external corners and edges. Deep internal bores can be coated by use of a wire counter-electrode positioned centrally within the bore. Processes where the coating is formed at the surface by chemical reactions involving the species in the environment (such as CVD or electroless plating) produce the most uniform coverage provided that the environment is not depleted in reacting species by poor flow or stagnation (this may occur in very narrow features or blind holes).

3.6 Future trends

At any one time, there are a large number of new coating technologies which are being researched, developed or even marketed commercially. Many of these technologies are variants or developments of processes that are well established, whilst others involve deposition of a coating by a truly novel technique. It is, however, difficult to predict which of these technologies will command a significant market in the future, since this depends amongst other things upon economic factors, industrial need and process robustness.

The main drivers for development of new processes are those of enhanced functionality and/or cost reduction. In many sectors, it is cost reduction and not enhanced properties that drives the development of new technologies. Such development usually proceeds alongside (and in competition with) development of existing technologies and materials. Processes that appear in the marketplace often have a long history of development and experimentation. For instance, plasma-enhanced oxidation is currently arousing much interest with a significant number of commercial operations able to offer the technology; however, this technology was being researched and developed as far back as the 1970s.

Apart from the normal market forces which drive technological development stand costs and concerns regarding the environmental impact associated with a number of existing processes. Whether such concerns will

prompt development of replacement materials produced by existing processes or development of a new process is difficult to predict. In a similar way, there is currently much interest in the area of nanostructured coatings. However, it is not clear whether the development and utilisation of such coatings will require development of entirely new deposition techniques or whether it can be realised with what might be termed traditional technologies such as electroplating.

It has been realised that a combination of a number of established surface engineering methods can deliver a working solution not achievable by one method alone; this is often termed 'duplex treatment'. Such duplex treatments may offer significant extensions to existing capability and are to be expected to grow in importance.

An excellent chapter by Rickerby and Matthews (1991) entitled 'Market perspective and future trends' was published more than 10 years ago as part of an edited volume *Advanced Surface Coatings: A Handbook of Surface Engineering*. In this chapter, a number of techniques were highlighted as having significant potential for growth or maintenance of market share; as expected, some of these predictions appear to be more accurate than others. However, Rickerby and Matthews suggested that much development of coating processes was based upon optimisation for a specific application which frustrated design strategies that incorporated options of surface engineering solutions. Moreover, they argued that process developments (including process monitoring and control) and process understanding will lead to expert systems for coating design and selection. In these areas, progress is still very much required and must continue in all sectors of the surface engineering industry, leading to wider application of appropriate technologies.

3.7 References

- Rickerby, D.S. and Matthews, A. (1991), 'Market perspective and future trends', in *Advanced Surface Coatings: A Handbook of Surface Engineering* (Eds D.S. Rickerby and A. Matthews), Blackie, Glasgow, pp. 343–364.
- Yerokhin, A.L., Nie, X., Leyland, A., Matthews, A. and Dowey, S.J. (1999), 'Plasma electrolysis for surface engineering', *Surf. Coat. Technol.*, **122**, 73–93.

3.8 Further reading

3.8.1 Handbooks and books

There are a number of books which address the subject of coating processes. A selection of the most useful are listed below in chronological order.

- Department of Trade and Industry, (1986), *Wear Resistant Surface in Engineering: A Guide to their Production, Properties and Selection*, HMSO, London.
- Rickerby, D.S. and Matthews, A. (Eds.) (1991), *Advanced Surface Coatings: A Handbook of Surface Engineering*, Blackie, Glasgow.
- Hutchings, I.M. (1992), *Tribology: Friction and Wear of Engineering Materials*, Edward Arnold, London.
- ASM Handbook (1994), Vol. 5, *Surface Engineering*, ASM International, Materials Park, Ohio.
- Stevens, K. (1997), *Surface Engineering to Combat Wear and Corrosion*, Institute of Materials, London.
- Burakowski, T. and Wierzchoń, T. (1999), *Surface Engineering of Metals: Principles, Equipment, Technologies*, CRC Press, Boca Raton, Florida.
- HEF Groupe (coordinated by M. Cartier) (2003), *Handbook of Surface Treatments and Coatings*, Professional Engineering Publishing, London.

3.8.2 Scientific journals

In addition to these sources of reference, scientific journals contain many articles relating to developments in coating processes for wear resistance. A number of search engines are available on the internet to enable papers addressing specific topic areas within the scientific literature to be identified. However, amongst others, the following journals, which are in alphabetical order, are of general relevance.

Journal of Thermal Spray Technology
Surface and Coatings Technology
Surface Engineering
Thin Solid Films
Tribology International
Wear

3.8.3 Individual papers of interest

Also, a list of papers from the scientific press which provide a broad overview of the technology in question are presented below, in alphabetical order.

- Bell, T., Dong, H. and Sun, Y. (1998), 'Realising the potential of duplex surface engineering', *Tribol. Int.*, **31**, 127–137.
- Celis, J.P., Drees, D., Huq, M.Z., Wu, P.Q. and De Bonte, M. (1999), 'Hybrid processes – a versatile technique to match process requirements and coating needs', *Surf. Coat. Technol.*, **113**, 165–181.
- Fauchais, P., Vardelle, A. and Dussoubs, B. (2001), 'Quo vadis thermal spraying?', *J. Thermal Spray Technol.*, **10**, 44–66.
- Kelly, P.J. and Arnell, R.D. (2000), 'Magnetron sputtering: a review of recent developments and applications', *Vacuum*, **56**, 159–172.

- Kerr, C., Barker, D., Walsh, F. and Archer, J. (2000), 'The electrodeposition of composite coatings based on metal matrix-included particle deposits'. *Trans. Inst. Metal Finishing*, **78**, 171–178.
- Nicholas, E.D. and Thomas, W.M. (1998), 'A review of friction processes for aerospace applications', *Int. J. Mater. Product Technol.*, **13**, 45–55.
- Pawlowski, L. (1999), 'Thick laser coatings: a review', *J. Thermal Spray Technol.*, **8**, 279–295.
- Yerokhin, A.L., Nie, X., Leyland, A., Matthews, A. and Dowey, S.J. (1999), 'Plasma electrolysis for surface engineering', *Surf. Coat. Technol.*, **122**, 73–93.

Chemical vapour deposition methods for protection against wear

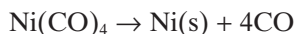
D.W. WHEELER

Atomic Weapons Establishment, UK

4.1 Introduction

Chemical vapour deposition (CVD) is a process by which volatile molecular species are transported in the vapour phase to a heated substrate where adsorption and/or reaction occur to deposit a solid film. It can be used to deposit a wide range of metals and compounds from submicrometre films to monolithic components several millimetres in thickness.

The earliest developments in vapour deposition technology occurred in the late nineteenth century; among the first recorded applications are the production of carbon filaments in the incandescent lamp industry (Sawyer and Mann, 1880) and the purification of nickel through the Mond process (Mond *et al.*, 1890). In the latter, nickel ore is reacted with CO at 50 °C and vaporised. The nickel tetracarbonyl is then transported to a deposition zone where decomposition occurs at 180 °C to give pure nickel. The reaction is



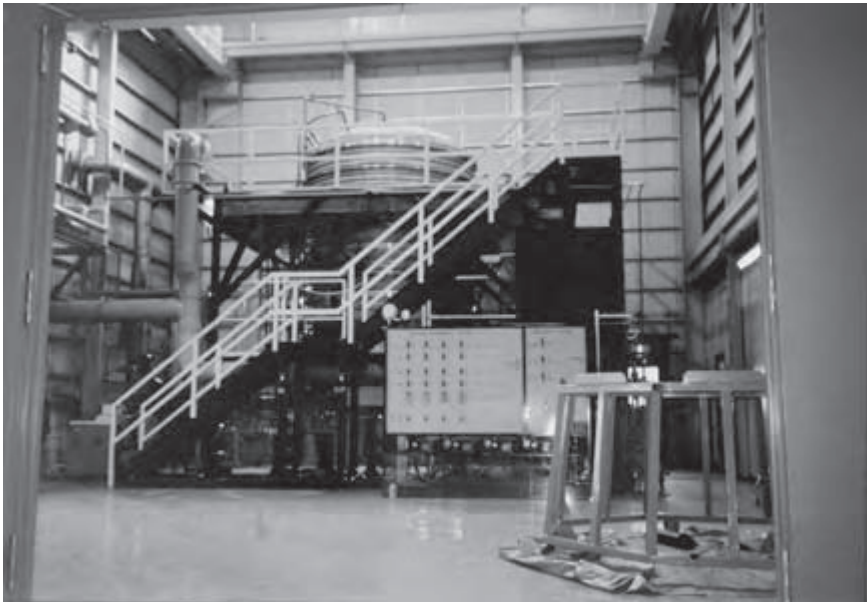
Although development continued on CVD during the early 1900s, chiefly on the production of refractory metals such as tungsten, it was not until the second half of the twentieth century that the process began to be more widely used. Starting with the semiconductor industry and continuing with applications such as machine tools, research on CVD coatings has undergone rapid expansion over the last 30 years. It is now used in many industries for mechanical and optical, as well as microelectronic, applications. It is now possible to deposit a large number of hard coatings by CVD including diamond, diamond-like carbon (DLC), boron carbide (B_{13}C_2), boron phosphide (BP), titanium carbide (TiC), titanium nitride (TiN), titanium carbonitride (TiCN), titanium diboride (TiB_2), silicon carbide (SiC), silicon nitride (Si_3N_4), alumina (Al_2O_3), tungsten carbide (WC), chromium carbide (Cr_7C_3), hafnium nitride (HfN), hafnium carbide (HfC), vanadium carbide (VC) and zirconium carbide (ZrC). Many of these coatings are now commercially available while others are still at the developmental stage. In

addition to coatings, CVD can also be used to produce free-standing components more than 10mm in thickness. One such example is ZnS, an infrared material that is valued for its optical properties and is used in infrared windows and domes in missiles. ZnS domes are grown on a mandrel, from which they are then separated (Goela and Askinazi, 1999). Later in this chapter, some of the CVD coatings that have reached the stage of commercial exploitation will be described. However, it is first necessary to examine the details of the CVD process itself.

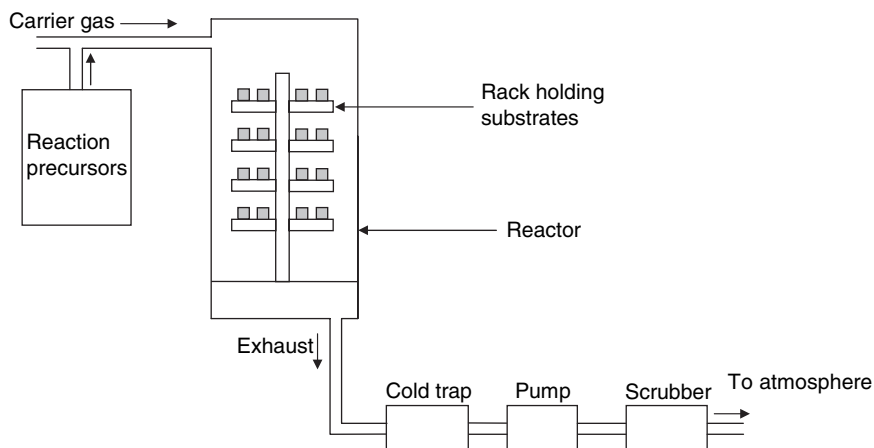
4.2 The chemical vapour deposition process

Figure 4.1 shows a CVD system used for the deposition of SiC, while a schematic diagram showing the generalised CVD process can be seen in Fig. 4.2.

Deposition takes place in the reactor, often at, or below, atmospheric pressure (760 torr), where the substrate is heated to the required temperature. The reactor can be either a hot-wall or cold-wall design. In the hot-wall reactor, the chamber walls are typically heated either resistively or by radiation from heating elements made from high-temperature materials such as



4.1 CVD system for the deposition of silicon carbide. (Photograph reproduced with the permission of Archer Technicoat Ltd.)



4.2 Schematic diagram of the CVD process.

graphite. Although temperature control is easier in such a design, hot-wall reactors suffer from a number of design deficiencies. Firstly, deposition occurs not only on the substrate but also on the reactor walls; over time the deposits can flake from the walls and contaminate the product, necessitating a laborious and time-consuming cleaning regime. Secondly, hot-wall reactors are also more prone to gas-phase pre-reaction of the precursors, which reduces the efficiency of the system and can, under some circumstances, have ramifications for product quality. Therefore, coatings which inhibit deposition on reactor walls and techniques which isolate reactor walls from the reagents have been used in large-scale CVD processing (Goela and Taylor, 1988).

In the cold-wall reactor, the substrates are typically heated by inductive coupling, electrical resistance or infrared heating (Bryant, 1977). Although deposition on the chamber walls is much reduced, the cold-wall reactor cannot be used in all systems owing to difficulties in achieving adequate temperature control, especially for large substrates of complex shape. These difficulties in maintaining uniform deposition conditions throughout the chamber can lead to unacceptable variations in coating thickness and morphology. Most hard coatings used in wear-resistant applications are deposited in hot-wall reactors.

During the deposition the precursor gases are delivered into the reactor, sometimes with a carrier gas such as hydrogen or argon, where they are transported to the substrate and subsequently decompose and/or react to form a coating on the surface of the substrate. The decomposition is usually thermally induced, although this can also be accomplished by other energy

Table 4.1 The types of CVD reaction, together with examples

Reaction	Example
Thermal decomposition	$\text{CH}_3\text{SiCl}_3 \rightarrow \text{SiC} + 3\text{HCl}$
Reduction	$\text{WF}_6 + 3\text{H}_2 \rightarrow \text{W} + 6\text{HF}$
Oxidation	$\text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2$
Hydrolysis	$2\text{AlCl}_3 + 3\text{H}_2 + 3\text{CO}_2 \rightarrow \text{Al}_2\text{O}_3 + 3\text{CO} + 6\text{HCl}$
Carbide formation	$\text{TiCl}_4 + \text{CH}_4 \rightarrow \text{TiC} + 4\text{HCl}$
Nitride formation	$\text{TiCl}_4 + \frac{1}{2}\text{N}_2 + 2\text{H}_2 \rightarrow \text{TiN} + 4\text{HCl}$
Co-reduction	$\text{TiCl}_4 + 2\text{BCl}_3 + 5\text{H}_2 \rightarrow \text{TiB}_2 + 10\text{HCl}$

sources such as microwave plasma. The various types of deposition reaction that can take place are listed in Table 4.1, together with some examples.

4.2.1 Precursors to the chemical vapour deposition reaction

The precursors for the CVD process can be in solid, liquid or gaseous form at ambient temperature. However, for those precursors not already in the vapour phase, it is essential that they be sufficiently volatile, while retaining thermal stability, to facilitate their easy transport to the reactor. Many precursors are toxic, corrosive, flammable or pyrophoric, e.g. trichlorosilane (SiHCl_3) and hydrogen, which are used to deposit silicon; the former is pyrophoric, while the latter is explosive in combination with oxygen (O_2) (Goela and Taylor, 1988). As a result, extensive safety precautions, such as leak detectors and extraction units, are required for their storage and handling.

A wide range of precursor chemistries are used, including both inorganic compounds (e.g. metal halides) and metal–organic compounds (e.g. coordination compounds such as metal acetylacetonate derivatives) and organo-metallics (e.g. metal alkyls or carbonyls). For the deposition of hard coatings, the most common precursors are metal halides (e.g. TiCl_4 , BCl_3 and AlCl_3) and hydrides (SiH_4 and NH_3). In addition, organic compounds such as methane (CH_4) and propane (C_3H_8) can be used as co-reagents. The metal halides, some of which are liquid at room temperature, can be volatilised by use of a heated bubbler assembly in which carrier gases such as hydrogen (H_2) or argon are passed over or through the halide to volatilise the precursor and transport it to the deposition zone. However, the bubbler has been largely superseded by other devices, the most common being a liquid mass flow controller and evaporation chamber; one such design has been described by Boer (1995). The carrier gas ensures even mixing of the reactant gases to ensure a uniform deposit and helps to maintain a tolerable

deposition rate by providing a large enough total flow rate through the CVD reactor (Rebenne and Bhat, 1994). It can also help to suppress nucleation in the gas phase.

It is important that the precursor be sufficiently stable so that (i) no significant decomposition occurs before it reaches the substrate (a problem more often associated with precursors containing organic ligands than the generally more robust inorganics); (ii) that the precursors are not condensed or deposited on the pipe walls during transport. Condensation can be reduced by independent heating of the pipework, e.g. by heating tapes.

4.2.2 Substrate treatments

In any coating–substrate combination a discontinuity exists at the coating–substrate interface, the magnitude of which is dependent upon the respective properties of coating and substrate. As a result, the interface represents an area of weakness and is often the location at which failure is initiated, even for well-adhered coatings. This can be exacerbated by the residual stress in the coating, which can arise from differences between the thermal expansion coefficients of the coating and substrate. For CVD coatings, undesirable phases formed by chemical reactions between the gases and the substrate can also be detrimental to coating integrity.

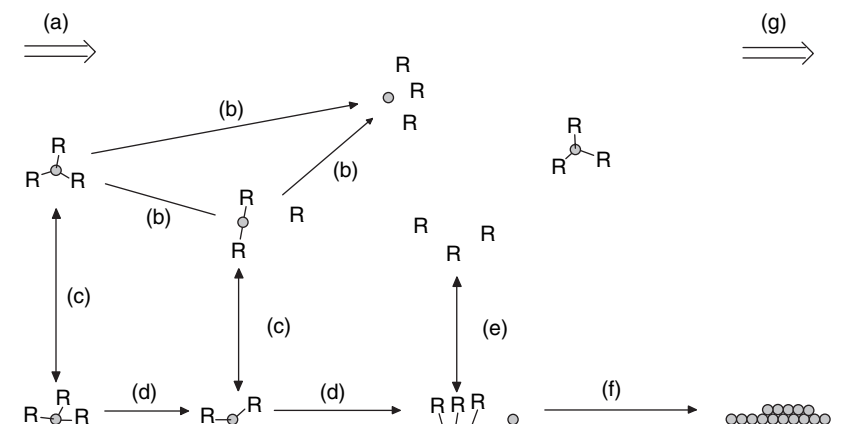
In order to prevent these chemical reactions from taking place an interlayer is often deposited, which acts as a diffusion barrier between the coating and the substrate. It can also act to reduce the residual stress in the coating if its thermal expansion coefficient is between those of the coating and substrate, provided that the mechanical strength is not compromised. One such interlayer is TiC, which has been used to enhance the deposition of hard coatings on WC substrates, including Al_2O_3 , B_{13}C_2 and TiN. In the deposition of B_{13}C_2 the presence of the TiC interlayer reduces boron diffusion from the gas phase to the substrate and, hence, reduces the formation of CoWB at the interface.

An alternative to depositing an interlayer is to alter the chemistry of the substrate itself by employing treatments such as carburising and etching. Carburising the WC substrate using an $\text{H}_2 + \text{CH}_4$ mixture at approximately 1000°C prior to the deposition of TiC was found to reduce the formation of the brittle η phase ($\text{Co}_3\text{W}_3\text{C}$ or $\text{Co}_6\text{W}_6\text{C}$) (Sarin and Lindstrom, 1979). Zhu *et al.* (1995) adopted a similar approach to enhance the adhesion of diamond coatings to tungsten and molybdenum substrates. The substrates were heated to 1100°C for 30 h in a CO atmosphere causing the formation of a carburised layer 2.2–2.4 μm in thickness, which resulted in a reduction in residual stress by approximately two thirds and improved coating adhesion.

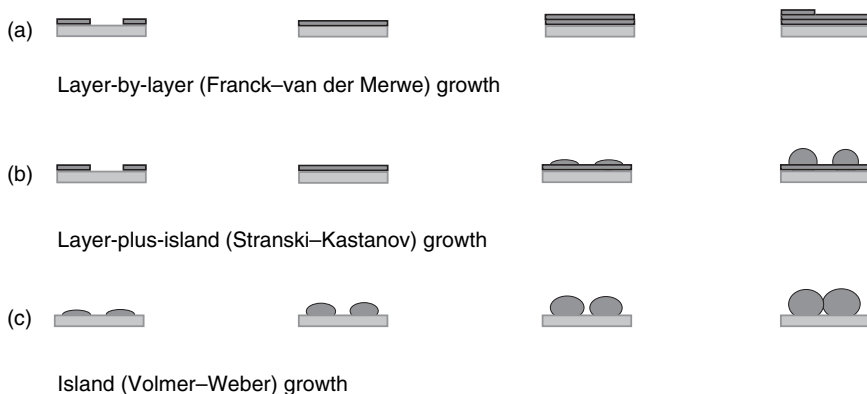
One of the difficulties in depositing diamond onto cemented WC substrates is that the metals that are used as binders in the substrate (most commonly cobalt and nickel) have the tendency to catalyse the formation of graphite. This problem is partially overcome by etching the substrate to remove the binder from the surface. Haubner *et al.* (1995) used Murakami's reagent ($K_3[Fe(CN)_6]$ in KOH) to attack the WC followed by $H_2SO_4-H_2O_2$, which was used to etch the remaining cobalt binder. The treatment was found to promote both adhesion and growth rate of the subsequently grown diamond.

4.2.3 Film formation

Figure 4.3 shows a schematic diagram of the deposition process. The molecular species are transported in the vapour phase to the substrate via diffusion and/or convection. Deposition begins by the adsorption of these species at the substrate surface. The deposit must have sufficiently low vapour pressure to prevent its volatilisation (Bryant, 1977). As the process continues, agglomeration of atoms leads to the film growth, which is shown in schematic form in Fig. 4.4. There are several different mechanisms of film growth



4.3 Schematic diagram showing the stages of film deposition: (a) mass transport of precursor to the deposition zone; (b) possible gas-phase reactions, which may lead to species more involved or less involved in the deposition process; (c) transport of precursors to the substrate surface where adsorption occurs; (d) reaction of the adsorbed species to generate the desired material and organic by-products; (e) desorption of organic species away from the surface; (f) surface diffusion of the adsorbed metal to growth sites and incorporation into the film; (g) mass transport of by-products and unreacted precursor material from the deposition zone (Harker, 1996).



4.4 Modes of film growth in CVD (Harker 1996).

(Jensen, 1993). Many of the coatings used in wear-resistant applications have been observed to grow by the nucleation of isolated crystals on the substrate. As deposition continues, these 'islands' coalesce, resulting in a continuous film, although some intergranular porosity at the coating-substrate interface may remain. The region of the coating adjacent to the interface will often consist of equiaxed grains. As the thickness increases, the more preferentially oriented grains grow at the expense of those less favourably oriented. This leads to a columnar microstructure with the grain size increasing with increasing thickness. It is sometimes desirable to limit grain growth as mechanical properties such as strength vary inversely with grain size. This can be achieved by interrupting the deposition process by stopping and restarting the gas flow. This causes a new layer of film to nucleate with finer grains, resulting in a smaller average grain size for the entire coating (Rebenne and Bhat, 1994).

Finished coatings typically have a density in excess of 99.9% of their theoretical value as well as identical chemistry. In some cases, CVD coatings possess superior mechanical properties to their bulk equivalent. This is demonstrated by Table 4.2, which compares the hardness values of various ceramics in their bulk and coated form. In some cases, the coatings are harder than their bulk counterparts, although considerable scatter is seen owing to variations in the deposition conditions.

In addition to the deposited film, unwanted gaseous by-products such as HCl also result from these reactions. Often highly corrosive or toxic, they require additional treatment, usually by chemical scrubbers or pyrolysis units, to neutralise them in order to prevent harmful emissions into the environment (Jensen, 1993).

Table 4.2 A comparison of the hardness values of CVD coatings and their corresponding bulk materials (data from Wood *et al.* (1999), Richter *et al.* (2000), Ajayi and Ludema (2004) and Chowdhury *et al.* (2005))

Material	Bulk hardness (GPa)	Coating hardness (GPa)
Diamond	95–117	93–117
B ₁₃ C ₂	35	59–67
BP	35	30
SiC	19–40	38
TiN	20	15–40
TiC	35	28–42
Al ₂ O ₃	20	20–21
WC	21	18–28

4.3 Factors affecting the coating characteristics

The characteristics of CVD coatings are dependent on many factors, the most important of which are substrate temperature, chamber pressure and gas composition as well as the chemistry of the substrate. While this multiplicity of variables confers a high degree of flexibility to the process by enabling a wide range of coating microstructures to be produced, it can also complicate the optimisation of the process conditions. The effects of these factors are now briefly considered in the following section.

4.3.1 Substrate temperature

Substrate temperature is the most important factor affecting the coating as it influences both the thermodynamics and the kinetics of the reaction. The reaction must be both thermodynamically favourable as well as able to proceed at a rate that enables the process to be economically viable. If the temperature is too low, the deposited film may differ considerably from that which was intended. In a study of the deposition of SiC on graphite substrates, Motojima *et al.* (1986) found that amorphous silicon coatings were deposited at temperatures below 750–800°C. Coatings deposited at low temperatures can also contain higher levels of impurities. An example of this is AlN where the presence of chlorine was detected in deposits below 800°C, increasing from 5 to 25 wt% with decreasing temperature (Goto *et al.*, 1992).

As the substrate temperature is increased, the higher diffusion rates result in higher rates of film growth. However, this trend does not continue indefinitely and a decline in the deposition rate may be seen if further increases in the temperature reduce the thermodynamic driving force.

Motojima *et al.* (1986) found that the optimum temperature for SiC growth was 1000 °C; the rapid decrease in deposition rate above 1100 °C was attributed to preferential deposition of SiC on the inner wall of the reaction chamber. Temperature also affects the microstructure of the coating; in a study of TiC on WC–Co substrates Lee *et al.* (1981) found that coatings deposited at temperatures below 1050 °C contained equiaxed grains, while above 1050 °C the grains assumed a more elongated appearance.

4.3.2 Pressure

Most CVD processes take place below atmospheric pressure as many coatings deposited under these conditions exhibit enhanced quality and uniformity. It also enables deposition to be carried out at lower temperatures as well as reducing the incidence of gas-phase nucleation.

Saito *et al.* (1986) investigated the effect of pressure on the character of CVD diamond deposited on silicon. They found that the highest-quality film was grown at the lowest pressure (67 Pa) while graphite was formed at the highest pressure (5000 Pa). This was because of the higher rate of dissociation of atomic hydrogen at low pressures (Pierson, 1993), leading to the presence of more hydrogen. Moreover, at subatmospheric pressure the hydrogen atom recombination is slow, which causes a super-equilibrium concentration of hydrogen radicals to be present (Butler and Woodin, 1993). At higher pressures the amount of atomic hydrogen present is inadequate to etch the graphitic deposits.

4.3.3 Gas composition

In CVD, the reactant gases are often diluted by carrier gases. Excessive levels of precursor gases in the total gas flow can result in nucleation in the gas phase. This has been seen in the deposition of Al₂O₃ coatings, where other effects have included poor adhesion and large microstructural variations owing to the formation of whiskers, needle-like crystals and dendritically branched crystals in the coating (Lux *et al.*, 1986). In order to deposit Al₂O₃ coatings that are free of these features a low concentration of reactants is required; however, this can result in low deposition rates (0.5–1.0 μm h⁻¹).

In diamond coatings, excessive levels of CH₄ can lead to unacceptable levels of graphite in the deposit and a concomitant reduction in mechanical properties. Sato and Kamo (1989) found that the elastic constant and thermal conductivity declined with increasing CH₄ content, the thermal conductivity at 0.5% CH₄ being less than half that of the value at 0.1%. The elastic constant also declined with increasing methane content, although it was less marked than that of thermal conductivity; the value at 5% CH₄ was still 78% of the value at 0.5% CH₄.

4.3.4 Substrate

The properties of CVD coatings are also dependent on the physical properties of the substrate. One of the most prominent examples is the mismatch between the thermal expansion coefficients of the coating and substrate. A large mismatch can result in excessively high residual stresses in the coating, which can promote cracking or buckling. In extreme cases, spontaneous delamination of the coating from the substrate has been observed during cooling following deposition.

Substrate chemistry also exerts a strong influence on the coating. Adverse chemical reactions between the gases and the substrate also serve to affect the quality of the coating. The effect of the cobalt binder on the deposition of diamond on cemented WC has already been discussed. For the deposition of TiC, cobalt has the opposite effect. Lee *et al.* (1981) found that it promoted both nucleation and growth of the coating owing to the higher rate of diffusion of carbon through the cobalt-rich phase, which was approximately 14 times faster than through the WC grains. As a result, the nucleation and growth rates were seen to increase significantly as the cobalt content in the substrate was increased from 3 to 25 wt%. Film growth was observed to take place in two stages. During the first stage, primary nucleation, TiC crystals were first seen at the interfaces between the WC grains and the cobalt binder. This was followed by secondary nucleation and growth, which extended to the interior of the WC grains. The enhanced nucleation of TiC on cobalt has been exploited in the latest generation of CVD coatings for WC tools; prior to the deposition of TiC, the near-surface layers of the WC are enriched with cobalt by gradient sintering to provide enhanced adhesion and toughness (Lassner and Schubert, 1999).

4.4 Advantages and disadvantages of chemical vapour deposition

The advantages of CVD are that it is capable of depositing a wide range of materials. Unlike physical vapour deposition (PVD), CVD does not suffer from line-of-sight limitations, which enables uniform coatings to be deposited on components with more complex geometries. It can also be used to produce refractory metals and ceramics at much lower temperatures than traditional processing routes. CVD coatings deposited under optimum conditions can be high in purity, adherent and greater than 99.9% of their theoretical density. Moreover, the deposition rates, which can exceed $25\mu\text{m min}^{-1}$ (depending on the coating system), are considerably higher than for PVD coatings (Wick and Veilleux, 1985). The versatility of the process enables a wide range of coating microstructures to be produced. Coatings

of up to 1270 μm can be deposited, while free-standing components several millimetres in thickness have also been produced by CVD.

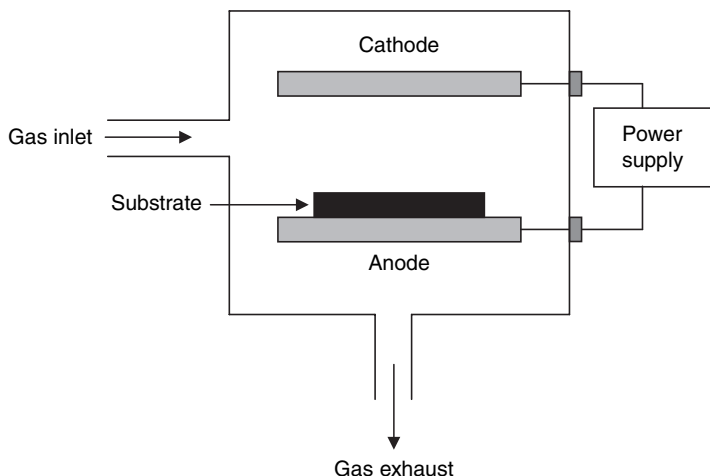
However, CVD also suffers from a number of disadvantages, most notably the high deposition temperatures; where lower temperature precursors are not available, the suitable substrates are limited to high-melting-point materials such as WC. Moreover, the fact that the CVD process is not a line-of-sight process (an advantage for coating components with complex shapes) can be a disadvantage as it is not possible to mask off areas easily. Although selective deposition has been proven in some systems, this is generally as a result of differences in deposition on adjacent materials of different composition. Another drawback with CVD is the extensive safety and environmental precautions that are needed to handle both the precursor gases and the reaction products.

4.5 Plasma-assisted chemical vapour deposition

The limited number of suitable substrates that can withstand the high deposition temperatures prompted the search for ways by which CVD coatings could be deposited at lower temperatures. This was accomplished by plasma-assisted chemical vapour deposition (PACVD) (or plasma-enhanced chemical vapour deposition (PECVD)) (Hess and Graves, 1993). First developed in the 1960s for use in the semiconductor industry, this technique was later applied to the deposition of wear-resistant coatings such as TiN (Archer, 1981).

Figure 4.5 shows a schematic diagram of the PACVD (or PECVD) process. The chamber contains two electrodes, one of which is sometimes used to support the substrate(s). Power is supplied by either a high-power radio-frequency current or a direct-current (DC) voltage, although the latter is more commonly used in the deposition of hard coatings. The DC voltage is often applied in pulses to reduce the incidence of arcing that can occur with this process and which can damage the substrate (Eskildsen *et al.*, 1999). When the reactant gases are introduced into the reactor, a plasma is generated by the electric field between the anode and cathode. The reactant molecules are dissociated by impacts from electrons in the plasma, which creates complex mixtures of highly reactive species (e.g. radicals, neutrals, ions and electrons).

The reduced deposition temperatures of the PACVD process allow the deposition of coatings on to steel substrates without the problem of distortion encountered with conventional thermal CVD. Coatings such as TiC, TiCN and TiN coatings, which are normally deposited at temperatures of between 900 and 1100 $^{\circ}\text{C}$, can be deposited by PACVD at temperatures in the range of 500 $^{\circ}\text{C}$ (Chu and Tian, 2004). The lower deposition temperatures also reduce the magnitude of the residual stresses in the coatings.



4.5 Schematic diagram of the PACVD (or PECVD) process.

However, PACVD coatings suffer from higher levels of impurities and defects, and lower densities, than CVD coatings deposited at higher temperatures (Bunshah, 2001).

4.6 Hard coatings produced by chemical vapour deposition

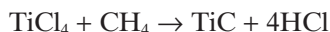
This section considers some of the CVD coatings that are available commercially. Some, e.g. TiC and TiN, have been used to coat components for over 30 years; others, e.g. diamond, are more recent entrants to the market. They are now described in turn, together with some applications.

4.6.1 Titanium carbide

TiC was one of the first hard CVD coatings to be commercially produced. Research into TiC began in the 1950s and reached the stage of commercial exploitation in 1969 with the introduction of the first TiC-coated cemented carbide indexable inserts for turning (Soderberg *et al.*, 2001). The succeeding decades have seen a steady increase in the proportion of tools that are coated, which now account for more than 80% of all turning inserts and 70% of milling inserts (Lassner and Schubert, 1999).

TiC coatings, which are typically between 5 and 10 μm in thickness, are most commonly produced by the reaction of titanium tetrachloride (TiCl_4) with a hydrocarbon such as CH_4 in a H_2 atmosphere. The substrate tem-

perature is usually between 850 and 1050 °C while the pressure is in the region of 1–760 torr. The coating is deposited via the following reaction:



The most commonly used substrates are cemented WC and high-speed steel; however, in the case of the latter, the high process temperatures necessitate rehardening of the coated components following deposition (Kessler, 2001).

Although it is 35 years since the introduction of TiC, it remains one of the most widely used coatings for machine tools; however, it is more commonly found as one constituent in a multilayer coating and is usually deposited as a bond layer to improve adhesion. These multilayer coatings include TiC/TiCN/TiN, and TiC/Al₂O₃/TiN. The latest multilayer coatings contain as many as 13 separate layers (Lassner and Schubert, 1999).

Another application of TiC is as a coating for high-chromium steel punches used in the manufacture of brass cartridge cases where the average punch lifetime has been increased by approximately an order of magnitude compared with the uncoated punches (Hintermann, 1981). Other forming applications include drawing rings and deep-drawing dies, which has led to increases in tool life of between 10 and 100 times that of the uncoated tools (Kessler, 2001).

TiC has also been used to coat bearings for the European Meteosat telescope and for gyroscope motors (Boving and Hintermann, 1987). It has been shown to increase the operating life of bearings under conditions of rolling contact fatigue. Radhakrishnan *et al.* (1998) evaluated TiC-coated tool steel ball bearings sliding against a tool steel raceway in the presence of a lubricant. The tests, which were conducted at a contact stress of 1875 MPa and a speed of 5400 rev min⁻¹, were continued until failure occurred. The time to failure of the TiC-coated bearings was 568 h, which was an increase of more than an order of magnitude compared with that of the uncoated bearings (47 h).

TiC has also been investigated for use in components in erosive environments, such as turbine blades. Shanov *et al.* (1992) compared the erosion performance of 5 µm CVD TiC coatings with 2.2 µm CVD TiN and 9.0 µm CVD Al₂O₃ coatings, all deposited on cemented WC (WC–6% TiC–9% Co) substrates. The erosion tests were carried out at particle velocities of between 140 and 260 ms⁻¹ and at temperatures of between ambient temperature and 650 °C. The impact angles were between 15 and 90°. The erodent was angular Al₂O₃ particles. The TiC offered the highest erosion resistance in almost all test conditions, followed by the TiN and the Al₂O₃. More recently, Tabakoff (1999) deposited 15 µm CVD TiC coatings onto various nickel-based superalloy substrates and evaluated their erosion performance in a high-temperature erosion test facility. The coating exhibited

an erosion resistance of approximately an order of magnitude better than the uncoated substrate.

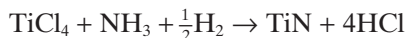
4.6.2 Titanium nitride

TiN coatings were developed soon after TiC, reaching the commercial exploitation stage in the early 1970s. Although the hardness of TiN is lower than TiC, it is still significantly harder than many materials for which it is used to machine. Its distinctive gold colour has also led to the use of TiN in aesthetic as well as functional applications. An example of this is the domes on the cathedral of Christ the Redeemer in Moscow, which was rebuilt in the late 1990s, although in that particular case the TiN coating was deposited by a plasma arc sputtering system rather than by CVD. The excellent diffusion barrier characteristics, good electrical conductivity and good adhesion of TiN have also led to its use in microelectronic applications (Price *et al.*, 1993).

TiN is deposited under similar conditions to TiC, the principal difference being the substitution of CH₄ by nitrogen (N₂). The deposition reaction is



At temperatures of between 900 and 1200°C, coatings can be deposited at rates of between 0.03 and 0.2 μm min⁻¹ (Rebenné and Bhat, 1994). An alternative nitrogen source is ammonia (NH₃), which enables deposition to be carried out at lower temperatures, as low as 400°C. The reaction is



Although the lower substrate temperatures enable TiN coatings to be deposited onto a wider range of substrates, the efficiency of the reaction is reduced. As a result, the coatings deposited contain higher levels of impurities with chlorine contents of not less than 5%, leading to a reduction in the hardness of the coating (Arai *et al.*, 1988).

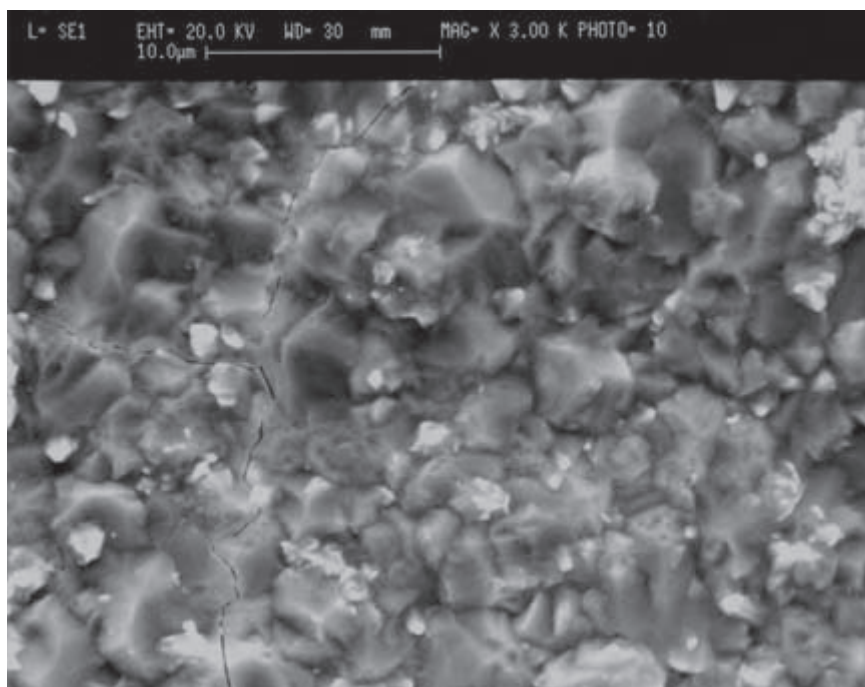
Like TiC, the thickness of TiN coatings is usually less than 10 μm. Most CVD TiN coatings have a composition close to stoichiometric composition (22.6 wt% N). Coatings with lower nitrogen contents exhibit reduced fracture toughness owing to the presence of the more brittle Ti₂N phase. For both TiC and TiN the maximum hardness has been measured on coatings having near-stoichiometric compositions (Kim *et al.*, 1988).

Although adherent TiN coatings can be deposited directly onto WC substrates, the reaction between the gases and the substrate can lead to a carbonitride zone at the coating–substrate interface. This can be avoided by increasing the pressure, which also results in a higher growth rate and a more pronounced columnar structure (Sundgren and Hentzell, 1986). Alternatively, an interlayer of TiC or TiCN can be deposited prior to the

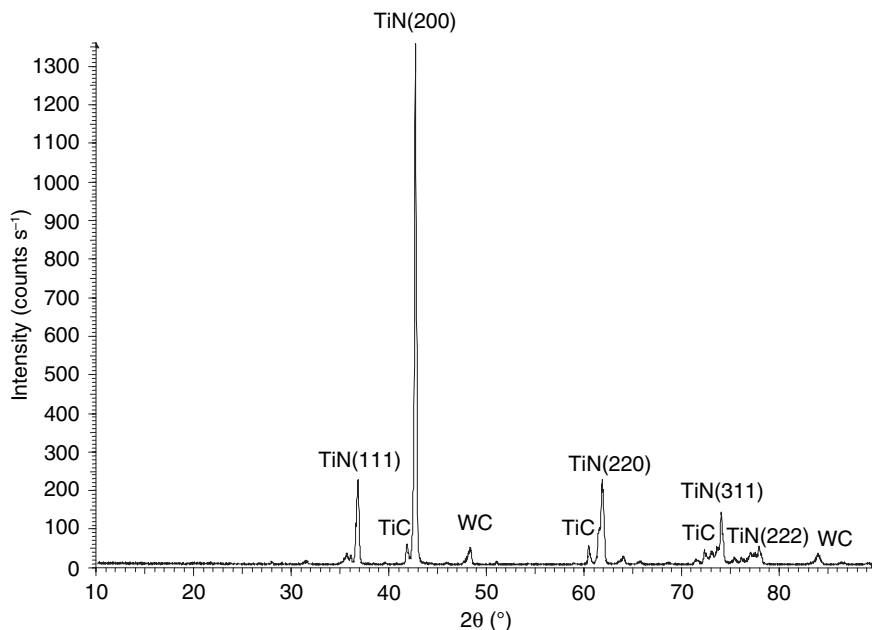
TiN to act as a diffusion barrier to enhance the adhesion (Rebenne and Bhat, 1994).

Figure 4.6 is a micrograph of a CVD TiN coating deposited on a WC substrate. An X-ray diffraction pattern for the coating is shown in Fig. 4.7. The most prominent peaks are those denoting the (200), (111) and (220) directions. In the turning of steels, it has been found that TiN coatings with a strong (111) orientation offer improved flank wear resistance, although for facing operations a stronger (220) orientation was beneficial in delaying the onset of crater wear and reducing the rate of cratering (Rebenne and Bhat, 1994).

CVD TiN is used widely as a coating for cutting tools although, as discussed in the previous section, it is often used as one constituent of a multilayer coating. Its greater chemical inertness compared to TiC and reduced tendency for adhesion to steel materials means that diffusion is reduced and cratering wear resistance at the top face is increased (Knotek *et al.*, 2001). However, in recent years, CVD TiN has been partially eclipsed by PVD TiN coatings. This is because the PVD coatings have smaller grain



4.6 Micrograph showing the as-grown surface of an 8 μm CVD TiN coating on WC.



4.7 X-ray diffraction pattern of an 8 μ m CVD TiN coating on WC.

sizes, and thus higher hardness, which confers increased operating lives for PVD coatings. Furthermore, the lower deposition temperatures (350–500°C) enable PVD coatings to be deposited on to a wider range of substrate materials. However, a recent comparison (Dubar *et al.*, 2005) of TiN coatings produced by both PVD and CVD for tooling used in a metal-forging operation has shown that CVD TiN coatings offered superior performance (e.g. lower friction) and tool life compared with their PVD counterparts.

TiN has also been used to coat forming tools used in sheet metal forming, e.g. the manufacture of automobile doors. The lives of the coated tools have been up to 50 times those of the uncoated tool steel components. TiN has also shown promise as a potential coating for use in the hot extrusion of aluminium (Bjork *et al.*, 1997).

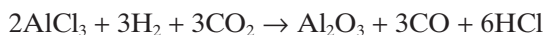
In addition to TiC and TiN, CVD has also been used to deposit other titanium-based coatings such as TiB₂, TiCN and TiAlN. All these materials exhibit high hardness and wear resistance. TiB₂ has been used as a coating to improve the erosion resistance of cemented carbide valve and pump components (Bunshah, 2001). TiCN has been shown to increase the operating lives of steel moulds used in the die casting of aluminium (Heim *et al.*,

1999); it has also been used to improve the tribological behaviour of titanium alloys (Kessler *et al.*, 2002), the untreated surfaces of which often exhibit a high and unstable friction coefficient in sliding contact, leading to severe adhesive wear and seizure. The rapid oxidation of TiN at temperatures above about 500 °C can be overcome by the use of TiAlN (Kim and Lee, 1996). Its superior high-temperature oxidation resistance is thought to be conferred by the formation of Al_2O_3 at the surface of the TiAlN coating, which protects the underlying film from further oxidation. Both TiCN and TiAlN have been deposited by PACVD, although TiAlN is more commonly deposited by PVD.

4.6.3 Alumina

Al_2O_3 coatings produced by CVD were developed shortly after TiC and TiN, reaching the marketplace in 1975 (Soderberg *et al.*, 2001). Although its hardness is lower than TiC at ambient temperature, Al_2O_3 retains its hardness to higher temperatures and at 1000 °C has a higher hardness than TiC. In addition to its high hardness, the thermal stability and oxidation resistance of Al_2O_3 make it an attractive option for use in coatings for machine tools. Owing to its poor adhesion on WC substrates, Al_2O_3 is often deposited onto TiC or TiN as part of a multilayer coating, its function being to provide thermal insulation, as well as protection from chemical and adhesive wear (Soderberg *et al.*, 2001).

CVD Al_2O_3 is most commonly produced by the hydrolysis of aluminium trichloride (AlCl_3) in excess hydrogen at low (approximately 1 torr) pressure at temperatures in excess of 900 °C. The coating is formed by the following reaction:



The same reactants have also been used in PACVD in a study of the feasibility of Al_2O_3 deposition at between 300 and 500 °C (Bunshah, 2001). However, the deposited coatings were found to be amorphous with unacceptable levels of impurities. Another study used mixtures of AlCl_3 , N_2O or O_2 , and H_2 or argon, to deposit Al_2O_3 coatings by PACVD at temperatures of approximately 700 °C (Täschner *et al.*, 1999).

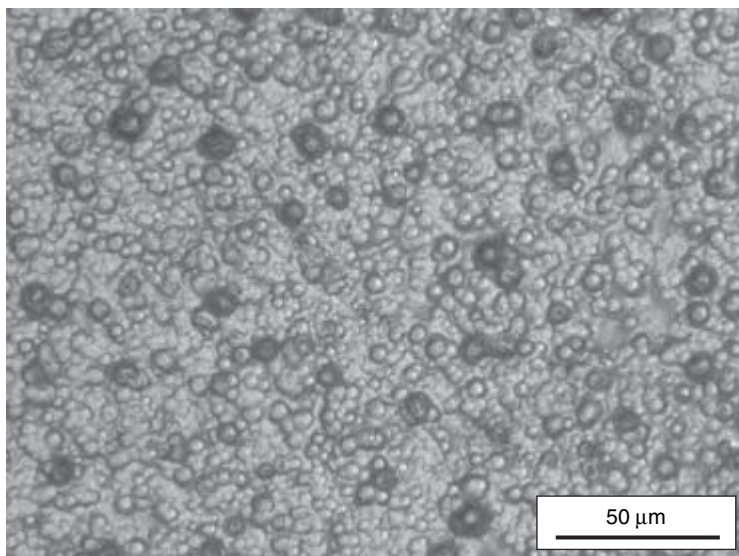
Al_2O_3 exists in a variety of different phases, although CVD Al_2O_3 coatings used for wear-resistant applications consist mainly of the thermodynamically stable α - Al_2O_3 and κ - Al_2O_3 (Lux *et al.*, 1986). The κ - Al_2O_3 phase is metastable and will transform to α - Al_2O_3 at elevated temperatures. This transformation has been shown to be highly temperature dependent, being three to four times faster at 1090 °C than at 1030 °C (Lindulf *et al.*, 1994).

The thermal conductivity of κ - Al_2O_3 is lower than that of α - Al_2O_3 , which makes it beneficial in machining applications. However, owing to the

differences between the densities of the two phases, the $\kappa \rightarrow \alpha$ transformation leads to a volume contraction of approximately 8% (Vuorinen and Karlsson, 1992), which can have potentially serious implications for coating integrity. The most desirable phase is $\alpha\text{-Al}_2\text{O}_3$ and, over the last decade, efforts have focused on maximising the $\alpha\text{-Al}_2\text{O}_3$ content. The deposition conditions have also been optimised to enable the latest coatings to have a preferred orientation in the (012) direction, which has improved both wear resistance and coating adhesion (Soderberg *et al.*, 2001).

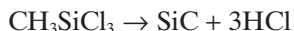
4.6.4 Silicon carbide

SiC has many properties that make it a potentially attractive choice in wear-resistant applications. In addition to its hardness, SiC also exhibits good thermal shock, as well as high-temperature oxidation and corrosion resistance. It is chemically inert in contact with acids and can only be dissolved by oxidising melts or fluorine at 300 °C (Brutsch, 1985). SiC can exist in one of two main phases, both of which have been produced by CVD; $\alpha\text{-SiC}$ has a hexagonal crystal structure, while $\beta\text{-SiC}$ has a face-centred cubic crystal structure. Figure 4.8 is a micrograph of a CVD SiC coating deposited on a WC substrate.



4.8 Micrograph showing the as-grown surface of a 10µm CVD SiC coating on WC.

CVD SiC is produced at deposition temperatures of between 1000 and 1800°C with the most common substrates being graphite, molybdenum, tungsten and tantalum. A comprehensive list of the routes by which SiC has been deposited by CVD has been given by Schlichting (1980a, 1980b). The most commonly used precursor for the deposition of SiC is methyltrichlorosilane (CH_3SiCl_3), which undergoes thermal decomposition in a H_2 atmosphere. The chemical reaction is



CH_4 can also be added to CH_3SiCl_3 and H_2 , the effects of which can be a reduction in the deposition temperature and an alteration in the microstructure and crystallographic orientation of the film (Kuo *et al.*, 1990). H_2 is often used as a carrier gas to transport the reactants to the hot surface. For SiC deposited using SiCl_4 and CH_4 as precursors, H_2 promotes the formation of SiC; without it, a film of pyrolytic carbon is the result (Schlichting, 1980a).

Chin *et al.* (1977) prepared CVD SiC by using a mixture of $\text{CH}_3\text{SiCl}_3 + \text{H}_2$ at temperatures of between 1150 and 1600°C. They found that the deposits ranged from smooth featureless and rounded columnar to angular, strongly faceted and needle structures. Coatings having a faceted appearance were obtained using higher deposition temperatures together with lower pressures and CH_3SiCl_3 contents. In contrast, lower temperatures and higher pressures and CH_3SiCl_3 contents resulted in smooth coatings with rounded growth features. X-ray diffraction showed the apparent coexistence of cubic SiC with a disordered phase and in some deposits single crystals of hexagonal SiC.

Other precursors have been used to reduce the deposition temperature. Motojima *et al.* (1986) deposited SiC onto graphite substrates at temperatures of between 500 and 1100°C using hexachlorodisilane (Si_2Cl_6) as the silicon source and C_3H_8 as the carbon source. They examined the effect of deposition conditions such as temperature and silicon, carbon and chlorine contents in the precursor gases. SiC peaks were not seen on X-ray diffraction spectra below 850°C; above this temperature, the SiC peak rapidly increased in prominence, although it was not possible to determine whether it was α - or β -SiC owing to overlap of the respective peaks. The optimum deposition temperature appeared to be in the range 950–1050°C: maximum deposition (as measured by weight gain of the substrate) occurred at 1000°C. This was supported by electron probe microanalysis data, which was used to measure the ratios of the C $\text{K}\alpha$ to Si $\text{K}\alpha$ peaks. The silicon content was constant over the range 900–1050°C, decreasing below 900°C and above 1050°C. The carbon content decreased with increasing reaction temperature, attaining a minimum at 1000°C and increasing again above 1000°C. The Vickers microhardness of the coatings

deposited at 1000°C was measured to be 38 GPa at room temperature and 21 GPa at 1000°C.

Brutsch (1985) deposited SiC films on a variety of substrates including WC–Co, graphite, steel, sapphire and Si₃N₄. Deposition took place at atmospheric pressure at temperatures of between 800 and 1200°C; the coatings were between 5 and 50 µm in thickness. The gas phase contained a volatile alkyl or arylchlorosilane and H₂ as the reactants together with N₂ as the carrier gas. A hydrocarbon was also added in some experiments to increase the carbon content. The deposited films, which had a nodular appearance, were primarily composed of β-SiC, although small amounts of α-SiC may have been present as these are easily obscured by the β-SiC. The maximum hardness (60 GPa) was recorded on films having a stoichiometric composition (30 wt% C); higher deposition temperatures also increased the hardness.

The good resistance to both thermal shock and oxidation of SiC has been exploited in coatings for C–C (carbon–carbon) composites used for variable orifice paddles on the exhaust for jet engines. These paddles, which are 450 mm in length, 150 mm width and 5–10 mm thick, are deposited with a SiC coating 100–200 µm in thickness. SiC has also been used in mechanical seals, where good sliding wear behaviour, as well as corrosion and thermal shock resistance are required. A common material currently used in seals is bulk SiC; recent research has focused on its replacement by SiC–SiC composites. They are produced by a variant of the CVD process, chemical vapour infiltration (CVI), in which a fibre-woven preform is coated or impregnated with SiC from the vapour phase. The deposited SiC fills the pores of the preform, resulting in a composite with high thermal stability and superior mechanical properties. However, it suffers from long processing times and poor run-to-run reproducibility (Mosebach *et al.*, 1995).

In addition to coatings and CVI composites, CVD has also been used to produce free-standing SiC discs up to 600 mm in diameter and plates up to 760 mm × 460 mm in size; the thickness of these pieces can be up to 13 mm (Pickering *et al.*, 1990). This material can be both transparent and opaque depending upon the microstructure; Kim *et al.* (1995) showed that transparent CVD SiC consisted of highly oriented, essentially defect-free columnar grains of β-SiC in the <111> direction. The translucent material was also predominantly cubic, albeit with a more significant level of defects, principally twins. The opaque SiC had no preferred orientation, a predominantly α-SiC structure with a high dislocation density. Free-standing CVD SiC has been considered as a candidate material for optical applications such as laser mirrors, solar collectors and concentrators, astronomical telescopes and optics in the vacuum-ultraviolet and X-ray regions (Goela *et al.*, 1991). Other applications include windows and domes for missiles, where high resistance to erosion from rain and dust particles is required (Goela *et al.*, 1994).

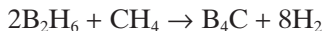
4.6.5 Boron carbide

Boron carbide is the fourth-hardest known material after diamond, cubic boron nitride (c-BN) and some types of SiC (Field, 1992). This property, coupled with its low density and chemical inertness, makes it a potentially attractive option for use in components that require wear resistance. However, the low fracture toughness of sintered boron carbide has limited its applications. CVD has emerged as a flexible method by which the problem of toughness can be overcome, enabling boron carbide coatings with a range of stoichiometries to be produced (Jansson and Carlsson, 1985; Rey *et al.*, 1989).

CVD boron carbide coatings have been deposited on a number of substrates including WC, silicon, graphite and steel (Lee and Harris, 1998; Moss *et al.*, 1998). Coatings of up to 50 μm in thickness have been reported (Loubet *et al.*, 1989), although they are more commonly less than half this thickness. The most common boron sources are boron halides, e.g. BCl_3 , BBr_3 and BI_3 , with CH_4 providing the carbon source. A typical deposition reaction is



Coatings are usually deposited at temperatures of 1200–1400 °C and pressures of between 10 and 20 torr. Boron carbide can also be deposited from diborane at more moderate temperatures (approximately 400 °C) by PACVD:



Boron carbide can exist in three different forms: two crystalline and one amorphous, depending upon the carbon content (Wood *et al.*, 1999). In the boron-rich region (not more than 5 at.% C) of the phase diagram is tetragonal B_{50}C_2 (Lartigue and Male, 1988). Boron carbide containing higher levels of carbon (8.8–20 at.%) exists in a rhombohedral form and is usually designated B_{13}C_2 or B_4C . Boron carbide with more than 20 at.% C is amorphous. The carbon content also exerts a significant influence on its mechanical properties. The hardness and fracture toughness of CVD boron carbide increase with increasing carbon content, reaching a peak at near-stoichiometric composition, before declining thereafter (Niihara *et al.*, 1984). When the carbon content is low, the excess boron results in diminished bond strength, while free carbon at grain boundaries is seen in super-stoichiometric boron carbide. B_{13}C_2 is the hardest of the three forms of boron carbide and hardness values of between 46 and 63 GPa have been recorded (Loubet *et al.*, 1989; Wood *et al.*, 1999). The hardness of B_{50}C_2 is less than half that of B_{13}C_2 , being between 15 and 25 GPa. The hardness of amorphous boron carbide lies between the two crystalline phases, at between

35 and 50 GPa. Elastic moduli, derived from indentation measurements, of 475 GPa and 410 GPa have been recorded for $B_{13}C_2$ and $B_{50}C_2$ respectively (Rey *et al.*, 1989). The carbon content also exerts a similar influence on the tribological behaviour of boron carbide coatings on WC. Olsson *et al.* (1988) found that the erosion resistance increased as the carbon content was increased from 8.8 to 22.5%. However, the amorphous boron carbide coatings exhibited poor erosion resistance, which was attributed to poor adhesion to the TiC interlayer.

In CVD boron carbide coatings, the presence of more than one phase is not uncommon; e.g. $B_{50}C_2$ and rhombohedral boron are sometimes co-deposited together with $B_{13}C_2$ at the boron-rich side of the $B_{13}C_2$ phase region. At higher carbon contents, free carbon and amorphous boron carbide can be co-deposited together with $B_{13}C_2$ (Vandenbulcke and Vuillard, 1981). The presence of these additional phases can be observed by mapping the mechanical properties by nanoindentation (Bose *et al.*, 2005).

The high hardness of boron carbide makes it an attractive candidate coating for components requiring high resistance to erosive and abrasive wear. The hardness of the coatings exceeds that of the particles commonly found in erosive environments such as SiO_2 and Al_2O_3 . As a result, the hardness of the erodent is insufficient to generate radial and lateral cracking on impact. Instead, the damage caused by individual particle impacts is limited to small-scale chipping with the gradual removal of the nodular morphology of the as-grown surface, leading to a smoother surface. The erosion performance of $B_{13}C_2$ at moderate particle velocity (64 m s^{-1}) has been shown to be superior to those of both Al_2O_3 and TiC coatings (Olsson *et al.*, 1989). The impacting Al_2O_3 particles caused material to be removed from the coating by a process of microchipping as well as a gradual reduction in the surface roughness of the as-grown coating (Stridh *et al.*, 1987). This continued until, at a critical particle dose, the coating was rapidly removed by spalling. Failure of the coating was observed to have occurred at the interface between the TiC interlayer and the WC substrate. The high erosion resistance of $B_{13}C_2$ is also seen at higher particle velocities. Bose and Wood (2005a) found that the erosion rate of $B_{13}C_2$ at 250 m s^{-1} was still half that of uncoated WC, although it was still more than four times higher than diamond.

Boron carbide also offers high abrasion resistance. In tests using the ball crater technique, Bose and Wood (2005b) recorded a wear rate of $6.4 \times 10^{-13}\text{ m}^2\text{ N}^{-1}$ for $B_{13}C_2$ on WC. This was lower than CVD TiC/TiN on WC ($9.5 \times 10^{-13}\text{ m}^2\text{ N}^{-1}$) although still more than an order of magnitude higher than diamond ($3.5 \times 10^{-14}\text{ m}^2\text{ N}^{-1}$). For sliding contact, Rey *et al.* (1988) recorded a coefficient of friction of approximately 0.2 for boron carbide sliding against itself in the absence of a lubricant. When in sliding

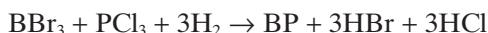
contact with other ceramics the superior hardness of $B_{13}C_2$ leads to two-body abrasion with removal of material from the counterface by the propagation of lateral cracking.

To date, one of the most widespread applications for boron carbide coatings has been the nuclear industry. Boron carbide has a high neutron capture cross-section owing to the presence of B^{10} atoms (up to 20% of the total boron content). Boron carbide coatings have been used for neutron flux control in nuclear reactors as well as shielding against neutron irradiation. Another application has been as a coating for fusion reactor walls to prevent impurities in the reactor wall from polluting the deuterium–tritium plasma, which can prevent ignition of the plasma (Veprek, 1990). Non-nuclear applications include sandblasting nozzles and fibres.

4.6.6 Boron phosphide

BP is a covalent III–V compound with a zinc blende (cubic) crystal structure (Kumashiro, 1990). It has a high stability, high decomposition temperature (1130°C) and a melting temperature in the region of 3000°C. Of particular interest from a tribological standpoint are its mechanical properties, principally hardness. Takenaka *et al.* (1976) reported a Vickers hardness of 47 GPa for loads in the range 100–300 gf carried out on epitaxially grown single-crystal BP. Nicholson and Field (1994) recorded hardness values of between 10 GPa (100 gf load) and 61 GPa (5 gf load) on a 17 µm BP coating on ZnS.

Cubic BP films can be produced by thermal CVD in the temperature range of approximately 900–1100°C. The boron precursor can be BCl_3 or BBr_3 . BBr_3 is often preferred as the high vapour pressure of BCl_3 at room temperature presents handling difficulties (Nishinaga *et al.*, 1972). Deposition occurs via the following reaction:



The last decade has also seen the production of BP coatings by reactive sputtering and PACVD. Of these, the latter is more easily scaled up for coating components of large area and/or complex geometry (Gibson *et al.*, 1994a). BP coatings are produced from diborane and phosphene precursors at substrate temperatures in the region of 400°C. The BP coatings produced in this way are non-stoichiometric and amorphous. They have been used to coat a number of infrared-transmitting materials, notably ZnS and germanium (Ge), to provide protection from damage caused by rain and sand impact. The infrared materials with the best optical properties often have poor mechanical properties and quickly degrade in erosive environments.

A number of liquid impact investigations have been conducted on BP coatings (Gibson *et al.*, 1992, 1994b; Goldman and Tustison, 1994; Mackowski

et al., 1994; Waddell *et al.*, 1994b; Seward *et al.*, 1995; Waddell and Clark, 1999; Clark, 2001). The parameter often used to quantify the rain erosion resistance of a material is the damage threshold velocity (DTV). This is defined as 'the velocity below which the material remains undamaged regardless of the number of impacts' (Jilbert *et al.*, 1995). The ratio of coated DTV to uncoated DTV for 20 μm BP coating on ZnS was 1.6, which increased to 1.8 for a 40 μm coating. Similar improvements were seen for BP coatings on Ge substrates (Goldman and Tustison, 1994). BP has exhibited a higher DTV than other similar coatings, for instance DLC and GaP.

The solid-particle erosion behaviour of BP films has also been studied. Waddell *et al.* (1994a) investigated the erosion performance of a 10 μm DLC/BP on ZnS and compared it with ThF₄ and DLC, both also deposited on ZnS. A number of particle sizes (less than 38–177 μm) and velocities (45–206 ms^{-1}) were used in the tests and it was found that the DLC/BP coating offered the best performance at all test conditions. Jilbert and Field (1998) looked at the effect of coating thickness on the erosion protection of Ge and ZnS substrates coated with BP. Using 200–500 μm silica sand at a velocity of 30 ms^{-1} , they found that the extent of erosion damage decreased with increasing coating thickness up to the optimum thickness (15 μm). Coatings thicker than 15 μm exhibited increased erosion damage, which was attributed to greater residual stresses.

BP coatings are now employed on infrared-transmitting windows and domes on aircraft and missiles. They are currently in service on a number of fighter aircraft including the General Dynamics F16, BAe Harrier GR7 and McDonnell–Douglas AV8-B (Hudson *et al.*, 1997). Owing to its high refractive index (about 3), BP is not an effective antireflection coating; this is overcome by depositing a thin layer (1–2 μm) of DLC on the BP coating (Waddell *et al.*, 1994a).

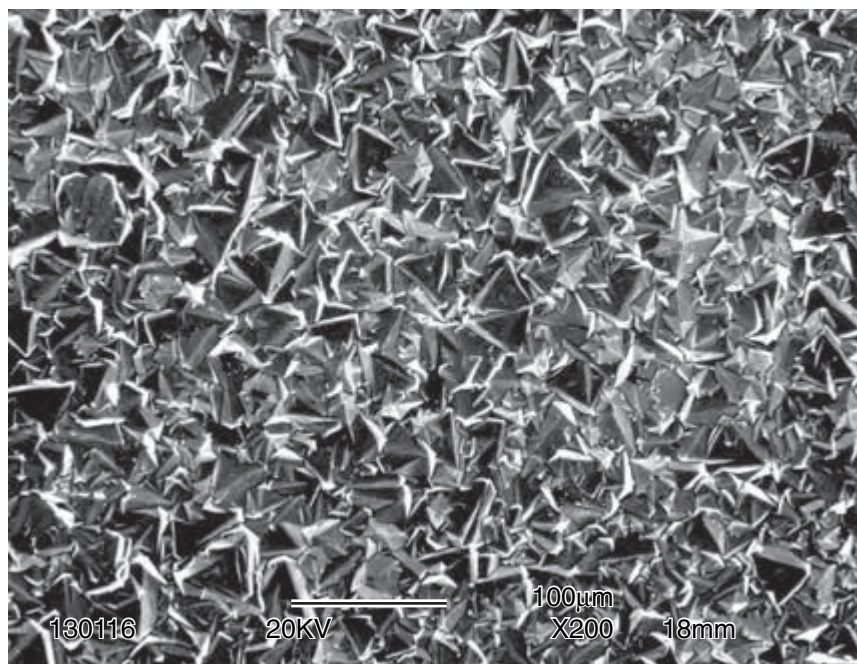
4.6.7 Diamond

The high hardness and strength of natural diamond make it an attractive option for components requiring high resistance to wear, such as machine tools, grinding wheels and wheel dressers. The advent of diamond coatings, applied by CVD, has significantly increased the number of potential applications. Like TiC, efforts to deposit diamond from the vapour phase first began in the 1950s, although it was not until the early 1980s (Spitsyn *et al.*, 1981; Kamo *et al.*, 1982; Matsumoto *et al.*, 1982) that it was possible to deposit diamond, first on diamond substrates, and later on non-diamond substrates. Two decades later, diamond can be deposited on a wide range of substrates including silicon, SiC, tungsten, molybdenum and WC. The last two decades have also witnessed significant improvements in the depo-

sition technology to such an extent that high-power microwave systems can produce CVD diamond films over areas of up to 200 mm in diameter and 1 mm in thickness (May, 2000). Figure 4.9 shows the growth surface of a 60 μm diamond coating on tungsten.

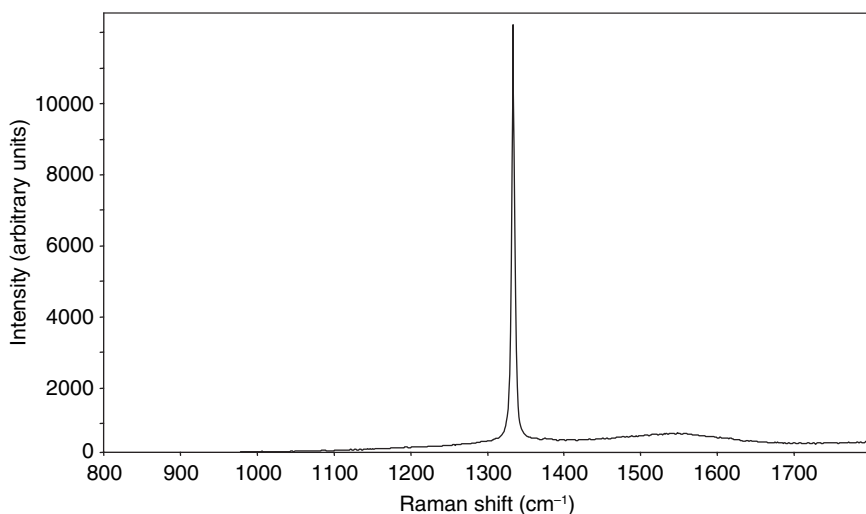
Diamond films are usually deposited at temperatures of between 800 and 1000 °C and pressures of 10–50 torr (Ashfold *et al.*, 2001). The reactant gases consist of a dilute mixture of a hydrocarbon, usually CH_4 , and H_2 . In order to deposit high-quality diamond the methane content generally does not exceed 1% of the total volume of gas. The choice of hydrocarbon gas is not limited to CH_4 ; other gases that have been used include acetylene, methanol and acetone.

There are a number of variants of the CVD process that have been used successfully to deposit high-quality diamond films including the hot-filament, microwave plasma, DC arcjet techniques and many others (May 2000). The main difference between these methods lies in the energy source used to dissociate the reactant gases. In hot-filament CVD, this function is performed by a tungsten or tantalum filament which is heated to tempera-



4.9 Micrograph showing the as-grown surface of a 60 μm CVD diamond coating on tungsten.

tures of approximately 2000 °C. In the microwave plasma process, a microwave source such as a magnetron generator creates a ball-shaped plasma; the CH_4 and H_2 molecules are dissociated by electrons in the plasma. H_2 molecules are dissociated to hydrogen atoms, while the methane is dehydrogenated into CH_3 , CH_2 and CH radicals (Saito *et al.*, 1986). The methyl radical (CH_3) is extremely reactive and on coming into contact with the hot substrate surface a bond is formed by chemisorption. The acetylene radical (C_2H_2) is also highly reactive, owing to its triple bond, and thus also adheres easily to the substrate. On the substrate the radicals form a mixture of amorphous carbon, graphite and diamond. The non-diamond deposits are etched by the H_2 gas and, although some residual graphite may remain, the resultant deposit is overwhelmingly diamond in nature. This is demonstrated by Raman spectroscopy, which is used to evaluate the quality of diamond coatings (Knight and White, 1989). The characteristic Raman shift of each molecular species enables the purity of the film to be determined on a qualitative basis. The main peaks of diamond (1332 cm^{-1}) and graphite (1580 cm^{-1}) are easily distinguished, making characterisation a relatively simple task. A typical Raman spectrum for CVD diamond is shown in Fig. 4.10. The scattering efficiency of graphite is approximately 50 times that of diamond (for a laser excitation wavelength of 632 nm); this fact enables even minute quantities of graphite to be detected in a CVD diamond film. However, Raman spectroscopy cannot be used to determine the quantities

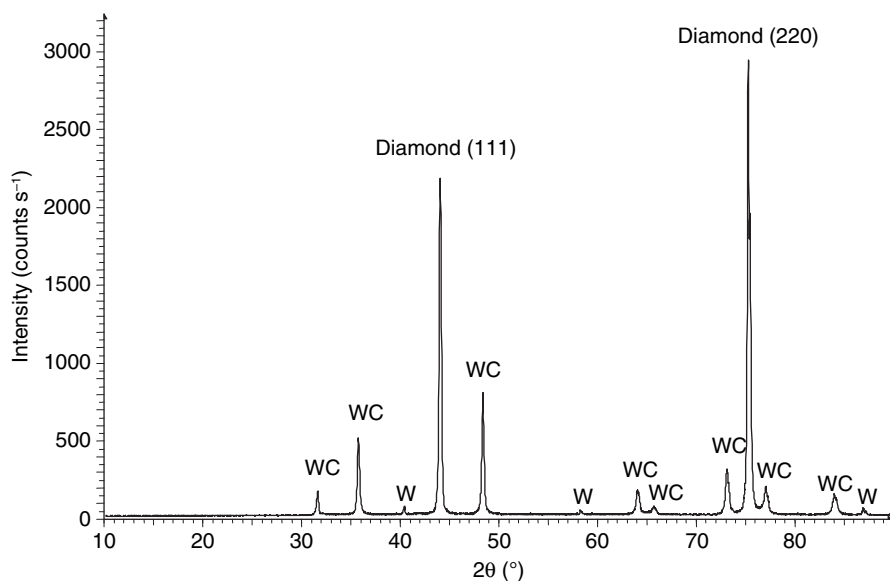


4.10 Typical Raman spectrum from the growth surface of a 60 μm CVD diamond coating on tungsten.

of graphite present and must be regarded as a qualitative method only. An X-ray diffraction pattern for a 120 μm diamond coating deposited on tungsten is shown in Fig. 4.11. It can be seen that the coating has a preferred orientation in the (220) direction. The WC peaks are thought to result from the reaction between carbon in the gas used in the deposition process and the tungsten substrate.

Natural diamond exhibits a low coefficient of friction, μ , sliding against itself, with values of between 0.05 and 0.15 recorded in most environments, the exception being high vacuum where μ can approach 1.0 (Field and Pickles, 1996). Similar behaviour is also seen with polished CVD diamond coatings, although μ is heavily dependent on the surface roughness of the coating (Bull *et al.*, 1994). The as-deposited diamond surface can be very abrasive, leading to high friction and wear of the counterface. Although CVD diamond films can be lapped to reduce the roughness of the as-deposited coating, this process is time consuming and is not feasible for non-planar surfaces. An alternative to polishing is the deposition of nanocrystalline diamond coatings (Erdemir, 2001).

To date, the most widespread application of CVD diamond is in cutting tools where coatings of up to 30 μm have been deposited on to tool materials such as cemented WC or Si_3N_4 . Alternatively, free-standing CVD



4.11 X-ray diffraction pattern of a 120 μm CVD diamond coating on tungsten.

diamond up to 1 mm in thickness can be brazed to the tool (Clark and Sen, 1998). Although the latter offers better adhesion, it is not possible to apply free-standing CVD diamond to anything more than the simplest of geometries.

Diamond-coated tools have been seen to offer superior performance in the machining of Al–Si alloys, ceramics and metal matrix composites, where they have exhibited lower wear rates and produced better surface finishes than sintered polycrystalline diamond (PCD) (Shen 1998). In one comparison the amount of flank wear on a diamond-coated tool was less than one fifth of that on a sintered diamond tool when used in the machining of aluminium alloy (Koike *et al.*, 1997). Diamond coatings also enable machining to be carried out at higher speeds than, for example, WC. Diamond-coated tools are now being used in the dry machining of AlSi7Mg rear axle supports used in the new BMW 5 series (Halwax and Pfaffenberger, 2004). The requirement for the machining to be carried out without a lubricant precluded the use of PCD tooling owing to the complexity of the tool geometry required to facilitate chip removal. The diamond-coated tooling, which consisted of a nanocrystalline layer 4 µm thick with a grain size of between 20 and 200 nm, delivered a tenfold increase in tool life over the uncoated WC–Co tools. Diamond-coated tools have also shown promise in the machining of wood-based composites such as medium-density fibreboard (Sheikh-Ahmad *et al.*, 2003). However, diamond cannot be used to machine ferrous metals owing to the affinity of carbon for iron, which can cause the diamond to transform to graphite.

Other applications where the low-friction behaviour of diamond has been exploited include surgical blades in ophthalmology, where the lower cutting forces leads to less tissue damage than the more commonly used stainless steel blades. On a larger scale, CVD diamond has been the subject of a development programme for possible use in mechanical seals. Hollman *et al.*, (1998) recorded a steady-state friction coefficient for CVD diamond sliding against itself of 0.2, which was considerably lower than other commonly used materials such as WC and SiC. This reduced friction can also result in reduced power consumption as well as reduced wear.

Laboratory tests have also demonstrated the excellent erosion and abrasion resistance of diamond coatings. When tested using the ball crater micro-abrasion test, CVD diamond was found to exhibit a wear rate of more than an order of magnitude lower than CVD B₁₃C₂ and TiC/TiN coatings (Bose and Wood, 2003). This has led to its exploitation in the dressing of vitrified bond grinding wheels containing abrasives such as Al₂O₃ or SiC. Grinding wheels dressed by CVD diamond tools require less frequent dressing operations than the previously used natural diamond dressers. Moreover, the tools themselves can be used for longer before replacement becomes necessary (Pricken, 1999).

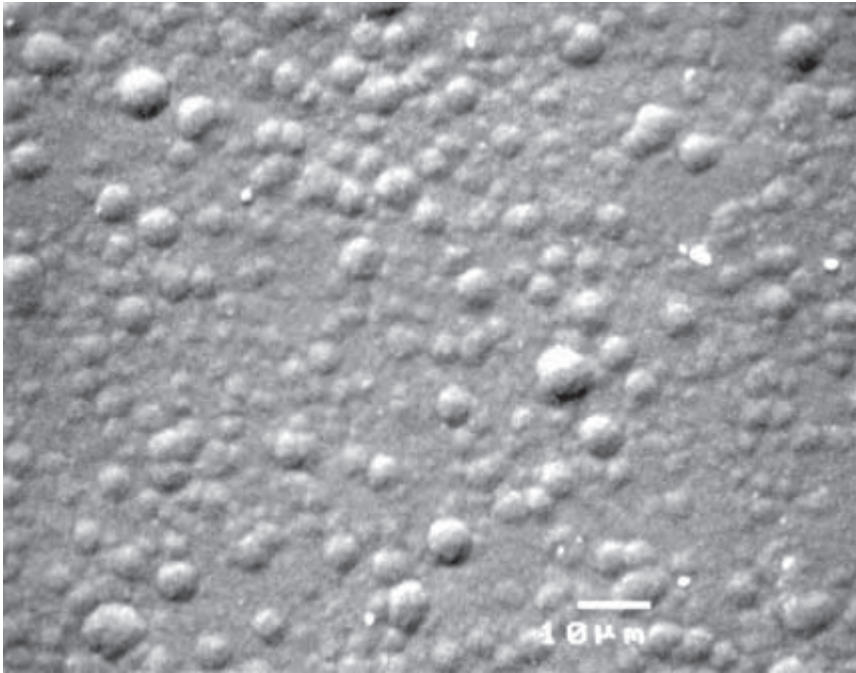
Diamond coatings have also been seen to exhibit a steady-state erosion rate up to 30 times lower than cemented WC (Wheeler and Wood 1999a, 1999b, 2003). Indeed, the superior mechanical properties of the diamond, particularly hardness, compared with the silica sand erodent means that the damage to the particles often exceeds that of the coating. However, subsurface shear stresses, which are generated by solid-particle impingement, are known to affect the integrity of the coating. If these stresses are of sufficient magnitude, coating debonding caused by crack propagation at the coating–substrate interface can be initiated, which can later lead to catastrophic failure of the coating. This debonding of eroded diamond coatings has been observed using scanning acoustic microscopy (Wheeler and Wood, 2001). When the depth of maximum shear stress occurs at, or close to, the coating–substrate interface, rapid failure of the coating can result (Wheeler, 2001). Nevertheless, diamond coatings have the potential to deliver significant increases in the operating life of components such as choke valves used in the offshore oil industry and which suffer from sand erosion (Wheeler *et al.*, 2005). The erosion resistance of CVD diamond has also been exploited in infrared-transmitting windows and domes for aircraft, which are vulnerable from erosion by both liquid-droplet and airborne dust particles.

4.6.8 Diamond-like carbon

DLC is a generic term used to describe a class of amorphous carbon coatings some of which have hardness values approaching those of diamond. The high hardness, together with their low-friction behaviour in many environments, has led to considerable effort to exploit these properties in commercial applications. General reviews of DLC have been given by Lettington (1993), Collins (1998), Gangopadhyay (1998) and Chhowalla (2001). DLC can be produced by PACVD as well as by other methods such as ion plating, laser ablation and ion beam sputtering (Bull, 1995); the following discussion will concentrate on DLC coatings deposited via the PACVD route.

DLC is deposited at lower temperatures than diamond (about 200 °C down to room temperature), which enables a wider range of substrates to be coated, including steel, glass and some polymers. Like diamond, the gases used are CH₄ and H₂. They are dissociated by the plasma that is formed between the two electrodes and the resultant radicals are deposited onto the substrate; deposition rates are typically between 0.5 and 2.0 μm h⁻¹ (Pierson, 1993). Owing to high levels of residual stress, DLC coatings are limited in thickness to no more than 5 μm. DLC coatings are often deposited on an interlayer such as silicon, chromium or tungsten to improve adhesion to the substrate.

An as-deposited DLC coating can be seen in Fig. 4.12. DLC films are amorphous and contain a mixture of sp³, sp² and C—H bonds. It is the pres-

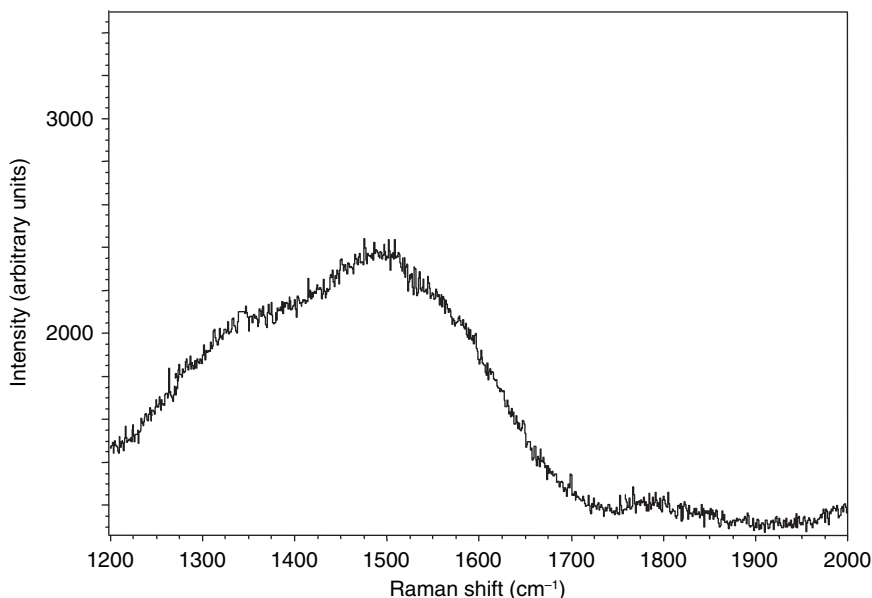


4.12 Micrograph showing the as-grown surface of a 3 μm DLC coating on WC.

ence of the sp^3 bonds that gives the coating its diamond-like character. A typical Raman spectrum for a DLC coating is shown in Fig. 4.13; it can be seen that it differs significantly from that of diamond (see Fig. 4.10). The spectrum consists of a graphite-like peak and a disorder peak in the regions of $1500\text{--}1550\text{cm}^{-1}$ and $1330\text{--}1380\text{cm}^{-1}$ respectively (Karve *et al.*, 2001).

The hardness is dependent on the structure and composition of the films; as a result a wide range of values have been reported, from 20 to 90 GPa (Pierson, 1993). Like diamond, DLC exhibits a low coefficient of friction in air, although this is dependent on the humidity; the friction is seen to increase with increasing relative humidity. In contrast with diamond, some DLC coatings continue to display low-friction behaviour, even under vacuum.

DLC coatings have been used to reduce both the friction and the wear of steel components. Kennedy *et al.* (2003) conducted reciprocating ball-on-flat tests using AISI type 4140 alloy steel under both dry and lubricated conditions. The balls and discs were coated with a DLC film 1 μm thick applied by PACVD. Coating one of the ball–flat combination resulted in a reduction in friction coefficient of between 75 and 85% (from 0.5 to 0.1)



4.13 Raman spectrum of a 3 μm DLC coating on WC.

under dry sliding conditions, while tests where both ball and flat were coated resulted in a further reduction in friction coefficient to 0.08. An even greater reduction in wear was seen where the wear rates of the coated specimens were approximately 200 times lower than those of the uncoated specimens. A similar, if less marked, reduction was also seen in the lubricated tests where the friction and wear were reduced by 50% and 75% respectively. This behaviour has led to its use in a variety of automotive applications including bearing surfaces, gears and internal combustion engine components (notably piston rings).

The low friction and corrosion resistance exhibited by DLC has led to its use as a coating for artificial hip joints. Another application is for tools employed in dry machining (Enke, 1999). However, DLC is unsuitable for use at elevated temperatures owing to its propensity to transform to graphite. Yamauchi *et al.* (2005) coated a magnesium alloy with a 2.5 μm film of DLC by PACVD. The coated specimens were tested under dry sliding conditions in an oscillating ball-on-flat apparatus in contact with an uncoated AISI 52100 steel ball at 150, 200 and 250 $^{\circ}\text{C}$. At all three temperatures the friction coefficient was high and unstable and increased throughout the test from about 0.2 to 0.5; in contrast, tests at room temperature recorded values of approximately 0.2. The increase in friction was attributed to softening of the magnesium substrate. Raman spectroscopy of the worn coatings indi-

cated that the DLC had not transformed to graphite. However, in order to avoid transformation the maximum recommended temperature for DLC is in the region of 300–350 °C.

4.6.9 Tungsten carbide

Although more commonly used in bulk sintered form or as a thermal sprayed coating, WC has also been produced by CVD. Depending upon the growth conditions, the deposited films have consisted of either the monocarbide, WC, or lower carbides such as W_2C and W_3C (Sundgren and Hentzell, 1986). Unlike thermal sprayed WC coatings, the CVD coating has a more uniform microstructure, no binder phase (e.g. cobalt or nickel) and lower porosity, all of which result in enhanced corrosion resistance as well as superior mechanical properties. Depending upon the process conditions, it is possible to deposit WC coatings with hardness values of up to 40 GPa. It is also possible to deposit coatings of up to 100 μm in thickness.

CVD WC coatings are produced by the reaction of WCl_6 and CH_4 at temperatures of between 900 and 1100 °C. However, Archer and Yee (1978) demonstrated that WC films could also be deposited at lower temperatures (325–600 °C) using WF_6 , C_6H_6 and H_2 , thereby enabling deposition on steel substrates to be achieved. At temperatures of between 500 and 700 °C the film growth rate was in the range 0.7–3.0 $\mu\text{m min}^{-1}$. Under these conditions, the coatings were predominantly W_2C with tungsten and W_3C also present. The carbides W_2C and W_3C are harder and more brittle than WC. The process was used to coat components such as journal gas bearings, air plug gauges and extrusion dies.

A relatively recent entrant to the market is the CVD WC coating Hardide. Originally developed in Russia, its manufacturers claim high wear resistance in both abrasive and erosive conditions. In the ASTM G65 abrasion test, the Hardide coating exhibited a wear rate four times lower than that of thermal sprayed WC and 12 times lower than that of hard chrome plate. A similar trend was observed in erosion tests in which erosion rate of the Hardide coating was half that of cemented WC and one third that of steel when tested using Al_2O_3 particles at 70 ms^{-1} (Mitchell, 2004). This performance has led to its application by the oil and gas industry for components such as valves, pumps and drilling equipment.

4.7 Conclusions

This chapter has shown that a wide range of coatings can be produced by CVD. It is instructive to conclude by considering the diversity of components to which CVD coatings have been applied in order to improve their wear resistance. Some examples are given in Table 4.3; this list, which is by

Table 4.3 Applications of CVD coatings in tribological components

Coating	Coating thickness (μm)	Application
TiC	5–8	Stamping and forming tools Cold deep drawing of alloy steels Cold forming of iron alloys Ball bearings
TiN	5–12	Turning of carbon, alloy and stainless steels Cutting, milling and drilling of superalloys and stainless steels Highly interrupted cutting and milling of alloy steels Sheet-metal-forming tools
Al_2O_3	6–8	High-speed extrusion of aluminium Hot and cold forming of steel Heavy-duty turning of cast iron and steel at high speeds Heat- and shock-resistant coating on cemented carbide for milling of forged, cast and corrosion-resistant steels
SiC	100–200	Exhaust paddles on jet engines Mechanical seal†
B_{13}C_2	3–50	Sandblasting nozzles
BP	5–20	Infrared-transmitting windows and domes
Diamond	30‡–1000§	Turning and milling of Al–Si alloys, ceramics and metal matrix composites Cutting of wood-based composites Dental tools Abrasive wheel dressing Surgical blades Mechanical seals
DLC	1–5	Artificial hip joints Machine tools Piston rings Journal bearings
WC	2–100	Extrusion equipment Pumps Ball valves Moulds and dies for ceramic forming

† SiC which is deposited by CVI on to a fibre-woven perform and, therefore, acts as the matrix rather than as a coating.

‡ Deposited directly on to the substrate.

§ Free-standing CVD diamond layer bonded to the substrate.

no means exhaustive, includes components varying in scale from machine tools to moulds and infrared-transmitting windows and domes.

In addition to the examples described above, it is instructive to consider cases where success has not been achieved; the lessons learned from unsuccessful examples can often assist the design process of other coated components. Perhaps the most obvious reason for an unsuccessful coating is poor adhesion. This can arise from a number of factors such as high residual stress, which itself could be due to a large difference between the thermal expansion coefficients of the coating and substrate. Adhesion could also be impaired by chemical incompatibilities between coating and substrate, which could result in the formation of deleterious phases at the coating–substrate interface. Another possible cause could be the presence of porosity or cracking at the coating–substrate interface. An example of poor adhesion is the SiC coating on WC–Co, which was shown in Fig. 4.8. Despite the high hardness of both coating and substrate, a study by the present author found that it offered minimal erosion resistance when impacted by silica sand at a moderate particle velocity (33 ms^{-1}). Individual impacts resulted in the ejection of fragments of the coating following their detachment at the coating–substrate interface.

However, highly adherent coatings can also offer equally poor performance if deposited on to unsuitable substrates. An example of this is the case of BP on stainless steel (Wheeler and Wood, 2005). Despite exhibiting excellent adhesion, the coating was found to offer poor erosion resistance and was rapidly removed by the initiation of radial and lateral cracks, which were caused by the particle impacts. It was thought that the hardness of the substrate was insufficient to offer effective support to the coating. This emphasises the importance of considering the component in its entirety rather than the coating in isolation.

The thickness of the coating is also important. Coatings that are too thin will be unable to withstand the contact stresses generated in the component, which could lead to premature failure (Wheeler and Wood, 1999b). Equally, coatings that are thicker than is necessary are, at best, economically wasteful and may even be detrimental to the performance as the level of the residual stresses is often seen to increase with increasing thickness. Therefore, it is important to understand the nature of the stress field generated in the component under service conditions. An example of this is the depth z_τ of maximum shear stress normalised to the coating thickness C_T . Work by the present author (Wheeler, 2001) has shown that, in erosive wear, rapid failure of the coating occurs when the depth at which the maximum shear stress occurs coincides with the coating–substrate interface (i.e. $z_\tau/C_T = 1$). For this reason, coatings used in erosive environments must be sufficiently thick to ensure that the maximum shear stress τ_m is contained within the coating and is remote from the interface.

4.8 Future trends

In the future, the number of commercially available products incorporating CVD coatings is expected to increase, in terms of both the range of coatings available and the complexity of the components that can be coated. Although many CVD coatings have hitherto demonstrated high wear resistance in laboratory-scale tests, for many components the deposition of highly uniform adherent coatings on to full-scale components of complex geometry is yet to be realised.

In addition to the development of existing coatings, it is expected that the current range of commercially available CVD coatings will be augmented by others that are still at the developmental stage. One of these is zirconia (ZrO_2), which is used as a thermal barrier coating for turbine blades to confer protection from the high service temperatures. Current deposition methods are air plasma spraying (APS) and electron beam physical vapour deposition (EB-PVD). However, the former suffers from high levels of porosity and defects, which can lead to premature failure of the coating, while the line-of-sight nature of the latter process limits coating uniformity and the ability to coat large and complex shapes. CVD has recently emerged as a possible alternative production route, which, if realised, could enable the deposition of thermal barrier coatings at reduced cost. Tu *et al.* (2004) have used metal-organic CVD to deposit yttria-stabilised ZrO_2 coatings from $\text{Zr}(\text{dpm})_4$ and $\text{Y}(\text{dpm})_3$ (dpm = dipivaloylmethanate), while Samoilenov *et al.* (2005) have used the acetylacetonates of zirconium and yttrium to deposit coatings up to $20\mu\text{m}$ in thickness. A different approach has been adopted by Goto (2005) who used a laser CVD process, enabling deposition rates in the region of $660\mu\text{m h}^{-1}$ to be attained, which is comparable with the deposition rates in APS and EB-PVD. The potential applications for CVD ZrO_2 are not limited to turbine blades; its high wear resistance (Soderberg *et al.*, 2001) also makes it a potentially attractive coating for applications such as machine tools.

Another CVD coating that could emerge in the near future is c-BN. The second-hardest material after diamond, c-BN has been used in sintered form for many years in the machining of ferrous metals. However, although the softer forms of hexagonal boron nitride (h-BN) and amorphous boron nitride (a-BN) have been produced by CVD, efforts to deposit c-BN have been hampered by the high compressive residual stresses, which cause coatings greater than 200nm in thickness to delaminate. In the last few years, researchers have reported some success in reducing the stresses in c-BN films. Matsumoto and Zhang (2001) used an $\text{Ar-N}_2\text{-BF}_3\text{-H}_2$ mixture in a DC jet plasma CVD system. Coatings of over $20\mu\text{m}$ in thickness were deposited onto silicon substrates and the compressive residual stresses were between 1.0 and 2.3 GPa, which were considerably lower than the previ-

ously reported values of between 4.0 and 20 GPa. Zhang *et al.* (2004) have reported the deposition of c-BN films onto silicon substrates with CVD diamond as an interlayer. Using an He–Ar–N₂–BF₃–H₂ gas mixture in an electron-cyclotron-resonance microwave plasma CVD system, they deposited coatings of up to 20 µm in thickness. Film growth was aided by the presence of fluorine, which preferentially etched the non-cubic BN phases, leaving a purely c-BN deposit. Transmission electron microscopy revealed the epitaxial growth of the c-BN on the diamond layer. Most recently, Bello *et al.* (2005) coated a WC cutting tool insert with a 1 µm c-BN layer with a 6 µm diamond interlayer. The coated inserts were tested by milling a mild steel plate. Although the tool failed, failure took place in the substrate rather than in the coating. Therefore, although this work is still at the early stages, it shows the potential of c-BN as a tool coating.

Another group of coatings that have emerged over the last decade are the nanocrystalline–amorphous composites. These coatings, the concept of which was first suggested in the mid-1990s by Veprék and Reiprich (1995), consist of nanocrystals of refractory metal nitrides (TiN, ZrN, NbN, VN, W₂N, etc.) less than 10 nm in size in an amorphous Si₃N₄ matrix. The microstructure has been shown to confer hardness and elastic modulus values of up to 50 GPa and 500 GPa respectively for films 4–5 µm in thickness (Veprék *et al.*, 1996), owing in part to the high coherency strains at the interfaces between the amorphous and crystalline phases. The coatings were deposited by PACVD at temperatures of between 500 and 550 °C, which allows deposition on steel substrates. Under these conditions, deposition rates of 2.2–3.6 µm h^{−1} have been reported (Veprék *et al.*, 1996). Other similar coatings include nanocrystalline (nc)-TiN/a-BN and nc-TiN/a-BN/a-TiB₂ (Karvankova *et al.*, 2003, 2005). The optimum properties appear to be achieved in coatings with a crystallite size of approximately 3 nm with the nanocrystals separated by one monolayer of amorphous Si₃N₄ or BN. Some of these coatings have exhibited hardness values approaching those of diamond. Veprék *et al.* (1998) reported hardness values of 65–70 GPa for a nc-TiN/BN coating produced by a combined PACVD–PVD process, while the same workers recorded values of 80–105 GPa for ternary and quaternary nc-TiN/a-Si₃N₄/a-TiSi₂ and nc-TiN/a-Si₃N₄/nc-TiSi₂ (Veprék *et al.*, 2000). It is clear that these coatings show great promise as potential coatings for machine tools. However, much work remains to be done and it may be some time before they complete the journey from the research laboratory to the production plant.

4.9 Sources of further information

A large body of literature exists on CVD ranging from research papers to books and conference proceedings. One of the earliest books is *Vapour*

Deposition by Powell *et al.* (1966), which remains a useful reference text. More recent publications include those edited by Hitchman and Jensen (1993) and Park and Sudarshan (2001). In addition to this, there are a number of extended reviews such as those by Bryant (1977), Hampden-Smith *et al.* (1998) and Choy (2003). CVD has also been the subject of two long-running series of conferences. The 1st International Conference on CVD was held in 1967, while the 1st European Conference was held a decade later. The most recent proceedings are from the joint meeting incorporating the 16th International and 14th European CVD Conferences held in 2003 (Allendorf *et al.*, 2003).

CVD coatings are available from a number of suppliers including Sandvik, Iscar, Element 6 (formerly De Beers Industrial Diamonds Ltd) and Hardide. Suppliers of CVD coating equipment include IonBond (formerly Bernex), Archer Technicoat and Surmetal AG.

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Physical vapour deposition methods for protection against wear

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5.1 Introduction

Coatings produced by physical vapour deposition (PVD) in which the coating vapour flux is created by a physical process such as evaporation or sputtering from a solid target have been available since the technology necessary to sustain the required vacuum was developed. The earliest PVD coatings were produced by evaporation of wires by Michael Faraday in the nineteenth century but the quality of the coatings was low and they were only a scientific curiosity until the development of better vacuum equipment. The first sputtered coatings were identified by Grove¹ in the middle of the nineteenth century in a study of fluorescent tubes, and sputtered coatings were subsequently used to make mirrors until the 1930s. The development of diffusion pumps in the 1920s made it possible to evacuate a deposition chamber to a low enough pressure for controlled vacuum evaporation. Indeed coatings produced by simple vacuum evaporation are still widely used in applications ranging from barrier layers for food packaging to mirror reflectors. Although evaporated metal coatings have been used in some tribological applications, such as to lubricate threads on fasteners for the food industry, it has been the development of more advanced PVD processes enabling compound and ceramic coatings to be deposited with a high density which has revolutionised the PVD wear-resistant coatings market.

Current tribological coatings deposited by PVD fall into three groups.

1. Hard wear-resistant ceramic layers.
2. Soft solid lubricant coatings.
3. Multilayer or composite coatings.

The same coating may often be deposited by a range of deposition technologies and in each case the deposition technologies have to be optimised to deliver coatings with acceptable performance. Whereas optimised coatings from conventional deposition technologies such as electroplating are

very similar, a major factor in the selection of PVD coatings is that their properties may vary from deposition technology to deposition technology even after optimisation and it is important that the material and coating process are treated together if successful products are to be developed. Failure to take this into consideration may lead to failures which could be avoided. It is therefore necessary to know something of the fundamentals of the different deposition technologies to enable correct coating selection.

This chapter will briefly introduce the fundamentals of the PVD process, the commercial deposition technologies available, the typical coating materials and several tribological applications.

5.2 Fundamentals of physical vapour deposition

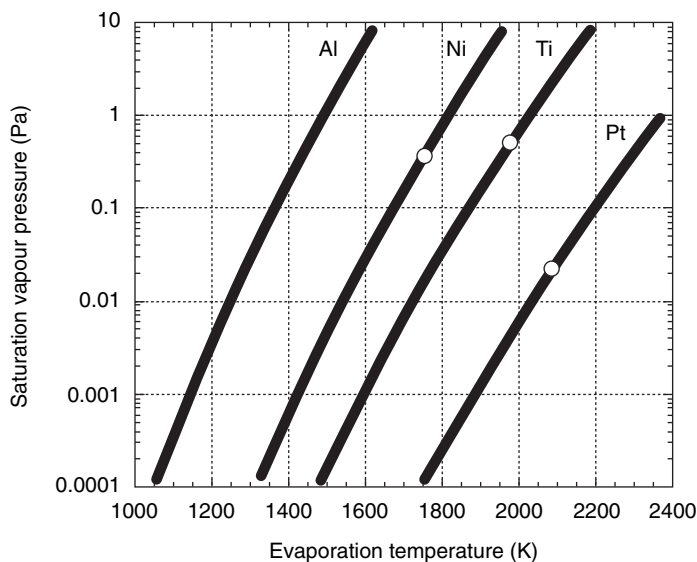
The PVD coating process involves deposition of the coating on an atom-by-atom basis from the vapour phase. There are four important stages to this.

1. Production of the vapour flux by a physical process (evaporation or sputtering).
2. Transfer of the coating atoms from target to components through the gas phase.
3. Deposition of the coating elements on the component surface.
4. Incorporation of coating atoms into the layer.

The following sections consider these in more detail.

5.2.1 Evaporation

Perhaps the easiest way to convert a solid material into a vapour flux is by evaporation. If the target material is heated, its vapour pressure will increase and at a critical temperature will exceed the ambient pressure and vapour will stream away from the target. Figure 5.1 shows the typical variation in vapour pressure with increasing temperature for a range of chemical elements. The vapour pressure increases with increasing temperature for all elements but there is a considerable variation in vapour pressure between different elements related to their melting temperature. Thus to develop a reasonable coating flux without an extreme heat input into the target it is usual to carry out the process under vacuum (typically 10^{-5} to 10^{-6} torr). The large variability in vapour pressure with element type² means that it is often very difficult to maintain the stoichiometry of alloy or compound systems during evaporation. Evaporated atoms are typically ejected with energies of less than 1 eV and remain charge neutral in the absence of plasma activation (see Section 5.2.3).



5.1 Variation in the vapour pressure with the temperature for several metallic elements.

A number of methods of heating have been developed for evaporation systems including resistive heating, electron beam heating, arc heating and plasma heating. In some commercial coating systems the solid metal to be evaporated is held in a water-cooled crucible to prevent contamination of the target and the heating is localised to the target region only (e.g. by steering of the electron beam in electron beam evaporation). In other systems a crucible or resistance heating support structure is used which does not chemically react with the material to be evaporated (e.g. TiB_2 boats for aluminium). In such cases a pelletised target charge may be placed in the boat which is then heated slowly until evaporation commences, but in some high-rate applications such as the metallising of polyester film for barrier layers in food packaging the metal to be evaporated is fed on to a hot boat in the form of a wire and the coating flux is produced by flash evaporation. This latter technique allows the highest coating rates, and good uniformity over large areas can be achieved using multiple wire feeds.

Metal coating rates produced by evaporation can be up to hundreds of micrometres per minute in some cases which makes the technique competitive with many other deposition technologies. However, rates are much reduced if compounds are evaporated.

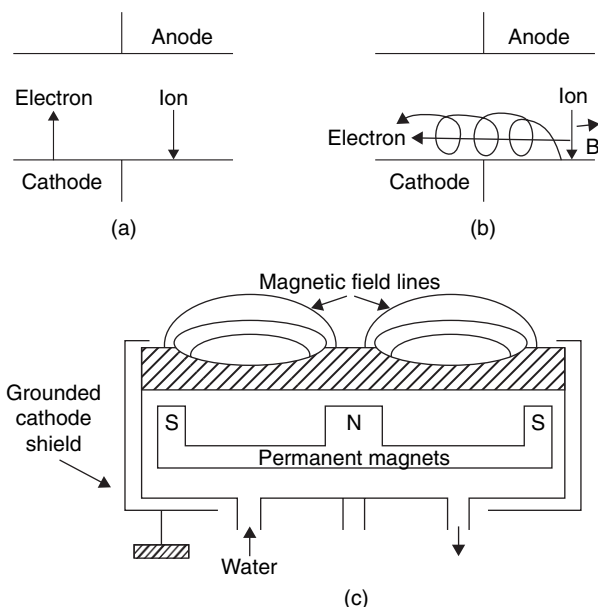
5.2.2 Sputtering

In the sputtering process the target is bombarded by heavy ions such as argon, and target atoms are ejected into the gas phase owing to the momentum transfer from the bombarding species. The ion bombardment can be created by the interaction of a plasma or ion beam with the target surface, both of which require operation in vacuum. Typically cathode sputtering takes place in an inert gas at a pressure of 10^{-2} to 10^{-1} torr and an applied potential of 500–1000 V. Electrons leave the negatively biased cathode and accelerate towards the anode, impacting with inert gas atoms in the coating chamber, ionising them and creating a glow discharge. The positively charged inert gas atoms are attracted to the cathode, causing sputtering on impact. A single high-energy ion of defined energy generally creates a fixed number of sputtered atoms given by the sputtering yield (Table 5.1) which is independent of temperature.³ The variation in sputtering yield with atomic number is much less than the variation in vapour pressure and for this reason it is easier to deposit alloys and to maintain compound stoichiometry using sputtering.⁴ However, the rate of coating flux production is generally lower with sputtering than with evaporation unless steps are taken to maximise the intensity of ion bombardment. For plasma-based systems this means increasing the plasma density close to the target which is conventionally achieved by the use of magnetic fields from magnets placed behind the target, the magnetron in Fig. 5.2.⁵ For ion-beam-based systems a high-beam-current ion source is required which can be focused on the target.⁶

Sputtered atoms are ejected with a range of energies that are related to the energy of the bombarding ion. For typical process conditions the mean energy⁷ of the sputtered atoms is around 10 eV. Only about 1% of the sputtered species is charged.

Table 5.1 Sputtering yields of some elements used in tribological coatings as a function of argon ion bombardment conditions

Target	Metal sputtering yield (atoms ion ⁻¹) for the following in energies				
	200 eV	600 eV	2000 eV	5000 eV	10000 eV
Silver	1.6	3.4			8.8
Aluminium	0.35	1.2			
Carbon	0.05	0.2			
Chromium	0.7	1.3			
Niobium	0.25	0.65			
Titanium	0.2	0.6	1.1	1.7	2.1
Tungsten	0.3	0.6		1.1	
Zirconium	0.3	0.75			



5.2 Comparison of sputtering processes in (a) simple direct-current (DC) sputtering (DC diode system) and (b) magnetron sputtering (DC magnetron system). (c) Magnetic arrangement in a magnetron cathode.

Simple sputtering methods suffer from two main drawbacks when compared with conventional evaporation: low coating rates and a high thermal load of the substrates due to bombardment by secondary electrons. By using a magnetron source it is possible to confine the electrons close to the cathode surface by means of a magnetic field, increasing the plasma density and reducing the electron heating of the substrates. Coating rates may be increased by an order of magnitude by this method.⁷ Lower discharge voltages are required since the plasma impedance is reduced by its higher density. Cooling of magnetron cathodes is essential to achieve the highest coating rates but this highlights the low electrical efficiency of the process because as much as 90% of the power supplied to the cathode is lost in heating the cooling water.

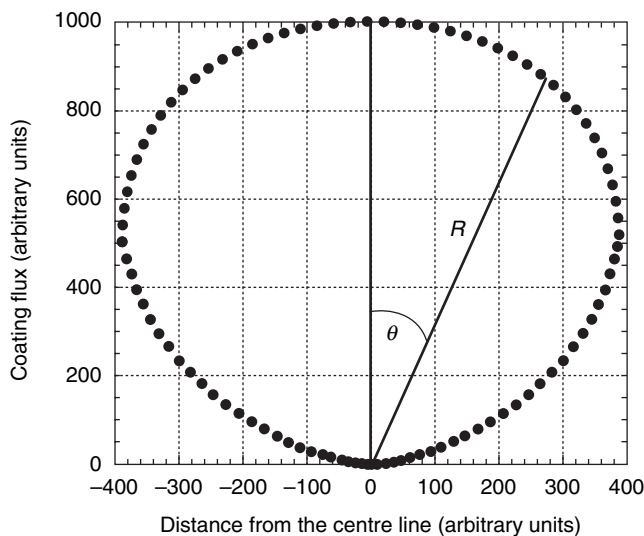
5.2.3 Vapour transport

In an ideal system, once the coating flux has been produced, it streams out into the vacuum chamber and travels in a straight line until it encounters the components, the chamber walls or the sample supports where it condenses to form a deposit. However, in practical systems the ambient pres-

sure is not always low enough for this to happen and the mean free path between collisions with the residual gas in the system is less than the distance between target and samples. Some gas scattering will therefore occur. Indeed, close to the targets where the coating flux originates, the local pressure will be higher and gas scattering between coating atoms is likely to occur. This can exacerbate the changes in stoichiometry in the evaporation of compound targets, as lighter atoms will tend to be scattered more than heavier atoms.

One advantage of gas scattering is that the direction of the coating flux is slightly randomised, enabling three-dimensional objects to be coated to a certain extent. In the absence of scattering, the coating flux will tend to deposit on the side of the components facing the target but, with scattering, some coating may be found all over the component, even if it will be thickest closest to the target. A more uniform coating can be produced using multiple sources or by manipulating the components in the vacuum system so that all sides face the target for an equivalent time during the coating cycle.

Since the source of coating flux tends to be small compared with the cross-section of the volume occupied by the components, the vapour flux tends to spread out as it is transported into the chamber. The flux distribution follows an approximately cosine-squared distribution (Fig. 5.3). This means that a flat component mounted at a fixed distance from the source



5.3 Variation in the coating flux R with the angle θ . The distribution is approximately $\cos^n \theta$ for many coating systems where $n \approx 2$ but varies with the process parameters.

will show a variation in thickness unless it is rotated in an appropriate fashion. Component manipulation must be optimised to avoid such thickness variations.

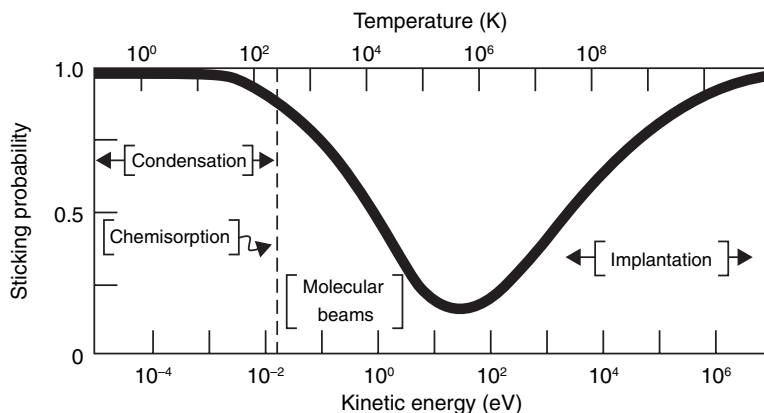
In some systems the coating flux passes through a region of plasma where some of it becomes ionised. The plasma is generated either by the coating process itself (e.g. in sputtering) or by auxiliary electrodes which are independent of it. This can help to densify the coating and to improve its properties (see Section 5.2.4). The proportion of the flux which is ionised by this method is usually very low (about 1%).

5.2.4 Coating deposition

When the coating flux encounters the components (or the chamber walls or other chamber furniture) it will condense and form the coating layer. A single coating atom will land somewhere on the substrate and then can move a short distance until it finds a site where it can become incorporated in the coating. The mobility of such an adatom depends on the substrate temperature and the energy of the arriving coating atom. For low-energy adatoms, such as those produced by evaporation, the mobility is low and the atom remains close to where it was first deposited. For this reason, vacuum-evaporated coatings are often porous and defective and have poor mechanical properties. The higher energy of the arriving sputtered atom generates greater mobility and denser coatings at the same substrate temperature. However, even this energy may not be enough to densify the film fully except at very high substrate temperatures.

A common method to avoid this problem is to use ion bombardment of the growing coating during deposition, a process which is known as ion plating.⁸ A small negative bias voltage is applied to the components (which must be conducting) which attracts the ions from the coating flux that bombard the coating surface as it is deposited. The energy transferred to the surface increases adatom mobility and the momentum transfer from the ion beam can densify the material significantly. Ion plating can also result in interfacial mixing and improvement of coating adhesion and tends to reduce the grain size of the coating, improving its hardness and fracture toughness. In addition, impurities may be resputtered from the surface of the growing coating, improving the purity of the deposited film.

The energy of the arriving ion is critical in dictating what happens to it once it arrives at the surface (Fig. 5.4). At low energies, the sticking coefficient is close to one and the ion will come to rest on the surface of the coating where it lands. As the energy increases, the sticking coefficient is reduced and the ion has sufficient energy to move around and escape from the surface if it does not find a structural site. At the ion energies produced by typical bias voltages used for PVD hard coatings (about -100 V) an ion



5.4 Variation in the sticking coefficient with the energy of the bombarding ion.

arriving at the substrate often has the lowest probability of sticking. As the ion energy increases above this, it has sufficient energy to sputter coat atoms and to create defects in the coating. Initially these defects are created in the surface layer of atoms and can be refilled by subsequent coating flux but, at higher energies, subsurface defects may be created (vacancies and interstitials) which remain in the coating during subsequent growth and are responsible for growth stress generation. Such defects are also created by ion implantation where again the sticking coefficient approaches one if the ion energy is high enough.

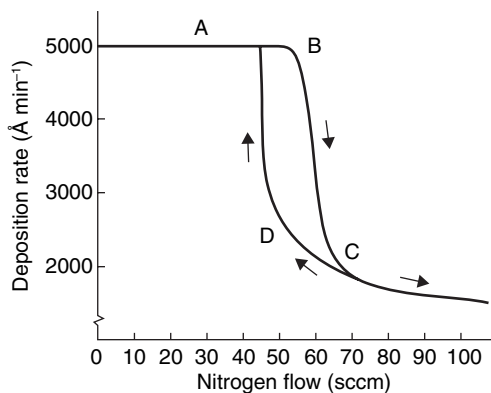
5.2.5 Reactive deposition processes

Reactive gases may also be added to the chamber in order to maintain the stoichiometry of compound coatings or to form compound coatings from metallic targets. Since the evaporation or sputtering rate of compounds is much less than that of the metallic elements that they contain, this is a way of increasing the coating rate, but the process control must be very precise to take advantage of this.

Direct evaporation is usually considered effective and reliable for metals but for ceramic materials is difficult because of their high melting points, low vapour pressure and tendency to dissociate. Consequently reactive methods are best employed to obtain stoichiometric coatings of carbides, nitrides or oxides, the metal being evaporated in the presence of an appropriate gas such as methane, nitrogen or oxygen.⁹ Activated reactive evaporation (ARE) operates at a pressure in the range 10⁻⁴ to 10⁻³ torr when a glow discharge is initiated by the incorporation of an anode in the coating chamber which ionises and increases the reactivity of the gas species.¹⁰

Figure 5.5 shows the variation in coating rate with the mass flow of the reactive gas into a sputtering chamber. It is clear that, on increasing the amount of reactive gas supplied to the system, the coating rate is reduced once a certain gas flow is achieved and drops to a lower plateau value at high gas flow. This represents the change from the coating rate of the pure metal to the coating rate of the compound. On reducing the reactive gas flow the change back to the metal coating rate occurs at a lower gas flow than on increasing and a noticeable hysteresis is produced. Control of the process by gas flow alone is therefore very difficult.

The reason for this behaviour is associated with what happens to the gas when it enters the chamber. The gas that is introduced can end up reacting with the deposited atoms to make the coating as required but some of it will react with the surface of the target to form a compound layer if the partial pressure of the gas in the chamber is high enough. This process is called target poisoning. If such a compound layer forms on the target, the sputtering yield drops and the coating rate is reduced. Reducing the partial pressure of reactive gas after this may not have an immediate effect as the compound layer needs to be sputtered from the target before metal behaviour is re-established. The amount of reactive gas required is therefore just enough to enable the desired coating to be produced, but in doing so it must be accepted that some target poisoning will occur and this must be limited if the highest coating rates are to be achieved.



5.5 Variation in the coating rate with the mass flow of reactive gas, in standard cubic centimetres per minute (sccm), into the chamber during magnetron sputtering of TiN. At A, no target poisoning occurs and the coating rate is high but stoichiometric TiN is not produced. At B, stoichiometric TiN is produced but target poisoning starts and the coating rate drops. A small increase in gas flow leads to a dramatic drop in coating rate at point C. Reducing the gas flow does not increase the coating rate until D when the poisoned target begins to clear.

In order to reduce the effect of target poisoning most commercial sputtering systems use some sort of partial pressure control based on analysis of the plasma in front of the target by atomic emission spectroscopy.¹¹ A piezovalue system can be used to let just enough reactive gas in to maintain the intensity of the metal emission line to limit target poisoning, but the gas inlet is placed closer to the components so that a coating of the correct stoichiometry is produced.

5.2.6 Deposition of alloy, compound and multilayer coatings

Compounds and alloys may be evaporated as well as elements but in general the composition of the coating is not the same as the source material because the vapour pressures of the different constituents are not the same and compound targets may dissociate on evaporation. In many cases, source alloys of one well-defined composition are developed which produce an alloy of a different desired composition when evaporated.¹² If the alloy contains elements with widely different vapour pressures, such as NiAl, this may be very difficult to achieve and the difficulty increases as more alloying elements are added. For this reason, evaporation is generally only used for simple alloys and compounds. The stoichiometry of compound coatings is often maintained by backfilling the chamber with a controlled partial pressure of an appropriate gas; for instance oxygen backfills are necessary to maintain the stoichiometry of evaporated oxide coatings.¹³

Producing conducting coatings such as metals or some transition-metal nitrides by sputtering is relatively straightforward by reactive sputtering from metallic targets. However, the quality of the target is very important to achieve this. Small non-conducting insulating inclusions such as oxide particles can lead to localised arcing on the target. For this reason, sputtering power supplies have been developed with good arc suppression circuitry and pulsed operation. Indeed it is now possible to deposit insulating oxide coatings by DC sputtering from metallic targets due to the development of high-specification solid-state power supplies (see for example Scholl¹⁴).

Traditionally insulating coatings have been produced from insulating targets using radio-frequency (RF) sputtering. RF plasmas are much more difficult to control than DC plasmas and insulating machine components from each other represents a more difficult problem. Complex component manipulation in RF systems is not possible for this reason and RF sputtered coatings are usually only deposited on to relatively simple component geometries. There is generally a change in stoichiometry during RF sputtering; for instance, oxides tend to lose oxygen and the stoichiometry of the coating is maintained by the use of an oxygen backfill in the deposition chamber, as mentioned previously.

One advantage of the sputtering process for producing alloy or complex

compounds is the fact that the sputtered atoms become intimately mixed in the gas phase and it is not necessary to have a target with the exact composition of the intended coating. Rather a compound target may be made with areas of different material added as inserts, or a powder target produced by mixing and pressing powders to achieve the correct average composition. After sputtering, the coating has a uniform composition which is close to that of the average target composition since sputtering yields do not vary much for different elements. This approach can be used to determine very rapidly the correct target composition required to deliver a specified coating. For this reason, more complex alloys and compound coatings are generally deposited by sputtering.

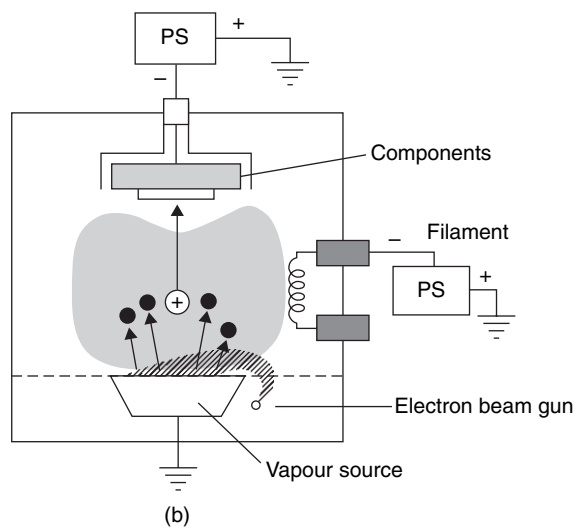
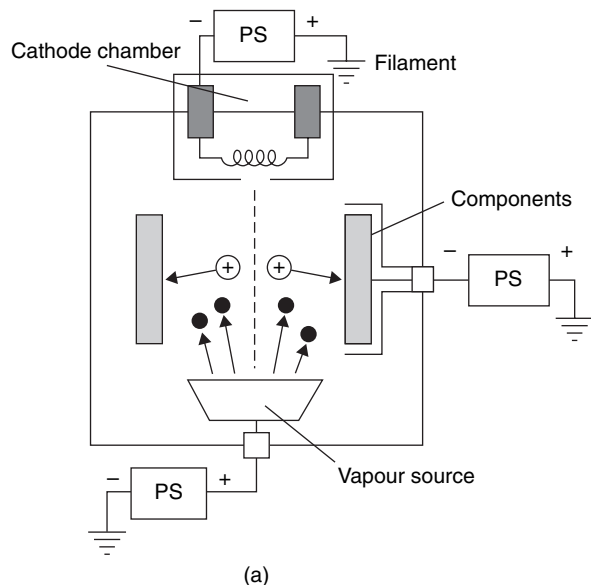
Multilayer coatings with different constituents can be produced by all PVD processes and are a subject of considerable current research. Multihearth evaporation systems have been used to create metallic multilayers by swapping the electron beam heating between hearths after preset intervals.¹⁵ Also rotating shutters have been used to control the arrival of the coating flux at the substrate. Commercial sputtering systems usually have two or more sputtering targets which may be arranged to deposit different layers. The components are rotated in front of each target in turn and a layered coating structure can be built up by control of the sample rotation system.

5.3 Commercial physical vapour deposition processes

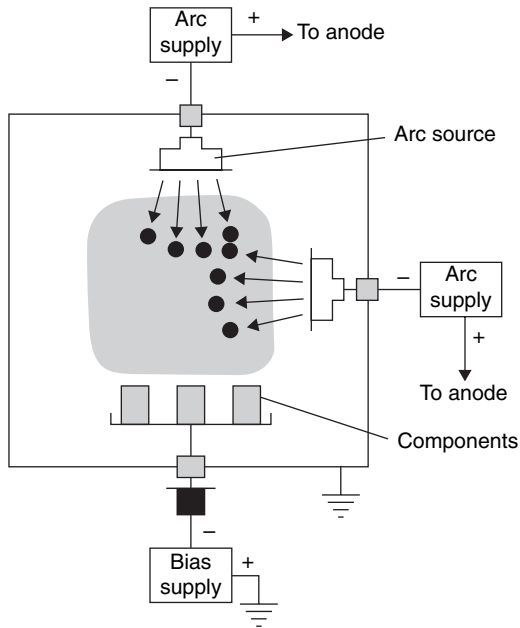
Many different PVD processes have been developed for applications including microelectronics and optics but the major developments in tribological coatings have occurred since the 1970s when Bunshah and Raghuram⁹ demonstrated the potential of TiC and TiN coatings by ARE and the Balzers company introduced the first commercial PVD TiN coating service. Since that time a number of suppliers have marketed commercial PVD coating systems aimed at tribological applications which have had some success in the marketplace. However, some suppliers produced coatings of insufficient quality in the early days and it is now the case that only a few commercially viable processes remain, which are discussed in more detail in this section. All these processes are ion-plating processes, since it is essential that tribological coatings are dense and well adhered to the substrate.

5.3.1 Thermionic arc ion plating

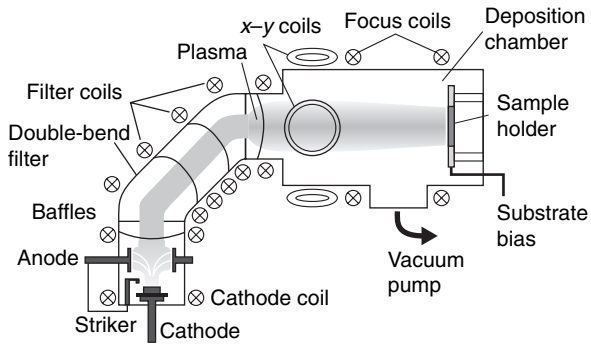
The first commercial PVD technology for tribological coatings was introduced by the Balzers Company in the late 1970s (Fig. 5.6(a)). The system uses a medium-pressure electron source operating almost in an arc mode to create a beam of electrons which passes through the coating chamber to



5.6 Commercial PVD deposition technologies (PS, power supply):
(a) Balzers; (b) Tectvac; (c) arc evaporation; (d) filtered arc evaporation;
(e) closed-field unbalanced magnetron sputtering; (f) ion-beam-assisted deposition.

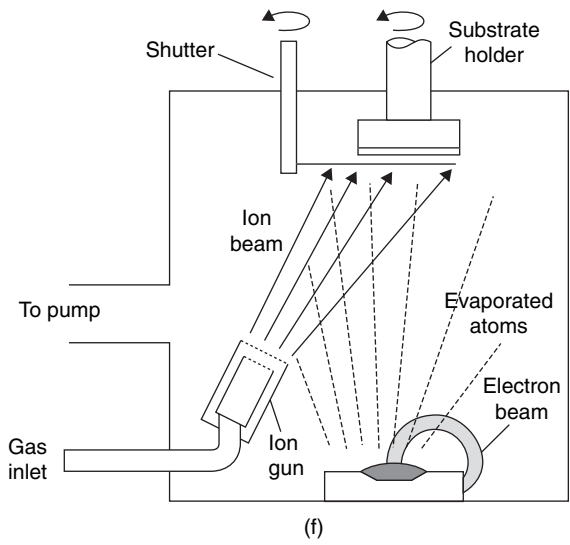
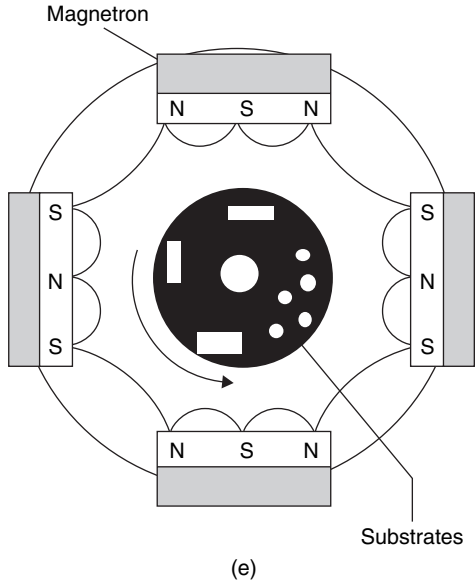


(c)



(d)

5.6 Continued



5.6 Continued

impinge on the crucible.¹⁶ The net effect is to increase the ionisation in the coating chamber. The specimens are heated by electron bombardment before coating, a unique feature of the Balzers process. This is achieved by making the substrate holders and thus the substrates themselves the anode of the arc discharge; sufficient uniformity can be achieved by magnetic dispersion.¹⁷ It is believed that the hearth is reciprocated vertically during coating to achieve a greater coating uniformity. Components are mounted around the perimeter of the chamber and are rotated during coating.

5.3.2 Thermionically assisted triode ion plating

If the evaporation system is operated at lower pressure, a higher-energy electron gun may be used.¹⁸ This is the principle of the Tecvac process (Fig. 5.6(b)), which uses a low-pressure electron beam gun system to evaporate the target and partially to ionise the coating flux, and additional thermionic assistance from a tungsten filament to enhance the discharge.¹⁹ This gives improved control of the process by ensuring that variables can be independently changed. These features permit argon ion bombardment of the components before coating (for heating and surface cleaning) without the need to have the vapour source in operation. The thermionically assisted triode ion-plating system was developed by Baum²⁰ and has the additional advantage that substrate heating is reduced compared with diode discharge techniques. The aim of this is to achieve a high ion current at the sample surface during coating but to minimise the ion energy so that the damage to the coating during deposition is minimised.

5.3.3 Arc evaporation

A technique which is widely used around the world is arc evaporation which is based on technology developed and patented in the USA and the USSR during the 1960s. The principle of the arc source is very simple. A metal cathode is configured so as to operate in arc mode (i.e. a low-voltage high-current discharge). The arc, once initiated, emits a dense metal plasma whose ions have high intrinsic energies. One or more arc spots are formed which move randomly over the cathode surface with velocities of the order of 10ms^{-1} . Typical spot diameters are of the order of $10\mu\text{m}$, giving current densities per spot of 10^6 – 10^8A cm^{-2} . The arc has a lifetime of the order of 10ns and, once it is extinguished, a new arc forms near the former arc, leaving a string of small craters. It is believed that no molten pool is formed on the source, which can thus be operated in an inverted orientation. This allows several arc cathodes to be fitted in a single chamber for greater coating uniformity (Fig. 5.6(c)). The plasma conditions lead to increased ionisation of metal and non-metal species.

Ignition of the arc is normally realised by shorting the arc circuit either by using a mechanical contact at the cathode surface or by using a metallic coating on the insulating border of the cathode, forming a conducting connection to an ignition electrode which can be momentarily shorted to the anode.

One problem of the arc source is that metal droplets can be ejected from the target by the passage of the arc which may become embedded in the coating. These droplets have diameters up to $3\mu\text{m}$; their number and size decrease with increasing target melting point, increasing spot velocity and increasing target contamination.²¹ One method to avoid this is the steered-arc technology of Hauser Techno Coatings, in which a magnetic field is used to speed up the motion of the arc.²² This leads to a reduction in macrodroplet formation but also a reduction in coating rate. Another method is to use a filtered-arc deposition system (Fig. 5.6(d)) in which the charged particles ejected in the arc are bent by a magnetic field before injection into the coating chamber and the droplets are captured on the filter walls harmlessly.²³ Again the deposition rate is reduced. However, good process control in the simple arc process can be enough to reduce macrodroplet deposition to an acceptable level for many tribological applications.

5.3.4 Unbalanced magnetron sputtering

Commercial sputtering systems generally contain two or more sputtering cathodes arranged around the edge of the chamber with the components to be coated at its centre. The chamber walls provide the anode for the discharge. Simple DC sputtering systems have been developed to coat tribological components such as the sputter ion-plating process developed at Harwell in the 1970s but the coating rates produced by such systems were unacceptably low when compared with those in evaporation-based systems.²⁴ More competitive systems were generated with the introduction of magnetron sputtering systems for hard coatings. Initially these were of the balanced type where the field strength of the magnets was controlled to isolate individual magnetrons from their neighbours and to keep the dense plasma just in front of the target.²⁵ This technique produced coatings at high rate but with inferior properties compared with coatings produced by competing systems. This was due to the low levels of ionisation of the coating flux and the low ion current at the component surface during deposition. The solution to this problem was to unbalance the magnetron with a stronger magnet at its centre to allow some of the plasma to extend out away from the target towards the components.²⁶ This can be achieved by shaped permanent magnets, as in the coatings systems developed by Monaghan *et al.*,²⁷ or by electromagnets in the system developed by Münz.²⁸ Placing several unbalanced magnetrons of appropriate polarity in the same system leads to the

closed field unbalanced magnetron sputtering system pioneered by Teer Coatings (Fig. 5.6(e)) in which the electrons are trapped inside the coating volume by the magnetic flux lines linking the targets. By such an approach it is possible to produce high-quality hard coatings at rates comparable with that achieved by evaporation-based PVD processes.

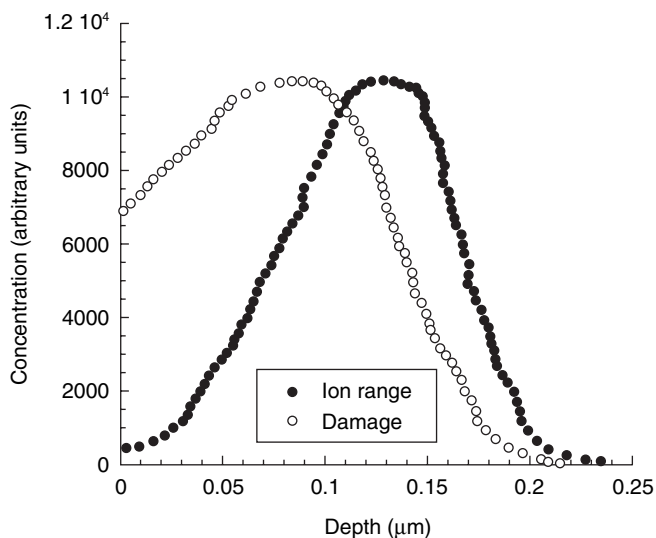
The benefits of arc evaporation and sputtering have been combined in a single system in the arc bond sputtering process due to Münz *et al.*²⁹ This process uses the arc sources in the initial etch step to ensure excellent adhesion of a subsequently magnetron-sputtered coating. This greatly reduces the duration of the etch step and improves the density and adhesion of the sputtered coating.³⁰

5.3.5 Ion beam processes

Ion implantation

Unlike the processes described above, ion implantation does not generally result in the growth of a coating on the surface but it does result in the modification of surface properties and can be used to improve the tribological performance of components. The process involves the injection of a chosen atomic species in the form of an accelerated ion beam into the surface of the material to be treated.³¹ Since the ions have a high velocity, they penetrate into the substrate and lose energy in a number of elastic and inelastic collisions with the sample atoms, eventually coming to rest with a slightly skewed Gaussian distribution (Fig. 5.7). Potential differences of 50–200 kV are commonly used for acceleration of the ions. In tribological treatments for steel a beam of nitrogen is often used and at a typical energy of 100 keV the peak of the Gaussian distribution lies about 100 nm below the surface and the total thickness of the treated layer is less than 250 nm. This is an extremely shallow depth compared with most PVD coatings developed for tribological protection which have a thickness of 1–10 μm . Nevertheless, significant improvements in component performance can occur.

Commercial ion implantation systems consist of an ion source from which the beam is extracted and accelerated, a beam transport system which may involve mass separation and electrostatic scanning and a sample chamber. The process is essentially line of sight and the components must be manipulated in front of the ion beam to ensure treatment on all surfaces. Semiconductor ion beam systems use magnets to separate individual isotopes of the element to be implanted and are highly controlled to deliver uniform low-dose treatments (e.g. $1 \times 10^{14} \text{ B cm}^{-2}$ in silicon). However, the typical ion doses needed to improve tribological performance (e.g. 4×10^{17}



5.7 Distribution of 90 keV nitrogen ions implanted in silicon and the damage that they cause.

ions cm^{-2} for nitrogen treatment of steel) require much higher beam currents to be economic and the mass separation is usually dispensed with. In such cases the ion source can be mounted in the wall of the sample chamber.³²

Ion-beam-assisted deposition

All the commercial deposition technologies described previously rely on excellent control of the energy and flux of the ions arriving at the sample during coating. In traditional PVD processes these ions are provided by a plasma and control of the distribution of ion energy and flux is achieved by control of plasma parameters. Owing to gas-phase collisions and the difficulty of defining the plasma volume accurately the level of control possible is limited. One solution to this problem is to replace the plasma with an ion beam in a process known as ion-assisted coating or ion-beam-assisted deposition.³³

In the ion-beam-assisted deposition process (Fig. 5.6(f)) the coating flux is made by a conventional PVD process, sputtering or evaporation and transport across the coating chamber occurs in the normal manner. However, an ion source is mounted in the chamber so that a beam of ions can impinge on the components as the coating grows. The ion source is usually a

relatively low-energy high-current-density source (e.g. a Kaufman source) which provides a similar intensity of ion bombardment to that achieved in a plasma-based coating system.³⁴

In dual-ion-beam sputtering, two ion beams are used. The first is a large-area high-current ion source which is directed at a target and is used to sputter material into the gas phase and the second is a lower-energy ion beam which is used to densify the coating when it is deposited on the substrates. In another variation on the ion-beam-assisted deposition process a low-vapour-pressure liquid is evaporated and condenses on the substrate and is converted to a hard coating by irradiation with a high-energy ion beam of the type which is usually used for ion implantation.³⁵

If the bombarding ions penetrate to the interface of the growing coating, intermixing can take place which greatly enhances coating adhesion. Alternatively it is possible to mix a thin coating with the substrate, a process known as ion-assisted coating. The controlled ion bombardment in ion-beam-assisted deposition during growth of the coating can produce dense coatings with a fine grain size and excellent mechanical properties at lower deposition temperatures than are conventionally used in PVD processes and this makes the process suitable for coating temperature-sensitive substrates.

5.4 Coatings for wear resistance

A range of PVD coatings is used for tribological applications. The most important coatings and their properties are summarised in Table 5.2 and are discussed in more detail in the following sections.

5.4.1 Hard coatings

Good tribological performance for hard coatings was initially demonstrated for TiC layers deposited by ARE.⁹ Similar CVD coatings were in service on cutting tools at the same time but the PVD coatings had a considerably lower deposition temperature (about 500 °C) which made them attractive for coating high-speed steel tooling. The coatings combined high hardness (35 GPa) and wear resistance with low friction when sliding against steel. However, scale-up of the deposition technology proved difficult as the process control necessary to produce high-quality carbide coatings on a chamber full of components was difficult to achieve. Too much reactive methane and nucleation of graphite occurred, leading to poor coating adhesion and friable coatings.

However, not long after this, it was realised that TiN was a much more forgiving coating which was easier to deposit reliably and was less sensitive to variations in coating parameters around the deposition chamber. The

Table 5.2 Properties and performance of some commercially available PVD coatings

Property	Value for the following coatings						
	TiN	TiAlN	TiCN	CrN	MoS ₂	(Pure DLC)	M-C:H
Deposition temperature (°C)	150–450	150–450	150–450	150–300	150–250	150–500	150–250
Typical thickness	1–10	1–10	1–10	1–50	1–10	1–2	1–5
Nanoindentation hardness (GPa) (5mN load; 2 μm coating)	22–30	24–32	28–35	12–22	3–16	25–70	8–22
Internal stress (GPa)	1–10	1–10	1–10	0.1–6	0.1–5	1–12	0.1–7
Friction coefficient (6mm 52100 steel sphere counterface; 20N load)	0.5–0.7	0.4–0.6	0.2–0.5	0.4–0.6	0.02–0.1	0.05–0.2	0.1–0.2
Abrasive wear	+	++	++	–	+++	+	++
Adhesive wear	+	++	+++	–	+++	+++	–
Corrosion†	++	+++	+	+++	+++	+	+

† +++, Excellent; ++, good; +, reasonable; – poor.

gold-coloured TiN was softer than TiC (about 25 GPa in commercial coatings) and had a much higher friction coefficient but was chemically inert and more resistant to oxidation than TiC. It was soon demonstrated to offer excellent tribological properties in a range of applications and became the first PVD hard coating to be developed commercially. In fact it is the colour of TiN which has contributed to its commercial success, giving an impression of enhanced value to the coated component even before it is used. It also provides an excellent indicator that the coating is still present after the component has been used in service for some time.

Many of the current commercial PVD hard coatings are just variants on the original TiN formulation. Initially TiCN coatings were developed to gain some of the advantage of the properties of TiC with the ease of processing of TiN. Most commercial TiCN coatings have an initial layer of TiN to promote adhesion followed by a gradual increase in the carbon content of the coating up to a plateau at its outer surface. Many suppliers offer coatings that have a carbon-to-nitrogen ratio equal to 1 but some suppliers increase this to 2 as the friction coefficient of this coating is reduced. Increasing the carbon-to-nitrogen ratio also increases the hardness of the coating.

TiN and TiCN coatings are not particularly suitable for operation at high speed or high temperature and so TiAlN coatings have been developed for service in these conditions. Again the amount of aluminium in the film varies with supplier but in all cases the coatings form a protective layer of aluminium oxide at high temperature which greatly improves the oxidation behaviour of the tool.³⁶

Coating formulations based on titanium are not particularly good for tribological applications involving copper since there can be considerable chemical reaction with the copper during sliding. Chromium nitride coatings have been developed for use in this case. In fact, PVD CrN and Cr₂N have been under development also as potential replacement coatings for hard chrome plate on environmental grounds. However, although the coatings have excellent performance, the cost of the PVD processed material is too high in many cases.

The most recent group of hard coatings to be developed by PVD is hard carbon coatings. Amorphous diamond-like carbon (DLC) coatings have been available by plasma-assisted CVD for some time but high-quality PVD coatings are less common but nonetheless show good properties.³⁷ Predominantly sp²-bonded DLC coatings by large-area ion-beam-assisted deposition have been available for some time and more recently amorphous coatings by unbalanced magnetron sputtering have been commercialized^{38,39}. These coatings offer reasonable hardness (about 15 GPa) and low wear rates when sliding against steel. The friction is low in such cases and remains low even if the counterface is not coated. This makes the coatings

very attractive for general engineering components. One problem is the relatively high residual stress and poor adhesion of the coatings. This has been addressed by the use of interlayers to promote adhesion and metal doping to reduce stress generation in the coating.⁴⁰ Nanostructures are produced when adding between 5 and 15% of carbide-forming elements to amorphous carbon coatings consisting of small carbide islands in an amorphous carbon matrix. Such films have a lower hardness than pure DLC, but a lower residual stress and a greatly improved fatigue life that makes them excellent coatings for bearing applications. Another type of PVD carbon coating is the tetrahedral amorphous carbon coatings with a high sp^3 carbon content which are much closer to diamond in properties. These are commonly produced by arc deposition processes.⁴¹ These films are very hard and wear resistant but have a high residual stress and consequently poor adhesion which has limited their use in tribological applications.

5.4.2 Solid lubricants

Thin soft metallic coatings on a harder substrate have been used to reduce friction for many years. Often these are deposited by electrodeposition but this process introduces many impurities into the coating and it is generally true that a PVD equivalent is much purer and therefore softer. For this reason, excellent friction reduction is possible using PVD coatings such as lead or gold. Ion-implanted lead is used in applications where rolling contacts occur in conditions where liquid lubrication is not possible.⁴² Similarly gold coatings are used to coat threaded components for use in applications where chemical contamination by lubricants cannot be tolerated (e.g. for components used in the food industry). Silver and gold coatings have also been used to lubricate ceramics.⁴³

When sliding is more severe, coatings with low-shear-strength layered structures have been used. Perhaps the most important of these is MoS_2 which has been developed for sliding components in vacuum applications such as bearings in satellites.⁴⁴ Initially the coatings were deposited by burnishing, but more recently ion-plated and unbalanced magnetron-sputtered films have been developed which show considerably greater durability and hence component life.^{45,46} The friction reduction which the coating produces is greatly reduced in the presence of water vapour and a number of different approaches to minimise the effect of water have been adopted in order to expand the range of applications of the material to terrestrial environments. The most successful is the doping of the film with titanium.⁴⁷ This both increases the film hardness and stability and greatly improves its tribological performance in air. However, titanium-doped MoS_2 films are still susceptible to environmental attack and coated components have to be carefully stored in dry conditions prior to use.

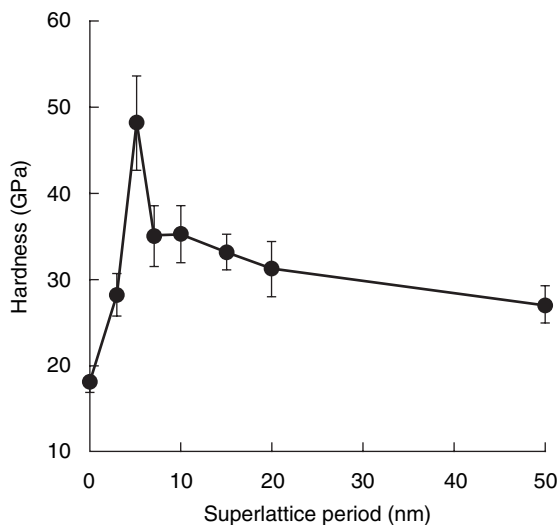
5.4.3 Hybrid processes, multilayer and composite coatings

It is often the case that a single-layer PVD coating does not show suitable properties to resist the tribological environment in which it is to operate on its own. One very significant concern is the fact that no thin PVD coating will offer any appreciable benefits if the substrate beneath it yields in the tribocontact. In such cases the coating will be bent into the hole caused by plastic collapse of the substrate and offer little protection to further wear. The load support of the substrate is therefore critical. In many cases the substrate cannot be made hard enough to prevent plastic deformation at the practical thickness of the PVD coating and another coating is deposited beneath the PVD layer to provide the necessary load support. For instance relatively thick (10–50 μm) electroless nickel layers are often deposited on to soft substrates (such as aluminium) to ensure sufficient load support for a TiN coating of a few micrometres thickness.

Another advantage of combining two (or more) surface engineering processes is that synergies occur which mean that the performance achieved is greater than might be expected from a simple combination of the benefits of the two individual processes. An example is the dramatic improvement in the life of PVD-TiN-coated tools by nitrogen ion implantation.⁴⁸

More recently, multilayer and superlattice PVD coatings have been developed which also show enhanced performance over the single-layer coatings initially commercialized.^{49,50} The presence of many interfaces within the coating is responsible, in part, for the improvements in performance.⁵¹ For instance PVD TiCN is nearly always deposited as a multilayer or graded coating with a pure TiN layer to promote adhesion and a carbon-containing outer layer of variable composition to give enhanced coating wear resistance and lower friction.⁵² Superlattice coatings, in which thin layers of two different coating materials with optimum thickness are repeated many times throughout the coating, have been found to show enhanced hardness and wear resistance if the superlattice period is correctly controlled.⁵¹ For instance a maximum enhancement in hardness is achieved at a superlattice period of 5 nm for a TiN/NbN system⁵³ when sharp boundaries between the individual layers are achieved. The hardness drops at lower superlattice period because of intermixing of the TiN and NbN layers (Fig. 5.8).

In addition to superlattice structures, coatings produced from a metastable mixture of insoluble phases which separate by spinodal decomposition have been demonstrated to give a very high hardness.⁵⁴ PVD⁵⁵ and plasma-assisted CVD⁵⁶ TiN/Si₃N₄ composite coatings produced in this manner with optimum grain size have been suggested to have hardness values approaching that of diamond, although this needs to more widely demonstrated. However, it is clear that such multicomponent and multilayer coatings offer



5.8 Variation in the hardness with the superlattice period for laboratory sputtered TiN/NbN multilayer coatings.

considerable advantages over the current generation of commercial hard coatings.

5.4.4 Microstructure–property relationships

The microstructures, and hence the properties, of PVD coatings are critically dependent on the processing conditions used to make them. The coatings are often considerably different from bulk materials of the same composition and have highly anisotropic properties due to their anisotropic microstructures; since the coating flux approaches the substrates from a restricted range of directions and adatom mobility is relatively low at low deposition temperatures, films are often deposited with a columnar microstructure. However, as the deposition temperature increases and adatom mobility is enhanced, denser equiaxed coatings are produced.

The first attempts to characterise the structures of PVD coatings by Movchan and Demchishin⁵⁷ recognised that there are three different structure zones as a function of homologous deposition temperature T/T_m (where T is the substrate surface temperature and T_m the melting temperature of the coating in kelvins). The low-temperature ($T/T_m < 0.3$) zone 1 structure corresponds to low adatom mobility and consists of tapered columns with domed tops. In zone 2 ($0.3 < T/T_m < 0.5$), surface diffusion becomes

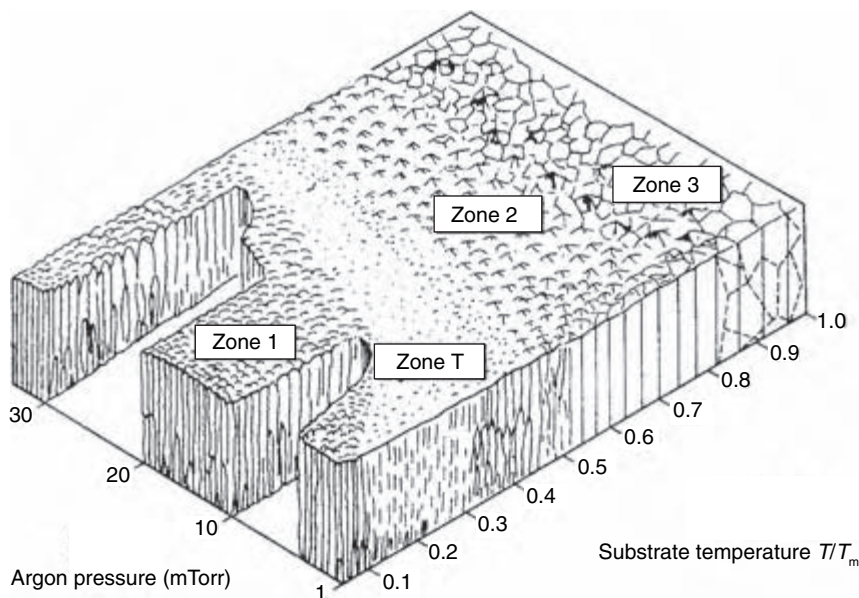
important and the structure is a straight columnar region with smooth surface topography. At higher temperatures ($T/T_m > 0.5$), bulk diffusion is the dominant process and the zone 3 structure produced is characterised by equiaxed grains.

Later work by Thornton⁵⁸ demonstrated that the presence of a sputtering gas could modify the model and a further region identified as zone T was inserted between zones 1 and 2 (Fig. 5.8) which consisted of poorly defined fibrous grains. Increasing the system pressure led to an increase in the size of the zone 1 columns. This is evidence of the effect of ion bombardment on the microstructure of the growing film. In practice both the flux and the energy of ion bombardment are important, the former being related to the specimen current and the latter to the bias voltage on the samples.

As an alternative to increasing deposition temperature, zone 1 microstructures can be overcome by subjecting the coating to ion bombardment by particles having sufficient energy that the resultant momentum transfer to the growing coating causes coating atoms to fill the voided boundaries. Messier *et al.*⁵⁹ have suggested improvements to the structure zone models which account for the evolution of microstructure with coating thickness and the effect of both temperature and ion bombardment. The model highlights the fact that ion bombardment promotes a dense structure of the zone-T type but that the necessary adatom movements can have a thermal or bombardment-induced origin.

The momentum transfer from the ion bombardment is characterized by $jV_b^{1/2}$, where j is the ion current density at the substrate and V_b the bias voltage. Increasing the ion current is therefore a much more effective method of densifying coatings than increasing the bias voltage.⁶⁰ A further disadvantage of depositing coatings with a high bias voltage is that the ion bombardment creates subsurface defects which are not removed by subsequent coating once a sufficiently high ion energy is used.⁶¹ Such defects lead to stress generation (Fig. 5.9) and can lead to premature coating failure by fracture or coating detachment. It is therefore not surprising that the most successful commercial coating processes have been optimised to enhance substrate ion current and operate with bias voltages less than 100 V.

The effect of bias voltage on the mechanical properties of hard coatings such as TiN is very dramatic.^{62,63} Figure 5.10(a) shows the effect of bias voltage on hardness for coatings deposited by a range of deposition technologies. At low bias voltages the hardness increases as the zone 1 microstructure is replaced by zone T but for some of the processes there is a reduction at bias voltages in excess of -100 V. This reduction is due to a change in the manner of growth of the coating leading to a more open layer and is controlled by the substrate used. The properties of the coating therefore depend on the packing density of the columnar units which make it up and the strength of bonding at the boundaries between them.⁶⁴ The same



5.9 Structure zone model for PVD coatings after Thornton.⁵⁸

bias voltages produce different coating properties for the different coating processes and so an optimum setting has to be determined for each; parameters developed for one process cannot be applied to another without modification.

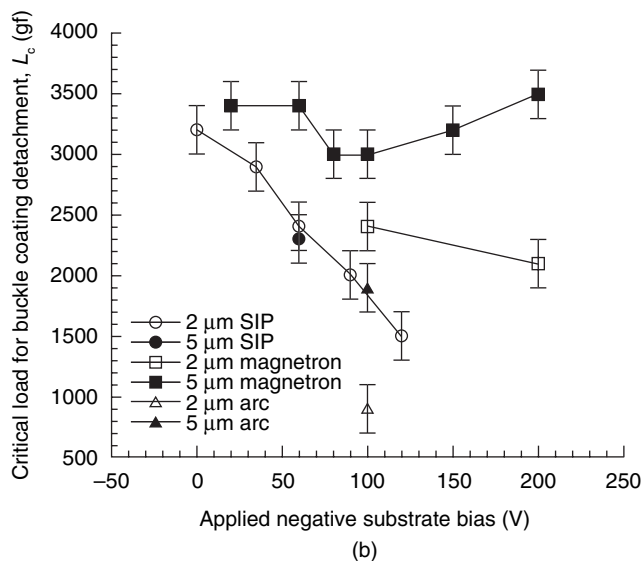
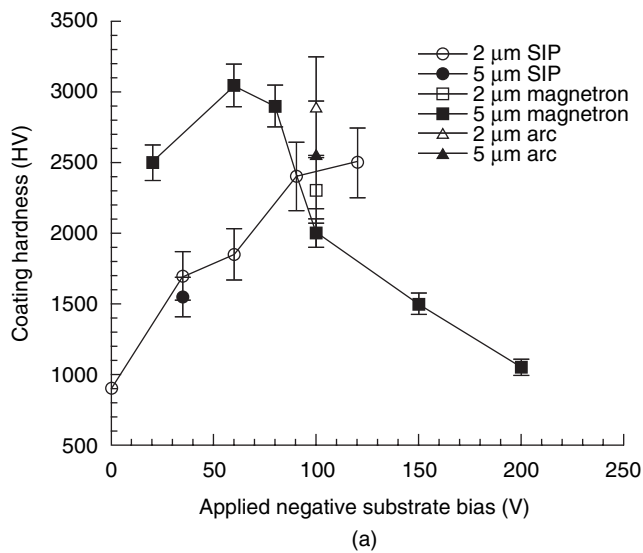
The use of PVD coatings to improve the wear resistance of a range of substrates is well established⁶⁵ and the effect of coating microstructure is key.^{66,67} Dense smooth films with the zone-T structure and a small compressive residual stress generally give the best performance provided that the residual stress is not too high and coating detachment can be avoided.

5.5 Applications

5.5.1 Cutting tools

For cutting tools the major wear modes are crater wear, adhesive wear, abrasive wear, oxidative wear and thermomechanical fatigue wear and any coating system must promote resistance to all these. This requires a hard, chemically inert, thermally stable coating which shows a limited thermal expansion mismatch with the substrate.

Commercial TiN coatings were introduced for cutting tools in the late 1970s, immediately opening up a market for the coating of sharp-edged



5.10 Variation in the properties of PVD TiN on 304 stainless steel with bias voltage for several commercial deposition technologies (SIP, sputter ion plating) (a) hardness; (b) scratch adhesion test critical load.

temperature sensitive high-speed steel tools that could not be successfully coated by the CVD techniques that were popular at the time. In addition, PVD coatings often had superior properties to the conventional CVD coatings (e.g. higher hardness⁶⁸). The benefits were often very impressive. For instance an uncoated $\frac{1}{4}$ in jobber drill would produce only one hole in a medium-carbon steel before failure due to excessive crater wear beneath the cutting lip, a form of chemical wear as the tool dissolved in the chip. This led to collapse of the cutting edge and blunting of the drill. This wear mode was almost completely removed by coating with a thin layer of chemically inert TiN and the main failure mode became heat generation at the outside edge of the cutting face. Initially over a hundred holes could be drilled in the same steel substrate and the ability to achieve a hundred holes by all tools in a sample selected from a single coating batch was used to qualify a coating process by some tool manufacturers. Nowadays, some of the best TiN coatings available will produce in excess of 700 holes in the same steel. In general, TiN coatings will not improve badly designed or manufactured tools and the performance benefits are very dependent on the application.

Many different edged tools are now coated with PVD hard coatings including machining inserts, drills, taps, broaches and hobs. The coatings are mainly used to increase the life of the tool but also to enable faster machining processes to be used in some situations. Tooling manufacturers have undertaken considerable work to identify appropriate tooling coatings for the machining of different base materials and typical choices are shown in Table 5.3. As the speed of cutting increases and heat generation becomes more difficult TiAlN coatings are preferred. Increasingly, as green manufacturing processes are developed which require less coolants or even dry machining, this high-temperature capability is a major advantage. In cases where chemical interaction occurs between titanium-based coatings and the workpiece, other coatings compositions have been developed. For this reason, CrN is widely used in the machining of copper and ZrN has been developed for machining some aluminium alloys.

The use of solid lubricating coatings to improve the performance of cutting tools was thought to be unlikely but successful trials by the Vilab Company showed that great improvements could be achieved by this.⁶⁹ The combination of a PVD hard coating topped with a solid lubricant (usually MoS₂) is now widely used because of the greatly extended tool life.

Increases in performance of cutting tools using multilayer and superlattice coatings have recently been demonstrated and the first commercial PVD coatings of this type are beginning to appear on the market. These tools are aimed at the machining of difficult materials, such as hard Al–Si alloys use in engine blocks.⁷⁰

Table 5.3 Basic ranking of PVD coatings for cutting tools for processing different workpiece materials

Workpiece material	Conditions	Excellent	Very good	Good
Steels	Medium and high cutting speeds	TiAlN	TiCN	TiN
Steels	Low cutting speeds	TiCN	TiAlN	TiN
Aluminium alloys		TiAlN	ZrN	CrN
Cast iron		TiAlN	TiCN	
Copper alloys		CrN	TiCN	ZrN
Titanium alloys		CrN	TiAlN	
Nickel alloys		TiAlN		
Graphite, plastics, green composites, wood		Diamond (CVD)		TiAlN

5.5.2 Forming tools

For forming tools the wear modes identified for cutting tools will also occur but, in addition, impact wear is a factor which requires a coating with good toughness (Table 5.4). PVD TiCN coatings have been particularly successful on a range of punch and die components made from die steels with a relatively low tempering temperature. Good process control to minimise substrate heating during coating is essential to achieve this. TiN coatings have been used on high-speed steel punches and dies in the manufacture of tools and lock components. MoS₂/Ti films have also been successful in such applications.⁷¹

In many cases the stresses introduced into the tool and its coating are very large during the forming process and excellent load support by the substrate is needed to achieve good performance with a thin PVD coating. High-speed steel dies may be plasma nitrided prior to TiN coating to improve tool life dramatically for this reason.⁷² Similarly, electroless nickel coatings are often used to provide load support for TiN coatings on aluminium injection moulding tools where the substrate hardness is sufficiently low that load support cannot be maintained.

Other forming tools that are now routinely coated include coining dies, CD stamping dies and cartridge punches.

Table 5.4 Basic ranking of PVD coatings for forming tools for processing different workpiece materials

Workpiece material	Excellent	Very good	Good
Steels	TiCN	TiN	TiAlN
Aluminium alloys	TiAlN		
Titanium alloys	CrN		
Copper alloys	CrN		
Plastics, filled plastics	TiAlN		
Nickel alloys	TiAlN		
Precious metals	TiAlN		

5.5.3 Engineering components

A very important application of sputtered TiN is in the provision of durable decorative coatings for consumer goods such as bathroom fittings, watch cases, pens and spectacle frames. The process can be controlled to give a colour almost identical with that of metallic gold.⁷³ Very dense coatings are necessary to prevent fingerprint marking by grease drawn into porosity; this may also be achieved by a thin metallic gold coating on top of a wear-resistant TiN or TiCN layer.

One of the disadvantages of PVD hard coatings for engineering components is that it is not always practical to slide the PVD coating against itself or something equally wear resistant and there is therefore a tendency to do much damage to the sliding counterface if this is not very smooth and well lubricated. Furthermore, if the coating becomes damaged and hard wear debris is produced, this can do considerable damage elsewhere in the system. Despite this, a number of applications have been developed for hard coatings where sliding is not significant. For instance 316L stainless steel gate valves for the food industry have been coated with TiN to prevent galling and to restrict the contamination of food with stainless steel wear debris. The ability of TiN coatings to prevent stainless steel from sticking to itself and other steels has been exploited by the nuclear industry where nuts and bolts and other fasteners used to join stainless steel components are coated with TiN to enable easy decommissioning to be carried out.

One advantage of DLC coatings is that they can slide against uncoated steel with little or no damage and generate low wear rates for the sliding pair. This material has been more widely used for general engineering components than other hard coatings for this reason. Applications include diesel injector valves, high-performance gears, video tape heads, sliding seals, textile industry parts and fly fishing-rod tips.

5.5.4 Bearings

Coatings for bearings need to provide low friction in cases where lubrication is marginal, to be resistant to contact fatigue, abrasive wear and plastic deformation when debris passes through the contact.

PVD coatings have been demonstrated to improve the rolling contact fatigue performance of a range of bearing steels (see for example Polonsky *et al.*⁷⁴). These have been exploited in a number of terrestrial applications but the main developments have been in bearings for satellites where liquid lubrication is not possible. For bearings where rolling is the dominant behaviour, ion-plated lead coatings have been successfully used but, as the amount of sliding increases, MoS₂ coatings have become more important.⁷⁵

Sputtered AlSi on bearings for automotive use has been developed which shows an increase of a factor of 2 in load-carrying capacity compared with conventional electroplated bearing surfaces.⁷⁶

Table 5.5 Designing with PVD coatings

Design requirements	Notes
The design should not contain deep blind holes	Plasma may form in holes during ion cleaning or coating; pumping out contamination is difficult. Penetration of coating flux is reduced in line-of-sight processes
Small bores are difficult to coat	Component should be designed to be split. Holes with a diameter to depth ratio of 1:1 can be coated but a higher ratio is preferred
Surface voids, cracks and fissures cannot be sealed by coating	Outgassing of pores can lead to problems with coating cast or powder metallurgy components. PVD coatings tend to follow the existing surface topography and will not bridge cracks
Burrs and manufacturing defects on machined components must be removed prior to coating	Vapour degreasing or sputter cleaning will not remove such defects which will be detached in service, removing the PVD coating that covers them
Large variations in cross-section should be avoided	These give rise to temperature variations during processing, leading to variable stress generation in the component

Table 5.5 Continued

Design requirements	Notes
Temperature-sensitive and non-conducting substrates are difficult to coat	and coating. This can lead to component distortion or coating detachment Coating needs to take place below the substrate tempering temperature. Ion plating requires a conducting substrate
Masking with close-fitting mechanical masks is possible; paint-on masks are not recommended	Paint-on masks can disrupt the coating process (e.g. by outgassing). There will always be some undercutting of a mechanical mask
Fixturing of the components is necessary, making complete coating of all component surfaces difficult	Electrical contact with the fixtures is necessary for substrate biasing. Barrel ion plating is possible for metallic coatings but hard compound coatings are damaged by the process
Surfaces of components should be bright and untreated prior to coating	Oxides, transit oils and protective layers must be removed to ensure good coating adhesion. Contamination and debris from polishing and cleaning must also be removed.
Dense pore-free coatings are required for corrosion resistance; some porosity is acceptable for wear resistance	Thin (less than 10 μm) pore-free single layer coatings are difficult to produce. Porous coatings may show fingerprint marks
Sharp edges can be coated provided that the process is set up to do it	Highly stressed coatings are easily detached from sharp edges. Excess ion current at sharp edges can lead to resputtering of the coating material. Processes optimised for sharp edges produce lower-quality coatings on adjacent flat regions
Substrates should offer sufficient load support for the coating	Plastic deformation of the substrate leads to bending of the coating in the deformed region which leads to fracture and detachment
Coating materials should be selected on the basis of the operating environment	For example do not use titanium-based coatings for copper applications, ensure that like-on-like sliding does not occur. Determine whether one or both parts of the contact pair need to be coated. Be aware that debris from elsewhere in the system can cause wear

5.5.5 Computer hard drives

The structure of a modern computer hard drive consists of an aluminium alloy platen coated with electroless nickel and magnetic layers and capped with a protective carbon layer. Both the magnetic layers and the carbon overcoat may be deposited by PVD or PVD–hybrid processes. As the information density on the disc increases and the fly height of the head is reduced, the chance that the head may touch the disc surface is increased. The thin carbon overcoat which may only be 10 nm thick is used to prevent damage to the disc and to reduce the frictional forces on the head.⁷⁷

5.5.6 Protective layers for functional coatings

A range of applications exist where functional coatings are used, such as antireflection of low-emissivity coatings for architectural glass, where the coating must be protected from handling damage or wear during transit and normal service. In such cases it is possible to deposit PVD transparent oxide coatings on the top surface as a protective layer. The role of this layer is to prevent contact damage from disrupting the functional behaviour of lower layers. Antiscratch layers on glass are an example of this.

5.6 Future trends

PVD coating technologies have matured since they were first introduced and are now well-established commercial processes. The cost of vacuum engineering and power supplies has also fallen in the period and so the economic disadvantages which the technology suffered in its early history are much less apparent. The drop in running costs and the increase in system reliability have meant that PVD coatings are increasingly competitive in the marketplace and the number of applications continues to grow. One area of current interest is the use of PVD coatings to replace similar electroplated coatings on the grounds that the environmental damage from the PVD process is significantly less. The fact that CrN coatings can be used in most applications where hard chrome plate has been traditionally used has been demonstrated in a number of studies but the major barrier to the uptake of the technology is still cost and work is ongoing to reduce further the cost of ownership of PVD plant.

New coating materials are also making it through to market. The emergence of commercial superlattice coatings after several years of academic research is an example of this. Improved coating formulations, hybrid and composite coatings continue to be developed and some of these will find niche applications in the market. Some materials which are still of mainly

academic interest such as fullerene-like coatings⁷⁸ of CN_x are about to be used in industrial trials.

The range of PVD coatings in use and the range of applications in which they offer benefits will also expand. This will partly be driven by improvements in the deposition technologies which produce them, by the characterisation techniques used for assessing the coatings and by the emergence of better rules for incorporating the coatings as an integral part of the component design process (see for example Table 5.5). True surface engineering solutions occur when the coating is considered as part of the design process and the substrate design is changed to accommodate it. This has been achieved in the case of the ADX drill which has been redesigned to achieve a performance which cannot be realised from the substrate or coating alone.⁷⁹ Such design changes will become more widespread as the benefits of PVD coatings are more widely understood. This is a major challenge to engineers working in the industry, but the gains are potentially very large.

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Electroless plating for protection against wear

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6.1 Introduction

Electroless deposition of metals was first demonstrated as early as 1844. A wide range of electroless deposition baths is now commercially available for a variety of metals and composites. Nickel is the most common metal deposited from electroless plating baths¹ and a large number of papers on this metal coating and its applications have been written. Extensive literature on the electroless deposition process and applications of other metals such as copper (particularly for metallization of printed-circuit boards (PCBs)), cobalt, tin, silver, palladium and gold is also available.

According to *Chemical Abstracts*, from 1967 to date approximately 575 literature reviews in English have been written on electroless deposition of single or multiple metals. These reviews have improved our understanding of electroless deposition processes and a number of applications have been developed. A review with over 100 references, published in 1979, discusses surface preparation and solutions for electroless nickel deposition on aluminium and its alloys.² A paper in 1982 focuses on the corrosion resistance and monitoring of Ni–P alloy coatings in various electrolytes including sea water, inorganic and organic acids and petroleum products and concludes that Ni–P has extraordinary corrosion resistance.³ The electroless deposition of copper into through-holes and blind holes was reviewed by Yung *et al.*⁴ who analysed the advantages and disadvantages of electroless and electroplated copper as well as mass transport deficiency in plating and criteria for quantitative evaluation. A review on the electroless deposition of gold for electronics applications included developments of non-cyanide electroplating baths, and a discussion on the contact and wear resistance of the coating.⁵ A 1997 paper discussed the advances in electroless deposition of copper, nickel, gold and palladium for the fabrication of PCBs, semiconductors, electromagnetic interference shielding and computer memories. The paper points out that despite advances in the understanding of the electroless processes the number of reducing agents

available at the time was the same as in the 1960s and they remain expensive and are not environmentally friendly.⁶ A more recent review highlights the environmental and health impact of electroless processes for the deposition of copper, nickel, palladium, gold, silver and metal alloys.⁷ Table 6.1 lists some reviews that focus on a particular aspect of electroless processes. Electroless deposition extend to fields such as catalysis,¹⁸ electrochemical sensors,¹⁹ composite materials,²⁰ corrosion prevention and wear resistance,²¹ electronics,¹³ lithium batteries,²² nanotubes²³ and three-dimensional structures.²⁴

The discovery that metallic nickel could be deposited from an aqueous solution of its salts by reduction with sodium hypophosphite was made in 1844 by Wurtz.^{25,26} The resulting electroless metal powder deposit had no practical application. Subsequently, the process was forgotten and no major plating baths were developed for over 100 years. Electroless nickel technology as it is known today is based on the work carried out by Brenner and Riddell in 1946. They developed a nickel-plating formulation²⁷ that was to become the first practical system for electroless nickel deposition. It was not until 1955, however, that a commercial plating bath was available under the trade name of Kanigen. The plating solution was adapted^{28–30} from the formulation devised by Brenner and Riddell and used to cover the interior face of tanks that transported concentrated caustic soda. Previous efforts by conventional electroplating methods had failed to achieve satisfactory nickel coatings for this application.

This chapter provides a brief introduction to electroless deposition followed by a description of the electroless process for the most common metals such as nickel, copper and cobalt. The electrolyte composition of electroless baths is then considered, followed by the characteristics and properties of electroless alloys and their applications.

6.1.1 Electrochemical methods of metal deposition

Metallic coatings can be produced on suitably prepared substrates by hot dipping,³¹ diffusion coating,³² by chemical vapour deposition and physical vapour deposition (PVD),³³ by thermal spraying³⁴ and by electrochemical techniques. Electrochemical methods have the advantage of good control over thickness and morphology of the deposit and are generally carried out at atmospheric pressure at temperatures in the range 20–90 °C. Three types of electrochemical deposition method are generally recognised: electrodeposition, immersion deposition and electroless deposition. Their main characteristics are summarised in Table 6.2.

Electrodeposition is based on the reduction of metal ions at the cathode using electrons supplied by an external direct current source. The oxidation reaction occurs on inert anodes, e.g. Pt/Ti, or at soluble anodes of the same

Table 6.1 Selected review papers on electroless deposition

Reference	Year	Title	Theme and contents
Dubin <i>et al.</i> ⁸	2005	'Electroless barrier and seed layers for on-chip metallization'	Electroless deposition of copper for liner/barrier and cladding layers, copper and PVD seed. Use the MPT* to verify autocatalytic reaction of Co-W-P alloys with hypophosphite
Baudrand ⁷	2004	'Electroless processes'	Post-plating, health impact, and environmental status of metal and alloys of copper, nickel, palladium, gold and silver
Kato and Okinaka ⁹	2004	'Some recent developments in non-cyanide gold plating for electronics applications'	Current status of both electrolytic and electroless non-cyanide processes for plating soft gold
Petrova ¹⁰	2004	'Chemical deposition of metal composite coatings on plastics'	Electroless deposition of Ni-P and copper on plastics including TiO ₂ and SiO ₂ particles. Tracks the effects of size, dispersion, concentration and influence of components and conditions
Agarwala and Agarwala ¹¹	2003	'Electroless alloy/composite coatings: a review'	Electroless alloys and composite coatings with respect to bath types and their composition properties and applications
Djokic ¹²	2002	'Electroless deposition of metals and alloys'	Electroless deposition for batteries, medicine, protective and decorative coatings
O' Sullivan ¹³	2001	'Fundamentals and practical aspects of the electroless deposition reaction'	Practical aspects of electroless deposition with emphasis on applications in the electronics industry
Duncan ¹⁴	2000	'Electroless nickel: past, present and future'	Evolution of electroless nickel and how the industry grew from this process, today's markets and forecast future directions
Kerr <i>et al.</i> ¹⁵	2001	'Electroless deposition of metals'	Electroless process and bath components for nickel and copper, advantages and limitations of electroless processes
Wen <i>et al.</i> ¹⁶	1999	'Electroless plating for the enhancement of material performance'	Electroless deposition emphasising metallization of bulk ceramics, modification of porous and powder ceramics
Khoperia ¹⁷	1999	'Microfabrication of microdevices by electroless deposition'	Metallization of dielectrics and semiconductors with nickel, advantages over gold and silver metallization. Electroless plating of silicon

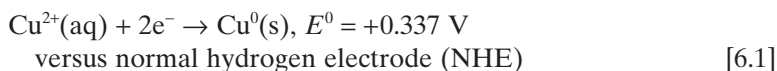
* MPT is the mixed potential theory, see section 6.3.2.

Table 6.2 Comparison of electrochemical methods for metal deposition³¹

Property	Electroplating	Immersion plating	Electroless deposition
Driving force	Power supply	Chemical displacement	Autocatalytic redox reaction
Cathode reaction	$M^{n+} + ne^- \rightarrow M^0$	$M^{n+} + ne^- \rightarrow M^0$	$M^{n+} + ne^- \rightarrow M^0$
Anode reaction	$M^n - ne^- \rightarrow M^0$ or $\frac{n}{2}H_2O - ne^- \rightarrow \frac{n}{4}O_2 + nH^+$	$M_1 - ne^- \rightarrow M_1^{n+}$	$R - ne^- \rightarrow O$
Overall cell reaction	$M_A \rightarrow M_C$ or $\frac{n}{2}H_2O + M^{n+} \rightarrow \frac{n}{4}O_2 + nH^+ + M^0$	$M^{n+} + M_1 \rightarrow M + M_1^{n+}$	$M^{n+} + R \rightarrow M^0 + O$
Site of cathode reaction	Substrate (workpiece)	Substrate (workpiece) which must remain partially exposed	Substrate (workpiece) which must have a catalytic surface
Site of anode reaction	Separate anode	Substrate (workpiece) which dissolves	Substrate (workpiece)
Anode reactant	M or H_2O	M_1 , dissolving metal	R, reducing agent in solution
Nature of deposit	Pure metal (or definite alloy)	Pure metal, but may be porous and poorly adherent	Usually M contaminated by O- or R-derived species
Thickness limit	Typically 1–50 μm	Typically only 1–5 μm in thickness	1–100 μm

nature as the metal being reduced at the cathode. The thickness of the deposit can be controlled by the time and quantity of applied current.

Immersion deposition, which is also known as cementation or galvanic displacement, takes place between a solid metal and a metallic ion. The metal ions to be deposited should be nobler than the immersed solid metal. For example the fact that the standard potential of $\text{Cu}^{2+}/\text{Cu}^0$ is more electro-positive than the couple $\text{Fe}^{2+}/\text{Fe}^0$ will allow Cu^{2+} to be reduced when mild steel (iron) is immersed in a copper sulphate solution:



and an immersion coating of copper will be deposited on the iron surface. The overall cell reaction of mild steel immersed into a solution of copper ions is



Immersion deposits are generally porous, exhibit poor adhesion and grow to an approximate thickness of only $1\text{ }\mu\text{m}$. Once the substrate (mild steel, in the example shown above) has been covered, dissolution of the base metal is prevented and the deposition ceases. Immersion deposits are mainly limited to precious metals used for decorative purposes, e.g. jewellery. They are also used industrially for gold contacts on PCBs.

Electroless deposition, like immersion deposition, does not involve an external direct current to form a metal coating on a particular surface; however, unlike immersion deposition where the process stops when the immersed metal is covered, electroless deposition continues even with the substrate covered. In the electroless process the metal ion to be reduced reacts with a reductant that is provided by a heterogeneous catalyst and does not reach equilibrium as quickly as the redox couple mixture used in immersion deposition processes. Electroless deposition can be divided into three categories.

1. Deposition of metals.
2. Deposition of alloys.
3. Deposition of composites.

6.1.2 Electroless nickel deposition

Chemical or electroless nickel deposition^{28–30,35} requires the reduction of nickel ions on a suitable surface by a reducing agent. The most widely used reducing agent is sodium hypophosphite, where phosphorus is co-deposited

with nickel, forming an Ni-P alloy. The main feature of electroless nickel deposits that distinguishes them from electrodeposits is the thickness and uniformity of the coating. This is possibly as a result of a relatively uniform mass transport and the absence of primary current distribution. For example, a smooth uniform electroless nickel coat can be deposited on components such as valves or pipe fittings of complicated geometry, which would be otherwise difficult by electrodeposition.

Electroless nickel coatings, which are deposited by autocatalytic reduction of nickel ions by hypophosphite,^{36,37} have a wide range of applications in the petroleum, automotive and electronics industries as illustrated in Table 6.3.

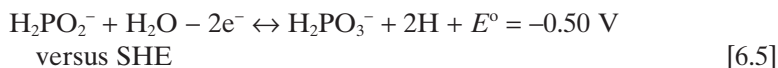
The co-deposition of phosphorus with nickel provides a coating with enhanced hardness, wear and corrosion resistance if compared with pure metallic nickel. On mild steel for example a wide variation of corrosion behaviour of electroless nickel coatings has been observed. This may be the result of local interferences with the autocatalytic reactions, preventing the oxidation of sodium hypophosphite, or the reduction of nickel ions taking place caused by oxide residues and organic contaminants remaining on the mild steel surface.

Electroless nickel can be deposited from either acid or alkaline solutions. Metallographic studies of deposits from alkaline baths exhibit a large number of delaminations in the dense homogeneous deposit structure which caused poor adhesion.¹⁵ Since the majority of the commercially available electroless nickel baths are in acid, this section will explore the mechanism of these solutions. An electroless nickel bath will produce a thicker

Table 6.3 Uses for electroless nickel coatings³⁶

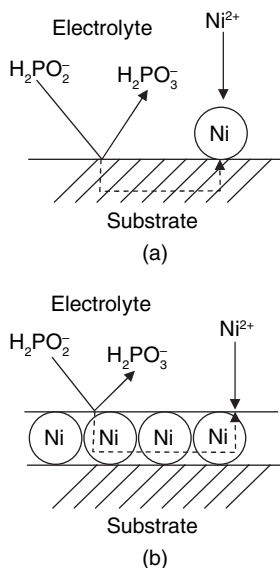
Uses for electroless nickel deposits
Printed circuits
Resistors
Temperature sensors
Valves for fluid handling
Moulds for plastics and glass
Wear-resistant coatings for gears, crankshafts and hydraulic cylinders
Magnetic tapes
Coatings on aluminium (to enable this metal to be soldered)
Corrosion-resistant coatings for components or structures
Plating on plastics

coating than an immersion deposit (greater than 1–5 μm), if an alternative oxidation process to metal dissolution such as that illustrated in equations [6.2] above occurs. Such an oxidation process should be carried out by a reducing agent and the reaction needs to occur on the base metal substrate and then on the deposit itself. The redox potential for the reducing agent must, therefore, be more electronegative than that of the metal being coated. Sodium hypophosphite is the most commonly used reducing agent in the electroless deposition of nickel from acid baths. The standard potential values E° , for $\text{Ni}^{2+}/\text{Ni}^0$ and $\text{H}_2\text{PO}_2^-/\text{H}_2\text{PO}_3^-$ redox couples are



The electrons produced by the oxidation of hypophosphite are utilised in the reduction of nickel ions (Ni^{2+}) at the cathodic sites as shown in Fig. 6.1.

From the electrode potentials of the above equations it is readily apparent that the metal ions can be reduced to the metal phase as the E° for the



6.1 Schematic diagram of the electroless deposition of nickel from a hypophosphite bath (a) initially on a ferrous substrate and (b) subsequent deposit onto a nickel substrate.³⁶

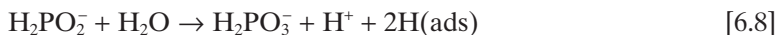
oxidation reaction is more negative than the E° for the reduction process and the overall reaction can be written as



The hypophosphite reaction also produces hydrogen gas, according to the reaction



However, the main mechanism for the autocatalytic reaction of nickel by hypophosphite is considered to be the following sequence of electrochemical reactions that involves hydride formation^{38,39}:



Reduction of the hypophosphite ion H_2PO_2^- by atomic hydrogen results in the co-deposition of phosphorus with nickel:



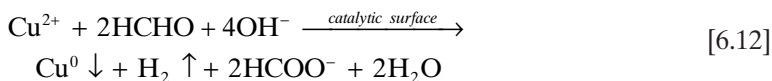
6.1.3 Electroless copper deposition

Electroless copper deposits were first produced in 1947 and commercial acceptance was achieved in the mid 1950s.⁴⁰ It started as a plated-through-hole processes for the (at the time) incipient printed-circuit industry. The first autocatalytic chemical reduction of copper was achieved from alkaline copper tartrate baths using formaldehyde as the reducing agent. Spontaneous precipitation of cuprous oxide particles limited the lifetime of the electroless bath but in the late 1960s a fast-plating 'heavy' electroless copper bath able to produce ductile copper deposits was developed. One of the first methods to stabilise electroless copper baths was by bubbling air through the solution to oxidise cuprous oxide particles, thus preventing the formation of catalytic nuclei for the precipitation of copper. Subsequently it was found that complexing cuprous ions with chemical agents such as mercaptobenzothiazole, thiourea, cyanide and divalent sulfur compounds among others stabilised electroless copper baths. In the 1970s, proprietary formulations were very stable and automated equipment to control the bath composition was commercially available.

The majority of the commercial electroless copper baths use formaldehyde as the reducing agent and usually operate in alkaline solutions at pH above 12. Other less common reducing agents for copper are hydrazine, hypophosphite and hyposulphite. To avoid the precipitation of cupric

hydroxide, complexing agents such as ethylene diamine tetracetic acid (EDTA), Qudrol and alkanolamines are necessary. The use of these agents affects the deposition rate, stability and quality of the copper deposit, and additives such as sodium cyanide, an increase in temperature and low deposition rates produce very ductile copper deposits.

The deposition mechanism for electroless copper reduced by formaldehyde involves 2 mol of formaldehyde and 4 mol of hydroxide⁴⁰:



Thin electroless copper deposits are used on non-conductive surfaces for subsequent electrolytic plating.

6.1.4 Electroless cobalt deposition

Electroless cobalt deposits are used for high-density magnetic recording in high-speed switch devices. The variation in bath conditions and constituents such as pH, complexing agents and addition agents can result in different magnetic coercivity properties. A reducing agent such as dimethylamine produces alloy deposits of Co-B in acid solutions. Co-B deposits used in magnetic applications can also be considered for use in corrosion prevention. The electroless deposition of cobalt on carbon nanotubes has been proposed as a method to produce high-density magnetic recording. The nanotubes were pretreated by etching with a CrO_3 solution followed by rinsing and dispersion in a 0.1 M SnCl_2 solution in 0.1 M HCl for 30 min and further activation in a 1.4 mM solution of PdCl_2 in 0.25 M HCl for 30 min, as described by Chen *et al.*⁴¹

6.2 Electrolyte composition and operating conditions

In order to produce the unique properties attributed to electroless deposits, the bath formulation must overcome various problems associated with this type of plating process. Electroless plating baths are very sensitive and need constant attention to the precipitation of metal salts, e.g. nickel, the alteration of pH, the instability of the plating solution, the suppression of the plating rate, the balance of additives and the adherence of gas bubbles.

6.2.1 Buffers

Electroless nickel-plating solutions contain buffer agents⁴² such as sodium or potassium salts or carboxylic acids such as citric, glycolic, malic or lactic acids. The buffers are used to maintain a constant pH that otherwise could

decrease owing to the production of hydrogen ions from the following two reactions:



It is desirable that the bath maintains a high buffer capacity⁴³ in order to support the increasing concentration of hydrogen ions and thus to maintain a stable plating solution with constant deposition rate and pH. An automated monitoring and adjusting device is normally used to control the pH. Despite the additives and careful monitoring, the plating baths may experience a pH imbalance.⁴² Commercial proprietary formulations contain inorganic alkali salts such as potassium carbonate to add to the reducing-agent replenisher. This might explain the fact that on addition of the reducing agent to a working solution, CO_2 is released.

6.2.2 Stabilisers

The presence of dust particles or unwanted precipitations resulting from the breakdown of bath reagents may lead to spontaneous decomposition of the bath during plating. Any nickel precipitation will accumulate and initiate further bulk or random nickel reduction. Heavy metals such as lead, cadmium or thallium will act as stabilisers by shielding the nickel fallout and inhibiting further growth of the particle.⁴⁴ Stabilisers also decrease metal plating on the sides and at the bottom of the bath containers which may present scratches or imperfections prone to catalyse chemical deposition during use. Only traces of these heavy metals must be used, typically less than 1 ppm, since larger quantities will lead to poor edge coverage (skip plating) of the workpiece which would preferentially absorb heavy metals. In extreme cases the heavy metal could poison the electroless bath. Small amounts of thiourea and sulfur-containing compounds such as mercaptobenzothiazole can be used in combination with lead, thereby making the concentration of lead less critical.^{45,46} Unfortunately, deposits produced from these solutions contain traces of sulphur which present poor corrosion resistance.⁴⁷ Other stabilisers used in electroless nickel-plating baths include molybdates, iodates and unsaturated organic acids.⁴⁸⁻⁵⁰ Their mechanism is still the subject of discussion.

One of the most difficult operating parameters affecting the stability of electroless solutions is adequate stabiliser replenishment. This is because depletion rates differ with the size and shape of the parts being plated, particularly in the case of barrel plating where the consumption of stabilisers is high and extra additions are required.

6.2.3 Complexants

In acidic conditions, nickel ions have a tendency to form precipitates with the oxidation products of the hypophosphite such as nickel phosphites. Additionally, at the pH levels of 4.5 used in most electroless nickel baths, nickel could precipitate as a hydroxide. To overcome these problems, ion complexants are added to prevent any localised precipitation. The choice of complexant is important as those with a low tendency to dissociate or with high stability constants can decrease the plating rate to negligible levels by trapping the metal ion, whereas completely dissociated complexants or those with low stability constants will not prevent metal precipitation. The concentration of chelating or complexant agent required in a formulation must be considered as this depends on the nickel concentration, its chemical structure and functionality. The most common complexant agents for electroless nickel bath formulations are glycolic, lactic, malic and citric acids or their sodium salts.

As the plating bath ages, the complexant concentration must be increased in order to prevent the solution from turning cloudy as a result of insoluble nickel phosphite build-up. Proprietary nickel replenish contain sufficient concentrations of complexing agent to make up for losses due to drag-out and to take care of the increased content of nickel phosphite precipitates. However, after five or six metal bath turnovers, the levels of this precipitate may be too high to maintain clarity of the bath and acceptable plating rates might not be achieved.

6.2.4 Exaltants (accelerators)

Stable plating conditions are achieved by choosing both the correct types and the correct concentrations of stabiliser and complexant. However, stabilising the plating solution could decrease the deposition rate and, therefore, addition of chemicals or accelerators to enhance the plating rate are often required. The best known inorganic exaltant is the fluoride ion^{51,52} which becomes incorporated within the metal lattice and has the added benefit of improving the hardness and stress resistance of the deposit. A proposed mechanism for exaltation occurs when the fluoride ion replaces an oxygen atom on the phosphorus. This weakens the P—H bond, thereby enhancing the hypophosphite oxidation process. The weakly bound hydrogen is then available to leave the molecule as a hydride ion and engage in metal ion reduction.

Three types of organic acid anion groups are commonly reported in the literature as exaltants⁵³: the first is saturated unsubstituted short-chain aliphatic dicarboxylic acids, e.g. malonic and succinic acids, the second is

aliphatic short-chain saturated amino acids, e.g. glycine, and the third is short-chain saturated aliphatic acids, e.g. propionic acid.

6.2.5 Other additives

The continuous generation of hydrogen bubbles on work surfaces during electroless deposition produces streaking and pitting unless the parts are mechanically moved during the process. Small amounts, typically 0.1%, of an anionic wetting agent⁵⁴ (sulphonate) accelerate the release of hydrogen bubbles by decreasing the surface tension between surface and solution.

Brighteners may also be added to the basic electroless nickel formulation in order to increase the lustre of the finished deposit, particularly in decorative applications. Cumarin and other unsaturated organic compounds are the most commonly used;^{55,56} traces of cadmium ions added to the bath are also a good brightener.

6.2.6 Operating conditions

For optimum deposition rates, the bath operating conditions³⁶ such as temperature, pH and concentration of nickel and sodium hypophosphite should be kept within strict limits. This serves to maintain a constant concentration of components in the deposit and a constant plating rate.

Temperature is the most important parameter that affects the plating rate with no significant reaction below 50°C. As the temperature increases, the rate of metal deposition accelerates reaching optimum values at 92°C. The pH of the bath also influences the plating rate, the phosphorus content and the adhesion and internal stresses of the final deposit. In practice, the optimum pH required for the acidic electroless nickel bath⁵⁷ is 4.5. The concentration of nickel ions and sodium hypophosphite vary with application; typical values are 4–6 g dm⁻³ and 36–50 g dm⁻³ respectively. Mechanical movement of the plated parts or stirring the solution is not necessary but is, however, advisable as reactants are transported more efficiently and hydrogen gas is taken away from the surface to be plated. A typical electroless nickel bath formulation is shown in Table 6.4.

6.3 Characteristics of electroless deposits

Different needs are required depending on the application; e.g. a non-porous film will provide protection against penetration of corrosive agents and will allow good conductivity for electronic and battery applications.

Table 6.4 A typical electroless nickel bath formulation.⁵⁴ The bath was operated at a temperature of 90 °C at pH 4.8. The plating rate was 12 $\mu\text{m h}^{-1}$ and the average phosphorus inclusion was 11–12 wt%

Compound	Class of additive	Concentration
Nickel (metal ions)	Metal ion	6 g dm ⁻³
Sodium hypophosphite	Reducing agent	36 g dm ⁻³
Lactic acid (88%)	Complexant–buffer	15 g dm ⁻³
Malic acid	Complexant–buffer	15 g dm ⁻³
Citric acid	Complexant–buffer	10 g dm ⁻³
Succinic acid	Exaltant	5 g dm ⁻³
Propionic acid	Exaltant	5 g dm ⁻³
MoO ₃	Stabiliser	5 ppm dm ⁻³

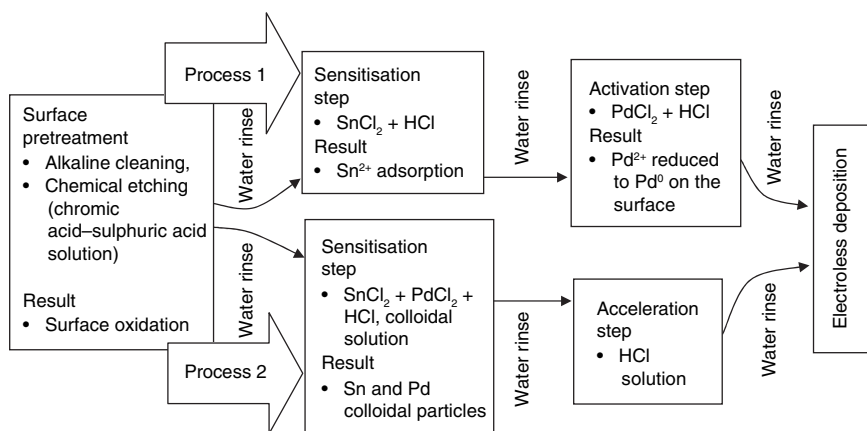
Electroless deposits also provide elastic and ductile deformation, absorbing and dissipating stress in hard ceramics materials.⁵⁸ For example, fractures in metal ceramic composites can be crack-bridged by electroless deposition of nickel on alumina composites;^{59,60} electrical and magnetic properties of a particular substrate can also be modified by electroless deposition, as in the case of nickel on mica fillers incorporated into an acrylonitrile–butadiene–styrene resin which is used as an electromagnetic interference shielding material in the electronics industry.⁶¹

6.3.1 Surface activation and pretreatment

Ramaseshan *et al.*⁶² reported the pretreatment of commercial titanium and aluminium powders of less than 75 μm and less than 45 μm particle size respectively mixed in an 80:20 ratio. The pretreatment consisted of immersing 50 g of the mixture in a 1 L solution containing 30 g of NiCl_2 , 7 g of NH_4Cl , 30 g of NaF and 20 g of sodium citrate, followed by rinsing with distilled water and drying under an infrared lamp. The purpose of the pretreatment was to remove the oxide layer on the surface of the titanium and aluminium particles and replace it with a monolayer of nickel atoms. The pretreated powder was then immersed in a 1 L stirred solution containing 30 g of NiCl_2 , 10 g of sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), 50 g of NH_4Cl and 100 g of sodium citrate at pH 9–8 and 88 °C. The immersion time varied from 5 to 40 minutes. Analysis by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed a very uniform coating thickness. This $\gamma\text{-TiAl}$ -based alloy coated with nickel has been proposed as a lightweight structural material for high-temperature aerospace applications.

Electroless deposition on non-conductive materials such as glass, silicone or polymers requires an activation procedure in order to provide catalytic sites on their surfaces. Two processes are used to condition the non-metallic surface for electroless deposition.⁶³ The first includes solvent cleaning and chemical etching followed by rinsing and surface adsorption of Sn^{2+} ions by immersing the substrate in an $\text{SnCl}_2 + \text{HCl}$ acid solution. The adsorbed stannous ions allow the activation stage by chemically reducing Pd^{2+} ions to Pd^0 on the surface which initiates the electroless deposition of nickel or copper. The second process, more commonly used in industry,⁶⁴ also includes solvent cleaning and chemical etching followed by an activation step with a colloidal solution of $\text{SnCl}_2 + \text{PdCl}_2 + \text{HCl}$. The colloidal tin and palladium particles are surrounded by stannous hydroxides that have to be removed with an HCl solution to allow the palladium particles to function as a catalyst for electroless deposition of nickel or copper metals. The acceleration step is sometimes included within the electroless plating bath. Figure 6.2 shows a schematic diagram of both processes.⁶³

The chemical affinity between Pd^{2+} ions and nitrogen-containing chemical groups has been proposed to avoid using Sn^{2+} ions in an attempt to introduce an alternative environmentally friendly electroless plating bath era.⁶⁵ The pretreatment process for non-conductive substrates such as glasses, silica, polymers or composite substrates consists of the use of plasma or vacuum ultraviolet irradiation or a plasma polymerisation process. The plasma treatment activates the inert surface by grafting specific functional groups such as NH_3 or N_2 on which Pd^{2+} ions chemisorb directly, avoiding the use of Sn^{2+} ions. The plasma grafting process allows selective activation



6.2 Conventional electroless activation-pretreatment processes.⁶³

of areas which is useful on substrates with complex geometry. It was found that Pd^0 atoms were the true catalyst of the electroless initiation reaction and that the adsorbed Pd^{2+} ions are reduced by immersing the substrate in a hypophosphite solution.

A pretreatment consisting of depositing copper seeds by PVD before the application of electroless copper is used in the integrated-circuit industry.⁶⁶

6.3.2 Deposition rate

Electroless metal deposition rates can be measured by two methods traditionally used to evaluate corrosion rates.⁶⁷

1. The interception of the vertical axis in a current versus potential curve at high polarization of the cathodic or anodic process.
2. Cathodic or anodic currents measured at the mixed potential at low polarization values.

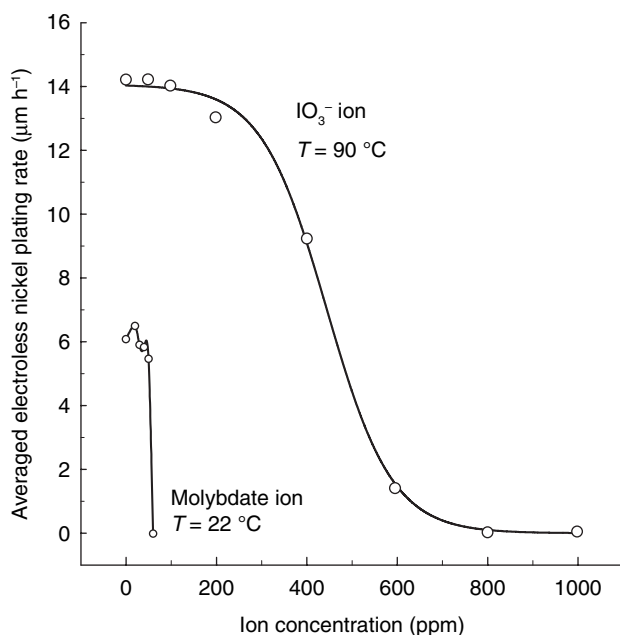
The mixed-potential value arises from the mixed-potential theory (MPT) that takes into account an electrochemical system consisting of two redox couples in equilibrium. When no faradaic process occurs, the total current is zero. However, the condition of zero current also exists in a non-equilibrium condition, when one component of the redox couple catalyses the electron transfer, the potential at this point is called the mixed potential.⁶⁸ Although the MPT explains heterogeneous processes involving mostly corrosion, the theory has generated a large amount of research trying to establish the mechanism of electroless deposition processes.¹³ El-Raghy and Abo-Salama⁶⁹ have pointed out the difficulty of explaining electroless deposition with the MPT model without simultaneous measurement of both oxidation and reduction processes. They found that in the electroless copper process the deposition rate decreased with time because of the anodic polarisation caused by the evolution of hydrogen as a result of the oxidation of formaldehyde while copper deposition took place.

Many other factors affect the electroless deposition rate and the thickness of the deposited layer. Since, as mentioned in Section 6.2, electroless baths include precursors, additives, complexing and wetting agents, buffers, stabilisers-inhibitors and catalysts, the deposits invariably contain a certain amount of these constituents and they can influence the deposition rate. Stabilisers are absorbed on active plating sites and so prevent the electroless metal from 'bombing out'. The higher the concentration of the stabiliser, the lower is the electroless deposition rate, as the active sites become covered and the bath is over-stabilised. Figure 6.3 shows the influence of two stabilisers for electroless nickel deposition: iodate and molybdate ions. The deposition rate was $14 \mu\text{m h}^{-1}$ when the concentration of iodate ion was

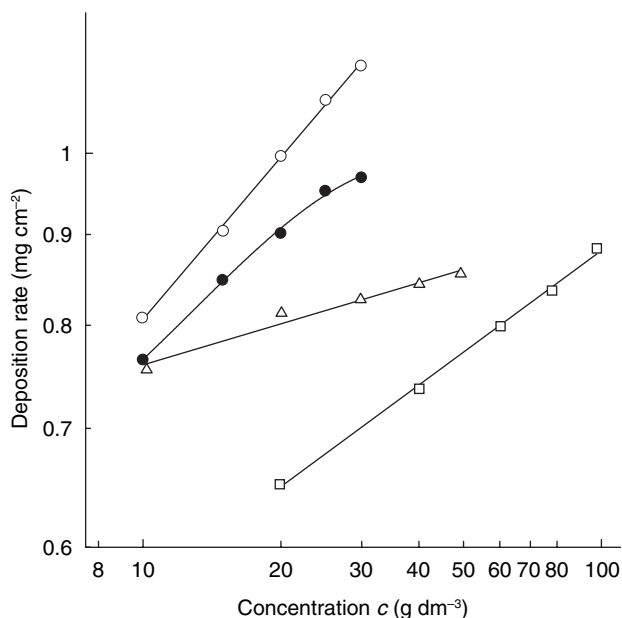
zero but the rate slowly decreased to $1 \mu\text{m h}^{-1}$ on addition of 600 ppm of the stabiliser. The iodine atom bonded to the surface reduced the possibility of contact between the surface and the oxidant agent. Similarly, when more than 50 ppm of molybdate was added to an electroless nickel plating bath the deposition rate decreased from 6 to almost $0 \mu\text{m h}^{-1}$.

Figure 6.4 shows the increase in deposition rate as components in the electroless copper deposition bath increased, one at a time for 30 min. Among all components in the bath, the figure shows that the rate was larger when the concentration of CuSO_4 increased.⁶⁹

Gravimetric measures are also used to estimate the deposition rate. For example gravimetric calculation of electroless copper deposition using formaldehyde and EDTA as reducing and complexing agents respectively showed that the deposition rate ranged from $1.8 \text{ mg h}^{-1} \text{ cm}^{-2}$, according to O'Sullivan,¹³ to $1.59 \text{ mg h}^{-1} \text{ cm}^{-2}$, according to Paunovic and Vitkavage.⁶⁷ These values compare well with the theoretical calculated value¹³ from the MPT of $2.2 \text{ mg h}^{-1} \text{ cm}^{-2}$. The electroless deposition rate also varies with concentration of metal ions, reducing agent, pH and temperature. When glyoxylic acid (HCOCOOH) was used as a reducing agent for electroless



6.3 The effect of the concentrations of iodate and molybdate ion stabilisers on the deposition rate of electroless nickel⁷⁰ at pH 5.



6.4 Effect of various bath components on the electroless deposition of copper:⁶⁹ ○, CuSO_4 ; ●, NaOH; △, formaldehyde; □, tartrate.

copper deposits instead of formaldehyde (H_2CO), the deposition rate was $3.3 \mu\text{m h}^{-1}$ at pH 11–12.5 and 60°C using EDTA as complexing agent and increased to $6 \mu\text{m h}^{-1}$ at 70°C . With formaldehyde, however, the deposition rate was only $2.3 \mu\text{m h}^{-1}$. The deposited film was able to elongate up to 10% when glyoxylic acid was used compared with 5–6% with formaldehyde and the uniformity in a plated through-hole was 20% for formaldehyde whereas with glyoxylic acid⁷¹ it was 90%. The plated-through-hole test probes the capacity of the electroless bath to penetrate into small cavities, leaving a uniform layer of metal. The electroless deposition rate of nickel in aminoborane baths varied between 7 and $12 \mu\text{m h}^{-1}$ while the values in sodium borohydride baths were $25\text{--}30 \mu\text{m h}^{-1}$ and in hydrazine baths $12 \mu\text{m h}^{-1}$, according to Agarwala and Agarwala.¹¹

6.3.3 Deposit thickness

One of the advantages of electroless deposition in comparison with electrodeposition is that the substrate surface on which a metal is deposited does not present problems of non-uniform current density distribution normally found in electrodeposition processes. This in principle should lead

to a more uniform and continuous coating. Kuiry *et al.*⁶⁰ described the formation of 120–140 nm nickel nanoparticles produced after a layer of electroless nickel of 30 nm thickness deposited on Al_2O_3 was laser irradiated. Further investigation by TEM revealed that additional 5 nm size particles were created owing to laser irradiation. They found that the number of nickel particles per unit volume decreased as the coating thickness increased. The thickness of the electroless nickel deposit depends also on the composition of the bath. Table 6.5 shows typical thicknesses of Ni–P coatings for different industrial applications.^{11,72}

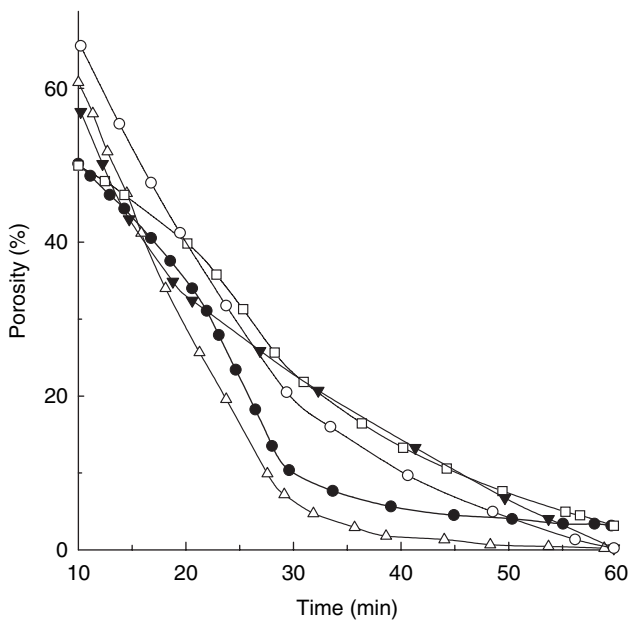
Electroless deposition of copper on copper seeds deposited by PVD provides a thin continuous uniform layer⁶⁶ of metal across wafers of 200 and 300 mm. The electroless deposit thickness can be as low as 100 Å because mass transport in electroless processes is slow and because of the absence of primary current distribution which is a characteristic of electroless deposition.

*Table 6.5 Applications of electroless Ni–P coatings.*¹¹ Further uses are considered: fuel injectors, fuel pump motors, water pumps and equipment, printing roles, fabric knives, plastic injection moulds, mirrors, electrical connectors, diesel engine shafts, motor shafts and stators, pressure vessels, valves, oil field tools and extruders⁷²

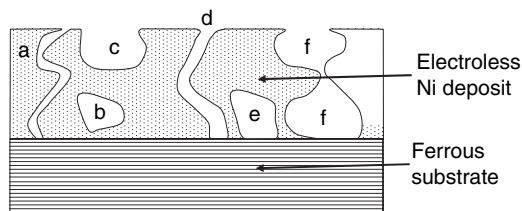
Application of Ni–P coatings	Typical deposit thickness (μm)
Automotive	2–38
Aircraft and aerospace	10–50
Chemical and petroleum	25–125
Electrical	12–25
Electronics	2–25
Food	12–25
Marine	25–50
Material handling	12–75
Medical and pharmaceutical	12–25
Military	8–75
Mining	30–60
Moulds and dies	15–50
Printing	≈38
Railroad	12–50
Textiles	12–50
Wood and paper	≈30
Chainsaw engine	≈25
Drills and taps	≈12
Precision tools	≈12
Shower blades and heads	≈8
Pen tips	≈5

6.3.4 Corrosion resistance and porosity

The corrosion and wear resistance of electroless deposits are closely linked to their porosity as noted by Kerr *et al.*⁷³ The presence of pores can accelerate the corrosion of the substrate and, therefore, it is important to assess this property in order to consider the life expectancy of an electroless coating. Pores can be classified by their size, geometry or by their point of origin; through-pores are those initiated at the substrate and traverse through the deposit, and pores originating in the deposit are masked pores. Through-pores can occur verti-



6.5 Percentage of porosity versus time of Ni electroless deposit on steel, calculated by the ammonium thiocyanate method. The samples were pretreated with alkaline soak cleaner Duraprep 115 solution at 60°C followed by different pretreatment cycles including; a) ● Hot rinse with deionised (D.I.) water at 50°C followed by immersion in 1:1 mixture of HCl and D.I. water at 25°C; b) △ Similar to 'a' with chemical polish at the end; c) □ Hot rinse with D.I. water at 50°C followed by immersion in Electroclean – Duraprep 215 solution at 60°C and electrochemical treatment consisting of 5 A dm⁻² of applied cathodic current followed by cold rinse in D.I. water and pickle in a 1:1 mixture of HCl and D.I. water at 25°C; d) ▼ Similar to 'c' with but with 2 A dm⁻² of anodic current; and e) ○ Immersion in Electroclean – Duraprep 215 solution at 60°C followed by: 5 A dm⁻² applied cathodic current, cold rinse with D.I. water, pickle in acid – as pretreatment 'a', cold rinse with D.I. water, immersion in Electroclean – Duraprep 215 solution at 60°C, applied anodic current at 2 A dm⁻² and cold rinse with D.I. water.⁷⁴



6.6 Illustration of various pore types: a, convoluted pore; b, void; c, dead end pore (pit); d, continuous pore; e, pore sealed at the surface; f, branched pore (combination of a surface pit and a pore sealed at the surface of the substrate, connected by a small channel).⁷⁴

cally or as part of the network and microscopic techniques are required to characterise them if they are smaller than 1 mm diameter. Masked pores can also be formed by stress in the coating and by further metal deposition on a cavity; these pores can be difficult to measure. Porosity decreases as the thickness of the electroless deposit increases by additional layers, as shown in Fig. 6.5 for various pretreated substrates coated with electroless nickel.⁷⁴

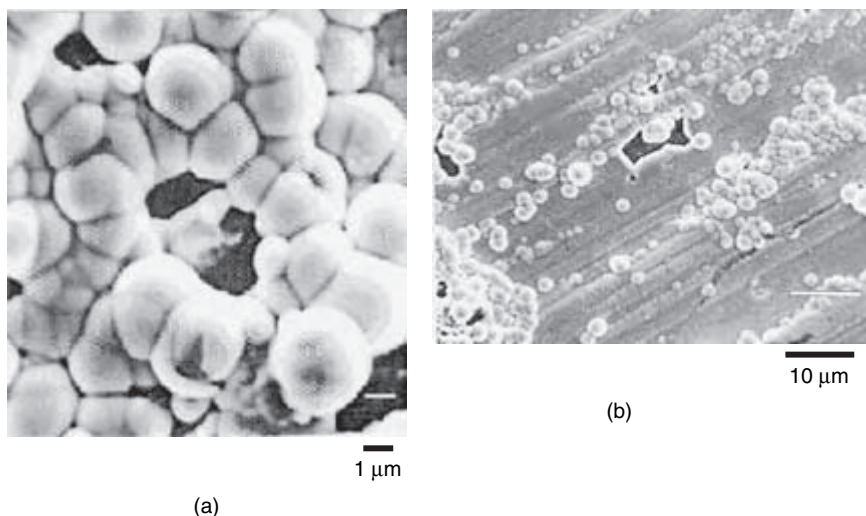
Porosity can be caused also by the roughness of the substrate; in general the smoother the substrate, the less porous is the electroless coating. Figure 6.6 shows a schematic illustration of the various types of pore.⁷⁴

The porosity of an electroless deposit can be caused by blisters formed by the incorporation and accumulation of hydrogen gas in the electroless deposited metal or at the metal–substrate interface. Blisters can weaken the adherence of the deposit and cause high porosity. The more porous the electroless layer, the more quickly corrosive agents can reach the substrate. Chemical additives such as $K_4Fe(CN)_6$ or 2-2'-dipyridyl and heat treatment reduce the amount of hydrogen trapped during metal deposition and improve the ability of the deposit to deform when the pressure of the remaining hydrogen gas increases in the metal network.⁷¹

Figure 6.7 shows SEM images of an electroless nickel coating on mild steel. Figure 6.7(a) is the image of a pore in a branched network system whereas Fig. 6.7(b) is a continuous through-pore.⁷⁴

Porosity can be measured by Tafel extrapolation, SEM analysis and cyclic voltammetry.^{73,75–77} Traditional porosity evaluation involves chemical spot tests by treating the coating with corrosive reagents such as SO_2 or by using it as an anode when covered with a filter paper impregnated with an indicator containing a 15% solution of NH_4SCN . Porosity is revealed by red–brown–coloured dots on the filter paper after passing a low current through the anode.

The corrosion potential of a substrate covered with electroless nickel serves as an indication of the porosity grade of the coating. For example Table 6.6 shows both the corrosion potential and the corrosion current density obtained from Tafel extrapolation experiments carried out on mild



6.7 Scanning electron micrographs showing surface pores in electroless nickel deposits of 6 μm thickness on mild steel: (a) nodular electroless nickel deposit showing a branched pore network; (b) surface pores extending through the deposit to expose the mild steel substrate.⁷⁴

steel substrates (BS 970) covered with three different electroless nickel thicknesses. Prior to plating, the substrates were mechanically pretreated as follows: milled (fly cut), grit blast coarse or grit blast fine. This was followed by a chemical pretreatment with an electrolytic alkaline cleaner, chemical polish and immersion in potassium permanganate.⁷⁵ The corrosion potential values of the mild steel samples shown in the table varied little for the different pretreatments with the same electroless nickel coating thickness; however, in all cases the potentials become noble, i.e. more positive, as the coating thickness increases, i.e. as the porosity decreases. The data also show that the corrosion current decreases as the electroless nickel coating becomes thicker; Reade *et al.*⁷⁵ suggested a critical coating thickness of 12 μm as a minimum requirement for good corrosion resistance on smooth surfaces.

The porosity of electroless nickel coatings on zincated aluminium substrates was evaluated by Tafel analysis in 5% NaCl and 0.05 M NaOH at 22 °C. Table 6.7 shows that the corrosion current density when the samples were treated in 5% NaCl decreases from 102 μA cm⁻² at 1 μm to 1.5 μA cm⁻² at 3 μm for an electroless nickel coating obtained from a commercial electroless nickel-plating process containing 10.5–13% of phosphorus.⁷⁰ The corrosion current follows a similar trend for another commercial plating process with slightly higher phosphorus content, 12–14%: from 268 μA cm⁻² at 1 μm to 2 μA cm⁻² at 3 μm. Above 3 μm thicknesses the corrosion current

Table 6.6 Data on the corrosion potential E_{corr} and corrosion current density j_{corr} obtained from Tafel extrapolation experiments on various electroless nickel deposits on several mild steel substrates⁷⁵

Nickel thickness (μm)	E_{corr} and j_{corr}	Electrolytic alkaline cleaner			Chemical polish			Potassium permanganate		
		Milled	Grit blast coarse	Grit blast fine	Milled	Grit blast coarse	Grit blast fine	Milled	Grit blast coarse	Grit blast fine
15	E_{corr} (V versus SCE)	-0.434	-0.482	-0.493	-0.451	-0.460	-0.415	-0.422	-0.441	-0.433
15	j_{corr} (mA cm^{-2})	0.046	0.045	0.048	0.046	0.044	0.051	0.036	0.038	0.044
60	E_{corr} (V versus SCE)	-0.264	-0.306	-0.184	-0.254	-0.277	-0.223	-0.196	-0.200	-0.167
60	j_{corr} (mA cm^{-2})	0.012	0.018	0.022	0.008	0.015	0.027	0.009	0.014	0.021
20	E_{corr} (V versus SCE)	-0.172	-0.190	-0.196	-0.201	-0.195	-0.179	-0.190	-0.132	-0.137
20	j_{corr} (mA cm^{-2})	0.0048	0.009	0.0081	0.007	0.0082	0.01	0.0052	0.005	0.0093

Table 6.7 Corrosion current density values obtained from Tafel analysis⁷⁰ in 5% NaCl and 0.05M NaOH at 22 °C

Electroless nickel deposit thickness (μm)	Corrosion current density (from 10.5–13% P bath) ($\mu\text{A cm}^{-2}$)		Corrosion current density (from 12–14% P bath) ($\mu\text{A cm}^{-2}$)	
	NaCl	NaOH	NaCl	NaOH
0	7400	13.2	7400	13.2
0.5	850	1.05	335	0.21
1	102	0.36	268	0.13
2	3.4	0.27	6	0.14
3	1.5	0.38	2	1.02
6	1.5	0.30	2	0.30
12	1.5	0.22	2	0.28

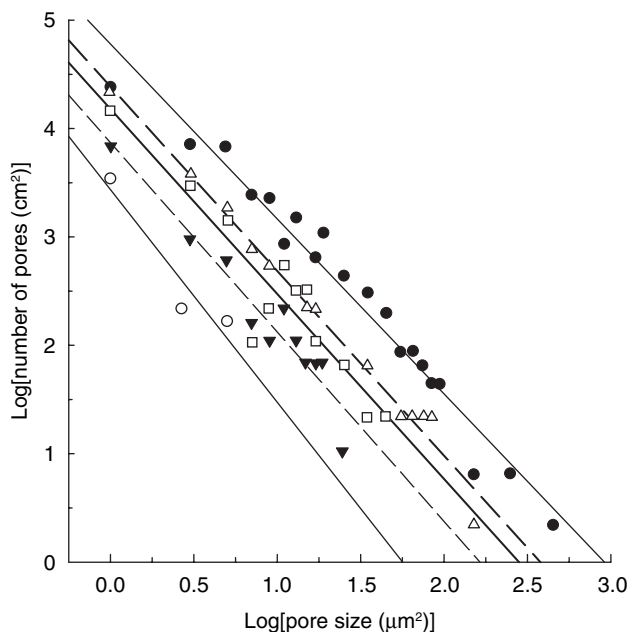
decreases to less than $3 \mu\text{A cm}^{-2}$ in both coatings, indicating a non-porous deposit. In the case of samples treated in 0.05M NaOH, both electroless nickel-plated samples showed a decrease in their corrosion current density from $13 \mu\text{A cm}^{-2}$ for bare aluminium to $1 \mu\text{A cm}^{-2}$ with a $1 \mu\text{m}$ coating.

Porosity is dependent on factors such as the following:

1. The composition of the electroless deposition bath.⁷⁷
2. The process conditions, including temperature and agitation.^{73–78}
3. The age of the electroless bath.⁷⁰
4. The nature of the substrate.⁷⁶

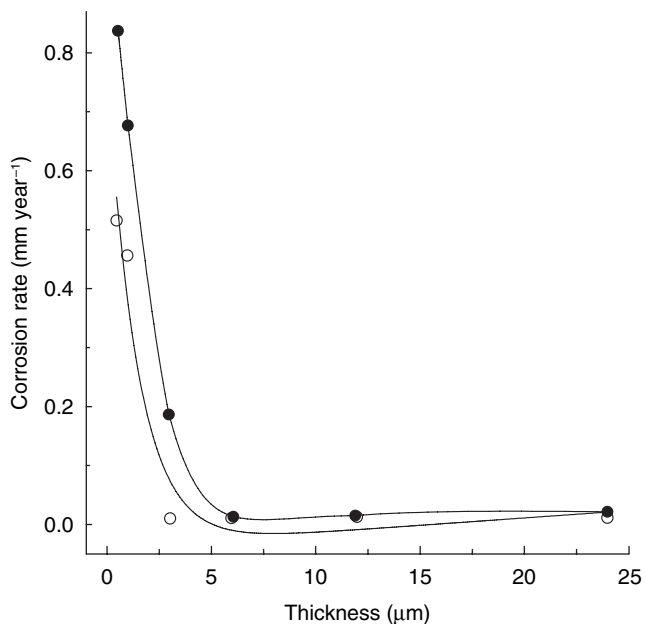
Figure 6.8 shows the log–log plot of the number of pores versus the pore size for an electroless nickel coating of different thicknesses on a Pyrene steel substrate determined from SEM images. The figure shows that the total number of pores decreases as the electroless nickel coating thickness increases on the Pyrene steel substrate.

Incorporation of polytetrafluoroethylene (PTFE) particles into a metal deposit adds additional properties such as lubrication, wear resistance, lower friction coefficients and non-stick surfaces.⁷⁹ A high percentage of PTFE in the composite can cause poor adherence and peeling of the coating; however, the corrosion resistance can improve if the PTFE content gradually increases with increasing distance from the substrate surface.⁸⁰ Electroless nickel also forms composites with P–Cu that act as a strong barrier for corrosion when deposited on copper or carbon steel.^{79,80} The corrosion resistance of Ni–P composites increases when the coatings are melted with a laser beam;⁸¹ the highest corrosion resistance was observed for coatings with a $180 \mu\text{m}$ thickness treated at the highest laser scanning rate of 5952 mm min^{-1} . The corrosion resistance was a function of the dilution and degree of crystallisation of the Ni–P composite on the steel substrate.

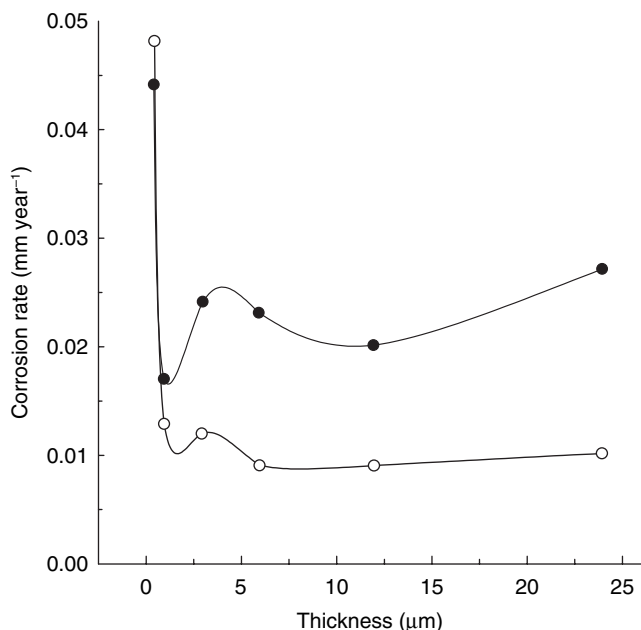


6.8 Log-log plot of the number of pores versus pore size for a Pyrene steel substrate electroless plated with different coating thicknesses:⁷⁴

●, 0.4 μm; △, 0.8 μm; □, 1.2 μm; ▼, 1.6 μm; ○, 2 μm.



6.9 Corrosion rate versus nickel coating thickness in 5% NaCl at 22°C measured by linear polarisation resistance:⁷⁰ ●, 10.5–13% P; ○, 12–14% P.



6.10 Corrosion rate versus nickel Ni coating thickness in 0.05 M NaOH at 22°C measured by linear polarisation resistance:⁷⁰ ●, 10.5–13% P; ○, 12–14% P.

Figure 6.9 compares two pretreated aluminium panels of 1 cm² covered with an electroless nickel layer deposited from two commercial plating baths of similar phosphorus contents. The figure shows the behaviours of the two coatings in a solution of 5% NaCl and demonstrates that the corrosion rate for the coating with 10.5–13% P decreases from 0.8 μm year⁻¹ at a thickness of 0.5 μm to 0.01 mm year⁻¹ at a coating thickness of 6 μm. In the deposit produced from a plating bath containing 12–14% P the corrosion rate decreased from 0.5 mm year⁻¹ to 0.01 mm year⁻¹ after a thickness of 3 μm was achieved.⁷⁰

Similarly, Fig. 6.10 compares the two nickel-coated aluminium plates immersed in 0.05 M NaOH at 22°C. The measurements show an initial decrease in corrosion rate from 0.045 mm year⁻¹ to a 0.015 μm year⁻¹ at a thickness of 1 μm for the deposit from the bath containing 10.5–13% P. The corrosion rate for the corresponding deposit obtained from the higher-phosphorus-content bath (12–14%) decreased to 0.01 mm year⁻¹ at a thickness of 1 μm.

6.3.5 Electrical resistivity

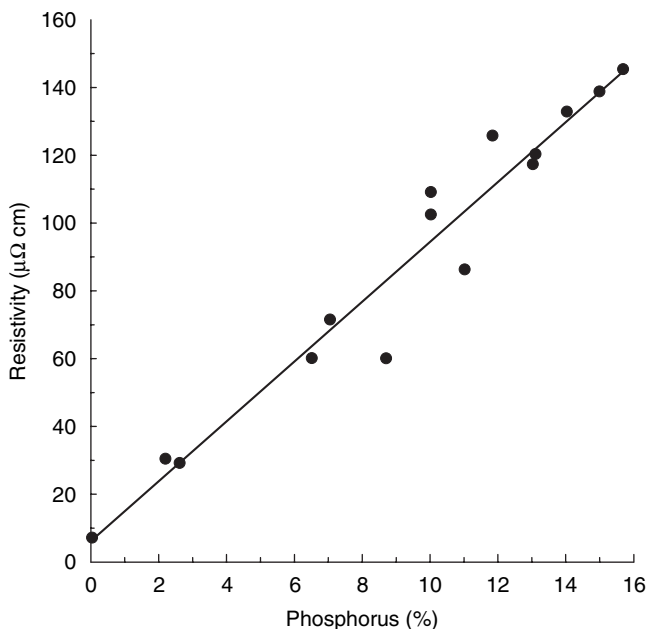
Because of the disruption of the regular lattice structure of pure nickel metal during electroless deposition and the inclusion of other components

in the metal lattice such as additives, complexants, inert matter or other metals, the resistivity of an electroless nickel deposit can be as high as ten times that of the pure metal. Figure 6.11 shows that the typical values of resistivity for an electroless nickel are of the order of 30–100 $\mu\Omega$ cm and illustrates how the resistivity increases linearly with increasing phosphorus content.¹ A resistivity value of $1.9 \pm 0.1 \mu\Omega$ cm, evaluated with a four-point probe, was found⁶³ in an electroless copper layer of 100 nm thickness annealed at 250 °C. The electroless layer was deposited on 10–100 nm PVD copper seed layers deposited on Si/SiO₂/ 25–30 nm wafers used as diffusion barriers for multilayered microelectronic structures.⁸²

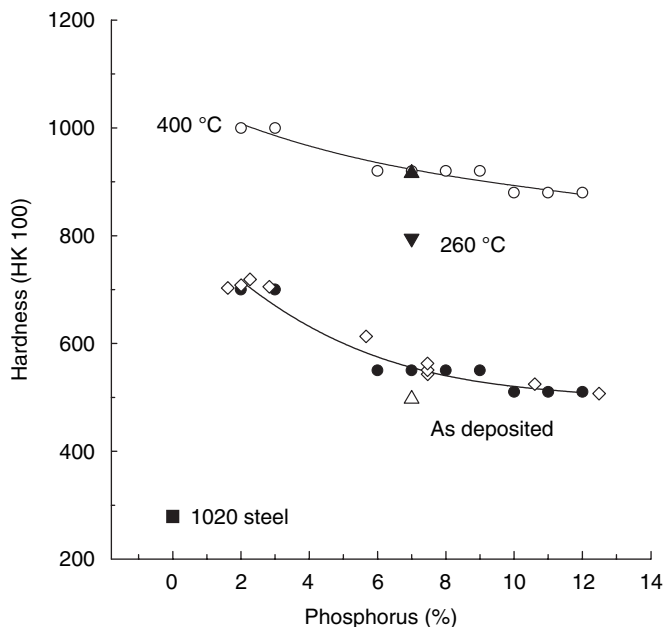
Non-conductive mica was treated with a Niklad 795 electroless plating bath⁸³ to deposit a 0.1 μ m (100 nm) thickness layer of nickel; the uniformity of the deposit changed the resistivity of the mica material from 10¹² to 1 Ω cm when the amount of nickel on 601 mm mica was changed from 20 to 60 wt%.⁶¹

6.3.6 Hardness

Figure 6.12 shows the Knoop hardness of electroless nickel phosphorus deposits from various literature sources compared with the hardness of a



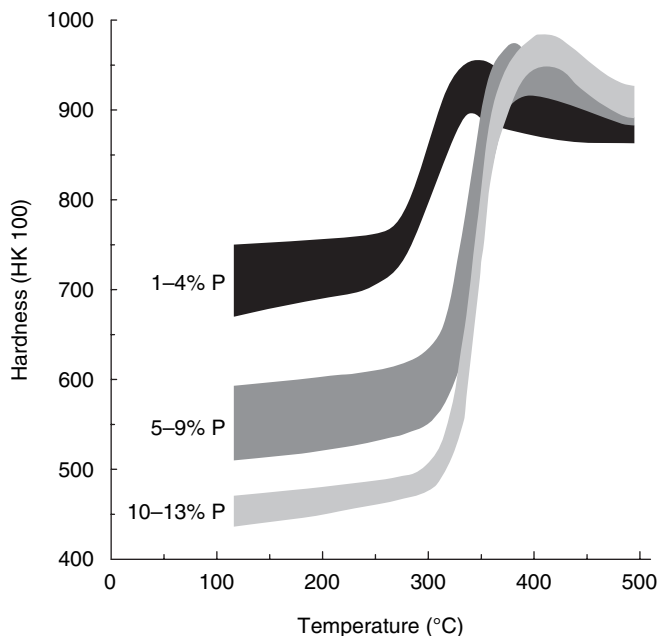
6.11 Effect of the amount of phosphorus in an electroless nickel deposit on the resistivity of the deposit.¹



6.12 Effect of phosphorus content on the Knoop hardness of an electroless Ni-P deposit: ■, 1020 steel;⁸⁴ △, as-deposited Ni-P;⁸⁴ ▼, Ni-P treated at 260 °C for 25 h;⁸⁴ ▲, Ni-P treated at 400 °C for 1 h;⁸⁴ ●, Ni-P as deposited;¹¹ ○, Ni-P treated at 400 °C for 1 h;¹¹ ◇, as-deposited Ni-P.¹

steel surface.⁸⁴ The figure shows that the hardness of the as-deposited Ni-P decreases as the percentage of phosphorus increases. Heat treatment at 260 and 400 °C increases the hardness of the deposit although a similar decrease in hardness with increasing percentage of phosphorus occurs for both as-deposited and heat-treated Ni-P deposits. Figure 6.13 shows the effect of 1 h heat treatment on the hardness of three types of Ni-P deposit classified according to their phosphorus content:¹ 1–4%, 5–9% and 10–13%.

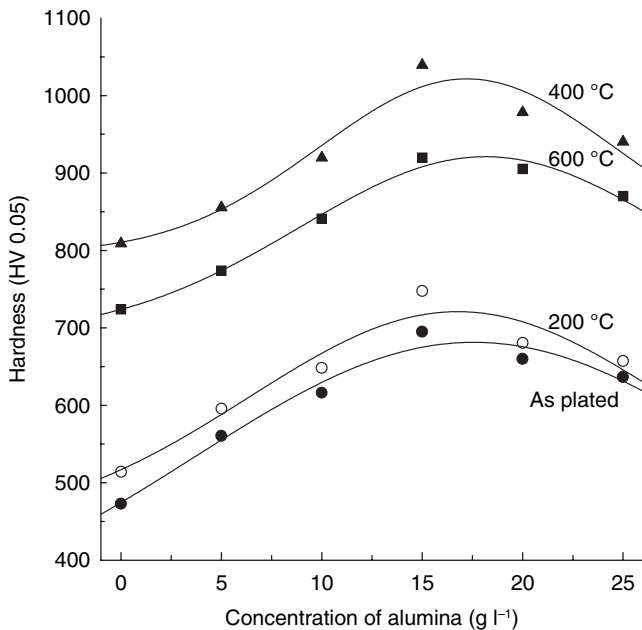
As indicated, the hardness of an electroless deposit is high at low concentrations of phosphorus and also increases with the inclusion of hard ceramic particles in the Ni-P structure of the composite. On the other hand, the inclusion of soft particles such as PTFE decreases the hardness, adding different properties to the coating such as water repulsion, corrosion and electrical resistance. The particle concentration within the electroless deposit increases with increasing concentration of particles in the bath and depends on the hydrodynamic conditions, pH, temperature and the physicochemical characteristics of the particles such as the zeta potential. The maximum level of particle concentration that can be reached in the deposit is normally between 15 and 30%. Hardness increases or decreases with the concentra-



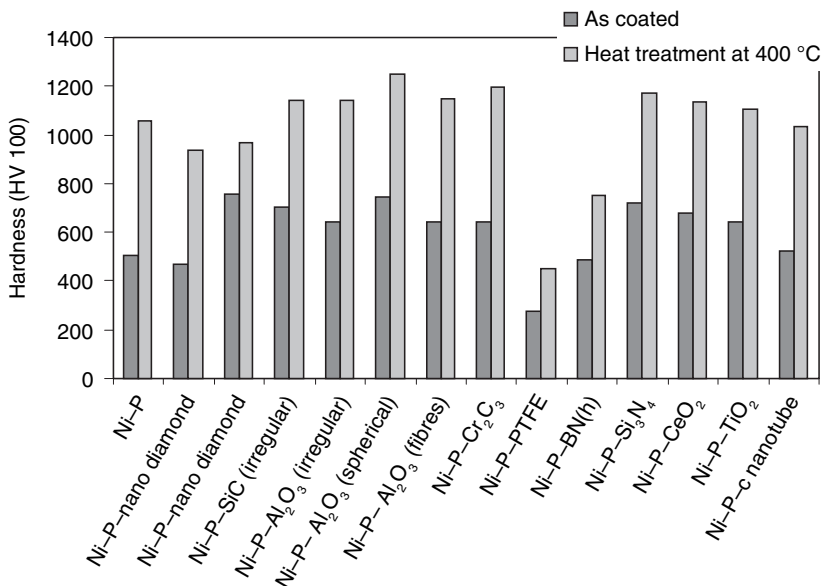
6.13 Effect of 1 h heat treatment and phosphorus content on the Knoop hardnesses of electroless Ni-P deposits.¹

tion of particles and a direct relationship between the number of particles and the composite hardness exists at low particle concentrations. Figure 6.14 shows the change in hardness as the concentration of Al_2O_3 in a Ni-P composite increases. The figure also shows the change in hardness of the composite after it was treated at different temperatures.⁸⁵ The figure indicates that, for Al_2O_3 concentrations up to 15%, the hardness of the composite increases as the particles add deformation resistance to the Ni-P matrix. However, at Al_2O_3 concentrations higher than 15%, the hardness decreases, probably as a result of the disruption of the Ni-P lattice by the particles. Similar behaviour was observed when the composite was heat treated at different temperatures; the harder composite was obtained by a 400°C heat treatment. It has been reported that, above this temperature, the Ni_3P precipitate changes from coherent to non-coherent, resulting in a decrease in hardness.

Incorporation of different particles such as TiC , Si_3N_4 , CeO_2 and TiO_2 can improve the hardness of the composite without significant alteration of the Ni-P structure.^{78,79} Figure 6.15 shows the hardnesses of electroless Ni-P deposits when different types of material are incorporated into the nickel lattice.⁷⁹ The percentage of phosphorus in the composites ranged from 6 to 10.4 wt%,



6.14 Effect of the concentration of Al₂O₃ particles and heat treatment on the Vickers hardness of Ni-P-Al₂O₃ composite coatings.⁸⁵



6.15 Comparison of the Vickers hardnesses of different composites⁷⁸ as deposited and after heat treatment at 400 °C.

whereas the percentage of particles varied from 0.52 to 7.44 wt% corresponding to 9.7 to 28.6 vol.%. The figure shows the hardness of the composite coating at room temperature and the hardness after heat treatment at 400°C, according to Balaraju *et al.*⁷⁸ The study showed that the hardness of the composites increased with increasing heat treatment temperature, reaching its maximum at 400°C and then decreasing. Balaraju *et al.* suggested that the Ni₃P hardening mechanism occurs to a certain degree in all composites.

6.3.7 Internal stress

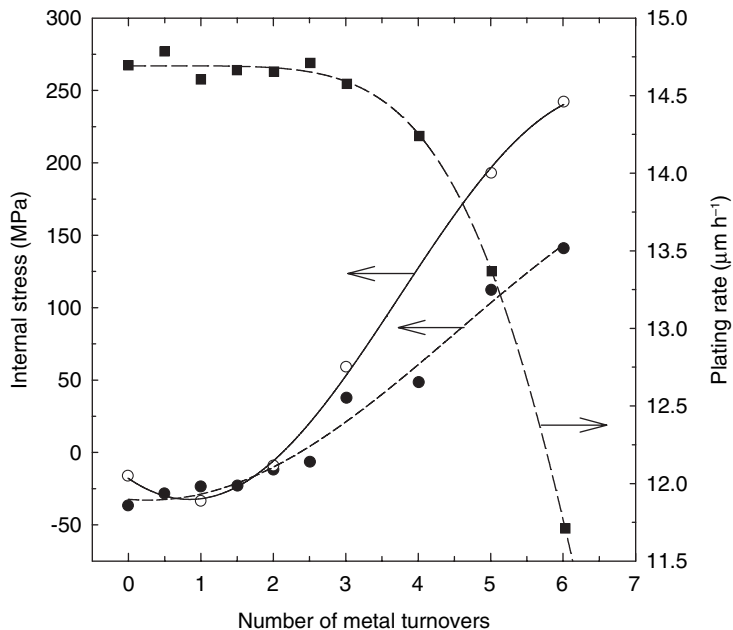
Metal deposited by electroless processes can present tensile, compressive or zero residual stress which will have a direct effect on the physical properties of the deposit. A coating with high tensile residual stress will lead to cathodic deposits prone to cracking, corrosion and poor adhesion. Compressive stress, on the other hand, can lead to a reduction in porosity. Electroless deposits from fresh solutions produce layers of metal with an internal compressive stress; in the case of nickel the compressive residual stress decreases with increasing phosphorus content and then becomes tensile with further increase in phosphorus content. The phosphorus content in the deposits depends on the age of the solutions, i.e. the number of turnovers, one turnover being the equivalent of plating out 6.1 g dm⁻³ of nickel from a solution with an initial concentration of 6.1 g dm⁻³. The electroless bath is semi-continuously corrected to maintain 6.1 g dm⁻³ concentration by addition of nickel salts. Figure 6.16 plots the internal stress and the plating rate from an electroless nickel solution as a function of the number of metal turnovers of the plating bath.

The internal stress increases as the number of turnovers changes and the deposition rate drops after about three turnovers, at which point the internal stress rises.⁸⁶

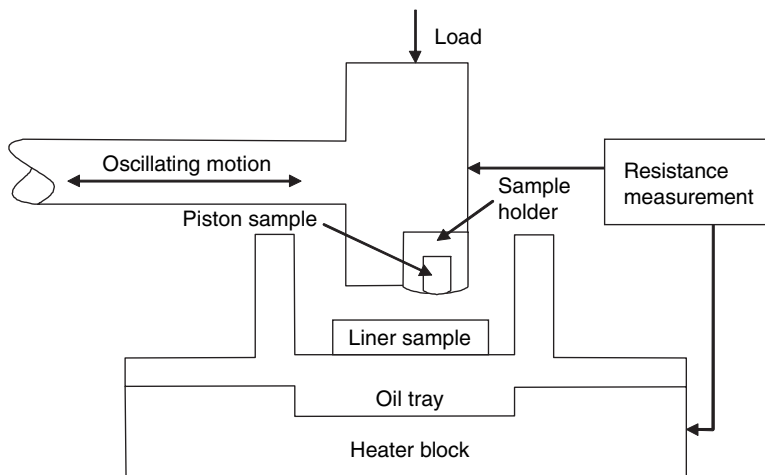
6.3.8 Wear resistance

Wear occurs in the area of contact between two solids; in uneven surfaces the contact is limited to points rather than areas on both surfaces, through which any load can be transferred. Hardness, ductility, surface finishing, lubrication, corrosion and temperature are key factors in wear resistance. The wear mechanism of materials is complex and can be originated by abrasion, adhesion, erosion, impact, compression, cavitations, corrosion, oxidation or thermal shock. Bench tests available for wear testing consist of surfaces sliding against each other and are designed considering the geometry, type of contact and type of motion; these could be flat disc or block, pin-on-disc, block-on-ring, crossed cylinders and four balls.⁸⁷

Figure 6.17 shows a typical set-up for evaluation of the wear resistance of a piston coating; a data acquisition system normally monitors friction,



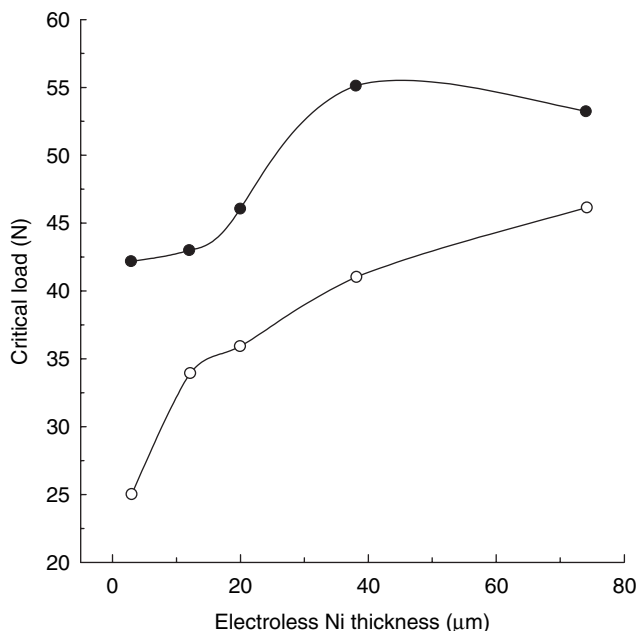
6.16 Comparison of internal stress and plating rates with numbers of turnovers for high-phosphorus electroless nickel baths:⁸⁶ ■, plating rate; ●, calculated internal stress; ○, internal stress according to the bath manufacturers.



6.17 Schematic diagram of the bench test arrangement for an aluminium piston skirt coating.⁸⁷

contact potential and temperature and tests can be carried out with or without a lubricant.

Hybrid techniques involve composite coatings with tailor-made properties for specific applications; in a study of the wear resistance of copper and brass substrates coated with electroless nickel followed by TiN coating by the PVD technique, the adhesion and abrasive wear properties were evaluated with a scratch tester.⁸⁸ The adhesion of the coating to the substrate was tested by load increase on the sample. The critical load increases with increasing electroless nickel thickness until a maximum value is reached, when the observed wear is free from substrate effects. Figure 6.18 shows the increase in critical load as a function of the electroless nickel interlayer thickness for copper and brass substrates. A maximum load for a brass substrate was found at an electroless nickel thickness of approximately 30 μm but no maximum was found for the copper substrate. Subramanian *et al.*⁸⁸ concluded that, in the case of copper, the electroless nickel interlayers still suffer the effect of the soft substrate at a thickness of 74 μm . Larger normal loads applied on to the electroless nickel coatings increased the average scratch peak height, the scratch valley depth and the scratch width

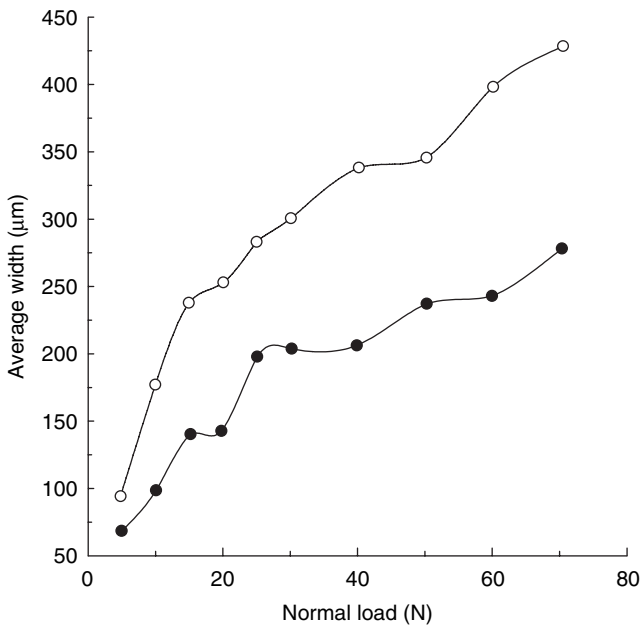


6.18 Critical load versus electroless nickel thickness for brass (●) and copper (○) substrates electroless nickel plated and coated with TiN.⁸⁸

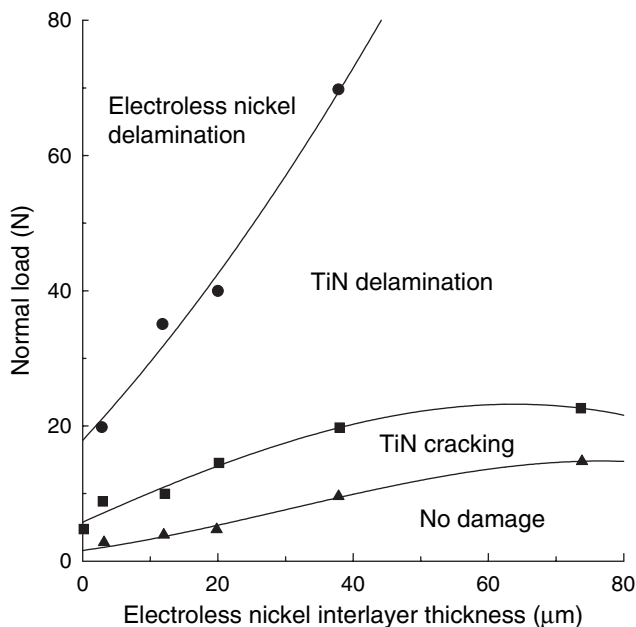
for a given electroless nickel thickness. The average scratch width as a function of the normal applied load for an electroless nickel thickness of $10\text{ }\mu\text{m}$ is shown in Fig. 6.19. From the plots it is evident that the deformation was larger on the softer substrate, copper.

Wear maps for copper and brass substrates coated with TiN with different electroless nickel interlayer thickness were constructed by observing the scratch tracks under the microscope. Figure 6.20 indicates the wear map for copper substrates, where four regimes of coating failure as a function of applied load and electroless nickel coating can be observed. The map shows the limits at which TiN coatings can be used; e.g. at normal loads below 10 N and an electroless nickel interlayer thickness of 30–40 nm there is no damage to the system; however, electroless nickel delamination occurs at high loads and with a thin electroless nickel interlayer.

The wear resistance of an electroless Ni–P coating on AISI plain carbon steel evaluated by the pin-on-disc test increased⁸⁴ substantially after heat treatment at 260 and 400 °C. The wear resistance tests were carried out under dry non-lubricated conditions using a pin made of AISI 52100 steel. The electroless Ni–P coating was obtained from a solution of NiCl_2 at pH



6.19 Average width of a scratch as a function of the normal load applied to copper (○) and brass (●) substrates coated with an electroless nickel interlayer of $10\text{ }\mu\text{m}$ and coated with TiN.⁸⁸

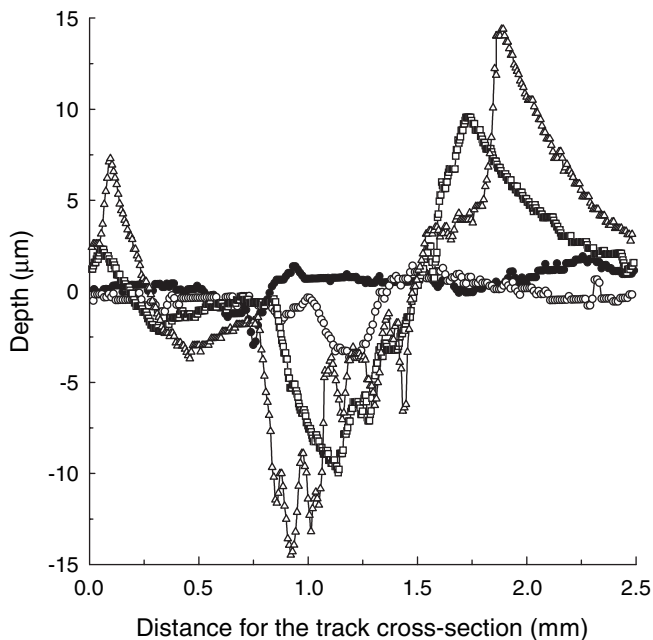


6.20 Wear map for TiN coatings on copper with an electroless nickel interlayer.⁸⁸

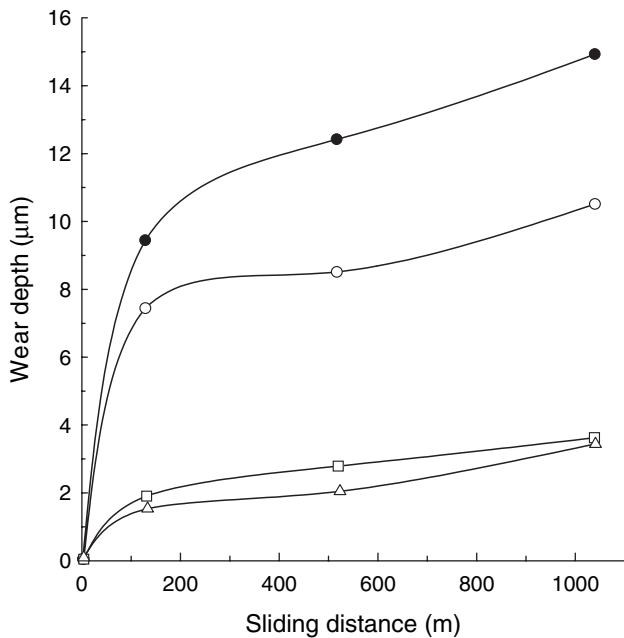
5.2 with NaH_2PO_2 as a reducing agent. Figure 6.21 shows the wear track depth profile produced by the pin-on-disc test for the as-deposited electroless Ni-P, the carbon steel substrate and the coatings heat treated at 260 and 400 °C after a sliding distance of 1040 m. The wear depth reached 15 μm for the as-deposited coating and 10.5 μm for the carbon steel substrate at sliding distance of 1040 m. The heat-treated samples showed a wear scar depth of only 3.5 μm (Fig. 6.22).⁸⁴

6.4 Conclusions

1. Electroless deposition takes place via an autocatalytic redox process.
2. In comparison with electroplating, electroless deposition has the advantages of more uniform deposit thickness (particularly on more complex workpiece geometries) and obviates the need for electrical connections to the workpiece. The cost of electroless deposition, however, is appreciably higher than electroplating, for a given deposit thickness.
3. While many metals have been deposited using the electroless technique, nickel-based coatings have dominated engineering applications. In



6.21 Track depth profiles for Ni-P samples after sliding for 1040 m: $\triangle$, Ni-P as deposited;⁸⁴ $\circ$, Ni-P heat treated at 260 °C;⁸⁴ $\bullet$, Ni-P heat treated at 400 °C;⁸⁴ $\square$, 1020 carbon steel.⁸⁴



6.22 Wear depth versus sliding distance: $\bullet$, as-deposited Ni-P;⁸⁴ $\circ$, 1020 carbon steel;⁸⁴ $\square$, Ni-P heat treated at 260 °C;⁸⁴ $\triangle$, Ni-P heat treated at 400 °C.⁸⁴

addition to the common Ni-P alloy coatings obtained from hypophosphite baths, it is also possible to deposit inclusions of hard particles (e.g. SiC or Al₂O₃) or soft particles (e.g. PTFE or MoS₂) to produce composite coatings having wear-resistant and self-lubricating properties.

4. In order to achieve satisfactory coatings for demanding engineering applications, due attention must be paid to the composition of the electroless bath (including electrolyte additives) and the operating conditions.
5. Adequate surface finishing and chemical pretreatment are also vital in the achievement of high-quality coatings.
6. Important properties of electroless coatings for engineering applications include corrosion resistance, porosity, electrical resistivity, hardness, internal stress and wear resistance.
7. Deposit properties are dependent not only on surface pretreatment, bath composition and process conditions but also on the age of the electrolyte; in practice with electroless nickel solutions, it is common to achieve an electrolyte lifetime of fewer than six metal turnovers before the electrolyte is replaced.

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6.6 Appendix: Professional associations

European Academy of Surface Technology (EAST)

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Germany

<http://www.east-site.net>

Institute of Corrosion

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NACE International

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USA

<http://www.nace.org>

Surface Engineering Association (SEA)

Federation House

10 Vyse Street

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<http://www.sea.org.uk>

The American Electroplaters and Surface Finishers Society, Inc. (AESF)

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Electroplating for protection against wear

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7.1 Introduction

Electrolytic deposition offers a versatile and powerful method for surface coating. Important properties for electrodeposits include wear resistance, hardness, ductility, porosity, internal stress, coating adhesion and corrosion resistance. All these properties and characteristics can be altered by the appropriate selection of a number of variables, such as temperature, species concentration, electrolyte pH, current density, electrolyte flow conditions and the use of electrolyte additives.

Producing a surface coating via electrolytic deposition may involve a number of important processes, including substrate preparation, coating formation and finishing. Table 7.1 presents a selection of processes that may be utilised for surface coatings.

The deposit thickness may be controlled by operating the process for a fixed time and at constant current density, as described by Faraday's laws of electrolysis. Consider a metal, M , deposited from a solution of its ions, M^{z+} , according to



Under steady-state conditions and with a constant current I , the rate of coating thickness x development with time t can be described by

$$\frac{dx}{dt} = \frac{MI\phi}{\rho AzF} \quad [7.2]$$

where M is the molar mass of the material, ϕ is the current efficiency, ρ is the density of the plated layer, A is the deposition area, z is the number of electrons transferred per deposited particle and F is the Faraday constant. Hence, assuming a current efficiency of 100% with a given current density and known electrode area, the development of coating thickness with time can be estimated for any metal. This has been tabulated for a selection of metals using a current density of 1 A dm^{-2} (Table 7.2). The deposit

Table 7.1 Processes involved in producing an electrolytic deposit

Process	Type	Description
Alkaline soak	Pretreatment	Surface wetting, degreasing and cleaning of substrate
Acid soak	Pretreatment	Removal of oxide films and surface roughening for keying electrodeposit to substrate
Solvent soak	Pretreatment	Degreasing and surface cleaning, typically with an organic solvent
Metal strike	Pretreatment	Formation of a thin metallic base layer. Used when the primary coating material does not easily deposit on to the substrate
Plating	Deposition	Electrophoretic or electrodeposition of the main surface coating
Polishing	Finishing	Smoothing or grinding the deposit for aesthetic appeal
Heating	Finishing	Heat treating the deposit to improve characteristics such as hardness
Sealing	Finishing	Application of a secondary electrolytic deposit or lacquer to protect the main deposit

Table 7.2 Data for various metals enabling calculation of coating thickness development with time (Barker and Walsh, 1991), assuming a current density of 1 A dm^{-2} and a current efficiency of 100%

Deposited metal	Number of electrons z	Molar mass M (g mol^{-1})	Density ρ (g cm^{-3})	Rate of thickness development dx/dt ($\mu\text{m h}^{-1}$)
Cadmium	2	112.4	8.65	24.3
Chromium	3	52.0	7.19	9.0
Chromium	6	52.0	7.19	4.5
Cobalt	2	58.9	8.80	12.5
Copper	1	63.5	8.93	26.5
Copper	2	63.5	8.93	13.3
Nickel	2	58.7	8.91	12.3
Silver	1	107.9	10.50	38.3
Zinc	2	65.4	7.19	17.1

thickness can vary from monolayers at one extreme to hundreds of micrometres (in the case of, for example, wear-resistant hard chromium coatings).

Two assumptions were made in Table 7.2.

1. The current efficiency is 100%. This is not the case in reality, although efficiencies approaching 100% can be obtained with some systems.
2. The density of the deposit is equivalent to that of the pure metal. Again, this is not necessarily the case, with some electrodeposits being highly porous.

Both the density and the current efficiency of electrodeposited coatings decrease with increasing current density.

It is important to bear in mind the appearance and quality of surface coatings; e.g. it is generally required that decorative electrodeposits need to be smooth and defect free, with a mirror-like finish. While engineering coatings do not need to meet aesthetic specifications, the deposits typically should be uniform, compact and must cover the substrate surface evenly. Some deposition media lead to the electrodeposition of unacceptable surface coatings. This can also occur with the use of excessive current densities which lead to deposits that are irregular and dendritic in nature. A widely used method for improving or altering the structure and appearance of electrodeposits is to incorporate additives into the electroplating bath. Figure 7.1 shows the effects of excessive current density and the use of additives on the morphology of electrodeposited lead layers.

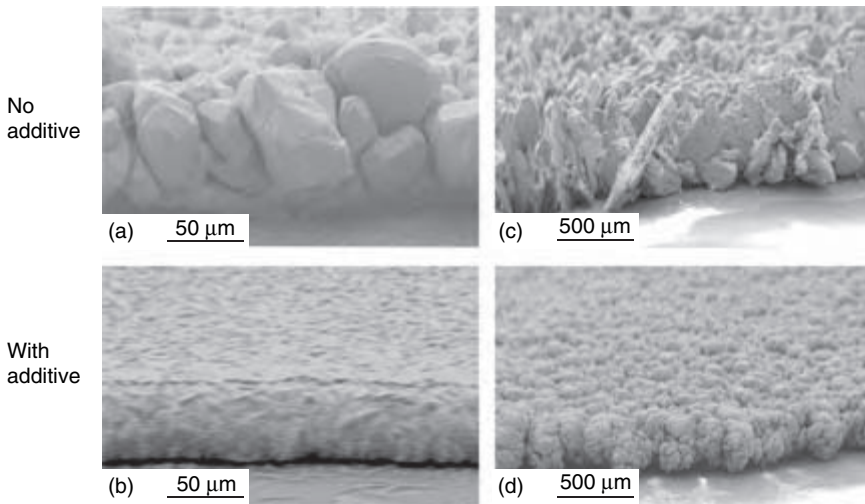
In addition to pure metals, alloys (binary, ternary and complex), oxide layers, conductive polymers and composite layers can be produced using electrolytic methods. A wide range of engineering applications can be met by electrodeposition including conductive coatings for the electronics industry, tribological layers for mechanical engineering and nanostructures for speciality magnetic semiconductor and optical uses.

This chapter discusses surface coatings produced via electrolytic methods (Fig. 7.2). The coatings are divided into metallic, composite and anodised groupings, with emphasis placed on the relationship between process conditions and deposit characteristics.

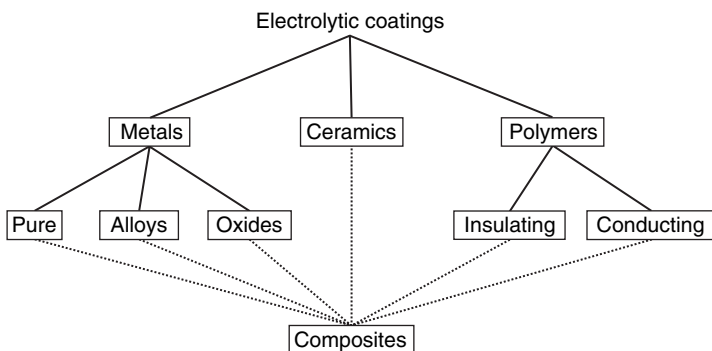
Electrodeposition can be broadly split into two methods, with this chapter predominantly focusing on the former.

1. *Electrolytic deposition.* Soluble ionic species, typically metal ions, are reduced at a cathode, resulting in precipitation of an electrodeposited layer from the electrolyte solution. The anode can be either soluble (the electrode is made from the material to be deposited and dissolution of the anode via oxidation acts as a source for the deposit) or insoluble (all species to be electrodeposited must already be present in sufficient quantity in the initial electrolyte solution).

2. *Electrophoretic deposition* (Van der Biest and Vandeperre, 1999). The material to be deposited (metal, polymer or ceramic) is present within the electrolyte as a fine powder or colloid suspension. A charge is applied to the particles by selective adsorption of ions on to the particles, removal of ions from the particles, interaction with bipolar molecules or electron transfer to the solution. Once a surface charge has been applied to the material, the initiation of an electric potential between the anode and cathode causes migration to the surface to be coated.

50 mA cm⁻²375 mA cm⁻²

7.1 Lead deposits on to a nickel rotating disc electrode (900 rev min⁻¹) (electroplating bath, 0.3 mol dm⁻³ of Pb(CH₃SO₃)₂ + 2 mol dm⁻³ of CH₃SO₃H + 1 g dm⁻³ of sodium ligninsulphonate; deposition time, 600 s.



7.2 Electrolytic deposition of materials.

Electrolytic coatings can be applied in a variety of configurations, ranging from simple homogenous layers to complex multicomponent deposits, as summarised in Fig. 7.3.

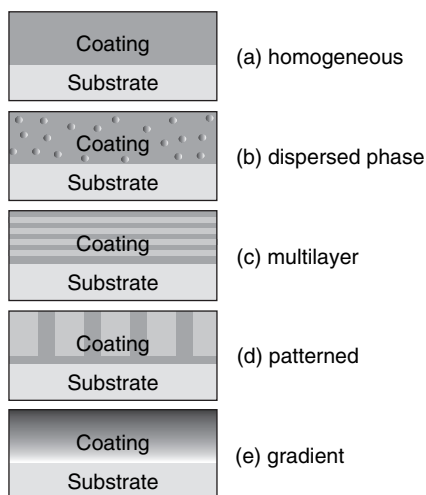
Electrolytic deposition techniques offer the following advantages for producing surface coatings.

1. Control of thickness as a function of time.
2. Control of the rate of deposition by adjustment of the current density.
3. The ability to stop the deposition process by turning off the current.

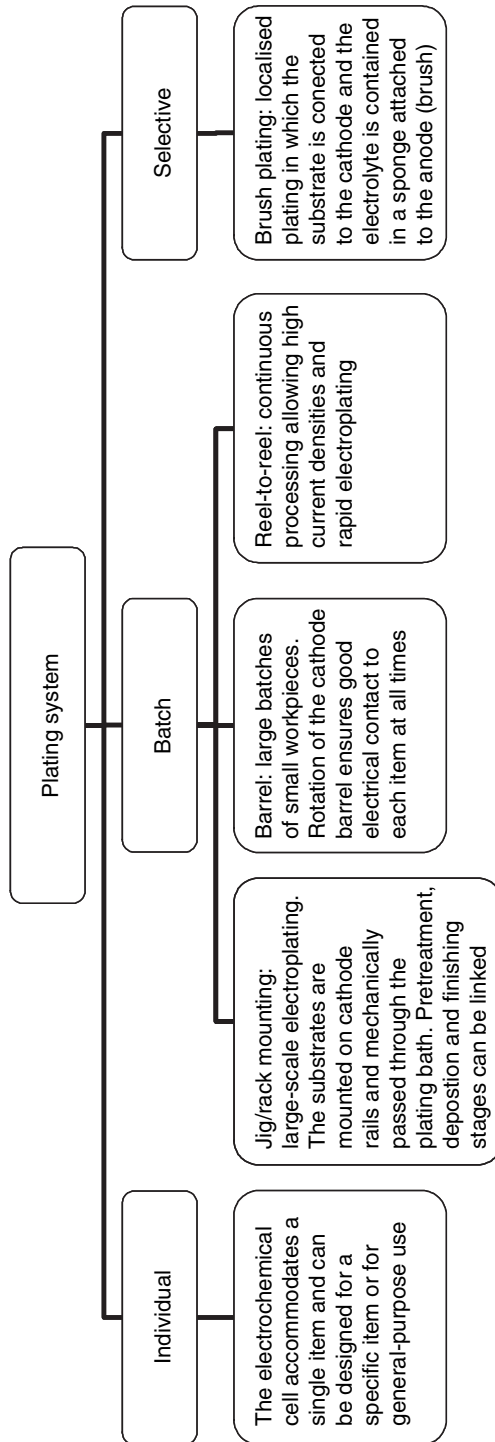
However, there are also some limitations.

1. A direct current power supply is generally required.
2. Current distribution can be non-uniform.
3. A conducting substrate is required although metallisation of non-conductors is well established (Weiner, 1977).

Electrodeposition can be tailored for specific tasks and workpieces. Dependent on whether a large number of identical objects needs to be plated, fast turnover or bespoke electroplating is required, and the design of the electrochemical cell can be adjusted accordingly. Figure 7.4 demonstrates the variety of possible reactors that are available.



7.3 Types of deposit: (a) homogeneous; (b) dispersed phase; (c) multilayer; (d) patterned; (e) gradient.



7.4 Plating systems for various workpieces.

7.2 Electrodeposited metallic coatings

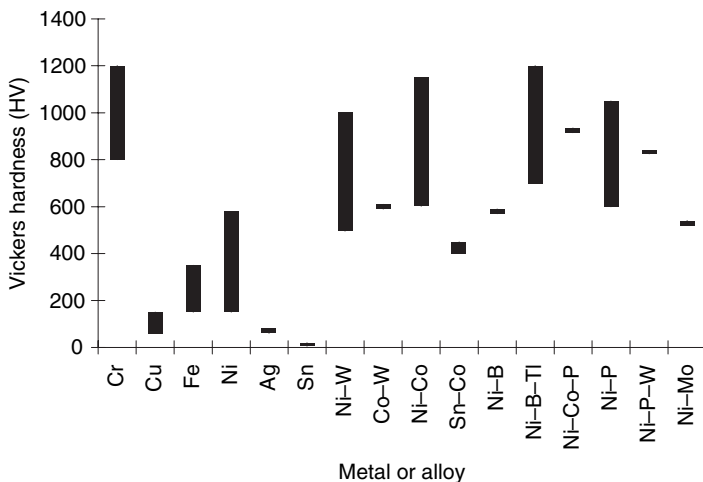
The morphology and properties of electrodeposited metallic coatings vary according to many factors including the electrolyte bath composition (including the use of additives), the plating method used (direct-current deposition, pulsed current or varying current density), the thickness of the deposit and the temperature of the electrolyte. As an example, Fig. 7.5 presents the Vickers hardness for a number of pure metal and alloy electrodeposited coatings.

7.2.1 Pure metals

Table 7.3 presents a selection of electrodeposited metals and, where available, typical electrolyte compositions and coating properties. A more detailed analysis of three widely used metals follows.

Chromium

Chromium is extensively used in industrial applications for wear, erosion and corrosion resistance; electrodeposited chromium layers have a low coefficient of friction and high hardness. Properties such as microstructure, hardness, residual stresses and cracks, and brightness of chromium layers electrodeposited from a hexavalent chromium electrolyte are strongly influenced by deposition temperature and current density. In the extreme, two



7.5 Vickers hardness for a selection of pure metals and metal alloy coatings.

Table 7.3 Electrodeposited metals, their properties and example electrolytic baths (Schlesinger and Paunovic, 2000; Kerr *et al.*, 2002)

Deposited metal	Example electrolyte and plating conditions	Typical properties and applications
Chromium	CrO ₃ (250–400 g dm ⁻³) SO ₄ ²⁻ (2.5–4 g dm ⁻³) Temperature, 20–30 °C Current density, 10–30 A dm ⁻²	Applied, predominantly in the automotive, aerospace and mining industries, to increase wear, abrasion, corrosion and fretting resistance, reduce static and kinetic friction, reduce seizing of threaded parts, fill undersize or worn parts
Cobalt	CoCl ₂ ·6H ₂ O (90–105 g dm ⁻³) H ₃ BO ₃ (60 g dm ⁻³) Temperature, 50–55 °C Current density, 3–4 A dm ⁻²	Wear-resistant coatings
Copper	CuSO ₄ ·5H ₂ O (150–250 g dm ⁻³) H ₂ SO ₄ (38–62 g dm ⁻³) Temperature, 20–60 °C Current density, 3–10 A dm ⁻²	Widely deposited for electronics applications. Copper is also used for forming deposits on plastic substrates
Nickel	'Watts nickel' NiSO ₄ ·6H ₂ O (225–375 g dm ⁻³) NiCl ₂ ·6H ₂ O (30–60 g dm ⁻³) Temperature, 45–65 °C Current density, 2.5–10 A dm ⁻²	Wear, abrasion and corrosion (particularly in alkaline conditions) resistance
Silver	Ag (35–120 g dm ⁻³) AgCl (45–150 g dm ⁻³) KCN (70–230 g dm ⁻³) K ₂ CO ₃ (15–90 g dm ⁻³) KNO ₃ (40–60 g dm ⁻³) KOH (4–30 g dm ⁻³) Temperature, 35–50 °C Current density, 0.5–10 A dm ⁻²	Printed circuits
Zinc	ZnSO ₄ (240–480 g dm ⁻³) NaCl (15–30 g dm ⁻³) H ₃ BO ₃ (20–100 g dm ⁻³) Al ₂ (SO ₄) ₃ ·18H ₂ O (25–35 g dm ⁻³) Temperature, 25–30 °C Current density, 0.5–3 A dm ⁻²	Corrosion protection

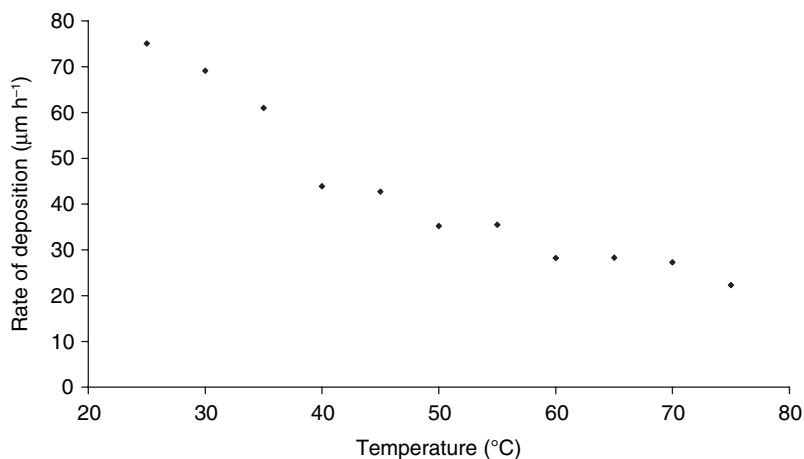
grades of electroplated chromium can be produced: firstly, hard chromium coatings which have high hardness and abrasion resistance but lower corrosion resistance due to a high degree of cracking throughout the deposit and, secondly, bright chromium coatings, which are crack free having lower hardness and abrasion resistance but much improved corrosion resistance.

The coefficient of friction increases with decreasing hardness. The hardness, residual stress and number of cracks are maximum when the deposit is laid down at about 40–50 °C and a current density of about 40–50 A dm⁻³. Figure 7.6 shows the effect of temperature on the rate of chromium deposition from an aqueous hexavalent chromic acid–sulfuric acid electrolyte on to a carbon steel substrate (Durut *et al.*, 1998).

The wear mechanisms for hard and bright electrodeposited chromium layers are predominantly abrasive and adhesive respectively, reflecting their differing properties (Durut *et al.*, 1998; Heydarzadeh-Sohi *et al.*, 2003). Heating electrodeposited hard chromium coatings, initially to about 600 °C, results in a volume decrease due to H₂ evolution (from chromium hydride, formed during deposition); further heating, to about 1200 °C, results in a volume increase due to thermal expansion. Thermal cycling often leads to thermal stresses which reduce the hardness and hence wear resistance of the hard chromium coatings. Susceptibility to thermal stresses is reduced if the coating is deposited using a pulsed-plating technique (Hadavi *et al.*, 2004).

Nickel

Nickel is electrodeposited for decorative as well as functional coatings. As a decorative coating, nickel layers can be deposited to a mirror-like finish,



7.6 Rate of deposition versus electrolyte temperature for the electro-deposition of chromium.

without the requirement for further polishing. As a functional coating, the appearance is less important and the deposits are, in general, produced with a matt or dull finish. These nickel and nickel alloys or composite deposits are used for wear, abrasion and corrosion (particularly in alkaline conditions) resistance and find use as alternatives to cadmium and chromium coatings. Corrosion protection is not sacrificial and is provided by the physical separation, by the nickel layer, of the substrate and environment (Brooman, 2000). Deposition parameters for nickel and the grain size of the resultant deposit strongly influence the wear resistance and coefficient of friction of the material. For example nanocrystalline nickel (grain size, 10–20 nm) gave 100–170 times the wear resistance and a 45–50% lower coefficient of friction than polycrystalline (grain size, 10–100 μm) nickel during pin-on-disc experiments (Jeong *et al.*, 2001).

Zinc

Zinc is typically used for corrosion-resistant coatings, e.g. galvanising steel. The standard potential for zinc is more negative than that for iron, which leads to the fact that zinc can provide sacrificial cathodic corrosion protection to iron and steel. Zinc is commonly plated in rack or barrel electrochemical reactors, which are suitable for bulk processing of components and can be deposited from zinc cyanide (for bright decorative coatings), alkaline or acidic electrolyte solutions. As with nickel and chromium, zinc can be electroplated for decorative or functional applications; however, bright zinc surfaces tarnish rapidly and a protective varnish or chromium layer is added to retain the lustre of the deposit. Nanocrystalline electrodeposits, prepared using pulsed-current techniques, have shown greater corrosion resistance than traditional electrodeposits produced using direct-current galvanic deposition (Youssef *et al.*, 2004).

7.2.2 Alloys

As with conventional alloys, electrodeposited coatings can combine specific properties from their constituents or exhibit enhanced characteristics unavailable with the pure materials and can therefore be tailored for specific applications. For example the incorporation of a harder element can increase abrasive wear resistance or the use of a softer element can lower the coefficient of friction. However, control of alloy deposition and component stoichiometry can be challenging.

Table 7.4 details a selection of metals and some common alloying components. Table 7.5 gives some specific alloys, their electrolyte baths and their applications. Alloys from widely used elements are detailed below.

Table 7.4 Metallic elements with alloying examples

Metal	Secondary alloys	Tertiary alloys	Complex or composite alloys
Co	Mo; W	W-P	Ni-ZrO ₂
Cu	Ni	—	—
Ni	B; Co; P; Mo; W	Co-P; Cu-P	Co-WC; Co-SiC; P-SiC; P-PTFE; Al ₂ O ₃ ; TiO ₂ ; P-MoS ₂ ; P-BN; Co-P-diamond; Fe-W-P-S; W-SiC
Pb	Sn	Sn-Ni	—
Sn	Co; In; Ni; Zn	—	—
Zn	Al; Co; Fe; Mn; Ni	Ni-P	Ni-Co-Fe

Table 7.5 Specific alloys, their electrolyte bath and common uses

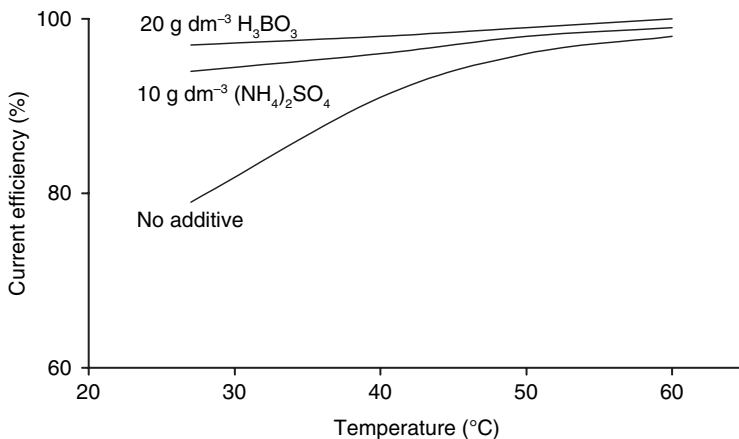
Coating	Example electrolyte	Comments
Au-Cu-Cd	KAu(CN) ₂ , 2.5 g dm ⁻³ K ₂ Cu(CN) ₃ , 60 g dm ⁻³ KCd(CN) ₃ , 2.5 g dm ⁻³ KCN, 25 g dm ⁻³	Antifretting and abrasion-resistant electrical contacts
Co-W	CoCl ₂ ·6H ₂ O, 100 g dm ⁻³ Na ₂ WO ₄ ·2H ₂ O, 45 g dm ⁻³ KNaC ₄ H ₄ O ₆ ·4H ₂ O, 400 g dm ⁻³ NH ₄ Cl, 50 g dm ⁻³	High-temperature stability and resistance to oxidation
Cu-Sn-Zn-Pb	Cu, 8 g dm ⁻³ Sn, 16 g dm ⁻³ Zn, 1.5 g dm ⁻³ Pb, 0.045 g dm ⁻³ KOH, 10 g dm ⁻³ KCN, 20 g dm ⁻³	Corrosion-resistant plating for aesthetic applications
Ni-Mo	NiSO ₄ ·6H ₂ O, 50 g dm ⁻³ Na ₂ MoO ₄ , 26 g dm ⁻³ HOC(COONa)(CH ₂ COONa) ₂ ·2H ₂ O, 88 g dm ⁻³ NH ₄ OH, 10 g dm ⁻³	Thermal stability and good wear and corrosion resistance
Ni-W	NiSO ₄ ·6H ₂ O, 13 g dm ⁻³ Na ₂ WO ₄ , 50 g dm ⁻³ HOC(CO ₂ NH ₄)(CH ₂ CO ₂ NH ₄) ₂ , 70 g dm ⁻³ NH ₄ OH, 40 g dm ⁻³	Higher wear resistance than Ni-Mo alloys
Zn-Co	ZnO, 0.12 mol dm ⁻³ NaOH, 2.5 mol dm ⁻³ SuperZINC ALCO cobalt additive, 5 ml dm ⁻³	Sacrificial coating for steel
Zn-Fe	Zn, 0.12 mol dm ⁻³ Fe, 0.01 mol dm ⁻³ NaOH, 2.5 mol dm ⁻³	Sacrificial coating for steel
Zn-Ni	Zn, 0.12 mol dm ⁻³ Ni, 0.02 mol dm ⁻³ NaOH, 2.5 mol dm ⁻³	Sacrificial coating for steel

Cobalt alloys

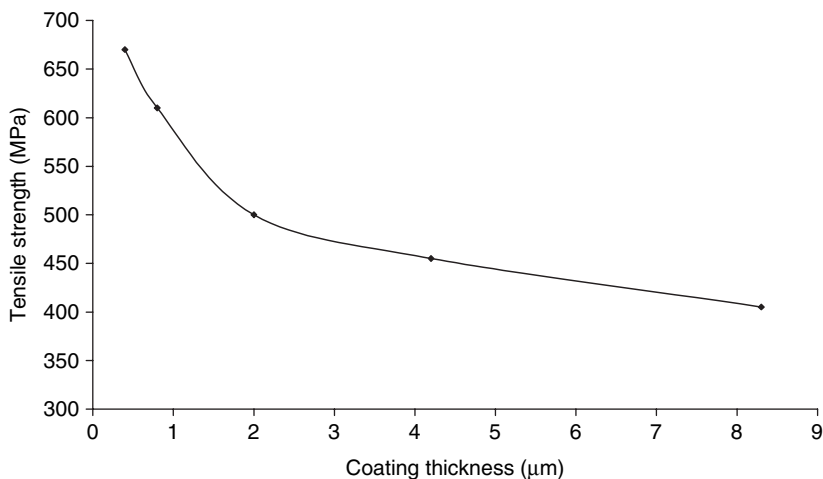
By alloying cobalt with tungsten (and with additional heat treating) it is possible to produce electrodeposits with hardness and wear characteristics comparable with hard chromium. Addition of iron to Co–W alloy improves the as-deposited hardness but slightly decreases the wear resistance (Capel *et al.*, 2003). Electrodeposited Co–Ni alloys have found use in the automotive industry as a pre-painting surface preparation for steel panels, while the magnetic properties of cobalt are attracting interest for specialist electronics applications. Alloys containing molybdenum, tungsten or nickel show good resistance to oxidation at high temperatures. Nanocrystalline deposits (grain size 90–150 Å) are finding use as replacements for hard chromium coatings. However, they tend to be less suitable for high-temperature applications because of cracking. Figure 7.7 shows the effect of using additives in the electrolyte bath to improve current efficiency during the electrodeposition of Co–Ni alloys from an acid sulphate electrolyte.

Copper alloys

Copper alloys have shown suitability for protection against environmental embrittlement and also improved ductility. Co–Ni alloys show particular promise for preventing stress corrosion cracking and crevice corrosion (Dini, 1997). Figure 7.8 illustrates the effect of coating thickness on the tensile strength of some Cu–Ni alloys (Gabe and Wilcox, 2002).



7.7 Current efficiency versus temperature for the deposition of a Ni–Co alloy with and without additives in the electrolyte solution (Lupi and Pilone, 2001).



7.8 Tensile strength versus coating thickness for Cu-Ni electrodeposits (Gabe and Wilcox, 2002).

Gold alloys

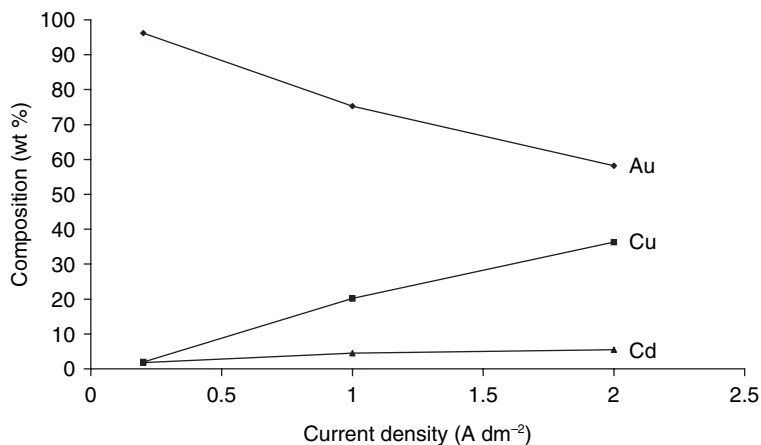
Electrodeposited gold alloys containing copper and cadmium show promise for use in electrical contacts in situations where high levels of abrasion and fretting occur. Increasing the current density increases the quantity of copper and cadmium incorporated into the alloy (Fig. 7.9) (Bozzini *et al.*, 2003).

Lead alloys

Alloys of lead have typically been developed for use as bearing coatings to improve wear characteristics; however the most significant alloying element is tin, for use in the electronics industry. Pb-Sn and Pb-Sn-Ni alloys also give low hydrogen permeability and thus inhibit embrittlement of steels (Dini, 1997). As a rough approximation the concentration ratio of tin to lead within the plating bath is the same as the ratio of the two elements in the electrodeposit.

Nickel alloys

Alloying cobalt with nickel can significantly improve the hardness, wear rate and coefficient of friction for electrodeposited layers. The wear rate and coefficient of friction reduce with increasing cobalt content, whereas the Vickers hardness is optimum (about 450HV) with a ratio by weight for nickel to cobalt of 1 to 1 (Wang *et al.*, 2005). The hardness of these alloys



7.9 Composition (by weight) of a Au–Cu–Cd alloy deposited at various current densities (Bozzini et al, 2003).

follows the Hall–Petch relationship, with the smallest grain size corresponding to the hardest deposit. Amorphous layers of Ni–W and Ni–Mo alloys can be electrodeposited from citrate solutions. These alloys show high surface hardness and wear resistance (Stepanova and Purovskaya, 1998). The electrolyte composition can significantly influence the stoichiometry of the coating, e.g. the quantity of tungsten or molybdenum incorporated in the deposit. By increasing the NH_4^+ concentration (to about 1.2 mol dm^{-3}) and raising the WO_4^{2-} -to- Ni^{2+} ratio in the electrolyte to 3 to 1, alloys with a high tungsten content (about 23%) are obtainable. However, alloys with a high molybdenum content (up to 33%) are deposited when the molybdenum concentration in the electrolyte is lower than nickel, with a ratio of about 2 to 3 and by lowering the NH_4^+ concentration (down to 0.2 mol dm^{-3}). Electroplated nickel is viewed as a more environmentally acceptable alternative to electroplated hard chromium for corrosion-, abrasion- and wear-resistant coatings. Nickel alloys incorporating boron, cobalt, phosphorous, tungsten, molybdenum, aluminium and titanium have been investigated (Brooman, 2004).

Corrosion-resistant Ni–W alloys, as alternatives to cadmium coatings, can be deposited such that the coating is either cathodic or anodic to a steel substrate, depending on the tungsten content.

Zinc alloys

It has been reported that zinc alloys containing cobalt and iron have lower coefficients of friction (decreasing with increasing concentrations of cobalt

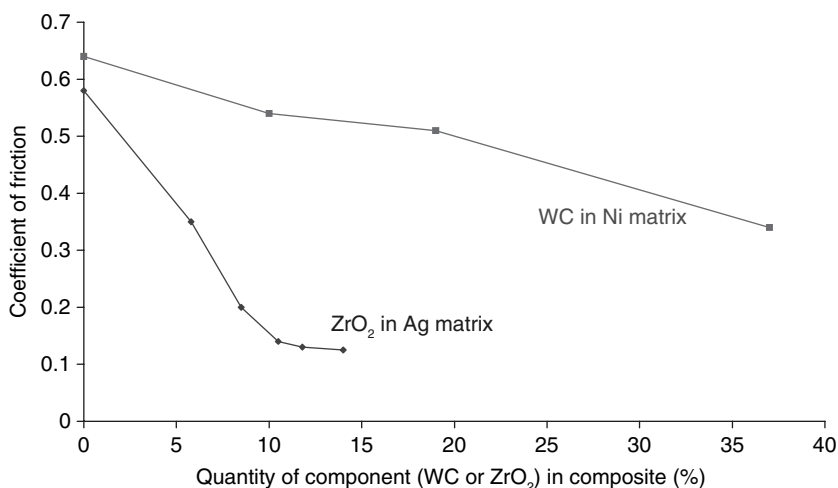
or iron), while nickel increases the coefficient of friction. Incorporating between 0 and 14% Fe can reduce the wear rate by as much as an order of magnitude (Panagopoulos *et al.*, 2004). Electrodeposited zinc alloys containing nickel and/or cobalt show higher corrosion resistance than zinc alone (Ramanauskas *et al.*, 1997).

7.3 Electrodeposited composite coatings

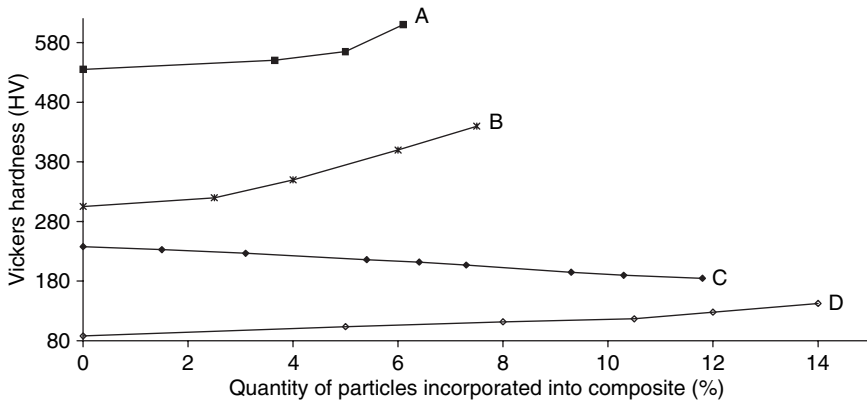
Composite coatings consist of an electrodeposited matrix layer into which is incorporated particles (typically with diameter below $100\mu\text{m}$) of another material. Predominantly the matrix is a pure metal or alloy, with the co-deposited material being either polymeric or ceramic. However, it is possible to use alternative materials, such as conductive polymers or oxide layers for the matrix (Musiani, 2000).

The individual components of composites impart characteristic properties to the final material. Composite coatings are of increasing interest for wear- and friction-reducing surfaces for engineering applications. For example, the inclusion of polytetrafluoroethylene (PTFE) into metal or alloy coatings gives a reduction in friction and mass loss during abrasion (Guo *et al.*, 2004) and the use of carbides increases wear resistance and hardness.

Figure 7.10 presents the coefficient of friction for two series of electrodeposited composites, Ag–ZrO₂ and Ni–WC with various quantities of ZrO₂



7.10 Coefficient of friction against quantity of particles incorporated into deposit for Ag–ZrO₂ (Gay *et al.*, 2001) and Ni–WC composite materials (Surender *et al.*, 2004).



7.11 Vickers hardness against percentage inclusion of composite particles for Si_3N_4 in an Ni-Co matrix (Shi *et al.*, 2005) (curve A), PTFE in a nickel matrix (Pena-Menez *et al.*, 1998) (curve B), graphite in a bronze matrix (Ghorbani *et al.*, 2005) (curve C) and ZrO_2 in a silver matrix (Gay *et al.*, 2001) (curve D).

and WC respectively. Incorporation of the harder particles into the metal matrix results in coatings with reduced coefficients of friction.

The electrodeposition of a wide range of composite materials is possible, with metal matrices including chrome, nickel, bronze and cobalt incorporating composite particles such as PTFE, WC, graphite and polyethylene to name just a small number. Figure 7.11 presents a plot of Vickers hardness against percentage inclusion of composite particles. As would be expected, particles incorporated into the coating which are harder than the matrix increase the hardness, and softer materials, such as graphite, decrease the hardness. However, graphite also decreases the coefficient of friction from about 0.43 (no graphite) to 0.2 (12% graphite).

7.4 Anodised coatings on light metals

Freshly exposed surfaces of reactive metals, such as aluminium or magnesium, quickly oxidise to form a thin protecting surface film. Under general atmospheric conditions this naturally formed oxide layer is sufficiently thick and inert to prevent severe corrosion or pitting. However, in corrosive environments it is necessary to enhance the thickness of the oxide layer by anodising.

7.5 Conclusions and further reading

The purpose of this chapter is to give an introduction to the engineering aspects of electrolytic deposition of surface coatings. However, the breadth

of electrochemical techniques, applications and electrolytic media cannot be exhaustively covered in a single chapter. Table 7.6 presents a list of selected review papers, altogether with their scope, to guide the reader in the direction of further information. The book by Pletcher and Walsh (1990), the books edited by Schlesinger and Paunovic (2000) and the Encyclopedia contribution by Elvers (2002) are also recommended for further reading. The Appendix 7.7 gives a list of professional associations which is also featured in Chapter 6.

Table 7.6 Some recent reviews on the electrodeposition of materials

Review	Scope	Number of references
Landolt (1994)	Theoretical and experimental aspects of alloy deposition detailed in terms of mass transport, current distribution and cell design (experimental) and non-interactive systems, charge-transfer-coupled systems and mass-transport-coupled systems (theoretical)	53
Winand (1994)	A review of the factors affecting the electrodeposition of metals and metal alloys from aqueous solution. Discussions of theoretical considerations and applications are given	72
Fan and Piron (1995)	Fabrication of large-surface-area electrodes via electrodeposition presented in the context of water electrolysis. Reviewed techniques include high-current-density deposition, composite deposition, reactive deposition and electrodeposition-activation processes	41
Van der Biest and Vandeperre (1999)	Electrophoretic deposition of materials	114
Kerr <i>et al.</i> (2000)	A review of the electrodeposition of composite materials, highlighting the importance of process control on deposit characteristics	45
Musiani (2000)	The electrodeposition of composites is covered, giving attention to applications such as conducting polymers, oxides and salts	75

Table 7.6 Continued

Review	Scope	Number of references
Krylova (2001)	The electrodeposition of paints on to metallic substrates. Concentrates on the factors affecting film formation and properties of the coatings	120
Boccaccini and Zhitomirsky (2002)	Application of electrophoretic and electrolytic deposition techniques in ceramics processing	88
DiBari and Chatham (2002)	A review, detailing chronological developments of nickel and nickel alloy electroplating and mentioning relevant patents	12
Dietz (2002)	The application of electrodeposited composite microcapsules, for self-lubricating coatings, is discussed. Written in German	9
Fieberg and Reis (2002)	The development of an ultraviolet-curable electrodeposited coating is presented, with discussion of anodic electrodeposition and binder chemistry	11
Gabe and Wilcox (2002)	A review of the use and future options for underlying and multilayered electrodeposits. Highlights the reduction of porosity and enhancement of mechanical and corrosion properties obtainable using underlayered and multilayered deposits	41
Gray and Luan (2002)	Coating and surface modification technologies, including electroplating and anodising, for improved corrosion and wear resistance. Specifically focuses on coatings for magnesium and magnesium alloys	171
Allcock and Lavin (2003)	Composite electrodeposits designed for extreme operating conditions, such as oil exploration and extraction and the steel industry. Takes into account temperature, corrosion, abrasion, fatigue, friction and erosion in manufacturing composite coatings	9

Table 7.6 Continued

Review	Scope	Number of references
Balaraju <i>et al.</i> (2003)	The formation of electroless Ni-P composite coatings. Assesses the method of formation, mechanism of particle inclusion and effect of particle inclusion on the wear, abrasion, corrosion and oxidation resistance of the composite. Also assessed are the structure, hardness and applications of such composites	100
Murphy (2003)	Relates to metal finishes, processes and equipment with a comprehensive list of references for the electrodeposition of various metals. Also includes a section on anodising	760
Myung <i>et al.</i> (2003)	A discussion concerning the integration of electrodeposited magnetic coatings in microelectromechanical systems. Soft and hard magnetic materials are assessed in terms of their corrosion resistance, residual stress and magnetic properties	33
Raj <i>et al.</i> (2003)	A review of alternating-current and direct-current anodising, concentrating on pulsed-current techniques	92
Bajat and Miskovic-Stankovic (2004)	Electrochemical deposition of Zn-Ni alloys and epoxy coatings. Reviews the influence of current density and electrolyte composition on chemical content, phase structure and corrosion resistance	81
Chen (2004)	Electrodeposition of heavy metals and oxidation of pollutants at titanium-based boron-doped electrodes during the treatment of waste water. Also covered are electrocoagulation and electroflotation techniques	221
Gabe (2004)	The use of flow eductors for agitation of anodising baths	26

7.6 References

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7.7 Appendix: Professional associations

European Academy of Surface Technology (EAST)

Katharinenstrasse 17

D-73525

Schwäbisch Gmünd

Germany

<http://www.east-site.net>

Institute of Corrosion

Corrosion House

Vimy Court

Leighton Buzzard

LU7 1FG

UK

<http://www.icorr.demon.co.uk>

NACE International

1440 South Creek Drive

Houston

Texas 77084-4906

USA

<http://www.nace.org>

Surface Engineering Association (SEA)

Federation House

10 Vyse Street

Birmingham

B18 6LT

UK

<http://www.sea.org.uk>

The American Electroplaters and Surface Finishers Society, Inc. (AESF)

Suite 250

3660 Maguire Boulevard

Orlando

Florida 32803

USA

<http://www.aesf.org>

The Institute of Materials, Minerals and Mining (IOM³)

1 Carlton House Terrace

London

SW1Y 5DB

UK

<http://www.iom3.org>

The Institute of Metal Finishing (IMF)

Exeter House

48 Holloway Head

Birmingham

B1 1NQ

UK

<http://www.uk-finishing.org.uk>

Thermal spraying methods for protection against wear

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8.1 Introduction

Ancient metallurgists and smiths were quick to realise that a vital requirement for their products was a hard surface coating on a strong but tough base. Examples of artefacts with such properties are swords and armour plate. Following the industrial revolution, there became an even greater demand for surface-hardened products and a variety of new methods were developed, which largely depended upon gas–solid reactions and solid-state diffusion. Partly because of the latter requirement, the hardening processes were strongly time dependent and they could only be applied to specific alloy-based materials; hence they were costly and inflexible. It is not surprising, therefore, that over the last century there have been concerted efforts to improve coating methods, the technology of which has now become classified as surface engineering.

One of the approaches to improved coating methods has been the introduction of thermal spray techniques which involve the projection of liquid or partially liquid particles on to the surface of the component to be coated. If the coating material and spraying conditions are adequate, an adherent deposit will be produced which will lead to a part with properties that satisfy service requirements.

This chapter introduces thermal spraying through a historical review, describes various thermal spraying processes and feedstock materials and presents specific examples of applications in various industrial sectors.

8.1.1 A brief history

Thermal spraying dates back to the early 1900s when Dr Schoop (1911) first carried out experiments in which molten metals were atomised by a stream of high-pressure gas and propelled on to a surface. The Schoop process consisted of a crucible filled with molten metal while the propellant, hot compressed air, provided enough pressure to break up the molten metal,

creating a spray jet. This system was quite rudimentary and inefficient. Following Schoop's work some improvements to the process were introduced but the disadvantages of the process, namely that it was only useful for low-melting-temperature metals, that the molten metal caused severe corrosion and that it was not possible to establish a continuous process, were enough to stop further progress.

Schoop then focused his efforts in another direction and in 1912 the first device for spraying metal wires was produced. The principle of this process is simple; a wire was fed into a combustion flame which melted the tip of the wire and then compressed air surrounding the flame atomised the molten metal and propelled the droplets on to a target to create a coating. Apart from improvements to nozzle and gun design as well as in wire feed drive rolls, the basic principle of the process is the same today. This technique is called flame spraying (FS) and covers a large group of thermal spray methods which use powder, wires or rods.

A completely new concept in thermal spraying was introduced by Schoop in 1914 when he used electricity to melt the feedstock material. The most advanced equipment made by Schoop was quite similar to current electric arc spraying. This technique is based on creating an electric arc between two wires of conducting materials, which are fed together inside the gun. This arc is created at the tip of the wires and a jet of compressed air propels the molten metal to the substrate.

The concept of powder FS was introduced by F. Schori in the early 1930s, when a metallic powder was fed into a flame by the Venturi effect. The powder was melted in the nozzle and the exhaust combustion gases (oxygen and acetylene) propelled the droplets. Improvements to the process incorporated in modern guns include an inert compressed gas that pressurises the combustion chamber and results in an increase in particle velocity.

The main problem associated with these early techniques was feedstock material. They all used low-melting-point materials and so applications were limited. Years passed, and the demand for high-temperature-resistant materials increased, until in the 1950s new systems that would boost the thermal spray market appeared. Firstly a modification of wire FS, the ceramic rod FS technique, which could use stabilised zirconias and aluminas appeared. However, it was the development, in about 1955, of the detonation gun (D-Gun®) and atmospheric plasma spraying (APS) in about 1960 that proved to be the watershed as regards thermal spray applications.

The D-Gun® was developed by The Union Carbide Corporation. Rather than using oxygen and fuel gases as a continuous combustion energy source a mixture of oxygen and fuel gases was repetitively ignited (detonated) inside a combustion chamber to produce shock waves (Poorman *et al.*, 1955). The resulting shock waves travelled along a water-cooled barrel, and supersonic speeds and high temperatures were achieved. This technology is

only available as a service (Praxair Surface Technologies) although new equipment is under development. With detonation FS, carbides and cermets could be applied to parts, giving a coating with superb wear resistance properties because of its good bonding to the substrate, high density and low porosity content.

Almost at the same time, in about 1960, Giannini *et al.* (2003) introduced APS based on the plasma generator of the Gerdien and Lotz (1922) type. A mixture of gases such as nitrogen or argon with hydrogen or helium is ionised by an electric arc and a plasma jet is created. The elevated temperatures associated with plasma sources are able to melt a wide range of materials and this allows the quality deposition of high-temperature materials, e.g. zirconias and aluminas, if the evaporation temperature of the material is at least 300 K higher than its melting point. Thermal barrier coating (TBC) applications in the aeronautics and space industry were originally the most common uses of this technique.

This was followed in the late 1970s and early 1980s, by the development and commercialisation of vacuum plasma spraying (VPS) and low-pressure plasma spraying (LPPS). VPS and LPPS were designed to alleviate some of the drawbacks of APS such as high rates of oxidation of metallic materials or substantial porosity in coatings. These techniques use a soft vacuum or inert-gas-controlled atmospheres (a technique called controlled atmosphere plasma spraying (CAPS)) to prevent the interaction of atmospheric oxygen with molten material. Moreover, owing to the vacuum present, the velocity of in-flight particles is higher in VPS systems than in APS. However, this equipment is more costly. Controlled atmosphere techniques find applications in the aeronautics industry where sometimes quality and durability rather than the cost of the process are most important.

A major leap forwards in thermal spray applications occurred in the 1980s when the Browning Engineering Corporation introduced a novel technique to spray metal powders, namely high-velocity oxy-fuel (HVOF). In this process, high pressure plays an important role in increasing the velocity of the in-flight particles to $700\text{--}800\text{ ms}^{-1}$. A mixture of a fuel gas (propylene, propane, hydrogen, etc.) and oxygen, or sometimes air (in high-velocity air-fuel (HVOF)), is burnt in a pressurized water-cooled chamber. The exhaust combustion gases expand through a nozzle to the atmosphere where shock diamonds are created inside the supersonic jet. Coatings with high density and high bond strength are obtained without the need for controlled atmospheres and with portable equipment. A wide range of materials can be sprayed with this technology and it has probably become the most useful thermal spray technique together with APS because of its versatility and ease of use.

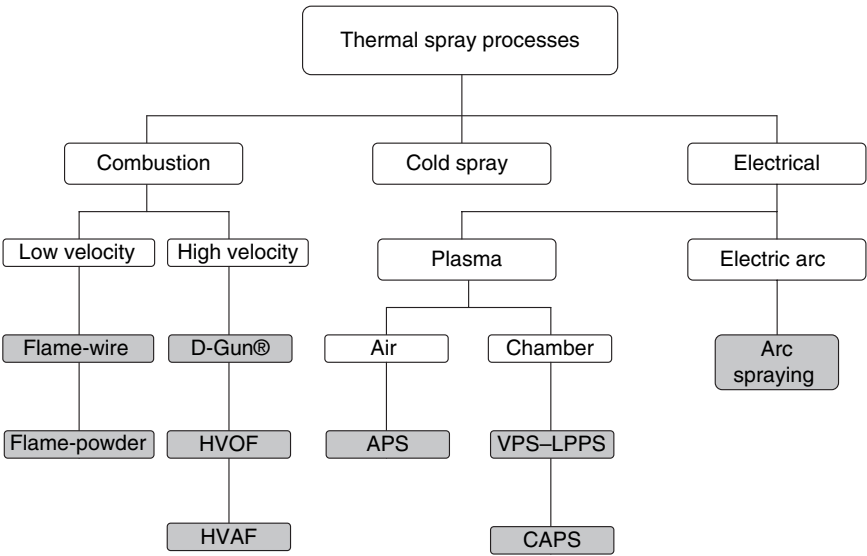
In the 1990s, new technologies appeared, among which perhaps the most promising is the cold-spray process. As its name indicates, cold spray is

based on high-velocity jets propelling material at a low temperature. There is no heat source, neither combustion nor electrical, only hot compressed gases that are fed into a gun with a de Laval nozzle. The particle velocity can be as high as 1200 ms^{-1} . The coating is built up by the deformation of ductile materials on impact. A coating with a low oxidation level, a high density and improved adhesion is achieved. Powder decomposition is also low but the main drawbacks to the process are the high cost and rapid degradation of nozzles due to erosion by high-velocity solid material.

Figure 8.1 summarises the above-mentioned thermal spray techniques. In essence, thermal spray processes can be classified into three families: one uses combustion as the heat source; another uses electrical energy, either in the form of a plasma or as an arc; cold spray is a family by itself.

8.1.2 Raw materials: types and classification

The feedstock materials used by all the techniques summarised in Fig. 8.1 can be divided into three groups: powder, wires and rods (Pawlowski, 1995). However, this is a commercial classification and, if material properties are taken into account, the following classification is more useful.



8.1 Types of thermal spray processes. The names of the techniques are shown as shaded.

Pure metals and alloys

Steels, stainless steels, nickel-, copper-, cobalt- and aluminium-based alloys, superalloys, M–Cr–Al–Y (alloys consisting of a metal M (typically nickel or chromium), chromium, aluminium and yttrium) are widely sprayed. These materials are used for corrosion, oxidation and wear resistance as well as for bond coats, e.g. TBCs.

Ceramics

Aluminium oxide (Al_2O_3), partially stabilised zirconia (ZrO_2), Al_2O_3 – TiO_2 mixtures, chromium oxides, titanium dioxide (TiO_2), calcium fluoride (CaF_2), hydroxyapatite (HAp), MgO – CaO , spinel and other mixtures formulated to decrease melting point are available in the marketplace. Ceramic materials can provide thermal or electrical insulation as well as wear and oxidation resistance.

Carbides and cermets

The carbides used most are tungsten carbide (WC), chromium carbide (Cr_3C_2) and titanium carbide (TiC). These are always combined with a metallic phase to form cermet materials. Among the metallic phases, cobalt (WC–Co), Co–Cr (WC–(Co–Cr)), Ni–Cr (Cr_3C_2 –(Ni–Cr)) are the most applied. These are commonly referred to as wear-resistant or hard coatings.

Polymers

Their low-friction characteristics and excellent chemical and sealing properties have made polymers a good alternative to protective coatings such as zinc, or conventional painting with organic solvents. Polyethylene, polyamide, poly (ether–ether–ketone), poly (methyl methacrylate) and other thermoplastics are amenable to spraying.

Others

Abradable materials formed by a low-friction material embedded in a soft matrix are used in applications where no clearance between moving parts is required, e.g. (Al–Si)–graphite, Ni–graphite, (Al–Si)–polyester, CaF_2 with a metallic matrix, (Al–Si)–polyamide and (Al–Si)–polyethylene. Self-fluxing alloys constitute another powder type. These are metallic alloys that are designed to be remelted once they have been sprayed. Typical self-fluxing alloys are nickel-based alloys with silicon and boron additions (self-fluxing

elements) as well as other elements such as chromium, molybdenum or tungsten. The elements boron and silicon react with oxygen to create a slag over the molten coating and produce a metallic matrix which is oxide free and with finely dispersed nitride and boride particles.

8.1.3 Powder production methods

The type of feedstock material determines the powder production method used. While oxide and carbides are often manufactured by fusion and crushing methods, metals and alloys are produced mostly by atomisation. Other techniques, such as spray drying, are versatile, allowing almost any kind of agglomerated powder to be produced using an organic binder phase. Other manufacturing methods are available such as self-propagating high-temperature synthesis (SHS) or sol-gel, but as of 2004 these methods are not widely used. Nanostructured powders are beginning to be increasingly used for their enhanced wear-resistant properties and are becoming a new thermal spray research topic (Schoenung and He, 2002).

Atomisation methods

The metal or alloy is melted in a crucible where it is kept molten. The liquid is poured into a heated funnel connected to a nozzle where it is finely dispersed (atomised) by a water or air stream which propels the droplets into a cooling chamber. Powder produced by this technique has a spherical morphology. The cooling media, water or gas, can lead to differences in phase compositions or non-equilibrium phases.

Spray-drying methods

A mixture of organic binder, water and the material to be agglomerated is sprayed in a chamber where there is a flow of hot dry gas. The water in the mixture evaporates and the organic binder covers the material particles, producing the agglomerated powder. The binder selected together with the processing parameters affects the final powder morphology and phase composition. Powders produced by spray-drying methods are porous and in some cases are subject to densification.

Fusion and crushing

The material to be used is melted in an oven or furnace and then solidified. The solidified mass is then broken up into small particles by industrial crushers and mills. The powders obtained in this way are dense and blocky

and have irregular shapes. To prepare cermets, fine carbide or oxide particles and metal matrix particles are mixed with an organic binder and sintered to form the cermet particle.

Clad powders constitute another powder type. These are formed by a dense core of material covered by a layer of another material (Fig. 8.2). The outer layer can be several micrometres thick and may be porous or dense.

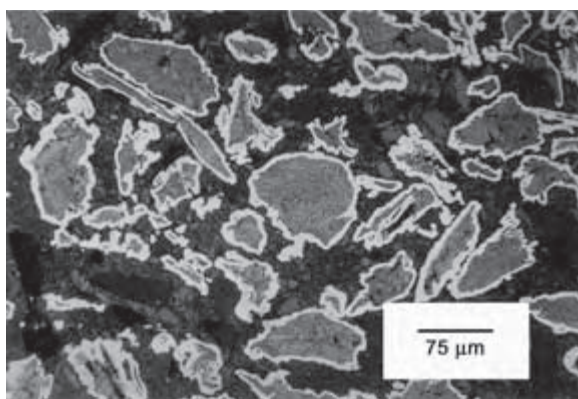
During the 1990s the production of cermets and complex metallic alloy powders by SHS has increased. In the SHS technique the heat released by exothermic reactions between reactants in solid–solid and solid–gas systems is utilised to increase the temperature of the system and to sustain reactions until complete conversion of reactants to products occurs (Pampuch, 1997).

8.1.4 Powder properties

The most important properties of the powders are as follows.

Grain size distribution

There are several grain size distributions commercially available. However, every spraying technique has its own powder size limits. Powder suitable for HVOF, for example, should be fine, ranging from 10 to 40 μm , whereas in other techniques such as APS the powders can be coarser. Particles that are too large lead to non-melted particles in the structure of the deposited layer while particles that are too small burn or degrade completely before reaching the substrate.



8.2 Cross section of Ni–graphite clad powder. A metallic nickel layer shrouds a graphite core.

Phase analysis and chemical composition

There are hundreds of commercially available powders covering most chemical and phase compositions. The thermal sprayer should know which is best for a given application and verify these properties by conventional chemical analysis techniques such as X-ray diffraction and energy-dispersive X-ray spectroscopy before using the feedstock material.

Flowability and density

These properties can be measured by following ASTM B 213-90 (flowability), ASTM B 212-89 (apparent density), ASTM B 527-85 (vibrational density) and ASTM B 238 (real density) standard tests. Table 8.1 shows some typical values of material flowability tested according to the ASTM standard using the Hall funnel. There are some cases where the powder does not pass through the hole in the funnel; so, in those cases, some improvement to the feeding process must be made such as heating the powder or increasing powder carrier gas flow. Both flowability and density can have an effect on powder feeding inside the flame or jet.

8.2 Thermal spray process fundamentals

8.2.1 Combustion and electric energy processes

As discussed in Section 8.1.1, thermal spray techniques can be divided into three families: two large groups depending on their energy source, namely combustion or electric, and the cold-spray process. Here we consider the combustion and electric energy processes.

There is no single best choice of coating process because each technique has its own merits and niche area depending on the properties of the coating

Table 8.1 Flowability values in seconds for some thermal spray powders (ASTM B 213-90)

Material	Flowability (s)
Stellite® 6, water atomised, 15–45µm	12
Polyamide, cryogenically milled, 85–225µm	86
WC–12% Co, fused and crushed, 15–55µm	13
Ni–Cr–B–Si, air atomised, 25–50µm	12
TiC–NiTi, mixture as produced by SHS, 19–61µm	61
HAp, fused and sintered	No

required, e.g. porous or not, or dense or not. In some cases, for instance, wire arc spraying is more suitable than APS although plasma coatings are theoretically better. Arc spraying has applications in restoration of worn and corroded parts outdoors because of the ease of use and high feed rates, whereas plasma spraying has to be performed in a spray booth and has lower feed rates. However, each technique has to satisfy the expectations of the customer.

Combustion methods can be split into two subgroups: low velocity and high velocity. In both groups, temperatures are similar because the same fuel gases or liquids are used. The fuels commonly employed are propylene, propane, kerosene (liquid), acetylene and hydrogen while oxygen or sometimes atmospheric air (in HVOF), can be used as an oxidant. In some cases (FS), compressed air is utilised to break up molten material in the nozzle and in other techniques it is used to pressurise the combustion chamber (HVOF and HVOF). The thermal history will not be the same for low- and high-velocity techniques because the velocity, and thus the dwell time of particles in the hot gases, is not the same. In low-velocity techniques (i.e. FS), particles stay longer in the jet and so oxidation and/or degradation of in-flight material will be higher. As a consequence of its low velocity, flame spray coatings have quite high porosity levels and only moderate bond strengths. However, higher spraying rates are commonly achieved as coarser powder and wires can be used. Flame spray processes are easy to use, are reasonably economical and can be used outdoors because the equipment is easily portable and not especially noisy.

On the other hand, in high-velocity techniques (HVOF and D-Gun®), dwell times will be shorter and so degradation of essential elements in the powder or interaction with the surrounding atmosphere will be less. A fine powder size must be used to avoid non-melted particles in coatings, as the thermal input is lower. Some HVOF guns capable of using wires (HVT wire; HV Techno Ltd) instead of powder are commercially available. Using wires enables the process to be continuous but, as there are far fewer types of wire available in the market than powders, only a limited range of coating compositions can be produced. The equipment used in HVOF is more expensive than FS techniques; skilled operators and more complex infrastructures (water cooling, compressed air and a spraying booth) are also necessary. Both the D-Gun® and the HVOF processes are noisy, especially the former, where a level of 150dB is reached.

As shown in Fig. 8.1, thermal spray processes using electrical energy can be split into two families, namely plasma and electric arc. Plasma spraying (whether performed in a controlled atmosphere or not) utilises electrical energy to ionise a gas medium, while wire arc spraying uses the high temperature created in an arc to melt the feedstock material. These two

electrical methods do not achieve similar temperatures or particle velocities, the values reached by APS being higher.

The benefits of wire arc spraying are ease of use, portability and low equipment maintenance cost. Wire arc coatings are often thicker than APS coatings and this technique has higher deposition rates than most other techniques based on combustion or electricity. On the other hand, coatings produced by this method have drawbacks such as high oxidation levels (but this can be reduced by using an inert gas as the propellant medium), a rough surface due to non-melted particles and some porosity. The main disadvantage, however, is the use of a wire because this must be electrically conductive which reduces the choice of materials available. The wires can be solid or have a metal conductive shell surrounding a non-conductive core (e.g. a WC core with Ni–C–B–Si, an Fe–Cr core with Cr_2O_3 and a WC– W_2C core with a cobalt binder). However, arc spraying has many applications and in some cases is replacing APS because of its lower costs and quite good coating quality (Sacriste *et al.*, 2001).

The great advantage of plasma spraying is its versatility. A wide range of materials can be sprayed and coarser powder can be used. Spraying conditions can be modified to achieve a range of velocities and temperatures and sometimes it is possible to use different gases with the same equipment. Each gas when ionised creates a plasma jet with certain properties (thermal exchange efficiency or viscosity) that can be modified to determine the particle velocity or temperature. The equipment is not easy to use and skilled operators are needed both to perform continuous maintenance and to select the correct parameters. As plasma jets emit harmful ultraviolet rays, adequate safety precautions must be taken. The coatings have low porosity levels, medium oxidation levels and few non-melted particles. Using controlled APS, large improvements in coating quality can be achieved, e.g. a bond coat adhesive strength 24% higher than conventional APS for Cr_2O_3 or an adhesive strength 25% higher for TiO_2 (Kim *et al.*, 2000), but the operational costs as well as equipment cost are greater (Gassot *et al.*, 2001).

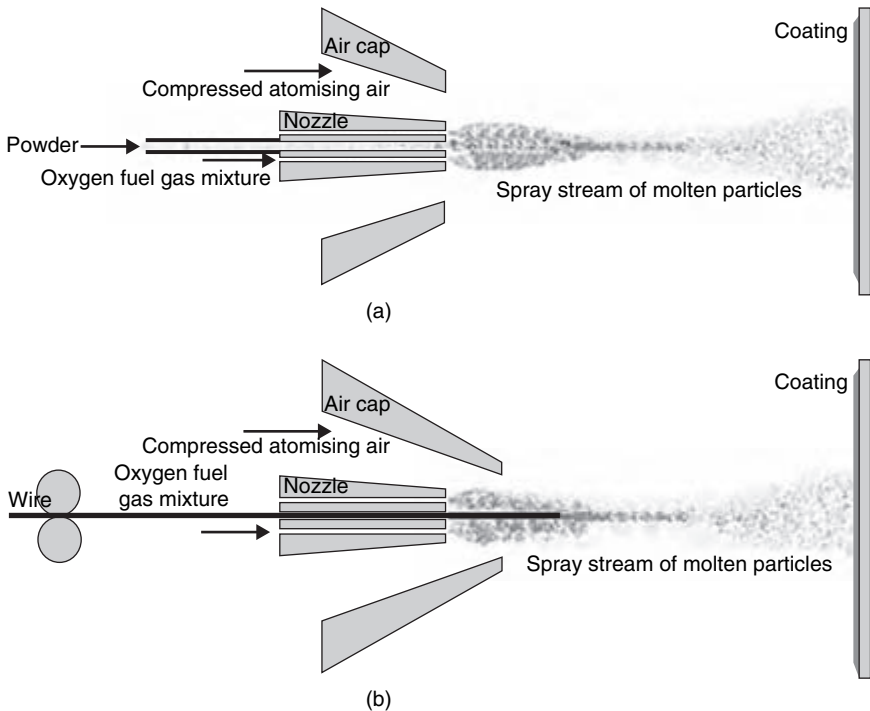
Table 8.2 summarises the main features of the major thermal spraying techniques. Additional brief explanations of the most used techniques, with a simple sketch of the guns are given below.

Flame spray powder and wire

The combustion gases are usually oxygen and propylene. The propellant gas, normally compressed air, projects the molten metal. While powder is fed by the Venturi effect, wires are fed by rotors that continuously pull the wire into the central region of the flame. Both powder and wire are fed axially; so injection takes place inside the flame (Fig. 8.3).

Table 8.2 Main features of thermal spray techniques

Deposition technique	Heat source	Propellant	Typical temperature (°C)	Typical particle velocity (m s ⁻¹)	Coating porosity (vol%)	Average spray rate (kg h ⁻¹)	Bond strength
FS	Acetylene-oxygen	Air	3000	30–120	10–20	2–6	Poor
APS (HVOF)	Plasma arc	Inert gas	16000	120–600	2–5	4–9	Good
	Fuel-oxygen or air	Exhaust jet	3000	800	0.1–2	2–4	Excellent
LPPS D-Gun® spraying	Plasma arc	Inert gas	16000	Up to 900	<5	–	Excellent
	Oxygen-acetylene	Detonation shock waves	4500	800	0.1–1	0.5	Excellent



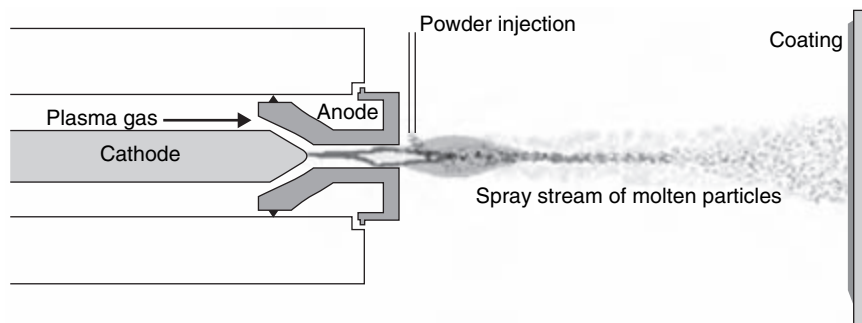
8.3 Sketch of (a) flame spray powder and (b) flame spray wire guns.

Plasma spray

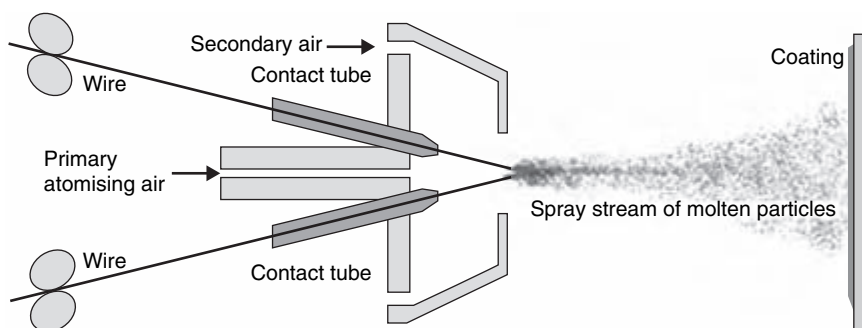
In the plasma spray technique an electric arc forms between two electrodes. This arc ionises a gas flow, creating the plasma state. Because of the gas pressure inside the plasma chamber, a plasma jet is created at the exit of the nozzle where injection takes place (Fig. 8.4). So, in this case, injection is radial and external.

Wire arc

As the name of the process indicates, wire is the feedstock. Two conductive wires are fed together and an electric arc is created between them when they are brought into close contact. In fact, both wires act as electrodes. The tips of the wires are melted and atomised by the propellant gas that carries the molten metal to the substrate (Fig. 8.5).



8.4 Atmospheric plasma gun sketch.



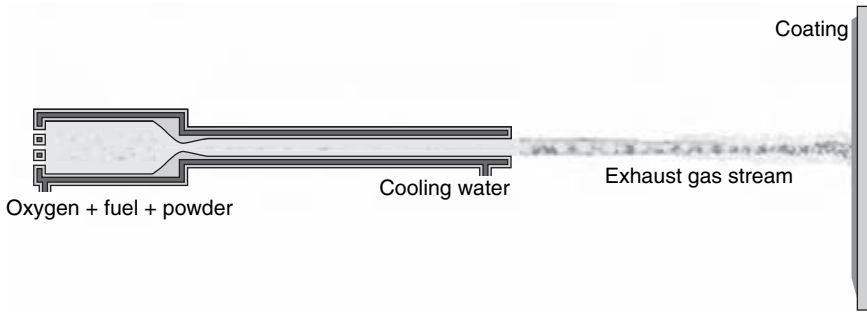
8.5 Sketch of electrical arc wire gun.

High-velocity oxy-fuel

The process utilises oxygen with several fuel gases, including hydrogen. They are ignited and continuous combustion takes place in a pressurised chamber (Fig. 8.6). Hot exhaust gases expand at the nozzle exit, creating diamond shock waves. Powder is fed in the combustion chamber axially. As stated previously, some modern guns can also use wires.

8.2.2 In-flight behaviour

This section deals with some of the physical and chemical processes that take place inside the jets. First, the chemical processes such as oxidation and vaporisation which take place in any kind of stream of hot gases will be described. Then the HVOF and APS processes will be explained in some detail.



8.6 HVOF gun sketch.

When the hot gases exit the torch through the nozzle, cold ambient air is entrained in the jet. This can trigger either oxidation or chemical reactions of vaporised material with elements in the air. In plasma spraying where the highest temperatures are reached, evaporation is more likely to happen. This phenomenon is especially important with fine powders and with plasmas with high hydrogen content as hydrogen enhances thermal conductivity. In processes where the velocity is high, e.g. HVOF, oxidation only takes place at the outer shell of in-flight particles and thus the oxide level in these coatings will be low. In APS processes, even for solid in-flight particles, the oxide content will be greater because of the high reactivity of ionised oxygen entrained from the atmosphere. Additionally, as an in-flight particle can fully melt in processes such as APS, convection processes inside the particle then control oxidation, resulting in a higher oxide content in the coatings. At the same time that in-flight oxidation proceeds, oxidation of the previously deposited layer when the jet spot has moved away takes place. Layer oxidation depends on the time that the hot gas stream remains over a specified area but it increases as the substrate temperature increases and especially if the stream is close to the substrate (short spraying distances).

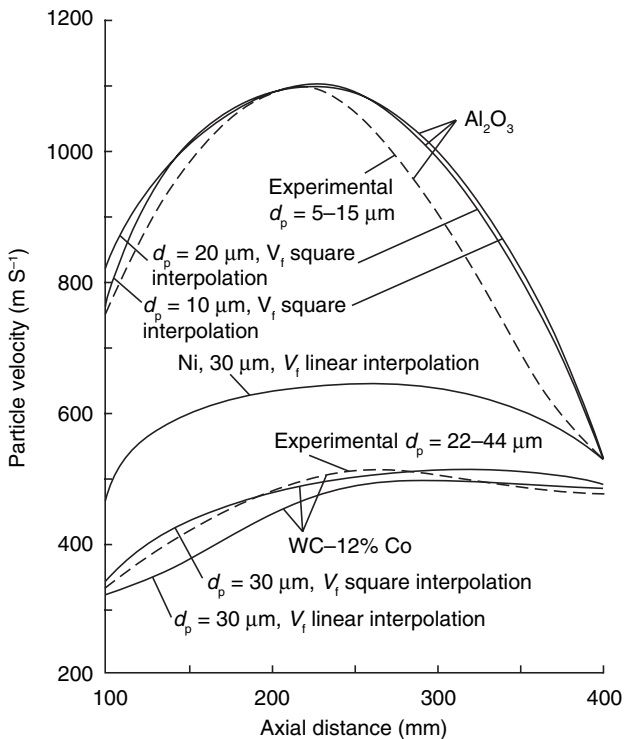
Reaction with the surrounding atmosphere can, however, be used to achieve desired chemical reactions between certain powder elements and a controlled atmosphere. This process is sometimes called reactive plasma spraying and is used to produce TiC , Si_3N_4 and several other ceramic coatings (Zhao and Lugscheider, 2002).

As will be seen in the particular cases presented below, the spraying distance plays an important role in thermal spraying. Thermal exchange will be greater with longer spraying distances because the dwell time of particles inside the hot stream will be greater, whereas in some cases the impact

velocity will decrease at spraying distances above a critical value owing to air turbulence.

In HVOF processes, a near-stoichiometric mixture of a combustible hydrocarbon and oxygen is burnt in the combustion chamber of the gun. In the results described below, the hydrocarbon gas was propane. The products of combustion achieve approximately the theoretical flame temperature of about 3000 °C, and then they leave the gun at a hypersonic velocity and so carry the entrained powder particles. Thus, from a standing start the particles are rapidly accelerated. The velocity attained will be higher with smaller particles than with larger particles and, for a given particle size, the velocity will decrease as the density increases.

After reaching a maximum, the velocity of the particles decreases as the length of the flight path increases. The results obtained from mathematical simulation of in-flight conditions are given in Fig. 8.7 (Sobolev *et al.*, 1994). High-density particles achieve lower velocities but the velocity profile is

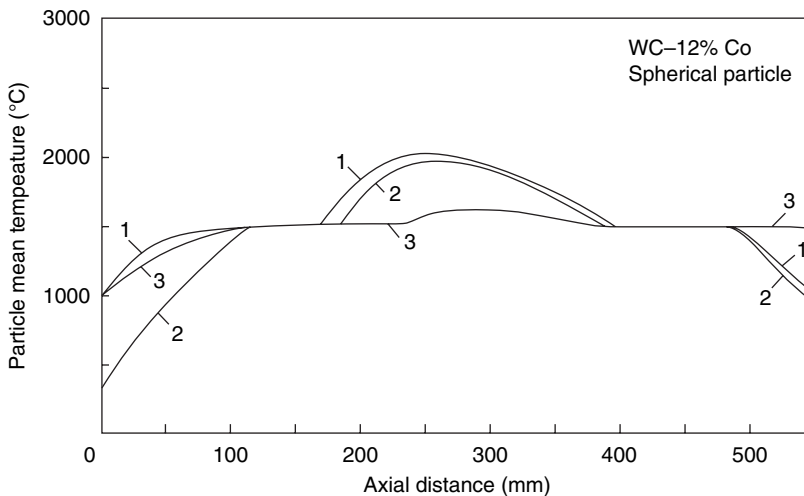


8.7 Particle velocity as a function of the axial distance along the flight path for different types of particles (Sobolev *et al.*, 1994). Results were obtained by mathematical modelling. V_f is the fluid velocity, d_p the powder diameter.

flatter, whereas low-density particles can achieve higher velocities but after a maximum the value decreases rapidly. The particle diameter has a certain effect on the velocity values because of aerodynamic concerns.

Under normal circumstances the spraying distance is set at 200–300 mm and, under these conditions, for example, WC–Co particles strike the component to be coated at a velocity of about 500 m s^{-1} , i.e. about the speed of sound. It is not surprising, therefore, that the HVOF spraying process is noisy and has to be carried out in a sound-proof chamber.

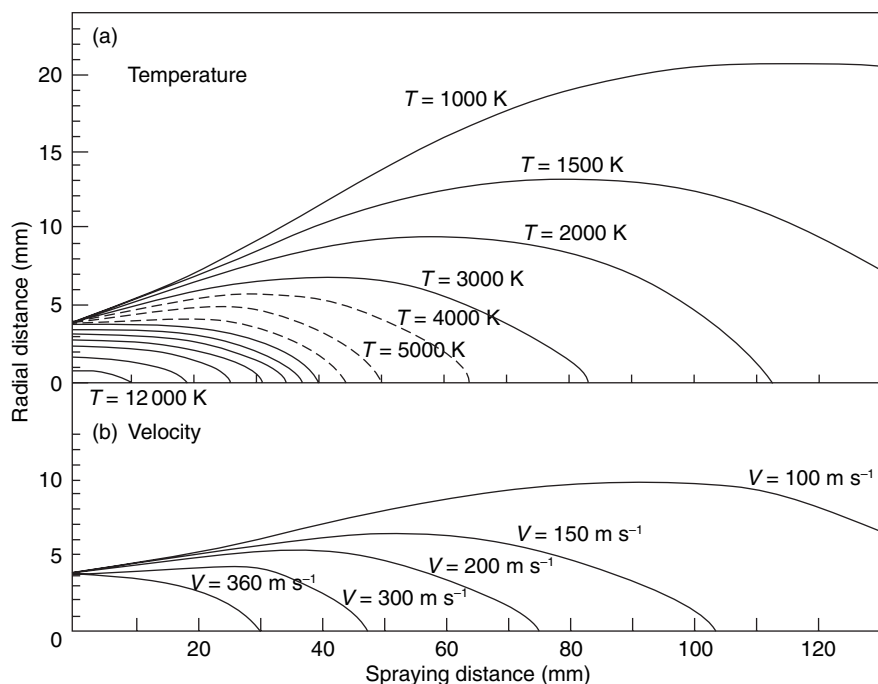
Whilst the particles are in the gun they may be preheated but, once they are projected from the gun, they are rapidly heated by the hot gases of the flame. As the time of flight is short, the particles never come into thermal equilibrium with the combustion gases. The influence of preheat and particle size on the temperature attained during flight, as determined by calculation, is given in Fig. 8.8 (Sobolev *et al.*, 1994). With WC–Co particles 40–50 μm in diameter, the temperature attained when they reach the component to be coated is believed to be about 1530°C , a value that seems to be in agreement with experimental evidence (Sobolev *et al.*, 1994; Nutting *et al.*, 1995).



8.8 Particle mean temperature as a function of axial distance with the effect of the particle radius and the preheating of the gun (Sobolev *et al.*, 1994). Curve 1, $d_p = 20 \mu\text{m}$, $T_0 = 1000^\circ\text{C}$; curve 2, $d_p = 20 \mu\text{m}$, $T_0 = 300^\circ\text{C}$; curve 3, $d_p = 25 \mu\text{m}$, $T_0 = 1000^\circ\text{C}$. Curve 3 is representative of normal spraying conditions. Results were obtained by mathematical modelling. d_p is the powder diameter and T_0 the initial powder temperature.

In the case of APS, high temperature and velocity gradients exist in both the radial and the axial directions. These gradients depend on the plasma viscosity and temperature. The example given in Fig. 8.9 shows that the highest temperature reached is in the zone of the plasma jet core. The temperature decreases as radial or axial distance from the nozzle increases, e.g. example at a stand-off distance of 80 mm and a radial distance of 15 mm, the temperature has diminished by about 90%. The radial temperature profile is very steep near the nozzle; at a radial distance of approximately 4 mm the temperature has only reached 1000 K (Boulos *et al.*, 1993). Another particularity of the APS process is that typical spraying distances are much shorter than those in the HVOF process.

Both the temperature and the velocity profiles suggest that the powder must ‘travel’ as close as possible to the axial direction where the thermal exchange is maximised. Powder feeding should be optimised in order to introduce the maximum amount of powder into the core of the plasma jet. A narrow powder size distribution is necessary; otherwise too coarse particles could pass through the core without being accelerated by the stream while too fine particles could be blown away by the jet.



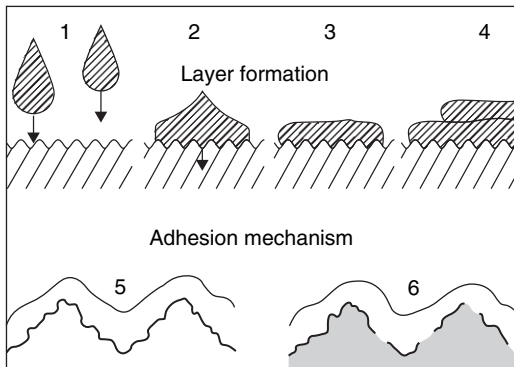
8.9 (a) Ar-H₂ plasma jet temperature and (b) Ar-H₂ velocity gradients. (Boulos *et al.*, 1993).

8.3 Coating structures

8.3.1 Coating metallography

The metallographic study of the powders, the coatings, the substrate and the interface between the coatings and the substrate, with the range of phases produced under conditions far removed from thermal and chemical equilibrium, taxes the skill of metallographers. It also requires the use, at the limit of their capabilities, of the full range of electron-optical instruments available for structural characterisation and microanalysis. However, it must always be remembered that structural characterisation is not just a metallographic exercise but it is from such studies that improvements in coating properties are achieved and better engineering components are fabricated.

Basically, thermal spray coatings are made up from a semicontinuous impingement of partially molten droplets on to a previously prepared substrate. Figure 8.10 shows this process in schematic form. During their passage through the hot gases, the particles partially melt. Thus, when they impinge on the substrate, they have a soft solid core with a liquid envelope. Figure 8.11 shows an HVOF process where the hot particle stream is seen to impinge on a rotating substrate, causing coating deposition, while at the same time some particles are observed not to adhere as they pass through regions of the substrate with open holes. As the impact energy is high, the liquid is forced into intimate contact with the substrate, where it adheres and forms a lamellar deposit, a splat, on the substrate. An initial coating



8.10 Coating build-up diagram during thermal spray process: 1, in-flight particles; 2, impact on surface; 3, heat transfer; 4, solidification and contraction of the coating material; 5, mechanical bonding; 6, local fusions.



8.11 HVOF process where particles in the spraying jet are seen.

layer is produced by moving the component relative to the impinging beam of particles. As the jet passes over the previously deposited lamellae again and again, the coating grows until the desired thickness is achieved. When the jet is not over a given area, oxidation of the top surface of the lamellar deposit, the splat, occurs and cooling takes place. The heat flux is directed through the recently deposited layers of the coating towards the substrate. The coating is built up by the superposition of individual particles. There are several different morphologies of splat particles depending on the thermal and kinetic history of the powder as well as its grain size and the feeding process. Particles of different sizes have different thermal histories; the finer particles have been fully molten while the coarser particles may still retain their original shape and morphology. This is the case of the so-called non-melted particles while completely melted particles will spread over the substrate, creating a splat. Impact morphologies affect lamellae adhesion, porosity and crack susceptibility and hence, to some extent, the final coating properties.

An undesired number of non-melted particles can appear in a coating if the powder has an unsuitable grain size for the technique used. In addition, if the feeding was not as precise as it should have been, owing to an unsuitable powder carrier gas flow, not all the powder grain size range is fed into

the flame core. Hence, if the powder grain size distribution is not narrow enough, the coating structure can be heterogeneous. If the coating structure is heterogeneous, its properties will also vary across each layer and at the surface.

As-sprayed thermal spray coatings have different levels of surface roughness, commonly being between 3 and 10 μm (R_a values). Smooth surfaces will be created if the particles spread well over the previously deposited layers whereas non-melted particles in the surface will lead to a coating with a high level of roughness. This is important only up to a point because coatings are not normally used as sprayed but only after machining to obtain a suitable surface finish.

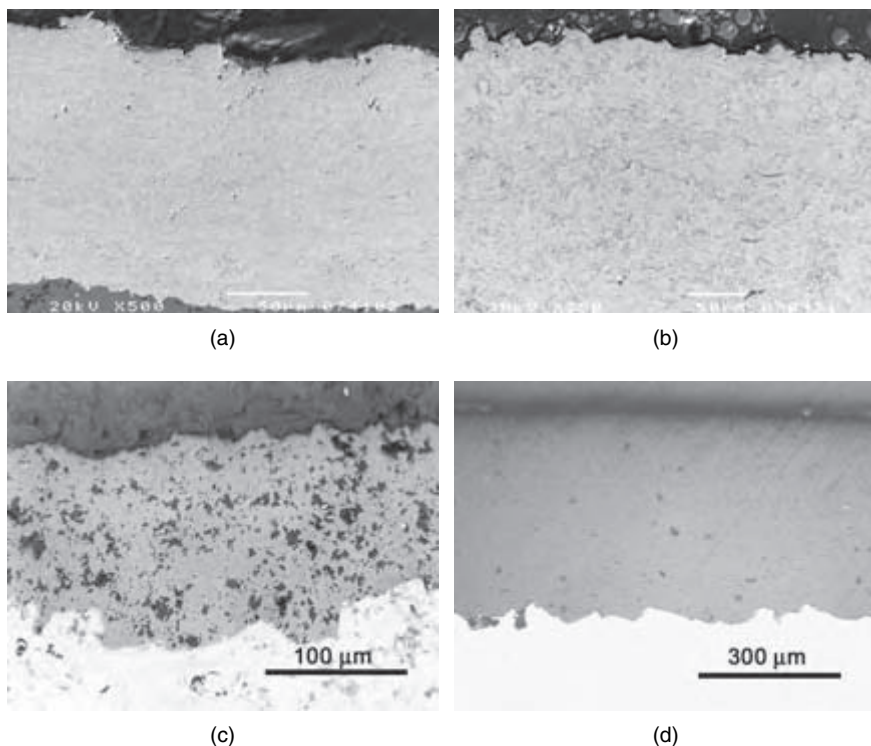
The adhesion of the splat lamellae to the previously deposited lamellae or to the roughened substrate is purely mechanical. There is no noticeable diffusion. For this reason, substrates must be grit blasted in order to achieve a suitable surface roughness (with an R_a value higher than 4–5 μm). Typically, the area of contact of particles attached to the substrate is not 100%. Normally it is about 25% but this can be increased with concomitant increase in coating adhesion by lowering the coating oxide level or by increasing particle velocity.

When particles spread over the substrate, the bottom layer of the lamellae will adhere to the substrate while the rest of the particle will contract, creating a stress. This stress is in addition to the stresses caused by the mismatch of coating and substrate coefficients of thermal expansion and causes the coating to have residual stresses. Residual stresses must be taken into account because they affect coating properties such as wear, corrosion and fatigue resistance as well as coating adhesion. Many studies are currently being devoted to *in-situ* measurements of residual stresses and how to control them (Renault *et al.*, 2000; Matejcek and Sampath, 2003; Matejcek *et al.*, 2003).

Some examples of common thermal spray coatings structures are shown in Fig. 8.12. It can be seen that TBC (Fig. 8.12(c)) has more porosity than metallic coatings. In the cermet coating (Fig. 8.12(a)), there is some porosity but the structure is very homogeneous while, in the Ni–Cr metallic layer (Fig. 8.12(b)), the oxide content is randomly dispersed inside the matrix.

8.3.2 Interfacial structures

With the arrival of the first splat on the substrate material, heat is rapidly lost from the liquid metallic phase to the relatively massive heat sink of the substrate material. It has been estimated that the cooling rate at a distance of 0.5 μm into the splat immediately adjacent to the substrate is about $10^6\text{ }^\circ\text{C s}^{-1}$ (Nutting *et al.*, 1995). The flow of heat from the splat to the sub-

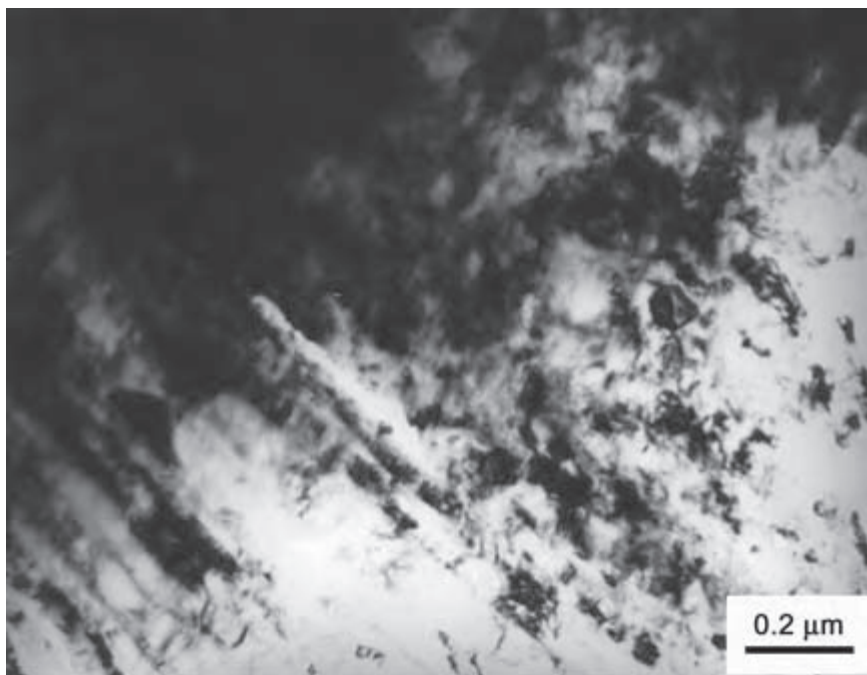


8.12 Coating examples: (a) an HVOF WC-Co layer; (b) an APS Ni-Cr layer; (c) a TBC with a Ni-Cr bond coat and a ZrO₂ ceramic layer both sprayed by APS; (d) an FS polyamide coating.

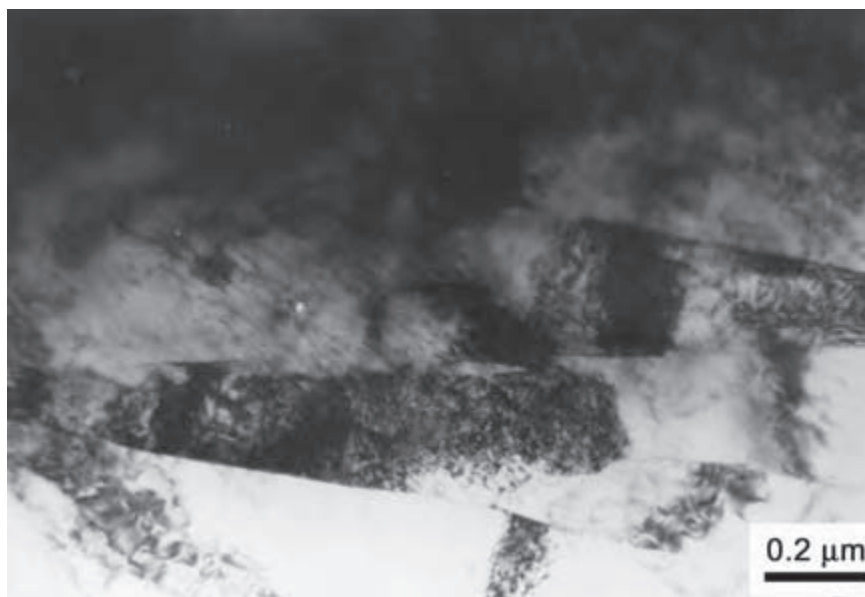
strate causes the substrate to heat and the temperature time profiles in the substrate at different depths from the coating-substrate interface can be calculated (Nutting *et al.*, 1995). Metallography on a steel substrate can be used to confirm the predictions of mathematical modelling as to heating and cooling rates. By careful specimen preparation techniques, thin foils from the interfacial region of the coating and the substrate can be prepared. Examination of foils by transmission electron microscopy from a region of substrate immediately adjacent to the coating shows a very complex fine crystalline structure, but it appears to consist of fine grains having a diameter of 0.1 μm with dark islands of smaller diameter within a range of 0.05 μm (Nutting *et al.*, 1995). Selected-area electron diffraction patterns from this zone indicated that the fine crystals were composed of a δ phase and a twinned high-carbon martensite, confirming that the temperature at the substrate interface must have reached about 1480 °C, since liquid has

been present. At a region situated approximately 3–10 μm from the interface, a transformation to martensite had occurred, which means that the substrate had reached the austenite transformation temperature and then had been cooled rapidly (quenched) by the bulk of the cool substrate. Figures 8.13 and 8.14 show the low-carbon martensite in this region. When the second layer of the coating is deposited, heat flows from the molten liquid in the splat to the first layer and from the first layer into the substrate. However, the first layer acts as an appreciable thermal barrier; thus the temperature rise in the substrate from the second and subsequent thermal pulses, is very low (Fig. 8.15). This is confirmed by the fact that the low-carbon lath martensite found at up to 10 μm into the substrate shows no evidence of tempering.

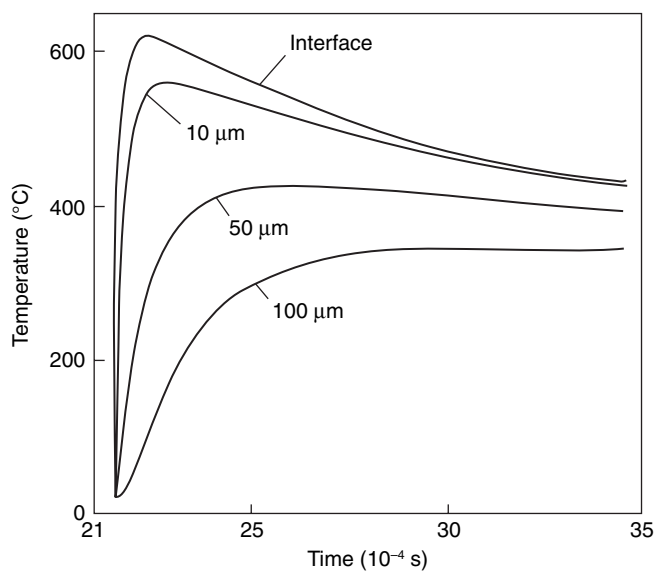
The modelling studies of Guilemany *et al.* (1994) and Sobolev *et al.* (1994) on heat transfer from an impinging splat to a steel substrate agree with the microstructural observations and predict a maximum temperature of 1480 °C at the interface, and about 1400 °C (range from 1350 °C to 1440 °C) 3 μm below the interface.



8.13 Transmission electron micrograph of the substrate adjacent to the coating.



8.14 Transmission electron micrograph of a low-carbon martensite structure formed in the interfacial region because of thermal spraying.



8.15 Time-temperature profiles induced in a steel substrate by the second layer of splats (Sobolev *et al.*, 1994). The temperature rise in relation to the time is insufficient to temper the martensite. Results were obtained by mathematical modelling.

Scanning transmission electron microscopy (STEM) can also be used to assess the chemical changes at the coating–substrate interface (Nutting *et al.*, 1995). Although it has been observed that the coating has been partially liquid, and that partial melting has occurred in the substrate and that there has been liquid–liquid contact, STEM analysis shows no transfer of elements from the substrate to the coating, a result which is not too surprising considering the rapid heating and cooling rates involved.

8.4 Post-spray treatments

In some applications, as-sprayed coatings may not be dense or pore free enough and/or may have an unsuitable roughness. For these reasons post-spray treatments may be carried out. The most common used processes to modify the structure are hot isostatic pressing (HIP), heat treatments and laser treatments. Heat treatments are carried out in furnaces, either with or without a controlled atmosphere, the main goal being to increase the bond strength, density and elastic modulus in ceramic materials. Lasers are used to remelt the whole thickness or the surface and produce a complete change in the microstructural features of the coating. Improvements in homogeneity and density occur and some precipitation of hard phases takes place following solidification of the molten zone when self-fluxing alloys are used. HIP treatments, although very expensive, are sometimes preferred as a method to decrease porosity. A reduction in porosity can achieve, for example, enhanced corrosion resistance (Malayoglu *et al.*, 2003).

Porosity can also be treated by sealants. Interconnected porosity can be sealed with glass-forming inorganic oxides, or with organic compounds such as waxes, epoxides or silicones. The amount of penetration by the sealant depends on the coating characteristic and also on the type of sealant used.

Finishing methods such as polishing and lapping can be used to modify the thickness and the roughness of the coating after the spraying process. A surface finish with $R_a < 0.2\mu\text{m}$ can be achieved.

8.5 Structure–property relationships

In this section, some examples of coatings and their most suitable fields of application are described. Most of the applications concern the wear, corrosion and thermal insulation properties of the coatings. Table 8.3 is a summary of some properties of coatings obtained by different techniques. Of course they can vary slightly if spraying conditions, type of powder used and gas types are changed. Tables of some other properties have been given by Pawlowski (1995) and Sinha (2003).

Table 8.3 Properties of thermal spray coatings obtained at the Thermal Spray Centre by various methods. Most Vickers microhardness values were obtained with 300gf loads but some were obtained with 100gf loads owing to their brittle nature. Bond tensile strength values were obtained using the ASTM C 633 test

Coating material	Vickers microhardness (load, 100gf† or 300gf††)	Bond tensile strength (MPa)
Composites and cermets		
WC-12% Co, HVOF§	879 ± 174††	>80
WC-12% Co, HVOF (conventional powder)‡	1236 ± 149††	>80
WC-12% Co, HVOF (nanostructured powder)‡	1568 ± 93††	>80
Cr ₃ C ₂ -20% (Ni-Cr), HVOF§	839 ± 63††	71 ± 4
Cr ₃ C ₂ -20% (Ni-Cr), HVOF‡	926 ± 60††	>80
TiC-(Ni-Ti), HVOF§	976 ± 30††	68 ± 1
WC-10% Co-4% Cr, HVOF§	1293 ± 48††	73 ± 2
(Al-Si)-23% graphite, APS	70 ± 35††	20 ± 3.2
Metals and alloys		
Ni-Cr-B-Si, HVOF§	905 ± 9††	75 ± 3
Ni-Cr-B-Si, APS	611 ± 15††	30 ± 4
Ni-Cr-B-Si, APS + remelting	667 ± 152††	>80
Bronze-Al (Al + 90% Cu), APS	176 ± 33††	35 ± 3
Mo, APS	440 ± 85††	45.8 ± 3
Ni-25% graphite, APS	82 ± 27††	26 ± 2
Ni-20% Cr, APS	292 ± 15††	52 ± 3
Ni-Cr-Al-Y, APS	318 ± 17††	40 ± 4
Ni-5% Al, APS	194 ± 13††	35.4 ± 2
Stainless steel 316 HVOF§	345 ± 25††	45 ± 3
Stainless steel 431 HVOF§	417 ± 17††	59 ± 4
Stainless steel + TiC, HVOF‡ (Sanchez et al., 2003b)	950 ± 94†	72 ± 2
Ceramic oxides		
Partially stabilised ZrO ₂ (ZrO ₂ + 8% Y ₂ O ₃), APS Al ₂ O ₃ , APS	570 ± 62†	16.2 ± 2
	866 ± 38††	26 ± 5
Polymers		
Polyamide 10/10, FS	8†	24 ± 4
Polyethylene, FS	<1†	15 ± 2

§ HVOF sprayed with a Sulzer Metco CDS gun.

‡ HVOF sprayed with a Sulzer Metco DJ/DJS gun.

8.5.1 Wear-resistant coatings

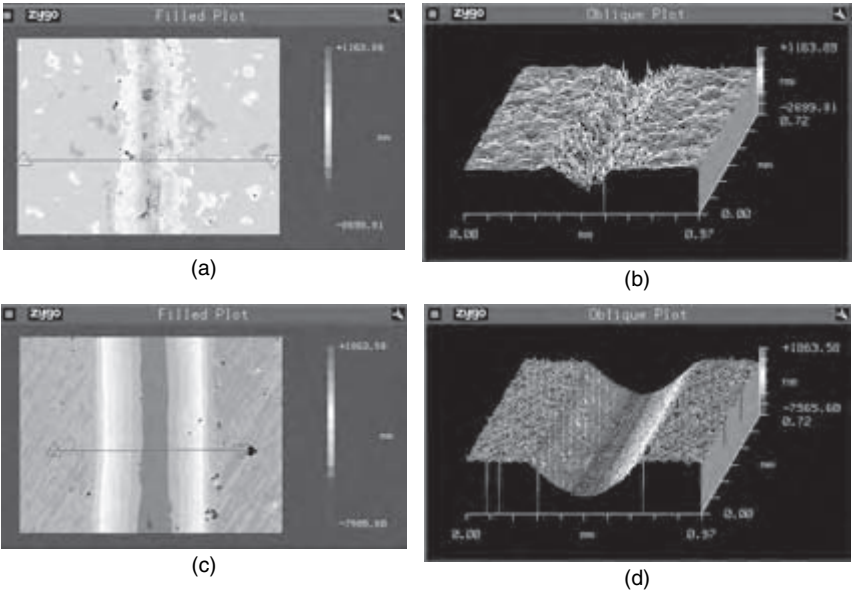
As wear can occur by several wear mechanisms, different types of wear-resistant coating are needed and are available in the market. The best choice of coating will be that suitable for a given application, bearing in mind the work conditions (Siegmann *et al.*, 2000). As previously stated, there is no overall best coating but there is an optimum coating for a specific application.

Sliding wear

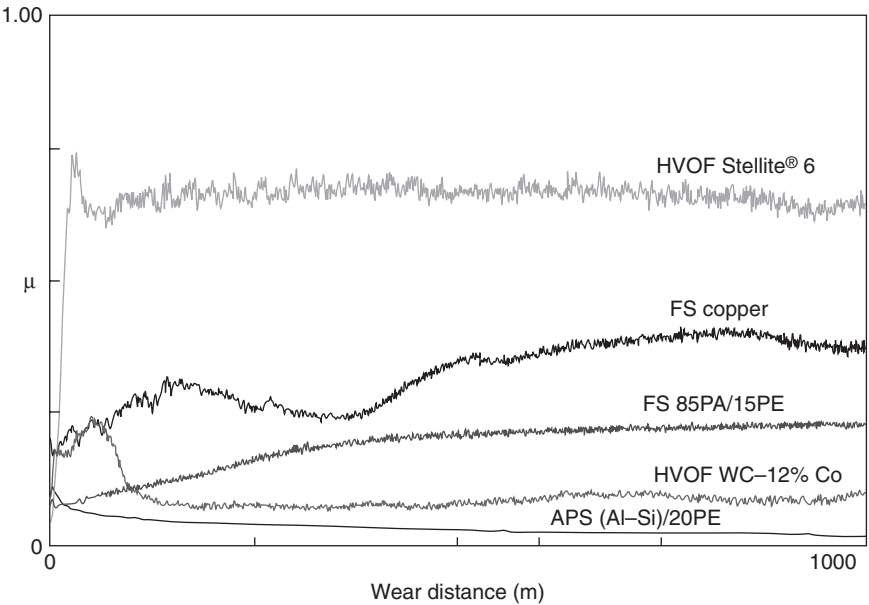
The materials most commonly sprayed for sliding wear applications are hard ceramics such as plasma-sprayed Cr_2O_3 and Al_2O_3 (Leblanc, 2003) and HVOF-sprayed WC–Co (Qiao *et al.*, 2003). Oxide coatings have higher thermal and chemical resistances than cermets although cermets, because of their metallic matrix, have a superior fracture toughness, a higher mechanical strength and a smaller coefficient of thermal expansion mismatch with a steel substrate. As a high thermal expansion mismatch can yield high residual stresses, thick coatings of oxide materials can spontaneously delaminate. Thermal spraying an intermediate coating (bond coating), with a suitable coefficient of thermal expansion, between the substrate and the outer wear-resistant coating may allow a thick oxide layer to be deposited without the occurrence of catastrophic cracking. Other materials used are metals and alloys such as molybdenum, Co–Cr–Mo, superalloys (Tribaloy, Stellite®, Inconel®, etc.) and Mo_3C . Thermal spraying as a technique of obtaining wear-resistant coatings is becoming increasingly important and an example of this is the use of HVOF spraying as a feasible alternative for hard chromium plating because of the excellent properties of the HVOF coatings and fewer environmental pollution problems (Nestler *et al.*, 1998; Dorfman *et al.*, 2000). A scanning white-light interferometry (SWLI) image of the wear tracks after a ASTM G 99-90 test is shown in Fig. 8.16. It shows that the wear track and thus the damage to the HVOF-sprayed Stellite® 6 (Fig. 8.16(c) and Fig. 8.16(d)) is much more severe than in the other example, a HVOF-sprayed blend of Ni–Cr–B–Si (60 vol.%) with WC–Co (40 vol.%). Wear tests also give information on the friction coefficient (μ), and Fig. 8.17 is a plot of friction coefficient against test distance (1000 m) for some materials including very low wear coefficient coatings developed by Sánchez *et al.*, (2003a).

Abrasive wear

Materials used in the thermal spray process when abrasion is the prevalent wear mechanism are Al_2O_3 , TiO_2 , Cr_2O_3 (Abdel-Samad *et al.*, 2000; Gawne



8.16 SWLI images of wear tracks of (a), (b) HVOF WC-12% Co/Ni-Cr-B-Si (40/60) and (c), (d) HVOF Stellite® 6.

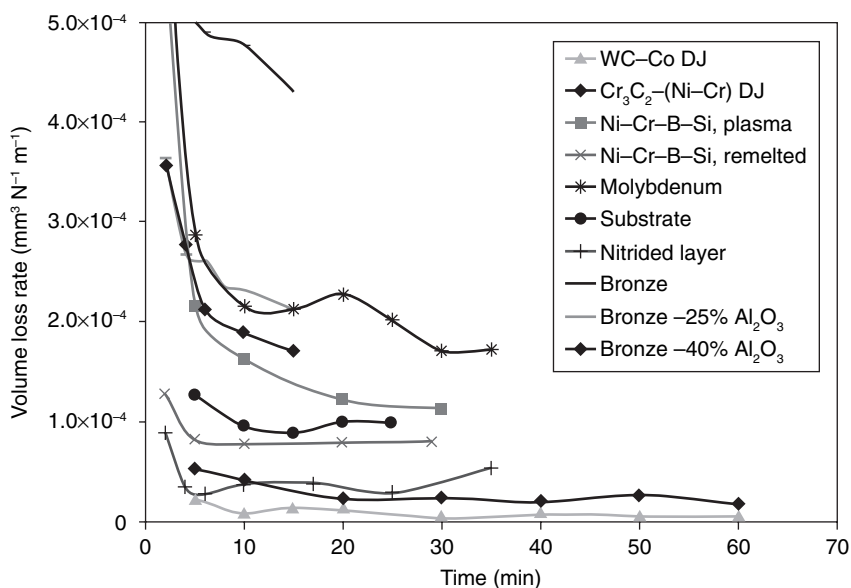


8.17 Plot of friction coefficient μ against wear distance for some materials. Copper and 85PA/15PE were subjected to a 10 N load and the others to 5 N.

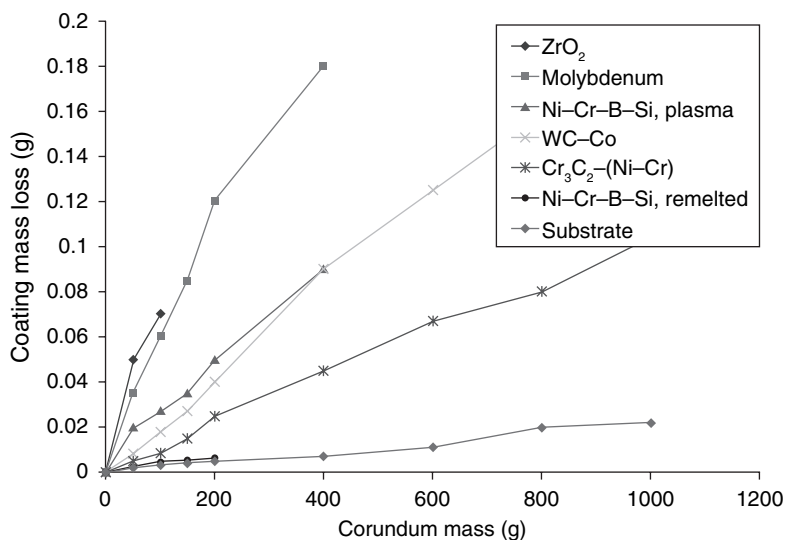
et al., 2001), and their blends sprayed by both APS and VPS. Also metallic molybdenum coatings and composites such as mixtures of self-fluxing alloys with carbides or oxides ($\text{Ni-Cr-B-Si} + \text{Cr}_3\text{C}_2$, Cr_3C_2 , WC, TiC, etc.) and cermets ($\text{Cr}_3\text{C}_2\text{-(Ni-Cr)}$, WC-Co, and WC-(Co-Cr)) are suitable materials for abrasion resistance applications. Figure 8.18 shows the wear rates of various materials as functions of test time in an ASTM G 65-91 abrasion test. It can be seen that the best materials for this kind of wear are cermets, carbides and nitrides, i.e. hard materials.

Erosion

Ceramics can resist erosion quite well, e.g. Al_2O_3 or WC-(Co-Cr) (Legoux *et al.*, 2003), if they are harder than the impinging particles. Ceramics and polymers have a wide range of wear resistances. Some elastomers show very good resistance but only under certain working conditions, whereas the performance of wear-resistant cermets depends strongly on binder content. Figure 8.19 shows mass loss for various coating materials against corundum mass in the ASTM G 76-83 test. As the corundum mass increases, so does the abrasion process and the material begins to lose mass owing to detachment of material by abrasive particle pull-outs.



8.18 Plot of volume loss rate against testing time to measure the abrasion resistance of some materials after an ASTM G 65-91 test.



8.19 Plot of mass loss against corundum weight after an ASTM G 76-83 test for some materials.

8.5.2 Corrosion- and wear-resistant coatings

Corrosion-resistant coatings are designed to withstand aggressive working conditions. These are mostly metallic coatings, although in several applications there is a need for both corrosion and wear resistance. For this reason, much effort has been devoted to improving the corrosion resistance of wear-resistant coatings such as WC-Co.

The coating parameters that affect corrosion resistance are porosity, oxide level, cracks, residual stresses and non-melted particles. Of these factors, porosity is the most important. Porosity can be divided into three types: surface breaking pores, which are harmless, discrete porosity in the interior of the coating, and interconnected porosity which is the most damaging as it creates a path for electrolyte to reach the substrate-coating interface. Severe cracking caused by residual stresses or fatigue can also allow electrolyte to pass through the coating. Non-melted particles can lead to electrolyte penetration via the porosity present around them. The oxide level also plays a role as a higher oxide content reduces the passivity of the coating layer and also creates a zone where crevice corrosion is likely to occur. Another undesirable factor is element depletion-during spraying. Metallic phases can become depleted in corrosion-resistant elements such as chromium or nickel if these elements oxidise or evaporate during the

thermal spray process. For example Ni–20%Cr alloy when sprayed by FS or APS (Guilemany *et al.*, 2002c, 2003).

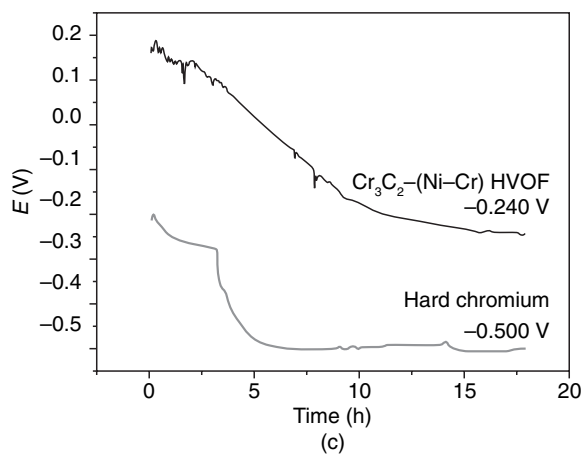
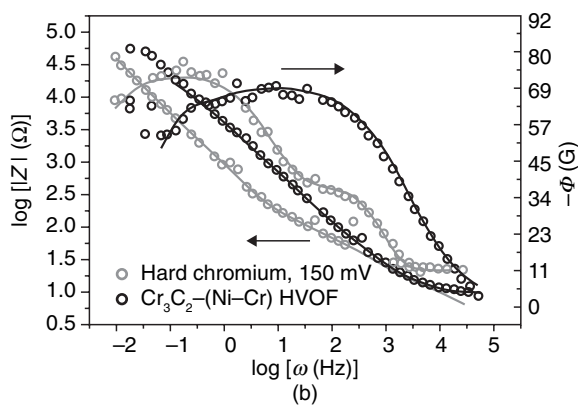
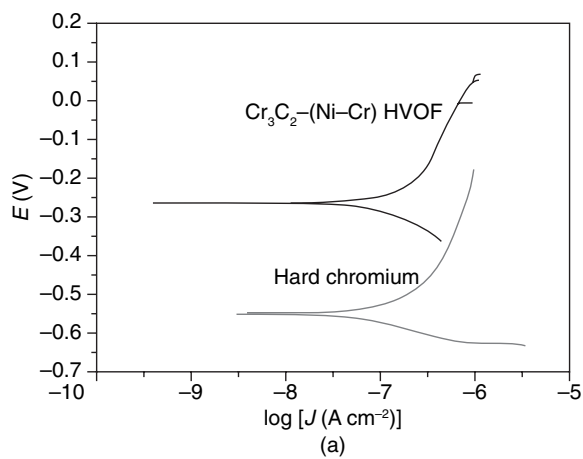
It must borne in mind that all these mechanisms occur as a result of certain microstructural features of the coating. These undesirable microstructural features provide a ‘tunnel’ for the electrolyte to reach the substrate and so, to maximise corrosion resistance, the sealant properties of coatings must be maximised.

On the other hand, there are corrosion mechanisms in coatings that depend on the creation of galvanic couples between dissimilar phases. This is the case for cermets, for example, where hard ceramic particles are in contact with a soft metallic matrix. It is for this reason that nickel or chromium additions to the cobalt matrix in WC–Co cermets are common in high-wear high-corrosion-resistance applications, although these coatings do have a lower wear resistance than WC–Co.

Aluminium sprayed by FS is very often used in applications in coastal environments. In more demanding hot corrosion applications, M–Cr–Al–Y, superalloys (Zhang *et al.*, 2003), 316 stainless steel (Zhao and Lugscheider 2003) and Ni–Cr can be used sprayed by HVOF or VPS. Figure 8.20 shows the results of corrosion tests (Sawyer and Roberts, 1974) carried out on coatings (Guilemany *et al.*, 2004). The corrosion tests detailed in Fig. 8.20 include cyclic voltametry (Fig. 8.20(a)), impedance (Fig. 8.20(b)) and open-circuit potential (Fig. 8.20(c)). All these tests were performed on an HVOF Cr₃C₂–(Ni–Cr) coating (black circles) and on an electrodeposited hard chromium (grey circles) (Guilemany *et al.*, 2004). The thermally sprayed coating is noted to perform better than the hard chromium plate.

8.5.3 Thermal barrier coatings

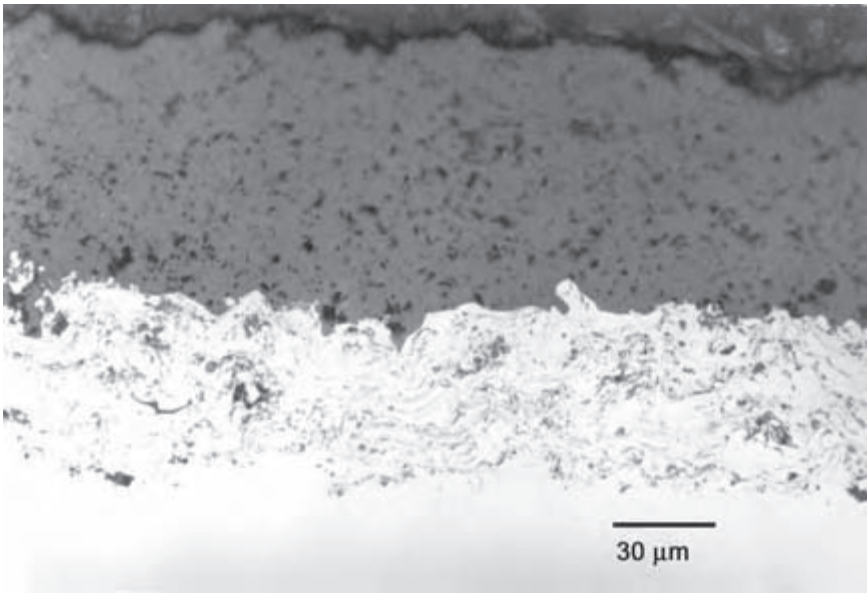
TBCs are coatings designed to protect critical engine components from excessive heat, enabling them to operate at higher temperatures than would otherwise be possible. TBCs should have a high melting point, a certain porosity level (Kulkarni *et al.*, 2003), low density (if used in aerospace and space applications), high thermal shock resistance, chemical stability, low thermal conductivity and good erosion resistance. The main uses of TBCs are in the turbine industry and in diesel engines. In turbines, the need for more sophisticated as well as more environmentally clean turbines places high demands on the materials used in their construction. The use of improved cooling systems as well as new material-processing methods and alloys allow current turbines to work at higher temperatures. The use of a TBC reduces the working temperature of the substrates by up to 110–130°C. The lower substrate temperature achieved in coated components enables them to work at high temperatures for longer times owing to reduced creep and fatigue rates. Moreover, there is a reduction in oxidation



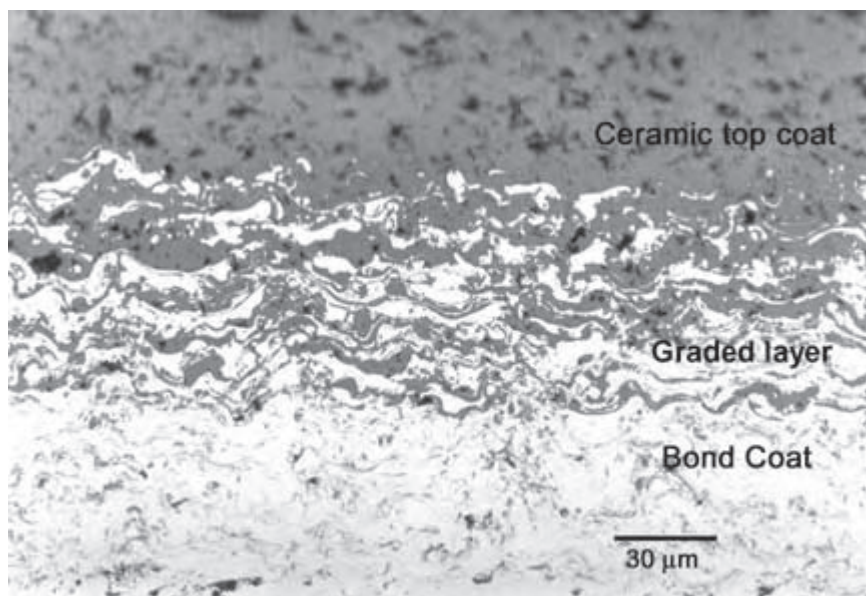
8.20 Corrosion test examples. Materials tested are HVOF sprayed $\text{Cr}_3\text{C}_2\text{-(Ni-Cr)}$ (black circles) and electrodeposited hard chromium (grey circles). (a) cyclic voltammetry, (b) impedance, (c) open-circuit potential (Guilemany *et al.*, 2004).

and hot corrosion of the substrate (Mifume *et al.*, 2003). The main problem resulting from the use of TBCs, however, is the aggressive turbine environment itself which causes hot corrosion and high-temperature oxidation of the TBC as well as mechanical fatigue and erosion wear, thus reducing the coating service life.

TBCs are composed of a bond metallic layer with a top ceramic layer. A TBC coating structure consisting of a Ni–Cr bond coat and ZrO_2 , both APS sprayed, can be seen in Fig. 8.21. The ceramic layer has a certain porosity level whereas the metallic layer is almost pore free but has some randomly dispersed oxide lamellae. The need for a bond coat arises from the mismatch of the coefficients of thermal expansion of the substrate and ceramic coating. The bond coat material should have a coefficient of thermal expansion between those of the substrate and the ceramic layer. Another engineering solution for coefficient of thermal expansion mismatch is functionally graded materials (FGMs) (Khor *et al.*, 2000; Guilemany and Armada, 2001; Cetinel *et al.*, 2003). In this case, there is not an abrupt bond coat–ceramic layer interface but a smooth interface (Fig. 8.22), where there is a graded zone between the Ni–Cr bond coat and the ZrO_2 top coat. Modifying the powder feeders during plasma spraying allows the material sprayed to



8.21 Optical micrograph of a cross-section through a TBC composed of a Ni–Cr bond coat and a ZrO_2 ceramic layer (grey in the image) both APS sprayed.



8.22 Optical micrograph of a cross-section of a FGM composed of a Ni–Cr bond coat (light phase) and partially stabilised ZrO_2 (dark phase) ceramic layer. There is a graded zone between the pure components.

change from 100% bond coat to 100% top coat; hence a graded coating is achieved.

The materials mostly used for bond coat applications are M–Cr–Al–Y alloys where M is nickel, cobalt or iron, and Ni–Cr coatings sprayed by APS or VPS techniques. Ceramic top coats are mostly made of partially stabilised ZrO_2 (Berndt *et al.*, 2001; Moreau *et al.*, 2001; Ballard *et al.*, 2003) and to a lesser extent alumina sprayed by APS although some are HVOF sprayed (Dobbins *et al.*, 2003). The lifetimes of ZrO_2 materials are maximised by adding 6–8 vol.% yttria (Y_2O_3). Other stabilised ZrO_2 compounds use ceria (CeO_2) instead of Y_2O_3 to increase hardness and crack resistance (Huang *et al.*, 2000).

8.5.4 Abradable clearance-control coatings

Abradable coatings based on a metallic matrix and a ceramic or polymeric filler phase can be employed in certain applications providing good reliability, high wear resistance, stability at moderate or even at high temperatures and reduced cost (Pleskachevsky *et al.*, 1997). The metallic matrix has to be relatively tough and fillers are usually solid lubricants that are weakly

bonded to the matrix. The whole system should have a low density and some porosity to decrease the wear damage of the counterpart surface. In addition, the distribution of the fillers in the matrix has to be good enough to maintain stable coating properties during the working lifetime of the engine. Some of these materials are used as abrasible seal coatings in modern aircraft engines (Comassar, 1991; Yi *et al.*, 1999), or turbines (Boddenberg *et al.*, 1998). In this case, the primary requirement is to prevent excess damage to the blade tip while reducing the operating clearance between the turbine and the shroud. The blade tip should be able to scratch the abrasible surface without creating severe damage to the blade surface to produce a groove in the abrasible coating, and so to maintain the seal. Nevertheless, high wear resistance, low friction coefficient and low counterpart damage are the most important factors when these coatings are used for sliding wear applications. These characteristics determine the minimum energy loss in systems working under sliding conditions, as well as their maximum service lifetimes and stable operation in conditions with limited or without lubrication.

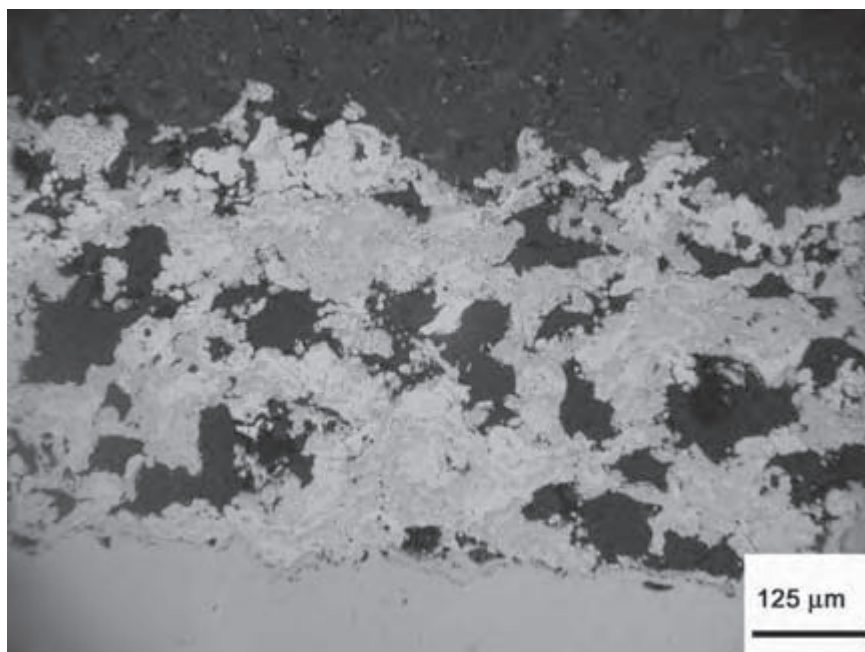
Aluminium-, cobalt-, copper- and nickel-based abrasible materials are available in the market, the cobalt-based and the nickel-based coatings being the high-temperature application materials. Blends of an aluminium matrix with various volume fractions of boron nitride (BN) (Nava *et al.*, 2001), graphite, polyester, polyimide, Co–Ni–Cr–Al–Y (Wei and Mallon, 2000), aluminium bronze alloys and bentonite (Dorfman *et al.*, 1992) materials are the most widely used. Other successful blends are an Al–Si matrix with polyamide (Fig. 8.23) or polyethylene (Sánchez *et al.*, 2003a), (Al–Si)–graphite, (Al–Si)–polyester and Ni–graphite (Guilemany *et al.*, 2001).

8.5.5 Other structure–property relationships

Polymer coatings can be applied as sealants because of their extremely low porosity and chemical stability (Leivo *et al.*, 2001; Guilemany *et al.*, 2002a; Vuoristo *et al.*, 2003). Spraying thermoplastics can allow a substantial reduction in the weight of parts. Moreover, they can be sprayed to form thick coatings.

Another interesting application field is that of self-lubricated systems. These systems have a lubricant phase dispersed in a metallic matrix (Zaluzcec and McCune, 1994; Newbery and Singer, 1995; Guilemany *et al.*, 2002b). The solid lubricating phase acts as a liquid lubricant and so the system does not need external lubrication. With this kind of application, environmental problems associated with the use of a liquid lubricant can be avoided.

During the 1990s thermal spray has been increasingly used in repair and overhaul applications (Dorfman, 2002) to restore worn or corroded parts of structures or installations. The materials sprayed are often materials with



8.23 Optical micrograph of a cross-section of an abrasion-resistant coating of (Al–Si)–polyamide. The dark phase is polymer filler whereas the light phase is the Al–Si matrix (Sánchez *et al.*, 2003a).

good corrosion resistance such as Ni–Al or stainless steel. Zinc, aluminium, Al–Mg and Zn–Al can be arc sprayed (Lester *et al.*, 1997; Ueno and Nava, 1997) or sprayed by FS (Ueno and Nava, 1997). Depending on the substrate material and the properties desired, various spraying techniques are possible, e.g. arc spraying Fe_3Al and Fe_3Al –WC materials on steel for boiler pipes in power stations (Xu *et al.*, 2003). In the case of turbine repair, spraying has to be carried out more carefully (McGrann *et al.*, 2000) in order to avoid any deterioration in performance of the repaired components. It is well known that spraying parameters affect the properties of the coatings and, if the coating is in demanding applications, such as in aeronautical components, high quality must be imperative.

8.6 Industrial applications

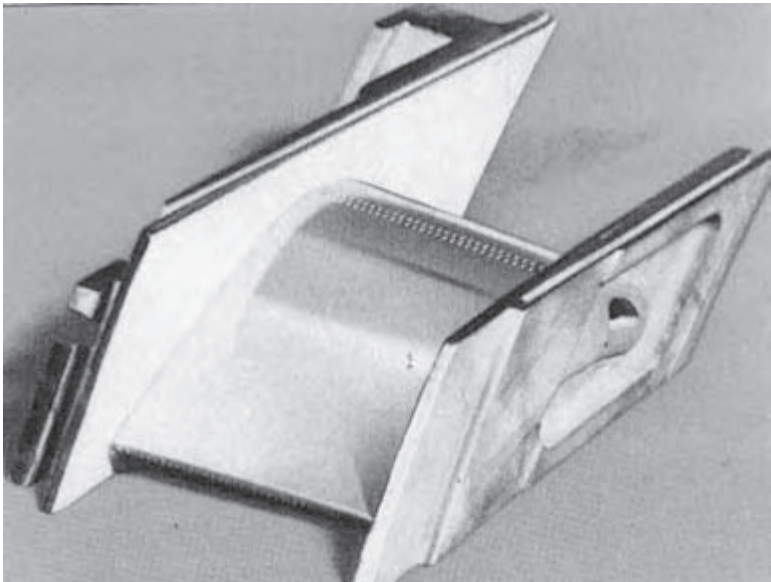
8.6.1 Gas turbines

In aircraft, land-based and marine gas turbines, thermally sprayed parts provide a wide range of solutions; e.g. wear-, oxidation- and corrosion-

resistant coatings, TBCs coatings and clearance-control coatings are found in several turbines (Hillery, 1996).

Marine propulsion turbines are susceptible to hot and salt corrosion owing to the high sulphur content of the fuel and a salt-water environment. Aircraft turbines are more exposed to hot corrosion and oxidation and in some cases to a salt-water environment if they operate quite often near oceans. Land-based turbines, on the other hand, are very different because of their larger size, lower rotational speeds, fewer on-off duty cycles, less weight penalties and large variety of locations. However, fuel type has the most important effect on coating selection. Coating degradation by hot corrosion mechanisms is the main failure process. For these reasons, M–Cr–Al–Y is VPS (Nakamori, 1990; Toma and Brandl, 1999), APS (Teratani *et al.*, 2001) or HVOF sprayed (Itoh *et al.*, 2001; Ajdelsztajn *et al.*, 2003a, 2003b; Bach and Lugscheider, 2003) on turbine blades and vanes (Fig. 8.24).

As stated before, neither the use of high-temperature-resistant superalloys nor improved cooling mechanisms can provide the increased operating temperatures needed in modern turbines and the use of a thermal insulator is essential in some parts of high-operating-temperature turbines. Thus ZrO_2 TBCs (Scrivani *et al.*, 2001; Dobbins *et al.*, 2003) are applied over some



8.24 Gas turbine nozzle guide vane where some parts can be coated with M–Cr–Al–Y HVOF sprayed or TBC plasma sprayed.

superalloys (Knight *et al.*, 1998) with a bond coat (typically M–Cr–Al–Y) to prevent the principal cause of TBC failure, which is oxidation of the interface between the coating and the superalloy substrate.

Vibration of fan and compressor blades in jet engines can be controlled by midspan dampers. WC–Co is HVOF sprayed on the contact surfaces of these dampers (Wigren and Pejryd, 1995; McGrann and Shadley, 1997) in order to increase the wear resistance of these parts. Other examples are Cu–Ni–In (Chakravarty *et al.*, 2000) sprayed in turbine blade roots or Inconel® sprayed to restore worn parts of airfoils, combustors and vanes in aircraft turbines.

8.6.2 Automotive applications

In the year 2000, more than 170 million vehicles excluding coaches, buses and trucks circulated in Europe (Merlo, 2003). There is an increasing demand for energy and, as a consequence, emissions of polluting gases to the atmosphere have risen. To cope with European emission legislation, car manufacturers are developing solutions, one of which is vehicle weight reduction. The use of light materials, such as aluminium and magnesium instead of cast iron for the engine blocks is one solution although neither of these materials has good tribological properties. This has been remedied by the use of surface treatment techniques such as thermal spraying; e.g. Al–Si cylinder bores are sprayed with an iron-based material (Barbezat, 2003; Cook and Zaluzec, 2003) using either HVOF or APS techniques. In the particular case of the cylinder bore there are two factors affecting the feasibility of HVOF spraying, namely the spraying distance and overheating of the substrate. As the internal diameter of the cylinder bores is not very large, and the coating must be applied to the bore, the spraying distance cannot be as large as typical HVOF spraying distances. However, if a short spraying distance is selected, the thermal flux from the HVOF gun to the substrate would be excessive for the Al–Si engine block. For this reason, APS is a more suitable technique for spraying cylinder bores. Other examples in the automotive industry are related to wear solutions such as APS and HVOF spraying of valves with self-fluxing alloys (Figure 8.25), stainless steel pistons APS coated with a Ni–Cr alloy (Rosso *et al.*, 2001), piston rings APS and HVOF sprayed with molybdenum and self-fluxing alloys or cermets (Herbst-Dederichs, 2003). TBCs have also been employed to improve the corrosion resistance and hence the life of valves and also to minimise heat loss and thus to increase engine efficiency (Yonushonis, 1997). However, degradation of TBCs by erosion has instigated the development of new CeO₂-stabilised ZrO₂ with improved tribological properties (Huang *et al.*, 2000).



8.25 Image of a self-fluxing alloy-coated car valve.

8.6.3 Oil and gas industry

Oil refineries, chemical plants and mining installations have pumps, valves, pipes and tools that are exposed to wear or corrosion mechanisms. In some applications, abrasive particles are involved whereas in others, sulphurous (Weber and Schutze, 1999) or corrosive environments increase corrosion rates. Drilling tools in mining and in oil rigs are subjected to high two- or three-body abrasive wear, and some components in chemical plants or refineries work under high-pressure high-temperature conditions.

Thus, in the oil and gas industries, several types of corrosion- and wear-resistant coatings are used (Tucker, 2002). Vessels in the chemical industries can be exposed to severe corrosion conditions and, because of their large shape, replacement is a costly option. Restoration of corroded parts with

coatings can be the solution to this kind of problem. Depending on the pipe, vessel or pump material, the coating solution will be different and hence knowledge of material compatibility and thermal spraying techniques is essential. Boilers in power generation plants and incinerators contain a large number of water-filled tubes. These tubes suffer from hot corrosion as well as erosion by hot exhaust gases and ash. A typical solution is the use of APS Ni–20% Cr alloy.

Pump parts are sprayed with molybdenum using APS which gives good sliding wear properties, Ni–Cr–Al–Y and Triballoys are used in demanding applications where both corrosion and wear are involved, Cu–Al is sprayed on pumps and valves for cavitation resistance, and stainless steels are very useful for restoring worn or corroded stainless steel parts in many industries. The spraying process sometimes can be carried out *in situ* with portable equipment, so reducing operational costs. Sometimes, owing to high noise emission or the automation required, the process must be carried out in a spraying booth.

8.6.4 Biomedical applications

New trends in the biomedical applications of thermal spray coatings are focused on calcium phosphate $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, i.e. hydroxyapatite (HAp), when in contact with bone, stimulates osseointegration and can even be transformed to osseous tissue. Thus an HAp coating can provide a pseudo-natural glue between human bones and bio-inert metals such as titanium or stainless steel. The main drawback of HAp coatings is their low fracture toughness and modulus of elasticity and, when sprayed as a thick coating, HAp suffers from thermal decomposition. Decomposition into C_3P and C_4P is highly undesirable because these products have a lower stability in body environments than HAp. The ideal HAp coating would be one with high cohesive strength, good adhesion, an optimum degree of porosity to enhance bone integration, a high degree of crystallinity and high chemical and phase stability (Clyne *et al.*, 1998).

Despite the large number of papers published on HAp spraying conditions, there is no universal agreement. Several levels of purity, crystallinity and bond strength have been proposed. For these reasons, HAp has been sprayed by APS (Fernández *et al.*, 2003), (Sun *et al.*, 2003), HVOF (Li *et al.*, 2000, 2002) or sometimes VPS (Gledhill *et al.*, 2001a, 2001b). VPS coatings have higher bond strengths and thus help to prevent coating detachment. Some biocompatible bond coats are also being studied, the aim being to increase bond strength as well as to seal titanium implants and so to prevent titanium ion release into body fluids. The parts commonly coated are hip replacements, joint replacements and dental applications (Fig. 8.26).

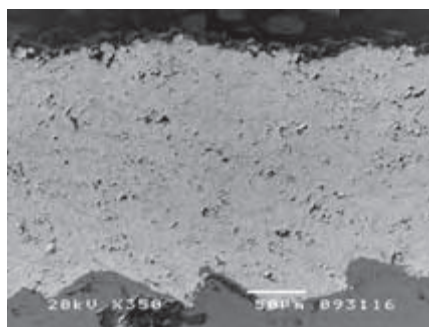


8.26 Titanium hip prosthesis.

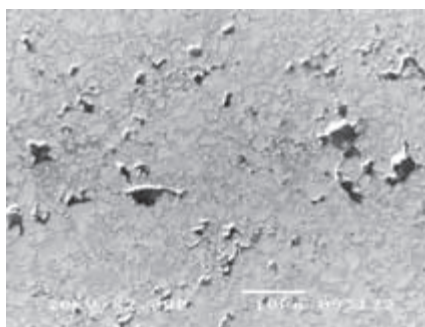
Thermal spray coatings have also some other applications: electronic industry (e.g. APS $\text{Al}_2\text{O}_3\text{--MgO}$ for electrical insulation (Pawlowski, 1995)), aerospace industry (e.g. TBCs of partially stabilised ZrO_2 with Co–Cr–Al–Y as a bond coat for combustors), printing industry (e.g. APS Al_2O_3 and Cr_2O_3 in Corona rolls and Anilox rolls), paper industry (e.g. HVOF cermets such as WC–Co, WC–(Co–Cr) and WC–(Ni–Cr) in rolls to increase service life) and mining industry (e.g. APS Cr_2O_3 in drilling components), among others (Sinha, 2003).

8.7 Unsuccessful coatings and applications

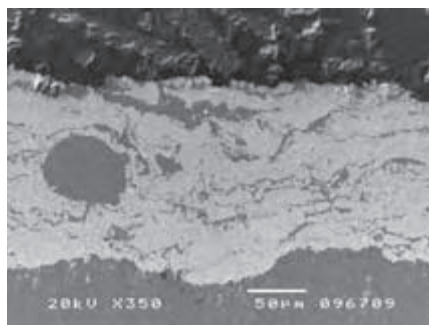
Thermal spray coatings have several problems and limitations. The inherent limitations of thermal spray coatings (e.g. lower elastic modulus, microhardness and corrosion resistance than bulk materials) are due to their microstructures, which contain variable amounts of inhomogeneities, porosity, cracks and oxide inclusions, the level of these imperfections depending on how well spraying has been carried out. Figure 8.27 gives various examples of coating defects caused by non-optimised spraying conditions. Unsuitable



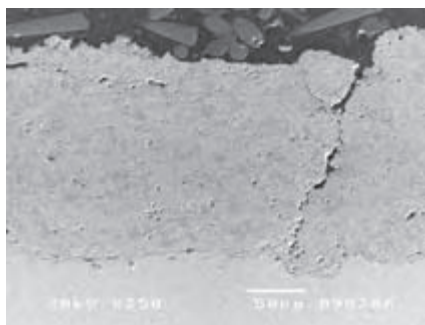
(a)



(b)



(c)



(d)

8.27 Examples of unsuccessful coating structures due to non-optimised spraying conditions: (a) WC-(Co-Cr) with too much porosity; (b) a detailed scanning electron microscopy image of this porosity; (c) Inconel® non-melted particle (clearly seen in dark contrast) in an Inconel® – (WC-Co) blend sprayed by HVOF; (d) vertical catastrophic crack in a Cr₃C₂-(Ni-Cr) HVOF coating.

spraying conditions, powder type and grain size distribution, axial feeding process or even impurities in feedstock materials or in the powder feeder from previous spraying operations can produce catastrophic failure of the layer.

Problems related to drift in spraying conditions during long-term spraying processes can be solved by using on-line monitoring devices (see Section 8.8). This kind of equipment, despite needing a large investment, is, in a short time, beneficial. To avoid problems with feedstock material, these should be checked on receipt from supplier because undesired phases or deviations in grain size distribution are sometimes detected.

Another restriction of thermal spray coatings concerns the substrate shape. Complex shapes with sharp edges are very problematic for thermal

spray owing to the stress concentration of those zones. The inner walls of pipes, tubes or shapes can be sprayed if the diameter of the bore is large enough to hold the spraying gun and to maintain an adequate spraying distance. For example cylinder bores are being coated with a special rotating plasma gun designed specifically for this purpose (Barbezat, 2003). However, if the shape is too complex to spray over a substrate, near-net shapes can be sprayed to reproduce the shape of a mandrel. The coating is then removed from the mandrel (see Section 8.8).

Other kinds of problem may arise if the coating materials are not properly selected for the service condition. For example where the service environment is not properly taken into account although, at least in theory, this kind of problems should have been eliminated by preliminary research.

Thus, as long as applications of thermally sprayed coatings are restricted to service applications where extensive laboratory and simulated service testing have been carried out to ensure that they have adequate properties, and care is taken to ensure reliability and repeatability in coating operations, satisfactory service performance should result and service failures avoided.

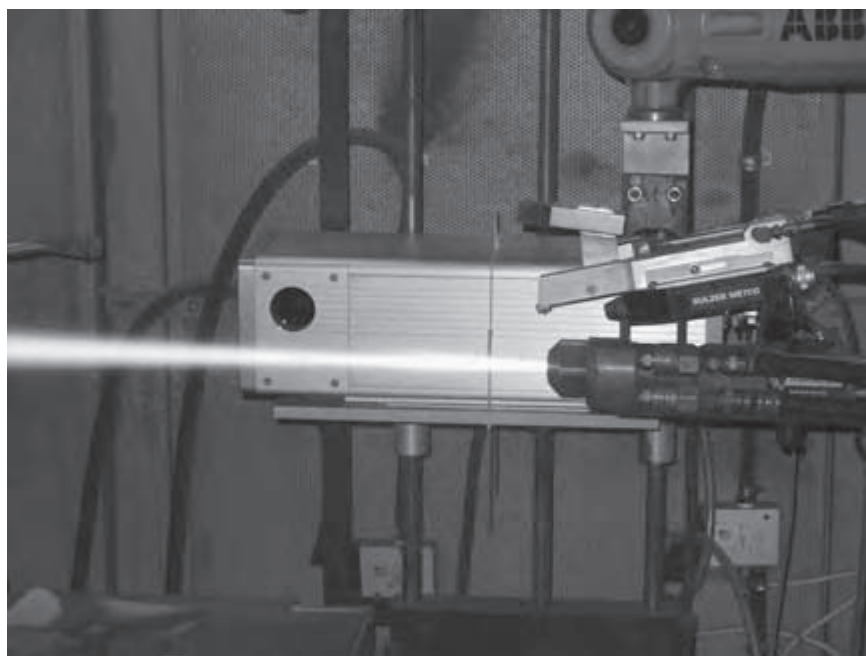
8.8 Future trends

Ever since thermal spray became a serious surface engineering technique, engineers and technicians have been striving to achieve better control and reproducibility. Reliability in thermal spraying processes is improved by new sensors and equipment design. The need for optimised spraying conditions has become essential, as has the use of the powders with more tightly controlled size distributions, shape and morphology and substrates with suitable preparation and temperature (Fauchais *et al.*, 2001).

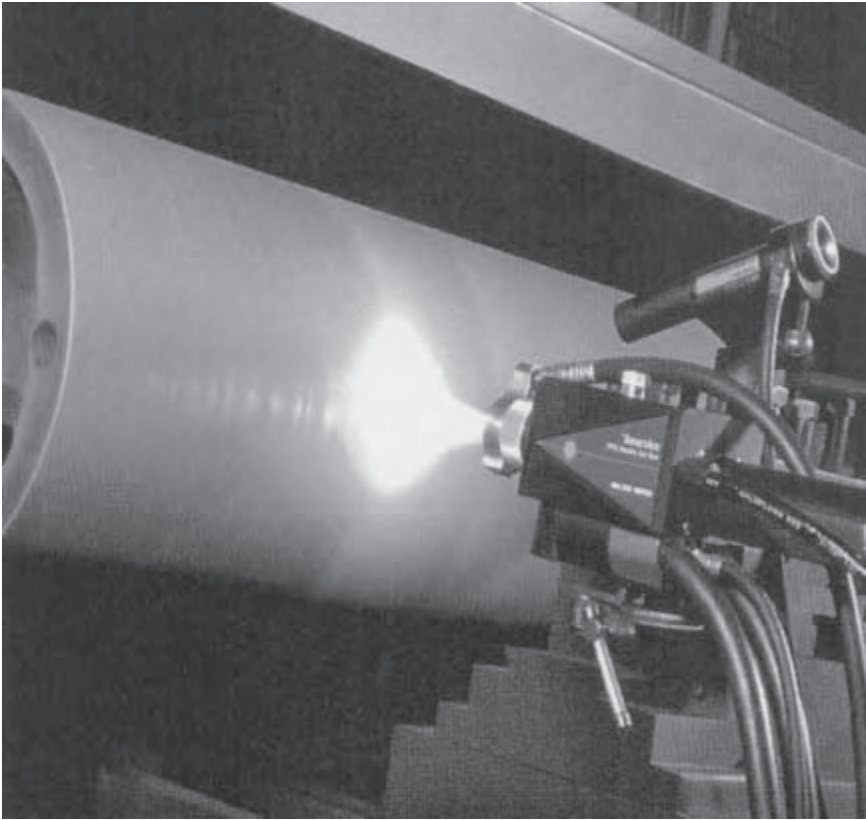
In the 1990s, sensors capable of monitoring in-flight particles inside the jet appeared, changing the optimisation concept radically (Lugscheider and Fischer, 2001; Refke *et al.*, 2001). Nowadays the use of this device to measure particle velocity, temperature, diameter and spatial distributions is indispensable (Vattulainen *et al.*, 1998; Vuoristo *et al.*, 2001). As in-flight particle conditions before impingement are directly related to coating properties, new trends in parameter optimisation concentrate on monitoring particle velocity and temperature. Thus, there is no need to select optimised spraying parameters, only to set in-flight parameters (velocity and temperature) in an optimised range (Guilemany *et al.*, 2002c, 2003). On-line control takes place in real time, so with slight modification to equipment parameters (power supply, gas flow rates, etc.) (Moreau *et al.*, 2001; Sampath *et al.*, 2003) the flame or jet can be adjusted to transfer the correct amount of heat and velocity to the particles (Fig. 8.28). With this procedure, coating quality

control is ensured. This is especially important during spraying large parts (Fig. 8.29), as drift in equipment parameters is likely to occur. For this reason, on-line sensors should be used to check, in real time, the in-flight parameters. This procedure ensures reproducibility between different zones of the same piece or coated component.

The use of the correct powder is also crucial. Using the proper spraying conditions and monitoring the process but using the wrong powder can lead to undesired coating porosity, more decomposition of phases in the coating or a decrease in a specific property. This is why many powder types are available in the market and powder-manufacturing companies are continually improving their methods as well as developing new blends and materials (He and Schoenung, 2002). For example, the use of agglomerated $\text{Al}_2\text{O}_3\text{--TiO}_2$ (Wang *et al.*, 2000; Shaw *et al.*, 2001) or WC–C nanosize powders is becoming popular because of their superb properties. Wear rates of up to one sixth of the conventional WC–Co coatings have been achieved (Zhu *et al.*, 2001) although, in general, nanostructured WC–Co coatings have higher wear resistances attributed to their enhanced hardness and toughness (Dent *et al.*, 2002; He and Schoenung, 2002). In $\text{Al}_2\text{O}_3\text{--TiO}_2$



8.28 HVOF gun and SprayWatch® on-line monitoring device from Oseir Ltd.

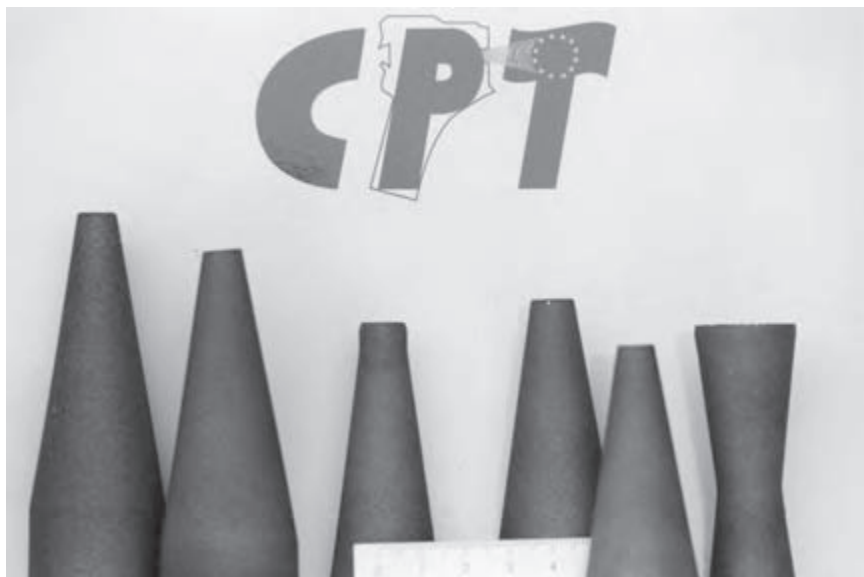


8.29 Electric arc thermal spray process of a large textile industry roll (by kind permission of Sulzer Metco).

nanostructured coatings, higher indentation crack resistance, spallation resistance and wear resistance are achieved (Gell *et al.*, 2001).

Another application of the thermal spray process is in the production of near-net shape components. The main feature of these components is their self-standing shape and the possibility of creating complex shapes impossible to obtain with traditional processes. To produce a near net-shape component a removable mandrel is sprayed and, after cooling, the complete layer reproducing the mandrel shape is released. Spraying can be carried out by APS or VPS (Geibel and Froyen, 1996; Hickman and McKechnie, 2001) and HVOF (Guilemany *et al.*, 1997, 1999). Figure 8.30, shows near-net shape components made with Inconel® and WC-Co.

The cold-spray process is also an emerging technology for producing high-bond-strength non-porous coatings but the fact that this process



8.30 HVOF near-net shape parts of Inconel® and WC-Co blends.

achieves a bond by impact means that only a limited number of feedstock materials are available to date (2004) (Stoltenhoff *et al.*, 2002; Kreye *et al.*, 2003).

Bibliography in the thermal spray field indicates that the nature of the in-flight and impact processes is under intense study. Knowledge of these aspects will allow on-line control of optimised spraying parameters and so lead to enhanced coating reliability which is seen as essential to enable thermal spraying to meet the challenges of the twenty-first century.

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Welding surface treatment methods for protection against wear

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9.1 Introduction

The use of a welding technique to deposit a coating is nearly as old as the use of welding to produce a joint and was first proposed in a patent by J. W. Spencer in 1896.¹ The deposit produced by welding is called a hardfacing or weld overlay while the technique itself is often referred to as surfacing. Surfacing processes can be used for the following.

1. Surface cladding, where a relatively thick layer of material is applied, normally to a carbon or low alloy steel to provide a corrosion-resistant surface, e.g. depositing a stainless steel overlay on a mild steel shaft. This is often referred to as overlay welding.
2. Hardfacing, where a layer of more wear-resistant material is deposited to provide a component which is more resistant to abrasion, impact, erosion or galling. The material deposited might also have to control combinations of wear, corrosion and oxidation.
3. Build-up, where a weld deposit is added to a component to restore its original dimensions. The build-up materials are sometimes used to resist combinations of impact and light abrasion. Alternatively a hardfacing might subsequently be deposited on built-up material.
4. Battering, where an intermediate layer of material is deposited on the surface of the component for metallurgical reasons before depositing the final top coat. This is similar, in some ways, to the bond coat applied when coating some materials by thermal spraying.

In this chapter we are primarily interested in the use of welding techniques to deposit a surface material for wear resistance, i.e. hardfacing, although the material deposited might also have to have adequate corrosion and oxidation resistance and strength at elevated temperatures.

9.2 Welding processes suitable for hardfacing

Most welding processes used to join components can also be used for hardfacing.² Fusion welding processes dominate but solid-state welding processes, such as friction surfacing are also becoming important in niche areas. Table 9.1 highlights the main features of the welding processes used for hardfacing. The principal differences between the various welding processes relate to the nature of the heat source, the form of the hardfacing welding consumable and the method of shielding the hot molten material from oxidation during the welding process. For a detailed description of these welding processes, reference should be made to standard welding texts.^{3,4} Laser surfacing is considered in Chapter 10 of this book. Table 9.2 summarises the advantages and limitations of different fusion welding processes from the surfacing perspective.

Just as multipass welds are used to produce joints between thicker materials, so multipass techniques are used to produce a surface coating of the desired thickness. The bulk of the materials deposited, i.e. the consumables used in the welding process, are iron based, but non-ferrous alloys (largely cobalt and nickel based) form an important market sector.

Friction surfacing and pulsed electrode deposition are the most recent welding processes to be applied to hardfacing and their comparative novelty requires a more thorough treatment here.

Friction surfacing is a process for depositing a thick coating on a flat surface by forcing the consumable to move parallel to the surface whilst simultaneously rotating it and applying load. Although first described in a patent in 1941⁵ it was in the 1980s when a viable technology arose.^{6–10} A proprietary process known as Frictec was developed. Figure 9.1 shows a schematic diagram of this process and the material being deposited. The coating material in the form of a solid consumable rod is rotated under a pressure of at least 100 MPa against the substrate material, a plate, disc or cylinder. A hot plasticised layer is produced, which reaches a temperature of approximately 40 °C below its melting temperature. By moving the substrate across the face of the rotating rod a plasticised layer typically 1–2 mm thick, depending on the diameter of the rotating rod and the coating material, is deposited. A high contact stress was found necessary to remove oxide films that would otherwise form at the interface between the consumable and the substrate. This unfortunately means that the equipment for friction surfacing tends to be expensive. Various materials including aluminium, mild steel, stainless steel, high-speed steel and Stellite® 6 and 12 can be deposited on to a range of substrate materials.¹¹ The coating is very regular; the surface is characterised by fine ripples and only 0.1 mm needs to be machined off after coating to produce a clean finished surface.

Table 9.1 Important features of welding processes used in hardfacing^{3,4}

Welding process	Description	Consumable material	Shielding
Oxy fuel welding (OFW)	Heat from a gas flame is used to melt hardfacing materials on to the workpiece surface	Bare cast rod, solid wire or rod, cored rod, sintered rod	Combusted gas
Oxyacetylene welding (OAW)	Modified OFW process in which powder application and fusion occur in a single operation using a special oxyacetylene torch	Powder	Combusted gas
Shielded-metal-arc welding (SMAW)	Consumable electrode process in which arc melts discrete lengths of filler material rod covered with a specially formulated coating on to workpiece surface	Flux-covered cast rod, flux-covered tubular rod	Coating on electrode decomposes to provide a shielding gas or slag
Open arc (O/A)	Consumable electrode arc process in which the arc between a flux-cored electrode and workpiece is shielded by a self-generated or self-contained gas or flux	Flux-cored tubular wire or rod	Flux in core of the electrode decomposes to provide shielding by CO ₂
Gas-tungsten arc welding (GTAW)	Non-consumable electrode arc process in which the heated area of the workpiece, the molten hardfacing alloy (from a filler rod) and the non-consumable electrode (thoriated tungsten) are protected by a flowing shielding gas	Bare cast rod, solid wire, rod or strip, tubular cored wire, rod, strip, sintered rod or strip	Argon gas flow

Submerged-arc welding (SAW)	Consumable electrode arc process in which the area between the continuous electrode and workpiece is shielded by a blanket of granular fusible material	Bare solid or tubular cored wire and strip, sintered strip, agglomerated alloy fluxes	Slag from particulate flux
Electroslag surfacing	Consumable electrode process where the electrode is melted by resistance heating in the molten flux surrounding the electrode and the workpiece	Cast or sintered strip, tubular cored wires or strip	Slag from particulate flux
Plasma arc welding (PAW) or plasma transferred arc (PTA) welding	Constricted arc between the electrode and work piece (transferred arc) generates plasma into which the consumable is introduced to form a molten pool on the workpiece. When the consumable is a powder, the process is known as PTA welding	Bare cast rod, solid strip or wire, tubular cored wire or strip, sintered strip Powder	Hot ionised gas supplemented by additional shielding gas, argon
Gas-metal arc welding (GMAW)	Consumable electrode process in which the heated area of the workpiece and the continuous filler metal electrode are protected by a flowing shielding gas	Solid wire, strip, tubular cored wire strip, sintered strip	CO ₂ , argon, helium gas flow
Laser welding	High-energy laser beam used to melt the hardfacing alloy and a thin layer of the substrate	Solid wire, strip, tubular cored wire sintered strip, powder	Argon, helium gas flow
Friction surfacing	Solid consumable rod is rotated under pressure against the substrate material	Solid rod	Mechanical shielding from two materials in close contact

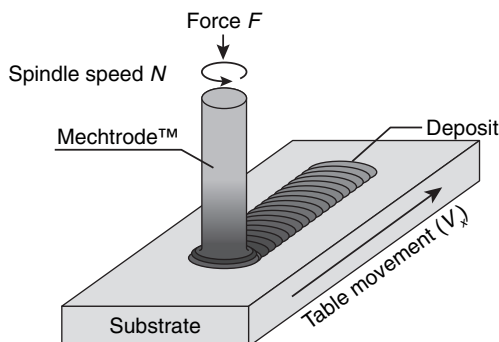
Table 9.2 Advantages and limitations of the various welding processes used for hardfacing^{3,4}

Process	Advantages	Limitations
OFW	Small areas can be surfaced Workpiece only superficially heated; brazing gives very low dilution, sweated surface Preheating permits use of softer flame Slow heating minimises cracking Versatile simple process All welding positions possible Capital costs low; equipment portable Good-quality smooth deposit Suitable for small repairs or hardfacing small areas Equipment is inexpensive and little operator skill needed Ideal for deposition of smooth thin hardfacing on flat surfaces Suitable for hardfacing small and large areas especially on heavy sections Permits hardfacing of large parts without preheat Little distortion when hardfacing small areas of components Versatile; suitable for all alloys Good accessibility; all position welding possible Low equipment costs; equipment portable Used on infrequent repairs	High welder skill needed Not suitable for surfacing large areas Carbon pickup on base material surface from reducing flame
OFW, powder torch		Similar to OFW
SMAW		Moderate operator skill needed More local melting than OFW Slag must be removed after hardfacing Deposit prone to cracking if low preheat used because of the high thermal gradient

SAW	Suitable for hardfacing large areas especially if using oscillating twin electrodes; beads up to 100mm wide can be produced Most widely used automated process; used in repeat applications Little operator skill needed No spatter; pore-free smooth deposits obtained No ultraviolet radiation By varying the arc voltage, different deposit compositions can be achieved when using agglomerated alloy fluxes as consumables High rate of deposition (greater than SAW) and area coverage Can apply to flat and curved surfaces Low heat input; small and uniform penetration of base material (less than in SAW); low dilution Can achieve extra-low carbon in the deposit in a single layer Very regular deposit profile; so little or no machining required No ultraviolet radiation Suitable for full range of sizes, flat, horizontal and vertical positions Low equipment costs; portable Easy to use; good visibility of deposit during welding; moderate operator skill level Used on more frequently repaired parts	Not suitable for surfacing small parts Mostly limited to flat position; can hardface simple cylindrical or flat workpieces Limited to low carbon and martensitic steels Deposit not visible during deposition Slag needs to be removed; slag removal difficult if preheat greater than 315°C High thermal gradients may cause cracking; so preheating and post-heating may be necessary Not normally portable Limited range of strip electrode materials although tubular cored wires can be used Strip widths from 30 to 300mm Minimum substrate thickness 40mm Surfacing of internal surfaces of tubes and nozzles only possible with specially designed equipment
	Electroslag	
O/A flux-cored arc surfacing		Not suitable for small components Accessibility restricted; cored electrode cannot be fed round small radius Slag needs removing Considerable spatter; some porosity Ultraviolet radiation

Table 9.2 Continued

Process	Advantages	Limitations
GMAW	No flux; gas shielding Versatile; can hardface complex shapes Deposit visible during process enabling high-quality deposition	High dilution in spray transfer mode; lower in short-circuit and pulsed modes Ultraviolet radiation
GTAW	Pulsed technique allows out-of-position deposition Good for hardfacing small intricate parts Alternative to OFW especially when large components or reactive base metals involved; freedom from carbon pickup No flux removal Arc action smoother and quieter, resulting in little spatter Requires little preheat; results in less heat build-up and minimises distortion	High operator skill needed Ultraviolet radiation
PAW or PTA	High-quality deposits produced Thin and thick layers can be deposited Dense homogeneous deposit with similar quality to GTAW. Wide range of materials can be deposited; suitable for surfacing lower-melting-point base materials Close control over surface finish No flux removal	Limited to straight-line or circular parts; when surfacing round or curved items, PAW performed in the horizontal rolled (1G) position Large parts need preheat, but excessive preheats and prolonged hardfacing times overheat the torch Some distortion expected Equipment costs relatively high Expensive equipment Safety precaution associated with use of laser
Laser	Can apply thin overlays; dilution zone, only 10–20 µm thick Can be used to hardface in a confined area, e.g. bores of pipes Superior quality to GTAW	



9.1 Schematic diagram of the friction-surfacing process.

Attempts have been made to produce a friction-surfaced deposit by using a lower pressure, a pressure in the 1–10 MPa range, the advantage being that this would simplify equipment requirements.^{12,13} Strongly bonded coatings of tool steels¹³ and stainless steel¹² were deposited, but friction surfacing with higher-conductivity materials, such as aluminium, or materials with low friction coefficients such as brass, on to mild steel substrates, was not achieved.¹⁴ Tool steel and Inconel 600 were efficiently deposited on to mild steel using an axial pressure¹⁵ of approximately 0.5 MPa; however, a nominal contact pressure as high as 21.8 MPa was required to obtain an adherent coating of uniform quality.¹⁶ Aluminium could only be deposited at higher contact pressures albeit with a poor bond strength.¹⁵ Stainless steel, mild steel and Inconel 600 could be deposited on to an aluminium substrate, higher pressures being needed to deposit stainless steel on an aluminium substrate (greater than 21.8 MPa) in comparison with mild steel (greater than 16 MPa).¹⁵ Mild steel bonded better than stainless steel to the aluminium substrate, which might be due to a lower hardness and plasticising temperature which facilitates plastic flow and leads to intimate contact between coating and deposit.¹⁷ However, only stainless steel displayed a lack of intermetallic compounds at the interface. Low-pressure friction surfacing thus requires more careful control of the operating parameters than higher-pressure friction surfacing but for limited combinations of coating–substrate has the potential to provide an efficient method of coating dissimilar metals.

Pulsed electrode surfacing (PES) or variants such as pulsed air arc deposition are high-energy-density arc microwelding processes that use short-duration high-current electrical pulses obtained via discharge capacitance to weld a consumable electrode material to a metallic substrate. It is thus

a fusion-welding technique, producing a metallurgical bond to the substrate, but the total heat input is low (approximately 0.10 MW m^{-2}) and so very little thermal distortion or metallurgical changes to the substrate material occur. Since the bulk material acts as a heat sink, heat is quickly dissipated, leading to rapid solidification and an extremely fine-grained coating. The consumable electrode with a positive polarity is brought close to the substrate, which has a negative polarity. This leads to the generation of a spark, the intensity of which is directly proportional to the voltage across the gap, the current and the pulse time. The energy of the spark determines the amount of material deposited and the bond strength between the coating and the substrate. The dielectric medium, which could be air, nitrogen, argon or any other environment, provides a path for the discharge plasma. A suitable choice of processing parameters leads to incipient melting of the electrode tip and material transfer through the discharge plasma. When air or nitrogen forms the plasma, globular transfer occurs while, when argon is used, a fine spray of molten material is produced. Spray transfer produces a smoother and more uniform deposit than globular mass transfer.^{18,19} The equipment required is very compact and simple, consisting of a pulsed power supply and an electrode holder. The electrode holder can be either held manually or integrated with a machine tool.

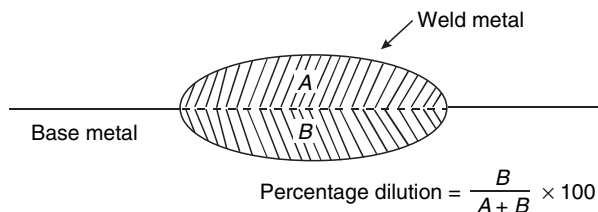
The majority of applications to date appear to be the treatment of cutting tools with tungsten carbide or titanium-based electrodes.¹⁸ WC-based hard alloys have been deposited on to low-carbon steel and pure titanium substrates using a pulsed air arc technique.^{20,21} The coatings increased the wear resistance of the steel and titanium substrates, as measured by a scratch test, by factors of 4.3 and 1.4 respectively. Pin-on-rotating-bar wear tests showed that PES-deposited WC-Co coatings had superior performance to substrates coated with titanium nitride (TiN) in this high-stress unlubricated wear test.²² Deposition of titanium boride (TiB_2) coatings by a PES technique have been made on copper, AISI 1018 and AISI 1020 steels using TiB_2 and nickel binder electrodes.^{23–26} Iron does not react chemically with the TiB_2 but migrates into the TiB_2 layer during solidification and acts as a binder similar to cobalt in the WC-Co system, promoting toughness to the ceramic layer.²⁵ Titanium carbide (TiC) coatings have also been deposited on AISI 8030 and 1018 by PES.^{27–28}

9.3 Nature of the deposit

Most of the processes used to produce a weld deposit are based on fusion-welding techniques which were originally designed to weld joints. These processes involve melting back some of the parent material (penetration in welding terms) so as to achieve a metallurgical bond between the filler material and the parent metal. Indeed it is this melting back of the parent

material that is one of the major differences between hardfacing and thermal spraying. This melting-back process means that the resultant alloy that solidifies is a mixture of the filler metal and the parent material, the composition of this alloy being defined by the dilution (Fig. 9.2). Dilution is a very important factor in hardfacing and causes the chemical composition and structure of the deposit to be not the same as those of the welding consumable used to produce it; e.g. if martensitic hardfacing wires are deposited on a 13% Mn steel, dilution effects mean that the first layer deposited will be austenitic, the second layer will be austenitic–martensitic and only in the third layer will it be fully martensitic. The second layer containing the mixed microstructure is brittle and can cause spalling in service.³

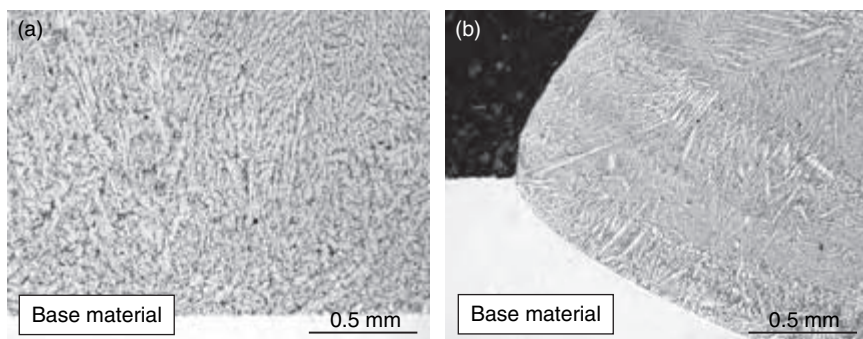
Ideally we require the dilution to be as low as possible or, to put this in welding terms, we require little penetration. The amount of dilution obtained is determined by both the welding process selected and the welding parameters chosen. Table 9.3 gives typical values of the dilution achievable, deposition rate and deposition efficiency and the minimum thickness capable of being deposited for the welding processes described in Table 9.1 operated in manual, semiautomatic or automatic modes. Typical operating factors, i.e. effective deposition time divided by total hours, varies between 20% for GTAW, 30% for SMAW and 60–65% for GMAW and SAW.²⁹ Note the low dilution levels obtained from oxyfuel (OFW), PTA, electroslog and laser welding processes. Figure 9.3 shows the very different shapes of the weld bead, and hence dilution, achieved by OAW and GTAW. The plasma-transferred arc process with its advantage of using two independent arcs (i.e. the non-transferred arc as a pilot arc and the transferred arc as the main arc) has become increasingly popular since the 1980s as a heat source for hardfacing, partly because of the low dilution achievable and the fact that it uses powder as the consumable which is available in a wider range of materials, some of which have a similar composition to those used in thermal spraying. The interfacial bond achieved is better than in plasma spraying and a thicker overlay can be produced than with laser treatment.



9.2 Dilution of weld metal.

Table 9.3 Characteristics of fusion welding processes used in hardfacing³

Welding process	Mode of operation	Weld metal dilution (%)	Deposition rate (kg h ⁻¹)	Minimum thickness (mm)	Deposition efficiency (%)
OFW	Manual	1–10	0.5–2	0.8	100
	Automatic	1–10	0.5–7	0.8	100
Powder welding	Manual	1–10	0.5–2	0.8	85–95
SMAW	Manual	10–20	0.5–5	3.2	65
O/A	Semiautomatic	15–40	2–11	3.2	80–85
	Automatic	15–40	2–11	3.2	80–85
GTAW	Manual	10–20	0.5–3	2.4	98–100
	Automatic	10–20	0.5–5	2.4	98–100
SAW	Automatic, single wire	30–60	5–11	3.2	95
	Automatic, multiwire	15–25	11–27	4.8	95
	Automatic, series arc	10–25	11–16	4.8	95
Electroslag surfacing	Automatic	3–20	Up to 44 with 20% dilution	4.2	
PAW	Manual	5–15	0.5–4	2.4	98–100
	Automatic	5–15	0.5–4	2.4	98–100
PTA	Automatic	5–15	0.5–7	0.8	85–95
GMAW	Semiautomatic	10–40	0.9–5	1.6	90–95
	Automatic	10–40	0.9–5	1.6	90–95
Laser welding	Automatic	1–10	Depends on powder feed rate and laser power	0.13	85–95



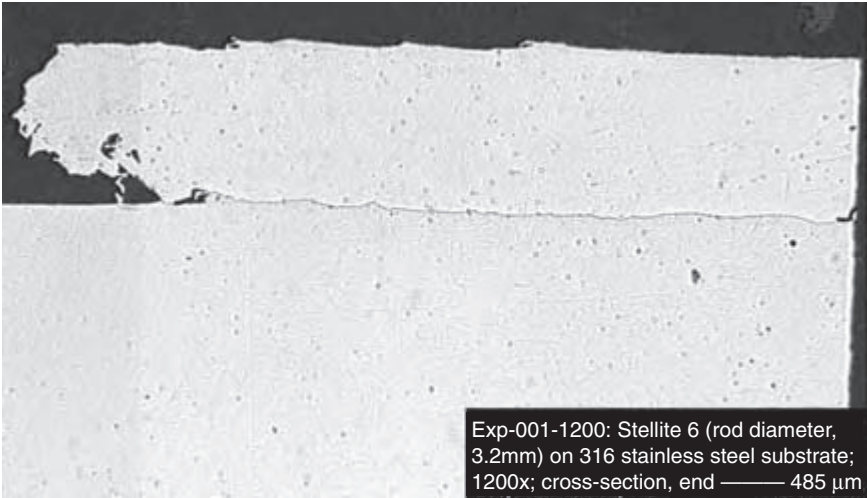
9.3 Weld bead profile and dilution achieved by (a) PTA-welded deposit of Stellite® 1 and (b) GMAW deposit of Stellite® 1. (Both samples courtesy of Deloro Stellite.)

Dilution is not only affected by the welding process selected but also by the welding parameters chosen. Table 9.4 details the effect of some of the SMAW parameter variables on dilution.⁴ As noted in Table 9.4, weld position and inclination together with the bead deposition pattern have a large effect on dilution. A tight bead spacing (more overlap) reduces dilution as more of the previously deposited bead and less of the substrate material is remelted and added to the weld pool. A deposit can be put down either in the form of a stringer bead or with electrode oscillation to produce a weave-type bead. In general, the greater the width and frequency of oscillation, the lower is the dilution. When surfacing shafts, a double-spiral technique can be employed to reduce dilution.³¹ The position of welding also influences the amount of dilution. Depending on the welding position or work inclination, gravity will cause the weld pool to run ahead of, to remain under or to run behind the arc. The more the pool stays ahead or under the arc, the less is the penetration and hence the lower is the dilution. The pool thus acts as a cushion and absorbs part of the arc energy, resulting in weld bead flattening and spreading. Inclining the workpiece at an angle and welding downhill produces minimum dilution.

Friction surfacing, on the other hand, produces a bond in the solid state rather than by the creation of a fusion zone. Thus no fusion zone, no porosity and a forged microstructure rather than a cast microstructure is produced. The fact that no fusion zone is formed is particularly important in hardfacing as that implies that no dilution occurs and the composition of the coating is the same as that of the consumable. Figure 9.4 shows a Stellite® 6 deposit on a 316 stainless steel substrate; the zero dilution should be noted. In addition, as friction surfacing is a solid-state process and does

Table 9.4 The effect of SMAW parameters on dilution^{4,30}

Variable	Change in variable	Influence of change on dilution
Amperage	Higher	Increases
Electrode polarity	Direct-current electrode negative	Decreases
	Direct-current electrode positive	Increases
	Alternating current	Intermediate
Current density	Higher	Higher
Arc length	Greater	Decreases
Bead spacing or pitch	More overlap	Decreases
Electrode oscillation	Greater width of electrode oscillation	Decreases
Travel speed	Lower	Decreases
Welding position	Vertical up (forehand welding)	Highest
	Vertical up (backhand welding)	Lowest
	Uphill	Lower
	Downhill	Higher



9.4 Friction-surfaced deposit of Stellite® 6 on 316 stainless steel. Note that no dilution has occurred. (Micrograph courtesy of Frictec Limited.)

not involve melting, materials that cannot normally be coated by fusion techniques because of incompatibility problems can be coated by friction surfacing. Another advantage is that friction surfacing is applied using machine tool technology and thus, once the settings (consumable rod, revolutions per minute, and the force and velocity of the substrate across the face of the rotating consumable rod), have been set so as to achieve the correct coating thickness, width and bond strength, consistent quality can be assured by monitoring these machine parameters. Optimisation procedures have been derived to aid in machine parameter selection.^{11,32,33}

Whereas many surface treatments such as nitriding give a smooth surface finish, welding generally gives a fairly rough surface, which may measure at least 2 mm between the peaks and valleys for SMAW and 1 mm for GTAW. For some components, e.g. bulldozer blades, a perfectly smooth surface is not required whereas, for gear wheels or valve seats, machining of the deposit is essential. Whether machining will be required will influence the choice of hardfacing alloy which must have adequate machinability. In some cases the deposit can be annealed, machined and rehardened followed by finish grinding.

9.4 Hardfacing materials

The American Welding Society (AWS) Specification A5.13 : 2000³⁰ covers shielded metal arc electrodes (alloy grades are prefixed by an E for electrode) and AWS specification A5.21 : 2001³⁴ covers non-coated products including bare rod as well as solid and cored wires (alloy grades are prefixed by ER for electrode and rod). The European Draft Standard prEN 14700:2003³⁵ specifies covered electrodes, solid wires, tubular cored wires, cored strips and sintered strips for hardfacing.

Hardfacing materials can be classified into five types.^{3,36}

1. Built-up alloys.
2. Metal-to-metal wear alloys.
3. Metal-to-earth abrasion alloys.
4. WC.
5. Non-ferrous alloys.

However, from a metallurgical viewpoint it is better to consider alloy types.

9.4.1 Iron-based alloys

Iron-based hardfacing alloys are the most widely used and constitute the largest volume use of hardfacing material. Iron-based hardfacing alloys offer a combination of low cost and moderate wear resistance which make

them ideal for the hardfacing of large equipment that undergoes severe wear, e.g. crushing and grinding equipment and in the earth-moving industry. These parts are also often restored to their original dimensions by hardfacing, i.e. are built up.

Iron-based hardfacing alloys can be classified, on the basis of microstructure, as follows.

1. Pearlitic steels.
2. Austenitic steels.
3. Martensitic–semiaustenitic steels.
4. High-alloy cast irons.

Table 9.5 gives the composition of several iron-based hardfacing electrodes.^{30,34,37} The large number of compositions covered by standard specifications should be noted.

Pearlitic steels

Pearlitic steels used for build-up are very similar to the same steels used for the welding of joints, i.e. they are weldable steels with low carbon (C less than 0.2% C) and limited alloy additions (e.g. up to 2% Cr) to ensure that the microstructure following cooling of the weld overlay is pearlitic. Submerged-arc welding is often used for repeat applications when the same part is surfaced on a routine basis, e.g. rollers, track shoes and drums. The chemical composition of the wire and the flux affect the composition and hardness of the deposited metal. Microstructure is also important, fine columnar grains giving better wear resistance than a coarse-grained structure.³⁹

Higher alloy additions (up to approximately 5% maximum) allow partially bainitic or even martensitic structures to be formed when cooled rapidly after welding. As the carbon and alloying element present in the steel increase, i.e. the carbon equivalent increases, it may be necessary, as in the welding of joints, to preheat the component to achieve crack free deposits. Table 9.6 gives the Rockwell C hardness and abrasion data for a two-layer deposit of a typical pearlitic low-alloy steel (EFe-1) produced by shielded-metal-arc welding. Table 9.7 summarises the principal features and fields of application of these materials.

Austenitic steels

Austenitic steels used for build-up are based on Hadfield manganese steel, e.g. ERFEMn-C in Table 9.5. These steels contain 12–16% Mn and up to 1% C. Although austenite is completely retained by quenching from 1000 °C, the material is metastable, and annealing, or slow heating and

Table 9.5 Chemical compositions of ferrous hardfacing electrodes (single values are maxima). E/ER indicates that electrodes are available for shielded-metal-arc welding (AWS A5.13:2000) and as a bare electrode and rod (AWS A5.21:2001). Compositions given are for ER where minor differences exist between the two specifications^{30,34,37,38}

AWS classification/ commercial name	Composition (wt%)									
	C	Mn	Si	Cr	Ni	Mo	V	W	Ti	Fe
E/ERFe-1	0.04–0.20	0.5–2.0	1.0	0.5–3.5		1.5				Balance
ERFe-1A	0.05–0.25	1.7–3.5	1.0	0.5–3.5						Balance
E/ERFe-2	0.10–0.30	0.5–2.0	1.0	1.8–3.8	1.0	1.0	0.35			Balance
E/ERFe-3	0.50–0.80	0.5–1.5	1.0	4.0–8.0		1.0				Balance
ERFe-4	1.0–2.0	0.5–2.0	1.0	3.0–5.0						Balance
ERFe-5	0.5–0.8	1.5–2.5	0.9	1.5–3.0						Balance
E/ERFe-6	0.6–1.0	0.4–1.0	1.0	3.0–5.0		7.0–9.5	0.5–1.5	0.5–1.5		Balance
ERFe-7	1.5–3.0	0.5–2.0	1.5	4.0–8.0		1.0				Balance
ERFe-8	0.3–0.6	1.0–2.0	1.0	4.0–8.0		1.0–2.0	0.50	1.0–2.0		Balance
E/ERFeMn-A	0.5–1.0	12–16	1.3		2.5–5.0					Balance
E/ERFeMn-B	0.5–1.0	12–16	1.3							Balance
E/ERFeMn-C	0.5–1.0	12–16	1.3	2.5–5.0	2.5–5.0	0.5–1.5				Balance
E/ERFeMn-D	0.5–1.0	15–20	1.3	4.5–7.5			0.4–1.2			Balance
E/ERFeMn-E	0.5–1.0	15–20	1.3	3.0–6.0	1.0					Balance
E/ERFeMn-F	0.7–1.1	16–22	1.3	2.5–5.0	1.0					Balance
E/ERFeMn-G	0.5–1.0	12–16	1.3	2.5–5.0	1.0					Balance
ERFeMn-H	0.3–0.8	12–16	1.3	4.5–7.5	2.0					Balance
E/ERFeMnCr	0.25–0.75	12–18	1.3	11–16	2.0	2.0				Balance
ER420	0.25–0.40	0.6	0.5	12.0–14.0	0.6	0.75				Balance

Table 9.5 Continued

AWS classification/ commercial name	Composition (wt%)										Fe
	C	Mn	Si	Cr	Ni	Mo	V	W	Ti	Nb	
ERFeCr-A	1.5-3.5	0.5-1.5	2.0	8.0-14.0		1.0					Balance
E/ERFeCr-A1A	3.5-5.5	4.0-6.0	0.5-2.0	20-25		0.5					Balance
EFeCr-A2	2.5-3.5	0.5-1.5	0.5-1.5	7.5-9.0					1.2-1.8		Balance
EFeCr-A3	2.5-4.5	0.5-2.0	1.0-2.5	14-20		1.5					Balance
ERFeCr-A3A	2.5-3.5	1.5-3.5	0.5-2.0	14-20							Balance
E/ERFeCr-A4	3.5-4.5	1.5-3.5	1.5	23-29		1.0-3.0					Balance
E/ERFeCr-A5	1.5-2.5	0.5-1.5	2.0	24-32	4.0	4.0					Balance
EFeCr-A6	2.5-3.5	0.5-1.5	1.0-2.5	24-30		0.5-2.0					Balance
EFeCr-A7	3.5-5.0	0.5-1.5	0.5-2.5	23-30		2.0-4.5					Balance
EFeCr-A8	2.5-4.5	0.5-1.5	1.5	30-40		2.0					Balance
ERFeCr-A9	3.5-5.0	0.5-1.5	2.5	24-30							Balance
ERFeCr-A10	5.0-7.0	0.5-2.5	1.5	20-25							Balance
EFeCr-E1	5.0-6.5	2.0-3.0	0.8-1.5	12-16					4.0-7.0		Balance
EFeCr-E2	4.0-6.0	0.5-1.5	1.5	14-20							Balance
EFeCr-E3	5.0-7.0	0.5-2.0	0.5-2.0	18-28		5.0-7.0	1.5	3.0-5.0			Balance
EFeCr-E4	4.0-6.0	0.5-1.5	1.0	20-30		5.0-7.0	0.5-1.5	2.0		4.0-7.0	Balance
Delcrome® 90	2.75	1	1	27							Balance
Delcrome® 92	3.7					10					Balance
Delcrome® 93	3	1	1.5	17		16					Balance
Delcrome® W	2.2	1.09	0.75	29.3							6 Co Balance

Table 9.6 Abrasion wear data from selected surfacing electrodes^{3,6}

Alloy	Material type	Number of layers and welding process	Rockwell C hardness (HRC)	Abrasion volume loss (mm ³)	
				Low stress†	High stress††
EFe-1 EFeMn-C	Pearlitic Austenitic manganese	Two layers, SMA	37	88	49
		Two layers, SMA	18	65	57
EFeMn-Cr	Austenitic manganese	Two layers, SMA	24	93	46
		Two layers, SMA	48	54	66
EFe-2	Martensitic	Two layers, SMA	59	60	68
EFe-3	Martensitic	Two layers, SAW	45	84	62
ER420	stainless				

† Data from a dry-sand-rubber wheel test (ASTM G 65, procedure B): load, 13.6 kgf; 2000 rev.

†† Data from a slurry-steel wheel test (ASTM B 611, modified): load, 22.7 kgf; 250 rev.

cooling, embrittles the steel by precipitating carbides at grain boundaries. Hence, Hadfield manganese steel components are kept as cool as possible during build-up, often by submerging the bulk of the component in water during the welding process. In addition, high-dilution passes over carbon and low-alloy steels present a risk of cracking because the diluted layer may not be stable austenite. This results in the hardfacing lifting or peeling away from the substrate on cooling. These materials, typified by EFeMn-C, are extremely tough, wear and shock resistant and very sensitive to plastic deformation. They have a high work-hardening rate and abrasion raises the surface Vickers hardness of this material from 200 to 600HV. Their high work-hardening rate is thought to be due to deformation twinning and a strain-induced $\gamma \rightarrow \alpha$ transformation,^{40,41} the nucleation of the α laths occurring at austenite grain boundaries and slip bands. This material of moderate yield strength but high work-hardening capacity is able to respond plastically to impact loading associated with abrasion. This plasticity dissipates energy, and cracking and spalling are avoided; hence there is good abrasive wear resistance.⁴² These materials find use in industrial applications, such as processing of earth materials, manufacturing of cement, etc. Table 9.6 gives the as-deposited Rockwell C hardness of this material and abrasive wear data of a two-layer shielded metal arc deposit.

Tensile strength and ductility reach a maximum at about 1.2% C and 12% Mn and so care must be taken with dilution. If high dilution cannot be avoided, a more highly alloyed steel, e.g. ERFEMnCr or ERFEMn-F (see Table 9.5) can be selected for the first pass. These highly alloyed compositions enable austenite to be stable even with high dilution. High interpass temperatures should be avoided as this can lead to carbide precipitation which embrittles the alloy. Table 9.7 summarises the principal features and fields of application of these materials.

Martensitic steels

Martensitic steels are designed to form martensite on air cooling after weld deposition and are thus often referred to as air hardening. They find uses in preventing unlubricated metal-to-metal wear in machinery. A typical electrode material would be ERFEM-2 and ERFEM-5 (see Table 9.5). A preheat of about 120°C is generally applied to prevent cracking. However, too high a preheat should be avoided so as to ensure a completely martensitic deposit. These deposits have inferior impact resistance to pearlitic or austenitic alloys but higher hardness and better resistance to abrasive wear (Table 9.6). However, martensitic deposits can be tempered at 425–650°C to improve toughness with some loss of hardness and abrasion resistance. More than one layer is normally applied to reduce dilution in the surface material. If a machined finish is required,

Table 9.7 Summary of ferrous hardfacing materials, microstructures, principal features, as-deposited Rockwell C hardnesses and application examples^{30,34,36}

Electrode material	Microstructure	Principal features	Rockwell C hardness (HRC)	Application examples
ERFe-1	Pearlitic	Tough economical machinable deposit. Preheat and post-heat not normally necessary. Can usually be deposited crack free	25–50	Build-up on low-alloy steel, e.g. mine car wheels, shafts, gears, rolls, cams
ERFe-2	Martensitic	Tough machinable deposit: harder than ERFe-1, but with poor impact resistance. Preheat to 120 °C; generally no need for tempering; if required can temper at 425–650 °C	25–50	Prevention of unlubricated metal-to-metal wear on rolling or sliding parts, e.g. crane wheels, undercarriage of tractors, cable sheaves, pipe forming rolls
EFe-3	Air hardening Martensite plus alloy carbides	Deposits comparable with many tool steels. Preheat to 200–315 °C. Deposits can usually be applied. crack free. Must cool to room temperature to complete martensitic reaction before tempering at temperatures up to 650 °C for secondary hardening	55–60	Overlay surfaces and edges requiring high hardness; good hot hardness; Generally used for metal-to-metal applications, e.g. forging dies and pincer guide shoes, but also performs well in earth abrasion applications where high impact is encountered Rebuild worn cast iron machinery parts
EFe-4	Graphite coating	Suitable for application on cast iron. Brittle deposit; crack free with care		
ERFe-5	Air hardening; cold-worked tool steel	High compressive strength with moderate abrasion and metal-to-metal wear resistance	50–55	Metal-to-metal wear applications such as machine components, shafts, brake drums and knife edges
ERFe-6	Air hardening; high-speed tool steel	Retains hardness to 593 °C	>60	Metal-to metal wear applications at temperatures up to 593 °C. Typical applications combine high-temperature service with moderate abrasion and severe metal-to-metal wear, e.g. shear blades, and trimming dies

Table 9.7 Continued

Electrode material	Microstructure	Principal features	Rockwell C hardness (HRC)	Application examples
ERFe-7	Air hardening	Higher-carbon modification of EFe-3. Higher abrasion resistance but lower impact resistance than EFe-3. Check cracks normal	>60	Parts requiring good low-stress abrasion resistance, e.g. cement chutes, fan blades, equipment for earth moving, and bulldozer blades
ERFe-8	Similar to H12 hot-worked tool steel. Martensite plus alloy carbides	Tough hard deposit but needs adequate preheat to ensure that it is crack free	54–60	Used for overlaying surfaces subject to moderate abrasive wear with high impact, e.g. machine tools and components subject to sliding metal-to-metal wear
ERFeMn series	Austenitic	Tough; excellent for heavy impact; moderate abrasion resistance. Dilution destabilises austenite. Slow cooling embrittles the steel. Nickel additions promote austenite stability. Chromium and molybdenum additions increase yield strength. EFeMn-F has higher manganese and carbon contents to ensure a fully austenitic structure even after dilution in a one-layer deposit	20, can work harden to 55	Rebuilding, repair and joining of austenitic manganese steels. Ability to absorb high impact makes ideal for rebuilding rock-crushing equipment and parts subject to impact loading, e.g. roll crushers, railway track build-up, breaker bars and hammer mill hammers
ERFeMnCr	Austenitic	Higher chromium content improves stability of austenite when compared with EFeMn deposits; so fully austenitic structure after dilution. Slow cooling embrittles the steel; higher yield strength than EFeMn-C	20, can work harden to 55	Can join austenitic manganese steel to itself and to carbon steel. Often used as a base for surfacing with EFeCr-X types for parts subject to abrasion and impact
ER420	Martensitic stainless steel	Good resistance to corrosion and thermal fatigue. Must cool to room temperature to complete martensitic transformation before tempering at 425–650 °C. Preheat at 95–315 °C	45	Blast furnace bells, cladding rolls for continuous casters

three layers are often deposited, the top layer being removed by machining.

Compositions with 0.7–2% C and from 5 to 12% Cr give a mixed microstructure of austenite and martensite after hardfacing, the proportion of each structure being governed by composition and cooling rate. These steels are often referred to as semiaustenitic. The austenite is unstable and transforms to additional martensite when deformed. As these alloys have limited ductility, cold cracking can occur which can be minimised by preheating. These deposits are generally not tempered and offer resistance to metal-to-metal sliding and rolling wear and, if work hardening occurs, provide some resistance to impact and abrasion.

If the service conditions are at elevated temperatures, martensitic steels with compositions similar to those of tool steels can be deposited, e.g. EFe-3, ERFe-6 and ERFe-8 (see Table 9.5). A preheat (200–315°C) is usually required to prevent cracking. The coated component should be allowed to cool to room temperature to ensure that the martensitic transformation is complete before tempering at a temperature up to 650°C. During tempering at this temperature, alloy carbides form and result in an increase in hardness (secondary hardening). These materials retain their strength at temperatures approaching their tempering temperature and thus can be used in service for resisting wear at high temperatures, e.g. in forging dies and similar applications. These materials maintain a cutting edge well. Table 9.6 gives the abrasive wear properties of EFe-3.

Where corrosion and wear resistance are important, martensitic stainless steels overlays can be specified. A typical electrode material would be ER420 (see Table 9.5). This material is austenitic at high temperatures but transforms nearly completely to martensite at room temperature. Preheat at 95–315°C is normally necessary to avoid cold cracking. The material should be slow cooled to room temperature after deposition to complete the martensitic transformation. Tempering is usually performed at 425–650°C. Table 9.6 gives the abrasive wear properties of this deposit. Table 9.7 summarises the principal features and fields of application of this material.

From the basic ER420 type, new alloys have been developed, e.g. 423 (0.12% C–12% Cr–1% Mo–Nb–V), 423N (0.05% C–12% Cr–1% Mo–Nb–V–N) and 423 mod (0.05% C–12% Cr–3% Mo–V–W) to improve thermal fatigue and corrosion resistance. Hardfacings on continuous caster rolls in 423N steel were reported to give a 50% improvement in average tons of steel produced over those hardfaced in 423.⁴³

Improvements in the mechanical properties of a submerged arc deposited 5% Cr–0.5% Mo–0.15% V–0.2% C tool steel can be made by plasma hardening the deposit. During plasma hardening, full dissolution of cementite occurs and partial dissolution of alloy carbides.

However, the rapid heat treatment allows only an inhomogeneous distribution of carbon in the matrix. On rapid quenching, at a cooling rate of $10^5\text{ }^\circ\text{C s}^{-1}$, a very-fine-grained lath martensitic structure is formed from this supersaturated solid solution. Some retained austenite is also present. Within the martensite laths, thin plate-like carbides are precipitated but the high cooling rate means that self-tempering of the martensite stops at an early stage. As a result the Vickers hardness increases from approximately 400 HV to 530 HV, an improvement in fracture toughness is seen and the wear resistance increases by a factor⁴⁴ of 1.65.

White irons

High-chromium white irons containing 8–35% Cr and 2–5% C are typical of the metal-to-earth hardfacing alloys. Typical electrode materials are ERFeCr-A1A and ERFeCr-A3 to ERFeCr-A10 (see Table 9.5). Various proprietary alloys such as the Delcrome[®] series, e.g. Delcrome[®] 90, 92, 93 and W, are available. Depending on the carbon and chromium levels the deposits can be hypoeutectic (approximately 2–3% C and 5–30% Cr), near eutectic (approximately 3–4% C and 13–30% Cr) or hypereutectic (approximately 4–7% C and 14–35% Cr) with spine-like primary carbides with a hexagonal cross-section. The carbides are mainly M_7C_3 (containing chromium, iron and, if present, molybdenum) but M_6C and M_3C are also found in certain high-chromium irons. The primary carbides can have sizes between 50 and 100 μm while the eutectic carbides are much smaller with a diameter typically less⁴⁵ than 10 μm . The matrix around these carbides may be austenitic, pearlitic or martensitic, austenite stability being achieved through the presence of manganese. In general, hypereutectic alloys have better abrasion resistance but poorer impact resistance than hypoeutectic alloys. The excellent abrasion resistance of the hypereutectic high-chromium white-iron alloys arises from the high volume fraction of hard chromium carbide particles having a Vickers hardness of 1200–1800 HV, i.e. harder than martensite.⁴⁶ However, cracks initiate at the large primary carbides and propagate readily through adjacent primary carbides, resulting in a low fracture toughness. White irons with an austenitic matrix have a higher fracture toughness than those with a pearlitic matrix, although a pearlitic matrix gives a slightly higher wear resistance (dry-sand abrasive wear test, ASTM G 65).⁴⁵ A martensitic matrix is beneficial to high-stress abrasion resistance because of the additional support that martensite provides to the surface carbides.³ Thus, where fracture toughness and wear resistance are both important, an austenitic matrix is preferred while, if fracture toughness is not important, a martensitic or pearlitic matrix gives slightly better wear resistance.

Additions of titanium, niobium and molybdenum are sometimes made so as to produce a fine dispersion of very hard carbides in addition to the primary carbides, e.g. in the EFeCr-EX series of hardfacings. This leads to an improvement of low- and high-stress abrasive wear resistance by both increasing the number of carbides and reducing the size of the chromium carbides.⁴⁷ Data on the abrasion resistance of a titanium-carbide-containing martensitic alloy (2% C–7% Cr–6% Ti) is given later in Fig. 9.6. Note that it performs very well when compared with iron-based alloys containing chromium carbide with similar carbon content. Modified chromium carbide hardfacings (5% C–25% Cr) have been developed through microalloying so as to form a finer carbide structure. This finer carbide distribution imparts enhanced wear resistance together with toughness, a factor of 2 increase in wear resistance being reported over the conventional chromium carbide grades.⁴³

The erosion resistance of these hardfacing materials strongly depends on the relative hardnesses of the erodents. The erosion resistance of high-chromium white iron was found to be 20 times, seven times and twice that of low-alloy steel when eroded with cement clinker, blast furnace sinter and silica sand, respectively, at an angle⁴⁸ of 30°. Sinter particles were unable to cause gross fracture of the carbides and so white irons with a high volume fraction of carbides showed the greatest resistance to erosive wear. Silica (SiO₂) and silicon carbide (SiC) were capable of causing fracture of the primary carbides. The concentration of plastic strain in the matrix then led to a high wear rate for the matrix. At normal impact with SiO₂ or SiC erodents, mild steel showed a greater resistance to erosive wear than white-cast-iron hardfacings.⁴⁹

Preheat has little effect on the deposition of these materials; many of the deposits develop a regular pattern of transverse stress relief cracks (often called check cracks) although some of the lower-carbon, more highly alloyed compositions may be crack free especially in limited thicknesses. These check cracks run from the surface to the substrate and the crack path is through fractured carbides or through the interface between the carbide and the matrix.

For a given hardfacing consumable the deposit microstructure is influenced by dilution effects with the substrate, by preferential loss of certain elements in the arc and by cooling rate. Welding processes which give high dilution, e.g. SAW, may give rise to a hypoeutectic microstructure in the first layer when depositing a hypereutectic electrode. The first layer would thus have a poorer abrasion resistance but better toughness than subsequent layers. However, lower-dilution processes would achieve a hypereutectic microstructure even in the first layer. Hence, different coating microstructures are achieved from the same electrode when using different processes. Table 9.8 includes the principal features and fields of application of these white-iron materials.

Table 9.8 Summary of white-iron hardfacing materials, microstructures, principal features and application examples^{30, 34}

Electrode material	Microstructure	Principal features	Rockwell C hardness (HRC)	Application examples
EFFeCr-A	Moderate amounts of chromium carbides in a high-carbon austenite	Two layers normally necessary to maintain uniform hardness; additional layers may spall. Greater impact resistance but decreased abrasion resistance compared with other ERFFeCr-XX	General-purpose hardfacing alloy which can be used when limited stress cracks are acceptable but severe abrasion is not present. Railway track work; crusher roll shell	Used for bucket lips and teeth, impact hammers and conveyors for crushing and transporting rock
ERFeCr-A1A and ERFFeCr-A4	Hypereutectic massive chromium carbides in an austenitic matrix	Excellent wear resistance and fair toughness. ERFFeCr-A1A has greater impact resistance than ERFFeCr-A4. Check cracks are normally present. Two layers necessary to maintain uniform hardness; additional layers may spall. Very low coefficient of friction develops with scouring by earth products		
EFFeCr-A2	Titanium carbide in an austenitic matrix	Build-up limited to three layers to minimise check cracking		
EFFeCr-A3	Similar to ERFFeCr-A1A but with a martensitic matrix	Lower manganese content than ERFFeCr-A1A gives rise to a brittle martensitic matrix	Hardfacing suitable for low-stress scratching abrasion with low impact	Hardfacing of mining, construction, earth moving and quarrying equipment subject to abrasion and moderate impact
ERFeCr-A3A	Near-eutectic chromium carbides in an austenitic matrix	Higher toughness but poorer abrasion resistance than ERFFeCr-A1A, ERFFeCr-A4, ERFFeCr-A9 or ERFFeCr-A10		
				Final overlay on roll crushers, hammer mill hammers and cone crushers over a build-up of austenitic manganese material

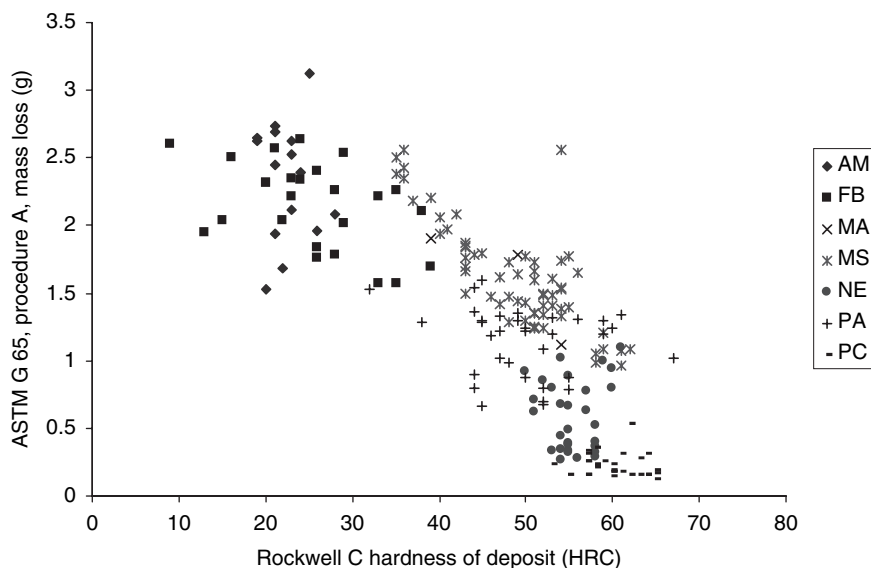
ERFeCr-A5	Hypoeutectic chromium carbides in an austenitic matrix	Build-up should be restricted to three layers to minimise check cracking		Metal-to-metal friction wear or earth scouring under low-stress abrasive conditions
ERFeCr-A6 and ERFeCr-A7	Hexagonal chromium carbides in an austenitic matrix	Higher-carbon version of ERFeCr-A5. Deposit develops check cracks. Molybdenum addition increases wear resistance to high-stress abrasion	50–60	Hardfacing suitable for low-stress abrasive wear plus moderate abrasion
ERFeCr-A8	Hexagonal chromium carbides in an austenitic matrix	Higher-chromium version of ERFeCr-A3. Increased chromium decreases toughness but improves abrasion resistance. Maximum check cracking	50–60	Hardfacing suitable for low-stress abrasion plus minimum impact
ERFeCr-A9	Hypereutectic hexagonal chromium carbides in an austenitic matrix	Deposit develops check cracks	50–60	Used for applications with abrasive wear combined with moderate impact
ERFeCr-A10	Hypereutectic massive hexagonal carbides in austenite–carbide matrix	Best low-stress abrasion resistance of ERFeCr-XX series but with reduced impact resistance. Limit to two layers. Hardness maintained to 760 °C	58–63	Used in most severe abrasive applications involving minimal impact, e.g. coal pulverising, handling equipment and glass sand handling equipment
ERFeCr-EX	Finely dispersed chromium carbide plus vanadium, niobium, tungsten or titanium carbides	Maintain hot hardness to 650 °C. Deposits check crack readily		Hardfacing for severe high-stress abrasion plus moderate impact

Summary of low-stress abrasive wear properties of iron-based hardfacings

As seen from the previous sections, iron-based alloys used for hardfacing can have the following microstructures.

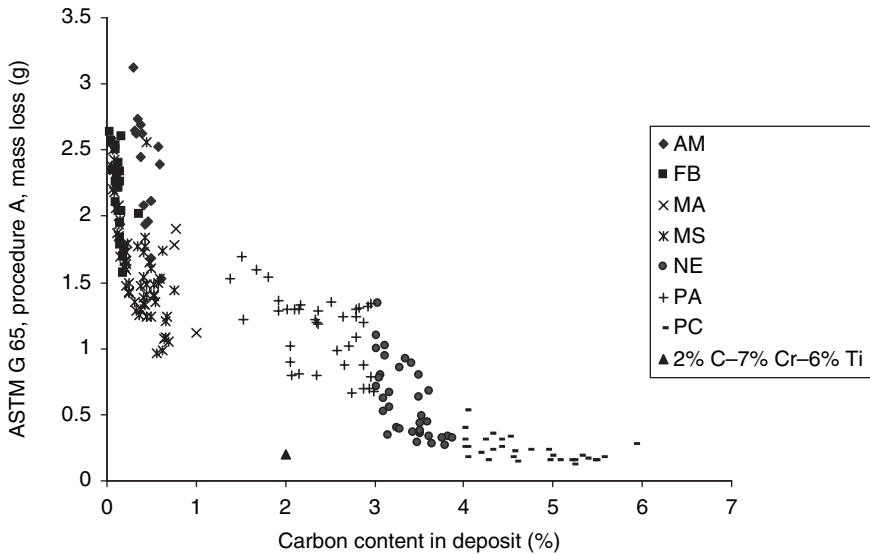
1. Austenitic manganese alloys (labelled AM in Fig. 9.5, Fig. 9.6 and Fig. 9.7).
2. Ferritic–bainitic as in build-up alloys (labelled FB in Fig. 9.5, Fig. 9.6 and Fig. 9.7).
3. Mixed martensitic–austenitic alloys (labelled MA in Fig. 9.5, Fig. 9.6 and Fig. 9.7).
4. Martensitic alloys (labelled MS in Fig. 9.5, Fig. 9.6 and Fig. 9.7).
5. Near-eutectic austenite–carbide alloys (labelled NE in Fig. 9.5, Fig. 9.6 and Fig. 9.7).
6. Hypoeutectic alloys containing primary austenite with austenite–carbide eutectic (labelled PA in Fig. 9.5, Fig. 9.6 and Fig. 9.7).
7. Hypereutectic alloys containing primary carbides with austenite–carbide eutectic (labelled PC in Fig. 9.5, Fig. 9.6 and Fig. 9.7).

A comprehensive assessment of the low-stress abrasive wear performance of iron-based hardfacings produced by SAW, flux core arc welding and SMAW with the above microstructures has been carried out by means of the ASTM G 65 procedure A dry-sand–rubber wheel test.⁵⁰ The actual chemical composition on the surface of the hardfacing was determined together with its hardness and related to the weight loss in the ASTM G 65 test. Figure 9.5 show the mass loss as a function of the hardness of the deposit for different microstructures. While a correlation of lower mass loss and hence greater abrasion resistance with increasing hardness is observed, the scatter in the results is large. Some clustering of data according to microstructure is seen; e.g. the primary carbide microstructures have greatest abrasion resistance. When the mass loss results are plotted against carbon content for different microstructures (Fig. 9.6), better correlation is noted. In the low-carbon regime of Fig. 9.6 (below 1% C) there appears to be two distinct trend lines of clustered data, the martensitic steels having better abrasive wear performance than the austenitic manganese steels. As the carbon content is increased, no significant austenite–carbide eutectic appears until a carbon content of 2% is reached, thus there is little improvement in wear resistance when the carbon content is between 1 and 2% over the lower-carbon martensitic steels; indeed steels with this level of carbon are less wear resistant than the martensitic steels. In the 2–3% C range there is more austenite–carbide eutectic and less primary austenite; so the abrasion resistance improves slightly, but the primary austenite microstructure is little better than martensite. In the 3–4% C range, where the microstructure is near eutectic, the abrasion resistance improves with increasing



9.5 Abrasion resistance from the ASTM G 65, procedure A, test as a function of deposit hardness for several iron-based materials with different microstructures: AM, austenitic manganese alloys; FB, ferritic-bainitic alloys; MA, mixed martensitic-austenitic alloys; MS, martensitic alloys; NE, near-eutectic austenite carbide alloys; PA, hypoeutectic alloys containing primary austenite with austenite-carbide eutectic; PC, hypereutectic alloys containing primary carbides with an austenite-carbide eutectic.⁵⁰

carbon content. Above about 3.5% C, primary carbides begin to precipitate, but they remain widely dispersed and the abrasion resistance is dominated by the austenite-carbide eutectic. From about 4% C the abrasion resistance is dominated by primary carbides with high wear resistance and there is slight further improvement above 5% C. When the mass loss was correlated with chromium content (Fig. 9.7), a great deal of scatter was noted and, for primary austenite with austenite-carbide eutectic microstructures (labelled PA), or for near-eutectic microstructure type (labelled NE), or for the primary carbide with austenite-carbide eutectic (labelled PC) microstructure, no improvement in G-65A abrasion resistance was observed with increase in chromium content. There would be a benefit with higher chromium content if corrosion was an issue as in wet abrasion. For these iron-based alloys it can thus be concluded that it is the microstructure that determines abrasion resistance and that microstructure is largely determined by the carbon content. It should be noted that, whereas under low-stress abrasion improvements in performance of a factor of 20 over mild

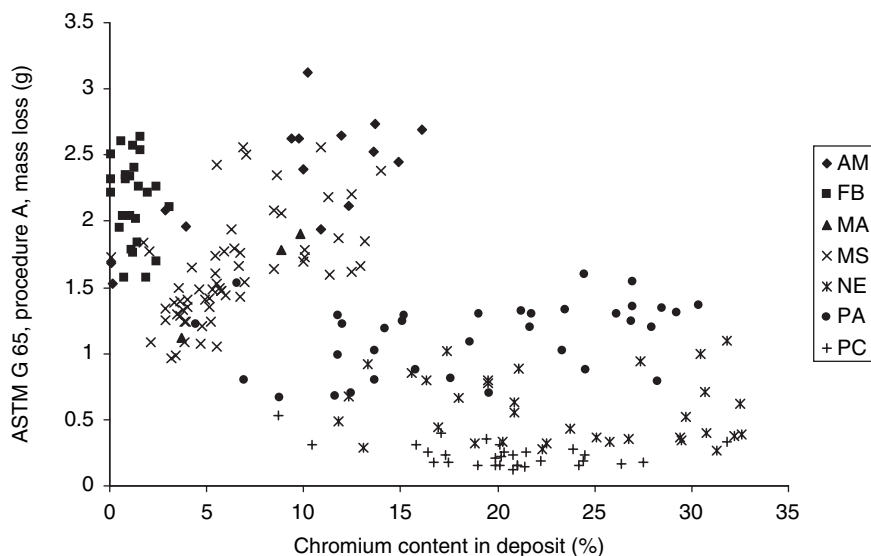


9.6 Abrasion resistance from the ASTM G 65, procedure A, test as a function of the carbon content of the deposit for several iron-based materials with different microstructures and alloy compositions: AM, austenitic manganese alloys; FB, ferritic-bainitic alloys; MA mixed martensitic-austenitic alloys; MS, martensitic alloys; NE, near-eutectic austenite carbide alloys; PA, hypoeutectic alloys containing primary austenite with an austenite-carbide eutectic; PC, hypereutectic alloys containing primary carbides with an austenite-carbide eutectic⁵⁰ and a 2% C-7% Cr-6% Ti alloy.⁴³

steel are possible with iron-based hardfacings, under high-stress abrasion the improvement might be considerably less.

Other ferrous alloys

Although carbon is the most common hardening element in steels, strengthening can also be achieved by borides which are harder than carbides, e.g. in alloys with 3% B and 25% Cr, and by intermetallic compounds formed from iron, niobium, silicon and molybdenum. The proprietary alloy Tribaloy T-500 is strengthened by Laves phase and has a nominal Rockwell C hardness^{51,52} of 53–58 HRC. In alloys where strengthening is from boron and carbon, the microstructure consists of a hard primary phase and a eutectic phase, itself consisting of eutectic hard phase and a metal matrix. Thus in the chromium-free and low-chromium-containing hardfacing alloys in the Fe-C-B system the hard phases are M_2B , M_3C or $M_{23}B_6$ with Vickers hardness values between 1090 and 1740 HV. In the Fe-Cr-C-B system, M_7C_3 ,



9.7 Abrasion resistance from the ASTM G 65, procedure A, test as a function of the chromium content of the deposit for several iron-based materials with different microstructures and alloy compositions: AM, austenitic manganese alloys; FB, ferritic–bainitic alloys; AM, mixed martensitic–austenitic alloys; MS, martensitic alloys; NE, near-eutectic austenite carbide alloys; PA, hypoeutectic alloys containing primary austenite with an austenite–carbide eutectic; PC, hypereutectic alloys containing primary carbides with an austenite–carbide eutectic.⁵⁰

M_3B or M_2B_2 phases form whose Vickers hardnesses range from 1190 to 2300HV. Addition of titanium to this system to form Fe–Cr–Ti–C–B alloys leads to the primary coarse hard phases being titanium carbide of the MC type and titanium boride of the MB_2 type whose Vickers hardness⁵³ values varied between 2300 and 4000HV. In order to achieve a high abrasive wear resistance it was found necessary to embed a sufficient volume fraction (more than 30%) of coarse hard phases, which were harder than the abrasive particles, in a hard eutectic.⁵⁴

Recently attempts have been made to deposit Fe–Cr–B metamorphic alloys by the PTA process. These are alloys that are primarily crystalline when deposited by thermal spraying or weld surfacing. An amorphous surface layer a few micrometres thick is said to form *in situ* under specific loading conditions, resulting in hardness increase⁵⁵ and a coefficient of friction of typically⁵⁶ 0.09–0.12. However, it has been found that the wear resistance of these metamorphic coatings depends more on the density and

microstructure of the coating rather than on the formation of an amorphous surface structure.^{56,57} Indeed when Armacor M (an iron-based powder containing 30–32% Cr, 17–19% Ni, 3.5–4.5% Mo, 3.5–4.5% B, 2.2–2.8% Cu, 1.0–1.8% Si, and 8.8–11% Co) and Armacor C (an iron-based powder containing 44.5% Cr, 5.9% B and 2% Si) were deposited by PTA as distinct from thermal spraying, no amorphous surface structure was detected by X-ray diffraction after wear testing.⁵⁸ The coating produced from Armacor M powder had better sliding and abrasive wear resistance than that formed from Armacor C. This was related to differences in the microstructures of these coatings which were an iron-based solid solution (austenitic in the case of Armacor M and ferritic for Armacor C), and chromium borides. The Vickers hardness and size of the borides in Armacor M were higher by about 200 HV and a factor of 4 respectively when compared with Armacor C. The lack of an amorphous surface layer after wear testing the weld-deposited coating was thought to be associated with the scale of the boride precipitates, much finer precipitates being achieved by thermal spraying.^{56,58}

9.4.2 Carbides

Hardfacings made by depositing martensitic steels and high-chromium irons owe their wear-resistant properties to the formation of carbides, either as a result of tempering martensite or from direct precipitation from the melt. Another approach is to incorporate particulate carbides, e.g. tungsten carbide, which has a Vickers hardness of 2400 HV 20, in the welding electrode and then transfer them to the weld pool.

WC additions to the welding electrode are normally made as a powder in a carbon steel tube (suitable for oxyacetylene welding) but other forms are available, e.g. a flux-coated form (suitable for shielded metal arc welding), and as a continuous wire with an internal flux for open arc welding. Various compositions are available, common compositions being 40, 50, 55 and 60 wt% tungsten carbide, 60 wt% being the most popular and covered by AWS A5.13:2000 and AWS A5.21:2001. The carbides can be a mixture of WC and W₂C. For each composition, several carbide size ranges are available, with mesh sizes from 12 to 120.

The performance of these coatings is governed by the volume fraction of carbide, the size of the carbide with respect to the abrasive particles and the welding technique used. Arc welding tends to dissolve the tungsten carbide more readily and, in extreme cases with very fine grains, may dissolve them completely. The dissolved tungsten carbide may precipitate as secondary carbides in the matrix on cooling. Such a matrix, although hard, is inferior to the composite consisting of tungsten carbide grains embedded in a hard strong iron matrix. Dilution effects with the base metal can also give rise to a reduction in tungsten carbide volume fraction and hence abra-

sion resistance. Thus welding processes with low heat input and dilution should be chosen. As the tungsten carbide grains have a high density, the grains tend to sink in the weld pool, leading to fewer grains at the surface and poorer abrasion resistance. A turbulent weld pool can produce a more uniform distribution of grains and thus ameliorate the wear resistance to some degree. The problems associated with the sinking of tungsten carbide particles due to their high density can be overcome by replacing tungsten carbide by other less dense carbides, such as vanadium, titanium or niobium carbides. These carbides produce a more homogeneous deposit.³⁶ Table 9.9 gives the abrasive wear properties of two tungsten carbide hardfacing materials. These data can be compared with those given in Table 9.6 as the tests were conducted under identical conditions.

Tungsten carbide hardfacings have been used to solve a wide range of industrial sliding and drilling abrasion problems, i.e. sliding abrasion with a limited amount of impact. Some common applications are in earth drilling, digging and farming, e.g. ploughshares, ditch digger teeth, ripper teeth and oil drill bits and tool joints. If the wear-resistant coating is only placed on the advancing edge of the tool, the back surface wears away at a greater rate and thus the tool is self-sharpening, e.g. in earth-cutting tools. Tungsten carbide hardfacings are not recommended for protecting both surfaces in sliding contact because the wear pattern is not smooth enough for bearing-type applications.³⁷

Complex carbide powders consisting of Fe–W–Ti–C and W–Ti–C powders manufactured by a self-propagating high-temperature synthesis method have also been deposited by submerged arc welding after producing a cored electrode.⁵⁹ W–Ti–C powders did not bond well to the matrix owing to the lack of an iron matrix binder. The microstructure of the deposit from Fe–W–Ti–C powder consisted of primary cuboidal carbides, having a titanium carbide core surrounded by tungsten carbide, and finer rod-type eutectic

Table 9.9 Abrasion wear data for tungsten carbide hardfacings³⁶

Carbide (wt%)	Material type (mesh size)	Number of layers and welding process	Abrasion volume loss (mm ³)	
			Low stress†	High stress‡
60	20–30	One layer, SMA	7.3	28.7
61	100–250	One layer, SMA	10.6	24.4

† Data from a dry-sand–rubber wheel test (ASTM G 65, procedure B): load, 13.6 kgf; 2000 rev.

‡ Data from a slurry–steel wheel test (ASTM B 611, modified): load, 22.7 kgf; 250 rev.

carbides uniformly distributed in a bainitic matrix. The Vickers hardness of these complex carbides was 2000–2500 HV. The average size of the carbides was about 2 μm , cuboidal carbides being slightly larger than rod-like carbides. The hardness and abrasive wear resistance (dry-sand-rubber wheel ASTM G65) increased with increasing volume fraction of the cuboidal but not the rod-like complex carbide. The wear resistance and fracture toughness of the hardfacings were found to be greatly improved over those of conventional high-chromium white irons. Hot-rolling simulation tests indicated that these hardfacings performed better than high-speed steel rolls.⁶⁰

9.4.3 Cobalt-based alloys

At higher temperatures in corrosive environments the properties of the iron matrix limit the performance of hardfacings. Thus a series of alloys is available where the iron matrix has been replaced by cobalt and nickel. Typical of the cobalt-based materials are the family of Stellite[®] and Tribaloy alloys. Two basic types are available: those containing carbides and those containing Laves phases.

Carbide-containing alloys

Carbide-containing cobalt-based alloys have been used since the early 1900s when an alloy of composition Co–28% Cr–4% W–1.1% C was developed. Table 9.10 gives the chemical compositions and as-deposited hardnesses of several carbide-containing cobalt-based alloys. The equivalent AWS grades are given where appropriate; the composition ranges of the AWS specified materials are greater than those of the proprietary alloys. High chromium levels are present for oxidation and corrosion resistance and tungsten or molybdenum provides increased matrix strength and carbide-forming ability. The main difference between these alloys is the carbon content which determines whether the alloys are hypoeutectic (Stellite[®] 21 and Stellite[®] 6), near eutectic (Stellite[®] 12) or hypereutectic (Stellite[®] 1). Figure 9.8 shows the microstructure of these alloys after being deposited by PTA. The carbide content controls the hardness and the level of abrasion resistance. The amount of carbide phase varies from about 29 wt% for Stellite[®] 1, to 12 wt% and 16 wt% for Stellite[®] 6 and 12 respectively.⁶⁰ Figure 9.9 shows the nominal Rockwell C hardness as a function of nominal carbon content³⁸ in Stellite[®] 1, 6, 12 and 21. Note the pronounced increase in hardness with carbon, and hence carbide content of the alloy. Low-carbon alloys (typically 0.25%) contain dispersed chromium-rich M_{23}C_6 and are reasonably ductile. These alloys provide metal-to-metal sliding wear resistance and cavitation erosion resistance. At a carbon level

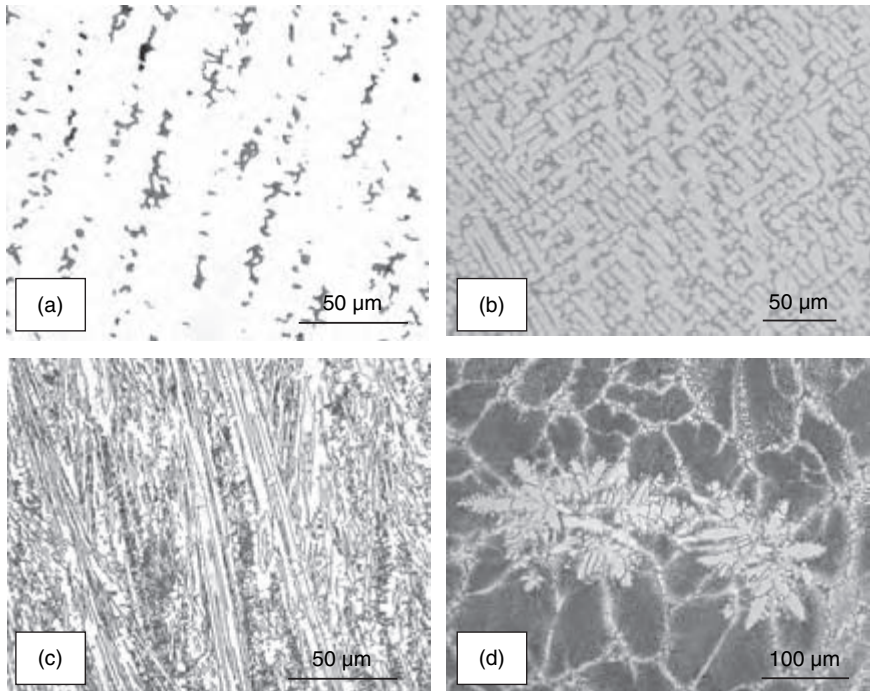
Table 9.10 Nominal compositions and Rockwell C hardnesses of selected proprietary cobalt-based hardfacing materials. The AWS specified ranges for solid cobalt-based bare electrodes and rod are also given^{34, 38, 51, 52}

Proprietary alloy†	AWS A5.21:2001, Table 2‡	Nominal composition (proprietary alloys) and specified ranges§ (AWS) (wt%)										Typical Rockwell C hardness (HRC)
		C	Mn	Si	Cr	Ni	Mo	W	Fe	Co	Other	
Carbide-containing CoCrW alloys												
Stellite® 1	2.45	1	1	1	31	<3	1	13	<2.5	Balance		55
Stellite® 6	ERC0Cr-C	2-3	1	2	26-33	3	1	11-14	3	Balance		43-58
	1.2	1	1.1	28	<3	1	4.5	<3	<3	Balance		40
Stellite® 12 AWS	ERC0Cr-A	0.9-1.4	1	2	26-32	3	1	3-6	3	Balance		23-47
	1.5	1	1.5	29.5	<3	<1	8.5	<2.5	<2.5	Balance		
Stellite® 12	ERC0Cr-B	1.2-1.7	1	2	26-32	3	1	7-9.5	3	Balance		34-47
	1.85			29.5				8.5		Balance		48
Stellite® 20	2.45	1	1	1	33	<2.5		17.5	<2.5	Balance		58
Stellite® 21	0.25	1	1.5	27	2.5	5.5			<3	Balance		32
Stellite® F	ERC0Cr-E	0.15-0.45	1.5	1.5	25-30	1.5-4	4.5-7	0.5	3	Balance		20-35
	1.75		1.1	25.5	22.5			12	<1.5	Balance		43
Stellite® 190	3.3	0.5	1	26	1			14	<2.5	Balance		52
		1	2	24-30	4	1	12-16	3	Balance			52-60
Carbide-containing Co-Cr-Mo alloys												
Stellite® 701	2.5	0.5	0.5	0.5	30-33	<3	13		<3	Balance		52-56
Stellite® 704	1	0.5	0.5	30	<2.5	14			<2	Balance		48-50
Stellite® 706	1.2	1	0.5	29	<3	5			<3	Balance		42-44
Stellite® 712	1.85	0.5	0.5	29	<3	9			<3	Balance		46-50
Stellite® 720	2.45	0.85	0.5	33	<3	18			<3	Balance	0.3 B	56-60
Cobalt base alloys with Laves phase												
Tribaloy T-400	<0.08		2.6	8.5		<1.5	29		<1.5	Balance		53-58
Tribaloy T-800	<0.08		3.4	18		<1.5	28		<1.5	Balance		54-60
Tribaloy T-900	<0.08		2.7	18		16	23		<3	Balance		52-53

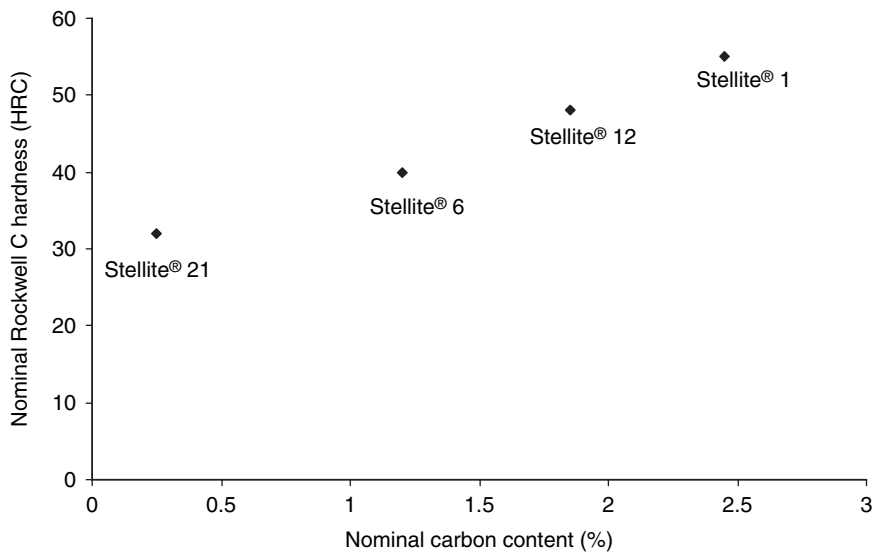
† Stellite® and Triballoy are registered trademarks of Deloro Stellite.

‡ AWS A5.13 :2000, Table 2 covers the chemical composition requirements of cobalt-based surfacing electrodes; AWS A%:21:2001, Table 2, covers cobalt-based bare electrodes and rods and AWS A5:21:2001, Table 3, covers metal-cored and flux-cored cobalt-based electrodes and rods.

§ (Single values in AWS classification compositions are maxima).

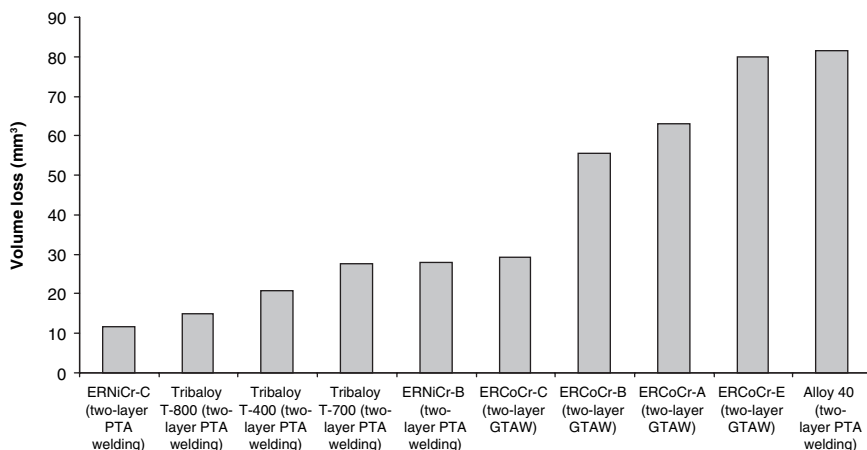


9.8 Microstructures of the PTA-welded deposits of (a) Stellite[®] 21, (b) Stellite[®] 12, (c) Stellite[®] 1 and (d) T-400. The Stellite[®] alloys have been etched in Murakami's reagent; T-400 was etched in Marble's reagent. (Samples courtesy of Deloro Stellite.)

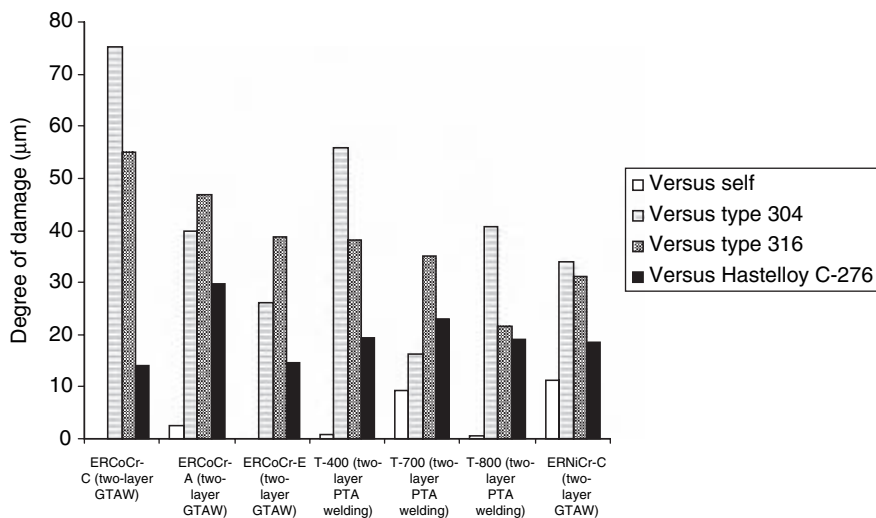


9.9 Nominal Rockwell C hardnesses of several cobalt-based hardfacing alloys as a function of their nominal carbon content.^{38,51,52}

of approximately 1% a network of $\text{Co-M}_7\text{C}_3$ eutectic is present. These alloys show limited ductility and may contain check cracks but have better abrasion resistance. At carbon levels of over 2%, large primary carbides and $\text{Co-M}_7\text{C}_3$ eutectic are present. These alloys have negligible ductility but cracking can normally be avoided in the overlay by using a high preheat (427°C minimum). They have very high abrasion resistance as can be seen in Fig. 9.10 which presents low-stress abrasion data generated by the ASTM G 65 dry-sand-rubber wheel test for several standard cobalt-based alloys, ERCoCr-A, ERCoCr-B, ERCoCr-C and ERCoCr-E.³⁶ These alloys also possess excellent cavitation erosion resistance and self-mated sliding properties. Figure 9.11 shows the sliding wear properties of various GTAW-deposited cobalt-based alloys sliding against themselves (self-mated) and against type 304 stainless steel, type 316 stainless steel and Hastelloy C-276. The data were obtained using the pin-on-block test with the following parameters: 2722 kgf load; ten strokes through a 120° arc.³⁶ Figure 9.12 shows the sliding wear properties of the same cobalt-based hardfacing produced by GTAW when sliding against themselves, Stellite[®] 1, Stellite[®] 6, Stellite[®] 12, Triballoy T-400, Triballoy T-700 and ERNiCr-C.⁶¹ This set of data were obtained from a Falex model 1 ring-and-block sliding wear machine with a 934 N load (equivalent to an initial Hertzian stress of 361 kPa), and a rotational speed of 80 rev min^{-1} . The good self-mated sliding wear properties of the Stellite[®] 6 and 12 alloys are due to their low stacking-fault energy, which indicates a decreased tendency to cross-slip, and which facilitates transformation from face-centred cubic (FCC) to hexagonal close-packed (HCP) during plastic deformation.⁶² In sliding contact a



9.10 Abrasion resistance as measured by the ASTM G 65 test for various cobalt- and nickel-based materials.³⁶

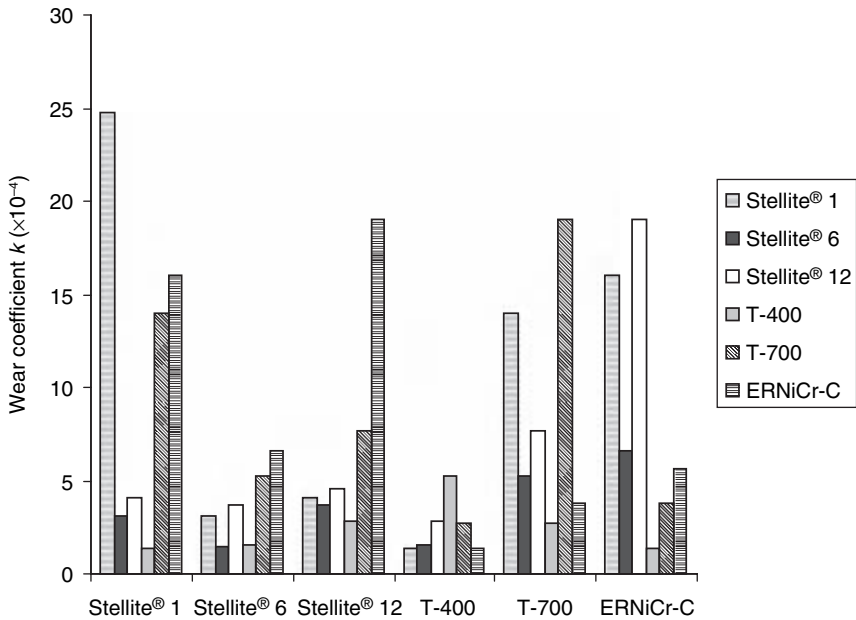


9.11 Gallings properties of various cobalt- and nickel-based hardfacing alloys (self-mated, versus type 304 stainless steel, versus type 316 stainless steel and versus Hastelloy alloy C-276). Data obtained using a pin-on-block test with the following parameters: 2722 kgf load; ten strokes through a 120° arc.³⁶

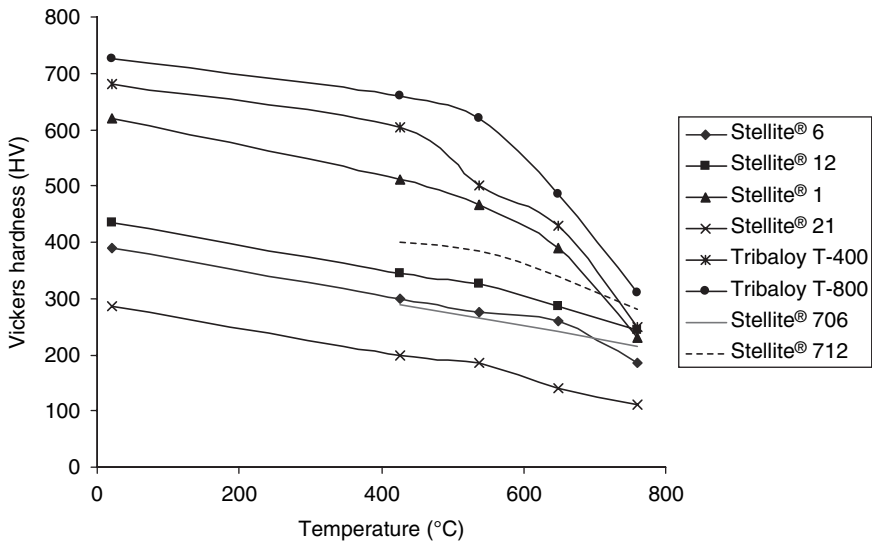
preferential orientation with the HCP basal planes parallel to the worn surface is generated.⁶³ This orientation gives the least resistance to shear in the sliding direction, which accounts for low friction. Significant strain hardening of the surface layers also occurs and thus the material self-generates an ideal surface layer that combines low friction with a high load-carrying capacity. The HCP phase acts as a solid lubricant on a harder substrate; hence the galling resistance of Stellite® 21 is good.⁶⁴

These alloys also possess good high-temperature strength as can be seen from Fig. 9.13 where the hardness of cobalt-based hardfacings is plotted versus temperature. Table 9.11 summarises the principal characteristics of these carbide-containing cobalt-based alloys and gives typical fields of application.

Recent research on these alloys has concentrated on attempting to improve the mechanical properties, such as hardness and wear resistance, by modifying the size and nature of the carbides present by additions of, for example, molybdenum to the basic Stellite® 6 composition.⁶⁵ As the molybdenum content increased, solidification led to the formation of two types of carbide, M_6C at primary cobalt-rich dendrite interfaces and eutectic $M_{23}C_6$ in the interdendritic region instead of just eutectic chromium-rich M_7C_3 and $M_{23}C_6$ in the interdendritic regions of molybdenum-free alloys.



9.12 Galling resistance, as measured by the average total mass loss of each pair of mating alloys, of various cobalt- and nickel-based materials (self-mated, versus Stellite® 1, Stellite® 6, Stellite® 12, T-400, T-700 and ERNiCr-C). Data obtained using a pin-on-block test with the following parameters: 934 N load (initial Hertzian stress, 361 kPa); 80 rev min⁻¹. Alloy couples with wear coefficients lower than 1.4×10^{-4} and 3.8×10^{-4} represent excellent and good alloy combinations respectively. Alloy combinations with wear coefficients in excess of 7×10^{-4} are considered to be poor.⁶¹



9.13 Vickers hardness as a function of temperature for various cobalt-based hardfacing alloys.³⁸

Table 9.11 Principal characteristics and applications of selected cobalt-based hardfacing materials^{30, 34, 38, 51, 52}

Alloy	Principal characteristics	Applications
Stellite® 1 ERCoCr-C	Hypereutectic structure High abrasion and corrosion resistance Retains hardness at temperatures >760 °C	Pump sleeves, rotary seal rings, wear pads, bearing sleeves, extruder screw flights and centreless grinder work rests
Stellite® 6 ERCoCr-A	Hypoeutectic structure; most widely used cobalt-based alloy Excellent resistance to chemical degradation over wide temperature range. Excellent self-mated antigalling properties	Valve seat and gates, pump shafts and bearings, erosion shields and rolling couples. Often used self-mated
Stellite® 12 ERCoCr-B	High-temperature hardness High resistance to impact and cavitation erosion Less tendency to crack than Stellite® 12 in multiple layers, but less ductile than Stellite® 21 Machinable with carbide tools Greater abrasion and galling resistance but less resistant to impact than Stellite® 6 Highest hot hardness of Co-Cr-W Stellite® alloys	Cutting edges on long knives in carpet, plastics, paper and chemical industries; saw teeth, rotary slitters, grid nozzles, burner tips, guide rolls, sleeves and bushing
Stellite® 20	Most abrasion-resistant standard cobalt-based alloy Poor impact resistance Good corrosion resistance	Slurry pump sleeves, rotary seal rings, wear pads, bearing sleeves and centreless grinder work rests
Stellite® 21 ERCoCr-E	Solid-solution-strengthened alloy with relatively low carbide content Good strength and ductility up to 1150 °C Excellent resistance to thermal and mechanical shocks Resistant to oxidising and reducing atmospheres up to 1150 °C	Valve trim for high-pressure steam, oil and petrochemical applications, turbine blades and vanes, components in combustion and or exhaust systems where high strength up to 816 °C and to oxidation to 1093 °C is required, medical and dental components and used for

Stellite® F	Material work hardens, has excellent self-mated galling resistance and is very resistant to cavitation Specifically designed for hardfacing internal combustion engine valves to give enhanced resistance to corrosion and erosion Slightly higher hardness and fluidity than Stellite® 6 and enhanced erosion and corrosion resistance Highest carbon content of Deloro Stellite Co-Cr alloys Care must be taken to minimise cooling stresses during hardfacing and to avoid service conditions with severe mechanical or thermal shock	building up forging or hot stamping dies Internal combustion engine poppet valves
Stellite® 190		Most severe abrasive environments such as the journals of tricone rock bits in oil-drilling industry
Stellite® 701	Superior wear and corrosion properties than conventional Co-Cr-W alloys at ambient and elevated temperatures Molybdenum improves corrosion resistance in reducing acids but impairs corrosion resistance in highly oxidising acids Good high-temperature oxidation and sulphidation resistance Molybdenum partitions in carbides to enhance wear resistance Good hot hardness	Similar applications to Stellite® 12 or 1
Stellite® 704		
Stellite® 706		
Stellite® 712		
Stellite® 720		
Tribaloy T-400	Outstanding resistance to galling and corrosion Excellent mechanical wear resistance	Valve trim, mechanical seals and thrust rings.
Tribaloy T-800	Excellent oxidation and corrosion resistance. Harder and better abrasive wear resistance than Tribaloy T-400 or T-700	Applied by PTA welding to numerous gas turbine components subject to high-temperature fretting
Tribaloy T-900	Good high-temperature fretting resistance Improved crack resistance, higher ductility than Tribaloy T-800 Good high-temperature wear resistance Good localised corrosion resistance	Used in applications with high-temperature and severe wear, abrasion and corrosion

In addition, as the molybdenum content increased, the dendrite arm spacing of the cobalt-rich dendrites decreased, the size of the chromium-rich carbides formed in the interdendritic region decreased but the size of the M_6C formed at the dendrite interfaces increased. The volume fraction of the chromium-rich carbides slightly increased, but that of the M_6C abruptly increased.

Attempts have also been made to improve their high-temperature wear and corrosion resistance. The Stellite® 700 series alloys (see Table 9.10 for nominal compositions) have been developed by replacing the tungsten present in the Co–Cr–W–C alloys by molybdenum. The molybdenum content of these alloys ranges from 5 to 17%. This improves the corrosion resistance in all types of reducing acid but impairs the corrosion resistance in oxidising acids because of its inability to form a tenacious oxide film. Nevertheless, owing to their high chromium content, these alloys possess good high-temperature oxidation and sulphidation resistance. The molybdenum partitions to the carbide and gives an improvement in hot hardness as can be seen in Fig. 9.13, the hot hardness of Stellite® 712 being greater than that of the equivalent Co–Cr–W alloy with the same carbon content (Stellite® 12). It also maintains its hot hardness better than Stellite® 1 which has a higher carbon content.⁵¹ Table 9.11 also includes the principal characteristic of these Co–Cr–Mo–C alloys.

Laves-phase-containing alloys

Laves phase is an intermetallic compound of general formula AB_2 , which typically imparts poor toughness but good wear resistance. Table 9.10 includes the composition of cobalt-based alloys containing Laves phase (Tribaloy T-400, T-800 and T-900). In these alloys, molybdenum and silicon are added so that a primary Laves phase of the $MgZn_2$ type with typical compositions such as $CoMoSi$ and Co_3Mo_2Si solidifies from the melt. This phase is hard and corrosion resistant. Note that the carbon level is restricted in these alloys to avoid carbide precipitation. As these alloys contain 35–70 vol.% of Laves phase, this phase effectively governs the properties and the matrix plays a lesser role than in the carbide-containing cobalt alloys. Figure 9.8(d) shows the microstructure of the T-400 alloy. The wear resistance of these alloys is thus highly dependent on the volume percentage of Laves phase, and dilution and cooling rate affect the properties considerably. The presence of the Laves phase restricts the ductility and impact strength of these alloys and it is difficult to obtain crack-free overlays on all but the smallest components. The fracture toughness of T-400 and T-800 has been reported as $21.9 \pm 3.0 \text{ MN m}^{-3/2}$ and $19.2 \pm 1.8 \text{ MN m}^{-3/2}$ respectively.^{66,67} These materials have superior high-temperature strength to Stellite® 1, 6 12 and 21 as can be deduced from the hot hardness data given in Fig. 9.13.

Tribaloy T-400 exhibits outstanding resistance to galling (Fig. 9.11 and Fig. 9.12) and corrosion and is particularly suitable when lubrication is a problem. Self-mated Tribaloy T-400 is seen to exhibit superior wear resistance (contact stress, less than 495 kPa) than Stellite® 6 (Fig. 9.12). Tribaloy T-800 with its high chromium content has excellent oxidation and good corrosion resistance. In a comparative study of hardfacing materials for diesel valve service it was found to have the best (but very similar to that of the nickel-based alloy Tribaloy T-700) hot wear performance in an accelerated rotating-sliding-wear test, outperforming Stellite® 6 and 12.^{68,69} However, its hot corrosion performance at 650 °C was inferior to that of the iron-based alloy Tristelle TS-2.⁷⁰ Hot sliding-wear resistance depends on the formation of a protective scale (glaze) on the material. However, the presence of refractory metal (e.g. molybdenum and tungsten) increases the hot hardness of the alloy (see Fig. 9.13) which is expected to reduce the deformation within the surface oxide glaze and hence to reduce the probability of the occurrence of scale fracture.⁶⁹ Data on the abrasion resistance of Laves-phase-containing alloys are also included in Fig. 9.10. Table 9.11 summarises the principal characteristics of these Tribaloy alloys and gives typical fields of application.

9.4.4 Nickel-based alloys

Nickel-based materials are cheaper than cobalt-based alloys. Three types of nickel-based hardfacing alloys are available.

1. Boride-containing alloys.
2. Carbide-containing alloys.
3. Laves-phase-containing alloys.

Table 9.12 includes the compositions and as-deposited hardnesses of several nickel-based hardfacing alloys. Table 9.13 summarises the principal characteristics of these nickel-based alloys and gives typical fields of application.

Boride-containing alloys

These were first available as a spray and fuse powder but are now obtainable as bare cast rod, tubular wires and powders. Their microstructure consists of borides and chromium carbides in a nickel-rich matrix. Figure 9.15 gives the microstructure of Deloro® 45. At low chromium content (approximately 5%), nickel boride (Ni_3B) is the main hard phase. As the chromium content is increased, the Ni_3B is replaced by chromium borides (CrB and, at still higher chromium levels, Cr_3B_2). Silicon is present to provide self-fluxing characteristics but is also an important matrix element

Deloro® N-6	1.1	1	1.5	29	Balance	5.5	2	3	3	0.6 B	28-37
Deloro® 716	1.1	1	1.5	27	23	3	3.5	29	11	0.5 B	24-32
ERNiCrMo-5A	0.12	1	1	14-18	Balance	14-18	3-5	4-7		0.4 V	
ERNiCrFeCo	2.5-3.0	1	0.6-1.5	25-30	10-33	7-10	2-4	20-25	10-15		
Nickel-based alloy with tungsten carbide											
Coltung 1	1.75		2.65	7	Balance		38.5\$	2.2		1.9 B	58-63
Colmonoy	0.5		3.5	11.5	Balance		16	3.5		2.5 B	52
57PTA											47¶
Colmonoy	2		1.4	20.3	40		34\$	1.4		0.9 B	50-55
83PTA											43-48¶
Colmonoy	2.3		3.1	20.3	Balance		30.8\$	2.4		1.9 B	58-63
635											
Colmonoy	2.2		2.5	8.6	Balance		48.2\$	2.2		1.5 B	58-63
705											
Nickel-based alloys with Laves phase											
Tribaloy	<0.08		3.4	15.5	Balance	32.5		<3	1.5		42-48
T-700											
High-silicon stainless steel											
Tristelle TS-1	1	0.1	5	30	10			Balance	12		38
Tristelle TS-2	2	0.1	5	35	10			Balance	12		45-46
Tristelle TS-3	3	0.1	5	35	10			Balance	12		47-51
Tristelle 5183	2		5	21	10			Balance	0.2		40
NOREM® 02	1.1-1.35	4-5	3-3.5	22.5-26	3.7-4.2	1.8-2.2		Balance		0.02-0.18 N	

† Tribaloy®, Deloro®, Nistelle® and Tristelle® are registered trademarks of Deloro Stellite, Colmonoy is a registered trademark of Wall Colmonoy.

‡ Single values in AWS classification are maxima.

§ Data for tungsten are given on www.matweb.com.

|| Double pass.

¶ Single pass.

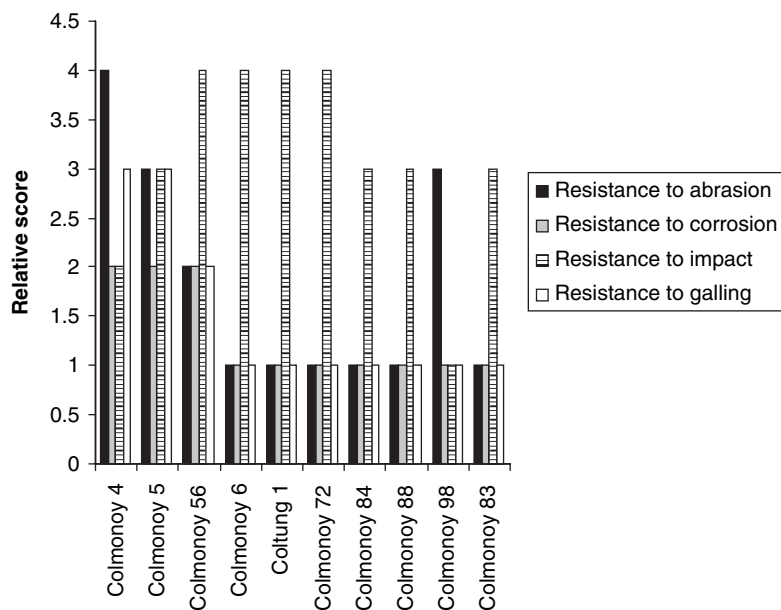
Table 9.13 Principal characteristics and applications of selected nickel-based and high-silicon stainless steel hardfacing materials^{30, 34, 38, 71}

Alloy	Principal characteristics	Applications
Deloro® 40 Colmonoy 4 ERNiCr-A	Contains chromium borides and carbides Takes a high polish; resists low-stress abrasion, heat, corrosion and galling Excellent impact resistance, greater than Colmonoy 5 Good machinability	Glass forming plungers, dies, moulds, valves
Deloro® 45 Deloro® 50 Colmonoy 5 ERNiCr-B	Intermediate between Deloro® 40 and 50 Contains chromium borides and carbides Hard dense corrosion-resistant coating with good fusing characteristics Suitable for mild impact (lower crack sensitivity but poorer abrasion resistance than Deloro® 60) Hot hardness maintained to approximately 400 °C Machine with carbide tools	Glass forming plungers Extruder screw flights, wear rings, plungers, dies, bearings, camshafts and diesel engine valve facings, seal rings, cylinder liners, stem guides and sleeves
Colmonoy 56 ERNiCr-B/C	Contains chromium borides and carbides Between Colmonoy 6 and 5 in chemistry and hardness. Better ductility and impact resistance than Colmonoy 6 Machine with carbide tools	Plastic extrusion screws and shafts and sleeves
Deloro® 60 Colmonoy 6 ERNiCr-C	Original nickel-based hardsurfacing alloy, contains chromium borides and carbides Good abrasion and corrosion resistance; low coefficient of friction	Pump plungers, seal rings, shafts, sleeves, valve trim, mechanical couplings and machine parts subject to sliding contact and abrasive particles

Nistelle C	Can be hot formed Best finished by grinding Good resistance to oxidising acids, such as nitric and sulphuric acids Good cavitation, metal-to-metal wear and abrasion resistance Excellent high-temperature strength (up to 1035°C) and resistance to oxidation Readily machinable More resistant to cracking during welding than ERNiCr-A, ERNiCr-B and ERNiCr-C	Pumps and valve parts in the chemical, pulp and paper industries, and hardfacing of drop-forging dies
ERNiCr-D and ERNiCr-E	More resistant to cracking during welding than ERNiCr-A, ERNiCr-B and ERNiCr-C	Trims of fluid control valves. Used as replacement for cobalt-containing weld overlays in the nuclear industry
Colmonoy 72	Excellent resistance to low-stress abrasion, and scouring action Wear resistance often superior to Colmonoy 6 Finish by grinding Nickel-based alternative to cobalt-based surfacing alloys Suitable for service up to 815°C	Pump parts Nuclear industry
Colmonoy 84	Fine (5–10 µm) complex bi and trimetallic borides and carbides uniformly precipitated in an Ni–Cr–B matrix	Glass mould plungers, pump plungers and sleeves, valve seats, plastic extrusion screws and barrels, centrifuges and wire-drawing capstans
Colmonoy 88	Excellent abrasion and corrosion resistance at high temperatures Low coefficient of friction Finish by grinding or CBN tools Superior resistance to corrosive liquids Low coefficient of friction	
Colmonoy 98		

Table 9.13 Continued

Alloy	Principal characteristics	Applications
ERNiCrMo-5A	Maintain hardness at 760 °C	Rebuild hot extrusion and forging dies, sizing punches, hot shear blades and guide rolls
ERNiCrFeCo	Excellent resistance to high temperature wear and impact Similar abrasive wear properties to ERCoCr-C or ERNiCr-C but poorer corrosion and galling resistance	Feed screws, slurry pumps, mixer components where high abrasion and low impact are factors
Coltung 1	Sensitive to cracking during cooling; poor impact properties Ni-Cr-B matrix alloy rich in chromium boride used to hold tungsten carbide particles	Cement industry conveyors pumps, screw flights, root cutters and coal cutter bits
Colmonoy 57PTA	Finished by grinding Ni-Cr-B alloy containing optimised amounts of precipitated tungsten-rich hard phases	Flights of new and rebuilt extrusion or injection moulding screws, feed screws, air locks and scraper blades
Colmonoy 83	Ni-Cr-W-B matrix containing chromium carbides with the addition of tungsten carbide particles	
Colmonoy 635	Excellent abrasion resistance; excellent edge retention Ni-Cr-B matrix used to hold tungsten carbide particles	
Colmonoy 705	Excellent protection against abrasive wear Ni-Cr-B matrix used to hold tungsten carbide particles	Screw conveyors and augers
Tribaloy T-700	Excellent protection against severe sliding abrasion High corrosion and oxidation resistance	Valve trim in the nuclear industry
Tristelle TS-1	Not susceptible to radiation activation	
TS-2 and TS-3	Outstanding resistance to sliding wear and cavitation erosion	
Tristelle 5183	Good resistance to corrosion Outstanding resistance to sliding wear and cavitation erosion Good resistance to corrosion	Cobalt-free alloy, alternative to Stellite® 6 for the nuclear industry

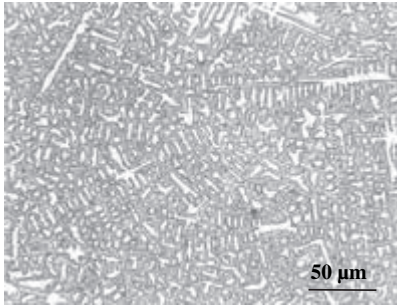


9.14 The relative performances of selected nickel-based alloys to abrasion, impact, galling and corrosion. A score of 1 is best, and a score of 4 is worst.⁷¹

and forms the intermetallic compound Ni_3Si . The higher the boron content, the lower is the silicon content required to form the silicide. The silicon content thus has a major influence on wear resistance. Complex carbides of M_{23}C_6 and M_7C_3 types are also present. When the silicon-to-boron ratio is greater than 3.3, e.g. as in ERNiCr-D and ERNiCr-E, a structure consisting of a nickel solid solution, a binary eutectic of nickel solid solution and a nickel silicide, and a ternary eutectic of nickel solid solution, nickel silicide and nickel boride is formed which has a greater resistance to cracking than the binary nickel solid solution–nickel boride binary eutectic present in the ERNiCr-A, ERNiCr-B and ERNiCr-C alloys.

The abrasion resistance of these alloys is a function of the amount of hard borides present in the matrix. Problems associated with the weld deposition of these nickel-based alloys include the high fluidity of the molten alloy, generation of residual stress in the deposit that can lead to cracking, and a significant dilution of the deposit by the substrate material due to the large difference in their melting temperatures.⁷²

Figure 9.10 includes data on the abrasion performance of some of the principal boride-containing nickel-based alloys while Fig. 9.14 shows the



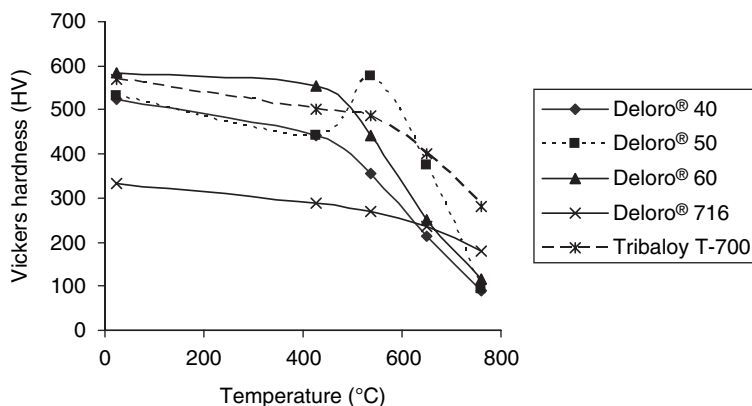
9.15 Microstructure of Deloro® 45 deposited by GTAW (peroxide etch). (Micrograph courtesy of Deloro Stellite.)

relative performances of these materials against abrasion, galling, impact and corrosion.⁷⁰ Low-stress abrasion resistance increases with increasing volume fraction of hard phases, and hence with increasing boron and carbon contents. These alloys exhibit moderate resistance to galling, Colmonoy 6 having the highest and Colmonoy 4 and 5 the lowest, the latter alloy types (ERNiCr-A and ERNiCr-B) having poorer galling resistance to Stellite® 6 when deposited by GTAW.⁷³ Figure 9.11 and Fig. 9.12 include adhesive wear data on ERNiCr-C (Deloro® 60 or Colmonoy 6). In general, this material exhibits poorer adhesive wear behaviour than Stellite® 6 and 12, but the nature of the mating surface is important. However, of the non-ferrous materials the boride-containing nickel-based alloys are least resistant to corrosion. This is thought to be due to the low chromium content in the matrix after boride and carbide precipitation. ERNiCr-A exhibits the best impact strength.

These boride-containing nickel-based alloys also exhibit good high-temperature strength as can be seen from Fig. 9.16 which gives the hardness of the GTAW-deposited coating at various temperatures. Comparing the data for these boride-containing alloys with those of the carbide-containing cobalt-based alloys given in Fig. 9.13 reveals that both alloy families have similar high-temperature hardnesses.

Carbide-containing alloys

After their use in the nuclear industry, cobalt-based hardfacing alloys are sources of the highly radioactive ⁶⁰Co isotope. Hence, carbide-containing nickel-based alloys with similar properties have been developed. Table 9.12 includes the compositions of several nickel-based alloys containing chromium carbide. These alloys, depending on the precise composition, contain



9.16 Vickers hardness as a function of temperature for various nickel-based hardfacing alloys.³⁸

M_7C_3 or M_6C in a similar way to cobalt-based alloys. Figure 9.14 also includes the relative performances of these materials (namely Colmonoy 72, 84, 88 and 98) against abrasion, galling, impact and corrosion. They exhibit excellent abrasion and galling resistances and their corrosion resistances are better than those of the boride-containing nickel-based alloys. In general, their impact strength is poor. Of this alloy family, Colmonoy 98 shows the best impact properties but poorest abrasive wear resistance.

ERNiCrFeCo alloys contain a large volume fraction of hypereutectic chromium carbides distributed throughout the microstructure, making the alloy prone to cracking on cooling after welding. They have similar abrasion resistances to ERNiCr-C and ERCoCr-C but their reduced nickel and cobalt contents with respect to those alloys results in a lower corrosion and galling resistance.

Laves phase alloys

Only one Laves-phase-containing nickel-based alloy is commercially available, namely Tribaloy T-700. The composition of this alloy is also included in Table 9.12. The Laves phase may be $NiMoSi$, Ni_3Mo_2Si or both. Chromium is present for oxidation and corrosion resistance. The amount of Laves phase constitutes normally approximately 50 vol.% by volume and has two distinct crystal structures: hexagonal and dihexagonal.^{74,75} The fracture toughness of this alloy is similar to that of Tribaloy T-400 and T-800 but the strength is some 40–71% less.⁷⁴ This is thought to be a consequence of

the larger size of the Laves phase precipitates in T-700 than in the cobalt-based alloys T-400 and T-800. Figure 9.11 and Fig. 9.12 include adhesive wear data for this alloy sliding against various substrates. In general, it has poorer adhesive wear properties than the corresponding Laves-phase-containing cobalt-based alloy T-400. In particular, it suffers poorer performance when self-mated; however, the nature of the mating surface affects the performance substantially (Fig. 9.11 and Fig. 9.12). Figure 9.10 includes the abrasive wear properties of this alloy while Fig. 9.16 gives the hardness of the as-GTAW-deposited alloy as a function of temperature. As for the cobalt-based alloys with Laves phase, the wear resistance is highly dependent on the volume fraction of Laves phase, which is a function of dilution and cooling rate. Dilution inevitably means that the coating contains iron from the substrate. This reduces the volume fraction of the Laves phase and increases the stability of the hexagonal-type structure at the expense of the dihexagonal structure. These microstructural changes bring about a significant improvement in strength, a modest improvement in toughness but a decrease in hardness.⁷⁴ However, the presence of iron gives rise to an increase in hardness after holding at 700 °C which is not obtained in T-700 without iron.

This hardfacing has good high-temperature corrosion and oxidation resistance; however, its hot corrosion resistance at 650 °C was reported to be slightly inferior to those of Stellite® 6 and 12.⁶⁹ This alloy can be readily deposited by GTAW or PTA welding processes. Although it has good metal-to-metal wear resistance, especially at elevated temperatures,^{68,69} and moderate abrasive wear resistance, its main limitation is that it possesses poor impact strength. As it does not contain cobalt, it finds use in valves and valve seats in nuclear reactors.

9.4.5 Composite materials

Chromium, tungsten and titanium carbides can be added to cobalt- and nickel-based materials in various proportions (20–70%) to provide enhanced resistance to abrasion and erosion, particularly at high temperatures. The compositions of several of these alloys are given in Table 9.12 and Table 9.14. Table 9.14 gives the hardnesses of the carbide and matrix of several of these materials. Figure 9.14 includes the comparative abrasion, galling, impact and corrosion resistance of two alloys (Coltung 1 and Colmonoy 83) which contain tungsten carbide. Excellent abrasion resistance, galling resistance and corrosion resistance are obtained at the expense of poor impact properties. Colmonoy 83 which contains chromium and tungsten carbides in a Cr–W–B matrix has excellent edge retention and galling resistance.^{70,76} Care must be taken to ensure that excessive dissolution of the tungsten

Table 9.14 Compositions and hardnesses of several proprietary composite cobalt- and nickel-based hardfacings^{51, 52}

Material, commercial name†	Composition	Rockwell C hardness of the matrix (HRC)	Vickers hardness of the carbide (HV)
Stelcar® 1215	15% TiC + pre-alloyed Stellite® 12	40	>3000
Stelcar® 60	47% WC + 53% Deloro® 60	60	2300
Super Stelcar® 40, 50, 60 and 70	Blends of coarse WC and Deloro® 50. Number indicates % WC	Depends on blend and deposition method	

† Stelcar® is a registered trademark of Deloro Stellite.

carbide does not take place during the hardfacing operation. Dissolved tungsten carbide precipitates either as WC in nickel-based and cobalt-based alloys with a high carbon content, or as W_2C or η -phase complex carbides in these melts with a low carbon concentration. The η carbides exist over a wide composition range and readily occur in the form of M_6C and $M_{12}C$ in the Ni–W–C and Co–W–C systems. Both W_2C and η carbides are very brittle and their corrosion and wear resistances are also inferior to those of WC.⁷⁷

The presence of carbide additions to these alloys can result in an increase in the propensity for thermal fatigue, cracks initiating at the incoherent carbides and propagating along their boundaries; e.g. under the same experimental conditions thermal fatigue cracks were found in PTA-welded Stellite® 6 with 30 wt% Cr_3C_2 but not in Stellite® 6 with no carbide additions.⁷⁸ However, the wear resistance of this composite material was about an order of magnitude better than without the carbide addition even when tested after a thermal fatigue treatment. The dry sliding-wear resistance at 450 °C of the composite material, but not Stellite® 6, improved considerably after an oxidation treatment at 700 °C for 100h when significant Cr_3O_2 formed on the chromium carbide phase as well as the matrix. The presence of this oxide layer seems to compensate for the presence of cracks in the thermally fatigued material and to account for only a moderate increase in wear rate of the thermally fatigued composite material compared with that of the as welded composite sample.

9.4.6 High-silicon stainless steels and cobalt-free iron-based hardfacing alloys

Several high-silicon stainless steels have been introduced as alternative lower-cost materials to cobalt-based alloys (see Table 9.12 for their compositions). These have similar antigalling and cavitation erosion resistances. Some are based on type 200 stainless steels (manganese- and nitrogen-containing austenitic stainless steels) and others are based on type 300 stainless steels, e.g. the Tristelle series of alloys. These alloys have inherently good corrosion resistance due to their high chromium and nickel contents but in addition contain silicon and cobalt additions which impart improved sliding wear and cavitation resistance. In a comparative study of coatings and hardfacings for corrosion and wear resistance in diesel engines, Tristelle TS-2 was found to have superior hot corrosion resistance^{69,70} to Stellite® 6, 12, 20, Tribaloy T-800 and T-700 at 650 °C. However, the hot wear performance of the former in an accelerated rotating sliding wear test was inferior to those of the latter alloys.

Carbide-strengthened austenitic iron-based alloys have been found to exhibit galling resistances similar to those of cobalt-based alloys. The austenite matrix is similar in composition to that of the galling-resistant alloy Nitronic 60 (Fe–18% Cr–8% Ni–8% Mn–4% Si–0.12% N).⁷⁹ Carbon and manganese additions improved the galling resistance; the effect of manganese was possibly through its effect on work hardening, as in Hadfield manganese steels. The corrosion resistances of these stainless steels can be better or worse than those of cobalt-based materials depending on the aqueous media.

As mentioned previously, cobalt-containing alloys are a source of occupational radiation exposure to plant maintenance personnel. This has recently led to the development of cobalt-free materials that have high galling resistances suitable for use in valves in the nuclear industry. Various iron-based hardfacing alloys have been proposed and their galling resistances determined.⁷³ Their microstructures consist of a continuous matrix of interdendritic carbide–austenite lamellae, which separates iron-phase dendrites that contain various amounts of austenite and δ ferrite.^{80,81} The microstructure of the austenite is of prime importance as, under sliding conditions, the galling resistance is generally dependent on the matrix structure, the amount of δ ferrite present in the dendrites, the strain-hardening behaviour and to a lesser extent the nature of any hard phases.⁸² Greater amounts of δ ferrite in the dendrites tend to result in higher values of threshold galling stress and hardness.⁸³ A higher hardness would improve resistance to adhesive transfer and galling. However, the δ ferrite content of the dendrite also has a strong influence on the amount of plastic stretching and necking of the dendrites in the wake of a propagating crack tip. This influences the amount of crack-bridging

toughening which controls the fracture toughness; thus the greater the δ ferrite content, the lower is the fracture toughness.

NOREM[®] 02 is one such iron-based alloy; the dendrites in its microstructure, although primarily austenite, contain a moderate amount of δ ferrite; its nominal composition is given in Table 9.12. The level of δ ferrite present is sufficient to provide a high level of galling resistance but the δ ferrite content is low enough that crack-bridging toughening is not limited, resulting in a fairly high fracture toughness.⁸³ It thus has a high resistance to galling, cavitation erosion and corrosion.⁸⁴ However, although laboratory tests showed that its sliding wear resistance was nearly equivalent to that of Stellite[®] 6 in the temperature range below 180°C, with further increase in temperature the wear mode changed abruptly to severe adhesive wear at 190°C and galling occurred⁸⁵ above 200°C. It is thought that its good wear resistance is based on the low stacking-fault energy of the matrix which suppresses cross-slip of dislocations, resulting in an increased work-hardening rate.⁸¹ Thus galling resistance is provided by preventing severe plastic deformation at the asperity contacts. However, the stacking-fault energy in general decreases with increasing temperature and thus cross-slip becomes easier at higher temperatures. This means that the wear resistance of an alloy based on a low stacking-fault energy can decrease significantly as the temperature increases. In addition strain-induced α' martensite forms during plastic deformation of this FCC structure and it has been proposed that this also helps, as in cobalt-based materials, to give rise to good galling resistance. The presence of δ ferrite provides a larger austenite–ferrite boundary area, which could promote the strain-induced phase transformation from austenite to martensite. However, the strain-induced phase transformation has a characteristic temperature M_d , above which it does not occur. For NOREM[®] 02 that temperature is located between 180 and 190°C. The amount of martensitic phase formed by strain-induced transformation decreases exponentially just below⁸⁶ M_d . Hence the dependence on temperature of the sliding wear resistance of NOREM[®] 02 can be understood. Raising M_d thus suggests itself as a means of increasing the temperature range over which the alloy exhibits good galling resistance. This can be achieved by alloying additions; e.g. an alloy of nominal composition Fe–20% Cr–1.7% C–1% Si was reported to exhibit similar sliding wear characteristics to Stellite[®] 6 in water⁸⁷ up to 250°C. However, care must be taken in drawing inferences from laboratory tests as to service performance as the nature of any oxide film also plays an important role in determining wear behaviour⁸⁸ and thus the precise test conditions and service conditions are important. This alloy also has a cavitation erosion resistance similar to Stellite[®] 6, which was attributed to the hardened matrix that could suppress the propagation of cracks initiated at the carbide–matrix interfaces.⁸⁹ Dilution during deposition can affect the chemical

composition of the coating, changing the δ ferrite content in the dendrites and M_d , which results in a decrease in galling resistance. Deposition parameters must therefore be closely controlled so as to maintain the optimum δ ferrite content needed for galling resistance and damage tolerance.⁸³

9.4.7 Copper-based alloys

Copper-based alloys that are used for surfacing fall into four copper alloy families. These are Cu–Zn, Cu–Si, Cu–Sn and Cu–Al. The Cu–Zn alloys are used for very soft bearing surfaces and mild corrosion, the Cu–Si alloys for corrosion-resistant surfaces, the Cu–Sn alloys for soft bearings and corrosion-resistant surfaces and the Cu–Al alloys for bearings of higher hardness and corrosion-, erosion-, cavitation- and wear-resistant surfaces. The compositions of typical alloys are given in Table 9.15, and Table 9.16 presents typical as-deposited hardness values.^{30,34,90} ERCuSn-A, ERCuSn-C, ERCuSi-A and ERCuAl-A2 are used for the restoration of corroded or eroded components, e.g. pump impellers. Thick sections are surfaced using GMAW, while thinner sections are usually repaired using GTAW. ECuNiAl and ECuMnNiAl are used for restoring naval propellers.

Copper-based materials can be utilised in metal-to-metal wear applications. In these applications, either the clad surface can wear in preference to the mating surface, or the clad surface acts as a hardfacing and resists wear. Typical materials in the first category are ERCuSn-A, ERCuSn-C, ERCuAl-A1, ERCuAl-A2, ERCuAl-A3 and a filler metal with a Brinell hardness some 50–75 HB below that of the mating surface should be selected. In the wear-resistant hardfacing category, typical materials are the aluminium bronzes ERCuAl-C and ERCuAl-D. Aluminium, silicon and iron are added to bronzes to strengthen their solid solution and, in excess of their solid solution limit, to promote precipitation hardening. Hardening is by β phase (Cu_3Al) and its partial or complete decomposition to Cu_2Al and copper. The bronzes with lower aluminium content are more ductile but less hard; the alloys with higher aluminium content have a Brinell hardness of 300 HB but very limited ductility. Aluminium bronzes possess anti-galling characteristics (self-coupled) similar to those of ERCoCr-E. This is attributed to planar slip during deformation which, as in cobalt-based materials, delays the onset and progression of microfatigue. Aluminium bronzes have high cavitation erosion resistance and biofouling resistance in seawater. The low-stress abrasion resistance is, however, very low. These alloys are not recommended for elevated-temperature use as their mechanical properties fall off considerably above 200 °C. Table 9.16 give typical applications of these materials.

When surfacing with copper-based alloys on iron-based material, care must be taken to minimise dilution as excessive iron pick-up will result in

Table 9.15 Chemical compositions of copper-based surfacing alloys; single figures are maxima^{34, 37, 90}

AWS classification	Composition (wt%)						
	Fe	Cu	Al	Zn	Si	Pb	Sn
CuZn-C	0.25-1.2	56-60		Balance	0.04-0.15		0.8-1.1
ERCuSi-A	0.5	Balance	0.01	1	2.8-4	0.02	1
ERCuSn-A		Balance	0.01			0.02	4-6
ERCuSn-C	0.25		0.01			0.02	7-9
ERCuSn-D		88.5 minimum	0.01			0.05	9-11
CuAl-A1		Balance	6-8.5				
ERCuAl-A2	0.5-1.5	Balance	8.5-11	0.02	0.10	0.02	
ERCuAl-A3	2-4.5	Balance	10-11.5	0.10	0.10	0.02	
ERCuAl-C	3-5	Balance	12-13	0.02	0.04	0.02	
ERCuAl-D	3-5	Balance	13-14	0.02	0.04	0.02	
ERCuAl-E	3-5	Balance	14-15	0.02	0.04	0.02	
ERCuNiAl	3-5	Balance	8.5-9.5	0.1	0.1		4-5 Ni
ERCuMnNiAl	2-4	Balance	7-8.5	0.15	0.1		0.6-3.5Mn 1.5-3 Ni 11-14Mn

Table 9.16 Properties and applications of copper-based surfacing alloys^{30, 34, 90}

AWS Classification	As-deposited Brinell hardness (HB)	Applications	Examples
CuZn-C	90†	Bearing and corrosion-resistant surfaces	Restore pump impellers
ERCuSi-A	80–100†	Corrosion-resistant surfaces	
ERCuSn-A	70–85†	Bearing and corrosion-resistant surfaces	Preferential wear applications include hydraulic piston heads, sheet mill guides, bushings, flood control valves and paper mill rolls. Corrosion applications include restoration of pump impellers
ECuSn-C	90†	Bearing and corrosion-resistant surfaces	
ERCuAl-A2	130–150	Bearing and corrosion-resistant surfaces	Surfacing drawing and forming dies for deep drawing mild steel, stainless steel, aluminium and titanium in the appliance, automotive and defence industries. Surfacing worn sleeves, sprockets, cams, pinions and gears
ERCuAl-A3	166	Bearing and cavitation-resistant surfaces	
ERCuAl-C	250–290	Bearing and cavitation-resistant surfaces	Restore nickel aluminium bronze components
ERCuAl-D	310–350	Bearing surfaces	
ERCuAl-E	340–380	Bearing surfaces	Restore or surface manganese nickel aluminium bronze components
ECuNiAl	160–200‡	Surface with high resistance to corrosion, erosion and cavitation in salt or brackish water	
ECuMnNiAl	160–200‡	Surface with excellent resistance to corrosion, erosion and cavitation	

† 500kg load.
‡ 3000kgf load.

poor machinability and impair corrosion, cavitation and wear resistance. Minimum current should be used to form the first layer and claddings made using a minimum of two or three layers in order to achieve the desired properties in the final finished deposit.

9.4.8 Materials deposited by friction surfacing

Typical materials that can be deposited by friction surfacing include low-alloy steels, tool steels, high-speed steels, and cobalt- and nickel-based alloys. A particular advantage of this process is that when depositing carbide containing materials the plastic work involved in depositing the coating leads to an ultrafine structure with fine carbides uniformly distributed throughout the structure.¹⁰ An inherent feature of friction surfacing of high-speed steels is the occurrence of self-hardening of the high-speed steel such that only a post-coating tempering treatment needs to be carried out. The hardness has an improvement in consistency of almost an order of magnitude over those obtained by the fusion-welding-based coating processes and this is important in ensuring constant properties along the coating length.⁹¹ Metal matrix composites can also be deposited by this technique; e.g. low-alloy steels containing 250 μm alumina particles can be used as the rod material to form a coating in which the alumina particles have been reduced to 20 μm in size. This coating has a Rockwell C hardness of HRC 66.

Underwater friction surfacing has been carried out to deposit a quench-hardenable martensitic stainless steel (1% C and 17% Cr) on to a low-carbon steel substrate.⁹² A uniform hardness distribution and a refined microstructure were achieved. The deposition efficiency was found to be greater under water than in air because of the cooling effect of the water. In addition, quench cracks were not observed in water owing to the reheating characteristics of the underwater friction-surfacing process.

Friction surfacing is particularly suitable when dilution would otherwise be a problem, when other methods for welding dissimilar metals are problematic and when a coating of approximately 1 mm thickness is required to be placed accurately. It is not recommended when working with thin components (under 2 mm thick), unless they can be adequately supported, because of the high forces involved in the process and in general for depositing high-melting-point materials on to a low-melting-point substrate.

The criterion controlling the component geometries that can be coated by friction surfacing is that of 'line of sight'. This means that most geometries can be coated but not the internal bores of tubes. A particularly suitable application of friction surfacing is that of industrial machine knives for the wood, paper, granulating and packaging industries.⁹³ In this application the ability to maintain a cutting edge is important and tool steels are the most appropriate hardfacing. The fine carbide distribution in the friction-

surfaced tool steel material gives between twice and 20 times longer life between sharpenings.⁹³ Derivatives of the basic friction-surfacing process can be used to deposit material on the ends of rods or tubes for manufacturing into a variety of tooling, such as punches and router cutters. Annular deposits can also be made and thus valve seats can be hardfaced.¹⁰

9.5 Hardfacing alloy selection

Hardfacing alloy selection is influenced by the following factors.^{3,94-97}

1. Wear resistance required.
2. Cost.
3. Base metal.
4. Deposition process.
5. Impact resistance.
6. Corrosion resistance.
7. Oxidation resistance.
8. Thermal properties.

In general, the wear resistance increases with increasing carbide content while the impact resistance shows the reverse trend. Thus, when both impact resistance and abrasion resistance are required, a compromise must be made and the most abrasive-resistant alloy that will probably withstand the expected impact is selected. Initial selection should err towards selecting a tougher material, as then any failure is likely to be gradual rather than catastrophic. When impact resistance dominates, austenitic manganese steels reign supreme.

When wear is accompanied by aqueous corrosion from acids and alkalis, such as in the chemical processing or petroleum industries, iron-based materials rarely possess the corrosion resistance needed. Hence nickel- or cobalt-based materials or high-silicon stainless steels are generally recommended.

Similarly, when wear resistance and oxidation and hot corrosion resistance are needed, iron-based alloys are seldom suitable. Adequate oxidation resistance normally requires a high chromium level in the matrix; hence Laves-phase-containing alloys or carbide-containing nickel- or cobalt-based alloys are selected in preference to boride-containing nickel alloys.

When high strength and wear resistance at elevated temperatures are important such as for hot forging dies or valves for service at temperatures above 870 °C, iron-based alloys are again not suitable as martensite tempers at high temperatures. Generally, as the high-temperature strength increases with increasing tungsten and molybdenum contents, cobalt-based alloys containing Laves phases are selected.

9.6 Hardfacing process selection

Service performance requirements influence not only hardfacing alloy selection but also hardfacing process selection. Factors to be considered include the following.

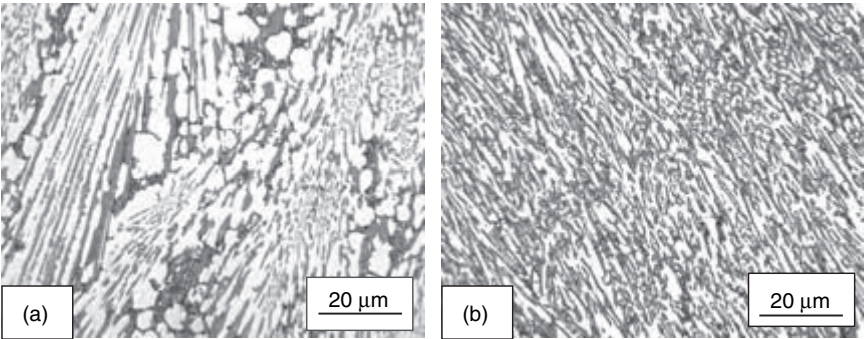
1. Hardfacing property and quality requirements.
2. Physical characteristics of the workpiece.
3. Metallurgical properties of the base metal.
4. Form and composition of the hardfacing alloy.
5. Welder skill.
6. Cost.

Cost is always important but the welding consumable cost need not dominate because welding labour costs are often more critical and expensive alloys may easily be justified when a longer life results.

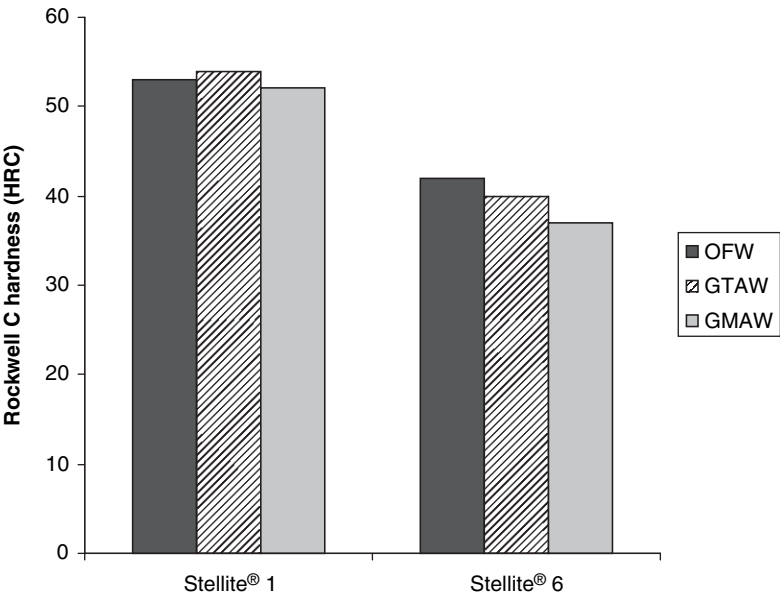
9.6.1 Property and quality requirements

Welded hardfacing deposits are basically fusion welds and so exhibit a cast microstructure. This cast microstructure is influenced by the rate of heat input and extraction, which determines solidification growth morphologies, their scale and microsegregation. As welding processes have different heat input rates, the microstructure varies with welding process. Figure 9.17 presents the microstructure of Stellite[®] 1 deposited by OAW and PTA welding, OAW generally giving a coarser microstructure. In addition, compositional variation also arises from dilution of the hardfacing alloy by the base material and this dilution changes with the welding process (see Table 9.3). Thus the properties of the hardfacing vary somewhat with welding process. Figure 9.18 shows that the room-temperature hardnesses of Stellite[®] 1 and 6 deposited by OFW, GTAW and GMAW differ slightly.

Some dilution is normally essential in order that a metallurgical bond is achieved at the base metal–hardfacing interface but, as the wear resistance and corrosion–oxidation resistance of the hardfacing alloy generally decrease with increase in dilution, this must be controlled. The maximum amount of allowable dilution will depend on specific service requirements and the alloy selected; e.g. the wear resistance of cobalt- and nickel-based alloys containing Laves phase are particularly sensitive to the amount of dilution. In general, a welding process and technique should be selected to give less than 20% dilution for the hardest (top) layer. A greater dilution may be acceptable for build-up layers and indeed might be desirable in some cases, as will be discussed in Section 9.6.3.



9.17 Microstructure of Stellite® 1 deposited by (a) OAW and (b) GMAW. (Samples courtesy of Deloro Stellite.)



9.18 Rockwell C hardnesses of Stellite® 1 and 6 deposited by OFW, GTAW and GMAW.³⁸

9.6.2 Physical characteristics of the workpiece

The size, shape and weight of the workpiece influence the choice of hardfacing process selection. For large heavy workpieces it is usually more convenient to move the hardfacing equipment to the workpiece and so manually operated portable welding processes such as gas-shielded metal arc processes and open arc processes are preferred. For smaller components, which

can be transported to the welding equipment, OFW, SAW, GTAW, PTA welding and GMAW are all suitable for in-plant surfacing of small workpieces. For small workpieces requiring thin, accurately placed hardfacing deposits, OFW and GTAW are normally selected. When large areas are to be hardfaced, processes such as SAW become suitable. When large quantities of small components need hardfacing, dedicated fully automatic equipment is selected. Table 9.2 summarises the advantages and limitations of the various welding processes with respect to the above considerations.

9.6.3 Metallurgical characteristics of the base metal

Steels are the most common base materials. When hardfacing, the main concern is martensite formation in the weld heat-affected zone, which would lead to the formation of a brittle layer and might lead to underbead cracking, causing a section of the hardfacing to spall. Thus the cooling rate must be controlled and preheating (or control of interpass temperature) is required when the carbon equivalent of the base material is greater than approximately 0.4%. The preheating temperature necessary can be obtained from the technical information supplied by the manufacturers of hardfacing consumables or from welding standards, e.g. BS 5135: 1984 (*Arc Welding of Carbon and Carbon Manganese Steels*) although it should be borne in mind that these standards were developed for joining rather than hardfacing. Alternatively the cooling rate can be calculated by the heat flow equations used for the welding of joints and a suitable preheat temperature determined to avoid martensite formation.³ The cooling rate is a function of the net heat input rate h_{net} (arc energy in joules per millimetre) defined as

$$h_{\text{net}} = \frac{\eta EI}{v}$$

where η is the welding heat efficiency (a function of the welding process), E the voltage, I the current and v the welding speed. Hence the welding variables and the welding process have important effects on the propensity to form martensite in a given steel-based material.

In alloy steels, hydrogen cracking can occur in hardfacing as in welding. Thus low-hydrogen processes or electrodes should be used. This can decrease the preheat requirements. With a high-carbon steel substrate a buttering layer from a mild steel electrode should be deposited before hardfacing so as to prevent underbead cracking.

When the base material is a martensitic stainless steel, tool steel or cast iron similar considerations apply. Post-weld heat treatments might be necessary to restore the base material to a suitable microstructural state. Austenitic stainless steels, with the exception of the free machining grades, and most nickel-based materials can be hardfaced by all welding processes.

Age hardening base materials generally requires solution and/or over-ageing heat treatments prior to hardfacing, as well as careful attention to preheat, interpass temperature and post-heat.

The coefficient of thermal expansion of the substrate material affects the thermal stress S developed in the hardfacing through the expression

$$S = E(\alpha_{\text{coating}} - \alpha_{\text{substrate}}) \Delta T$$

where E is Young's modulus, α the coefficient of thermal expansion and ΔT the temperature difference. Thus, when depositing a brittle hardfacing, the workpiece may have to be heated to relatively high temperature during welding so as to reduce the ΔT term in the above equation and so to permit the deposition of a crack-free hardfacing. Insulating the hot part immediately after hardfacing with dry sand, lime or a fibreglass blanket aids more uniform cooling and can help to control residual stresses, weld cracking and distortion.

Differences in the coefficient of thermal expansion of the hardfacing and the base metal can generate thermal stresses in service, leading to thermal fatigue failures. Thus, buffer layers are sometimes deposited between the base metal and the hardfacing to counteract the large differences between the thermal expansion coefficients of the hardfacing and the base metal. In this respect, dilution (normally undesirable) can help to produce a 'graded coating' or *in-situ* buffer layer. Welding process selection is thus important as different welding processes produce different dilution levels.

9.6.4 Hardfacing product form

Hardfacing process selection is obviously affected by the form in which the hardfacing material is available. Table 9.1 indicates the form of the hardfacing consumable required for each welding process. Almost all hardfacing material is available as powder and most can be produced in some type of rod form. Rods can be in bare cast form, if the alloy characteristics permit this, or as tubular rods or wire consisting of a highly alloyed powder core encased in low-alloy sheaths. Metal cored wires are defined as those where metallic materials constitute 95% or more of the core; flux cored wires have more than 5% non-metallic constituents in the core. Bare cast rods and tubular rods are available in diameters from 3.2 to 8 mm and lengths of 250–700 mm. Cored wire diameter can range from 0.9 mm to 6.35 mm and are available in 2–227 kg packs.

Hardfacing with cored wires is increasingly replacing the relatively slower SMAW because of the advances made in weldability, the ease of use and the ability to automate wire application processes.⁴³ Cored wires offer higher deposition rates at lower heat inputs, lower dilution, minimal spatter and smooth tie-ins with multipass beads so as to reduce machining. In addi-

tion, the small-diameter wires now available allow hardfacing applications on thin components at low heat inputs and the cladding of the bores of small-diameter tubing. Wires that can be deposited by spray transfer allow out-of-position welding for situations where a component cannot be positioned for welding to be performed in the flat position.

Electroslag surfacing is normally carried out with strip electrodes, either cast or sintered, which limits the range of materials that can be deposited. Recent developments using a hollow channel electrode filled with particulates⁹⁸ or cored wires⁴³ have extended the range of materials that can be deposited, e.g. Fe–C–Cr alloys. The low penetration and dilution characteristics of this process permit uniformity in composition from the surface to the weld metal–base metal interface, thus allowing wear and corrosion resistances to be maintained during wear of the component.

The non-consumable electroslag process also allows loose fillers such as grit, powder, granules and chips to be used as the consumable material. Conventional microstructures can be achieved, e.g. high-chromium white irons; however, if large-diameter granules are used as a filler or if surfacing is carried out at a high feed speed, the deposited metal will have particles either partially melted or not melted at all and thus a composite structure will result.⁹⁹

9.6.5 Welder skill

In general, manual hardfacing processes such as OFW and GTAW require high welder skills while automatic welding processes such as SAW and PTA welding require a minimum of operator skill once the machine control parameters have been established. Models are being derived to predict the effect of surfacing parameters on the dimension of the weld bead and dilution. These models allow the rapid selection of process parameters to achieve the desired quality of the hardfacing and lead to a reduction in the amount of material deposited and enhanced mechanical and metallurgical properties of the hardfaced layers.¹⁰⁰ Where quality is not at a premium, e.g. when hardfacing earth-moving and mining equipment, lower welder skills when using a manual process are permissible.

9.6.6 Cost

Labour and materials are the main elements of cost. Labour costs depend on the welder skill required, the process deposition rates and the operating factors. Table 9.3 gives typical deposition rates for various welding process used for hardfacing. Deposition rates are normally lowest for manual processes; automatic processes can give deposition rates of the order of 30 kg h⁻¹. For maintenance applications the cost advantage

(CA), of hardfacing over replacement can be studied by means of the expression

$$CA = \frac{CN}{PN} - \frac{CR}{PR}$$

where CN is the cost of a new component plus downtime, CR is the cost of hardfacing plus downtime, PN is the work output during the service life of the new component and PR is the work output during the service life of a hardfaced component.⁴ When the CA is positive, hardfacing is likely to be the best solution. The costs of hardfacing can be determined by taking into account flux costs, shielding gas costs, power costs, welding material costs, labour costs and overhead costs.²⁹ In general, deposition rates for the arc welding processes can be increased by the incorporation of auxiliary electrodes and powders into the molten weld pool; e.g. electrically heated wires can be fed into the weld pool as in the hot-wire GTAW process; extra wire or strips can be fed into the SAW pool. Hardfacing powders can also be fed on to the surface of the work ahead of the arc before the flux is added in SAW. These techniques also have the advantage of reducing dilution as more hardfacing material is deposited for a given amount of base material melting by the arc.

The cost of the welding consumable depends on raw material costs and the form of the welding consumable. For cobalt-, tungsten- and nickel-based hardfacing materials the raw material cost dominates whereas for iron-based material the product form is the dominant factor. Deposit efficiency, measured as the percentage of hardfacing consumable retained on the workpiece (see Table 9.3), must also be taken into account when estimating the total hardfacing cost for a given process.

9.7 Distortion and residual stresses

Distortion and residual stresses in the hardfacing arise owing to the contraction of the deposited metal. Thus when the deposit cools it tries to contract against the resistance of the substrate and the work distorts, as shown in Fig. 9.19. When hardfacing the bore of a die or the periphery of a sleeve, radial contraction occurs, causing rings to become dished or concave. The greater the resistance of the substrate to contraction, the less is the distortion but the higher are the residual tensile stresses, which can either result in hardfacing cracking or fatigue cracking when the component in service is subjected to fluctuating stresses resulting from a fluctuating load or varying temperatures.

Distortion and cracking from tensile residual stresses can be reduced by preheating. As discussed in Section 9.6.3, preheating may also be necessary



9.19 Distortion caused by contraction of the hardfacing deposit.

to prevent the formation of martensite in the substrate. If the part is uniformly heated, the expansion of the part can be used to counteract somewhat the contraction of the hotter hardfacing. The greater the coefficient of expansion of the substrate material, the less is the distortion produced after hardfacing the preheated component. Conversely the greater the coefficient of expansion of the hardfacing, the greater is the distortion. However, during hardfacing a preheated material the contraction of the deposit is partially dissipated by plastic compression of the hot base metal and the plastic extension of the hardfacing; the higher the preheat, the lower is the yield strength and thus the easier is the plastic deformation. This may cause excessive distortion especially when hardfacing hollow sleeves or rings. Another factor that limits the preheating temperature is scaling of the surface of the component and comfort of the operator. Thus, although it is feasible to heat a small article to 600°C, larger components, where the heating time would be longer, can normally only be preheated to a maximum of 450°C.

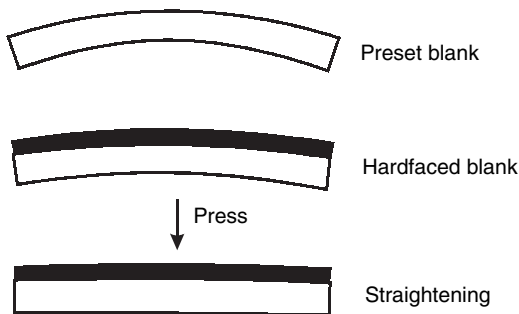
Numerical simulation studies have recently been carried out to reveal the magnitude of the residual stresses present after hardfacing with Stellite® and to quantify approaches that can be taken to reduce these stresses.¹⁰¹ Reducing the base metal thickness, using a base material with a higher coefficient of expansion and preheating were found to give lower residual stresses, as expected. The heat transfer conditions at the surface also affect the residual stress distribution in the hardfacing. If the surface heat transfer was increased by applying additional cooling to the surface, the average residual stresses were reduced. Local post-heating at a specific distance from the hardfacing and the use of an austenitic stainless steel interlayer between the carbon steel and the hardfacing layer could reduce the tensile residual stress in the hardfacing.

When hardfacing with a martensitic steel on a steel with lower carbon content, the formation of martensite in the deposited material and in the heat-affected zone of the substrate as the hardfacing cools to room temperature also affects the residual stresses present as the formation of martensite from austenite is accompanied by a volumetric expansion which on its own would cause a residual compressive stress to develop. The actual

residual stress distribution at room temperature is influenced by the temperature, and thus the time, at which the martensitic transformation takes place in different regions of the hardfacing–substrate heat-affected zone as the component cools to room temperature. The temperature at which the martensitic transformation starts, M_s , is itself a function of the composition of the steel which will be affected by dilution. Numerical simulation has been used to study this effect and it was established that decreasing the martensitic start temperature of the hardfacing material brings about a decrease in the peak values of residual stresses present which were located at the centre of the hardfacing and in the heat-affected zone of the substrate.^{102,103}

Control of distortion and residual stress in the hardfacing also depends, as in the construction of a component or structure by welding, on the skill of the operator and the sequencing of the deposit. The thickness deposited should be limited so that shrinkage stresses do not become excessive. If thicker deposits are required, build-up electrodes should be used before hardfacing. Peening each layer during cooling in a thick build-up can also be carried out to help to relieve residual stresses.

Simple flat components can be pre-bent in the opposite direction to which distortion will take place, as shown in Fig. 9.20 so that the contraction of the deposit on cooling straightens the component. Some mechanical straightening may be necessary but care should be taken to ensure that this generates residual compressive stresses rather than tensile stresses in the deposit. The component can also be restrained by clamps. Intermittent application of the coating so as to produce a discontinuous coating, provided that this is acceptable, can also reduce distortion. Correct sequencing of deposits can reduce distortion considerably by balancing stresses; e.g., to prevent warping when hardfacing a shaft, a short run of deposit should



9.20 The effect of presetting on distortion after hardfacing.

be made along one side parallel to the axis and the shaft should then be turned over and a similar run made on the opposite side to equalise the stresses. Applying the hardfacing in a dot pattern can minimise local overheating and distortion. For components that have to be machined after hardfacing, the part can be hardfaced oversize and machined or ground to size.

When hardfacing is completed, the deposit normally contains residual tensile stresses. For components that are stressed in service or where fatigue loading is present, a stress relief heat treatment should be carried out if possible. Typical stress relief temperatures for carbon steels commence at 450°C, but 600–650°C would be preferred.

9.8 Successful and unsuccessful applications

Hardfacing produces a metallurgical bond to the base material and thus there should be no line of weakness at the interface as can be found in some thermally sprayed coatings. Thick coatings can be deposited using multipass techniques. Successful applications exploit these features of the welding process and examples of successful applications have been given in Section 9.3 where the different hardfacing consumables were described. Unsuccessful applications normally occur for the following reasons.

1. The hardfacing alloy itself is not capable of withstanding the service conditions.
2. Too much dilution has occurred and the microstructure and properties of the deposit have been compromised.
3. Cracking of the deposit has occurred owing to thermal stresses developed in the hardfacing. This is more of a problem when hardfacing massive, highly rigid parts, shrink-fit parts, etc.
4. Cracking of the base metal has occurred in its heat-affected zone.
5. High residual tensile stresses are present in the hardfacing and these stresses have summed with the applied stresses to bring about premature failure under the service stresses acting.
6. Cracking of the hardfacing occurs in service after repeated heating and cooling owing to thermal fatigue induced by the difference between the coefficients of thermal expansion of the base material and the hardfacing. Thermal fatigue cracks can also result from the difference between the thermal expansion coefficient of the matrix and carbides, e.g. between the thermal expansions coefficient of vanadium carbide and the thermal expansion coefficient of the Stellite® 21 alloy to which it is added.¹⁰⁴
7. Cracking of the hardfacing allows a corrosive to penetrate to the base material.

8. Dilution in layers deposited under the top layer has impaired the wear resistance on these layers, leading to more rapid wear once the top layer has been compromised, which hence reduces the total life of the hardfacing.
9. The coating is insufficiently thick to withstand the subsurface stresses caused by the wear process.
10. Defects, namely porosity, cracks and microsegregation, are present in the hardfacing, which impair its fracture toughness and reduce its impact strength.
11. Hard particles present in the hardfacing consumable have either dissolved or decomposed during the deposition process, leading to a hardfacing with a lower wear resistance than expected on the basis of the electrode composition.

Selecting a more suitable hardfacing material or varying the deposition process or parameters so as to achieve the desired microstructure can overcome many of these factors. What cannot be easily changed is the fact that the hardfacing has a different coefficient of thermal expansion from the base material. However, buttering or using dilution to produce a graded microstructure can assist.

9.9 Conclusions

The production of hardfacings by using welding processes to achieve the bond is a well-established industry. It competes directly with thermal spraying and indeed similar coating chemistries can be deposited by both processes. The manufacturers of welding and hardfacing consumables have developed a wide range of alloys with different microstructures and properties. The composite materials involving tungsten carbide particles in a variety of matrix alloys which can be deposited from cored wires allow materials that exhibit extremely good abrasive wear properties to be achieved. Development in the electronics of welding sets has allowed far greater control on deposition parameters than was previously possible and this permits greater quality control on the deposited material. Friction surfacing offers much potential in allowing incompatible materials with a refined microstructure to be deposited with no dilution. These factors suggest that hardfacings produced by a welding process will still find applications in the future in spite of the ever-growing number of different coating processes and coating chemistries available in the marketplace.

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Laser surface treatment methods for protection against wear

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10.1 Introduction

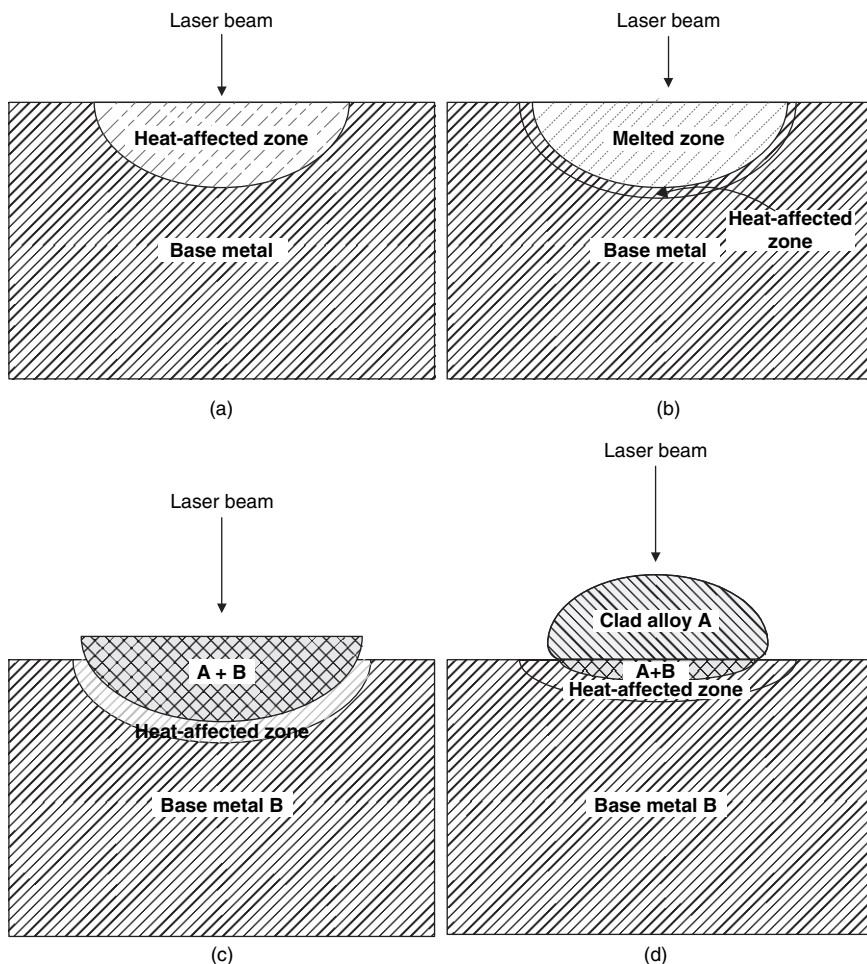
Since high-power kilowatt-range carbon dioxide lasers became commercially available in the mid-1970s, there has been a persistent and enthusiastic research and development effort to turn this high-energy-intensity optical beam into a useful surface engineering tool. In the past 30 years, a large number of research papers and monographs have been published reporting mainly on the laboratory success of various laser surface engineering (LSE) techniques in improving corrosion resistance and wear resistance. However, published reports on successful industrial applications of LSE technologies for the improvement of wear resistance are relatively rare. An attempt is made in this chapter to review some of the latest findings in the laboratory environment and some real industrial applications of LSE for enhancing wear resistance. It must be emphasised that different types of laser have been successfully employed in a range of industries to improve various material surface properties for different applications and this chapter will only focus on the application of high-power infrared lasers for the enhancement of the wear resistance of metallic components.

10.2 Operation principles

LSE represents a group of laser processing technologies, namely laser transformation hardening (LTH), laser surface melting (LSM), laser surface alloying (LSA) and laser surface cladding (LSC), which are depicted in Fig. 10.1.

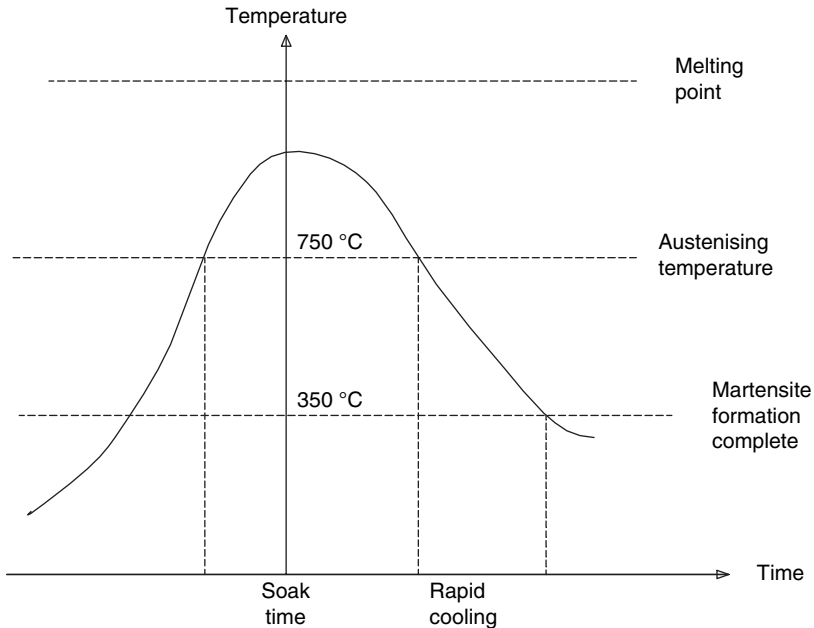
10.2.1 Laser transformation hardening

LTH is mainly used for the surface hardening of ferrous alloys (e.g. carbon steel and cast iron) by a solid-state transformation mechanism from austenite to martensite under a rapid heating and cooling thermal cycle, as



10.1 Various LSE techniques and the terminology used: (a) LTH; (b) LSM; (c) LSA; (d) LSC.

illustrated in Fig. 10.2. When the laser beam irradiates the metal surface, the infrared energy absorbed by the electrons and atoms at the metal surface causes very rapid heating of a thin layer of metal near the surface. When the beam is moved to a different area on the surface, the heat deposited in this layer will be quickly conducted away to the substrate. As there is no interfacial gap between the heated region and the substrate, the cooling rate of the heated volume of metal can be as high as $1 \times 10^5 \text{ }^\circ\text{C s}^{-1}$. The cooling rate depends on the laser processing parameters such as power intensity, total energy absorbed, interaction time and volume of the heat sink, i.e. thickness of the substrate. The microstructure of the martensite and hence the hardness obtained at the surface are affected by the cooling



10.2 The rapid heating and cooling cycle of LTH and the formation of martensite.

rate and the base metal composition. Careful process control with an optimum combination of power intensity and interaction time leads to a hardened surface without any sign of surface melting. Surface melting should be avoided as it will ruin the surface dimension, and post-heat treatment machining is then required. LTH has found application mainly on ferrous alloys, as discussed in Section 10.5.

10.2.2 Laser surface melting

LSM involves the use of a high-energy-intensity beam to scan the surface of a metallic substrate in a shielded gas atmosphere. The laser energy density, interaction time and shielding gas affect the nature of the melted region. The heat input from the laser has to be sufficient to achieve melting of a thin surface layer, normally less than 1 mm thick, and no vaporisation should occur. The rapid solidification rate associated with this technique leads to refined microstructures and in certain alloys to the formation of metastable crystalline or non-crystalline phases. Most research effort have been directed to surface melting of ferrous and non-ferrous alloys for refining and homogenising surface microstructures which can enhance corrosion- and wear-resistant properties.^{1,2}

10.2.3 Laser surface alloying

The objective of LSA is to mix an additional material with the molten surface of the substrate so that, upon solidification, an alloy surface with a different composition from that of the substrate can be obtained. The properties of the alloyed surface can be tailored to suit different requirements. Much research work on LSA has been directed towards producing a hard-facing layer or an improved corrosion-resistant layer. The structure of the laser-alloyed layer often contains supersaturated solid solutions and sometimes intermetallic compounds. In addition to the metallic components that can be alloyed to the substrate surface, ceramic components can also be added so as to achieve a metal matrix composite surface with significantly increased hardness on the metal substrate. The additional material can be applied by pre-pasting or electroplating on the substrate surface prior to the laser melting process. Because of the Marangoni convective flow within the molten pool, a good composition distribution can be obtained. By varying the process parameters, the level of dilution and the degree of melting of the hard-phase ceramic powders, in the case of a metal matrix composite coating, can be controlled. A surface-alloyed layer of the order of 0.1–1 mm is often used.

10.2.4 Laser surface cladding

LSC uses a high-power laser beam to melt the coating material and a thin surface layer of the substrate to form a coating 50 μm –2 mm thick with low dilution. The clad layer is metallurgically bonded to the substrate. Laser cladding has found applications in improving wear and corrosion resistance, reclamation of worn parts, and improvements to electrical and thermal conductivity. Similar to LSA, only the area of components that are subject to wear are clad. LSC with coaxial or off-axis powder injection is most popular and has found practical application in industry because it is more energy efficient and permits better process control and reproducibility. The properties of the clad layer can be tailored so as to meet service requirements.

10.3 Lasers for laser surface engineering

Carbon dioxide (CO_2) lasers and neodymium-doped yttrium aluminium garnet (Nd-YAG) lasers with output wavelengths of 10.6 and 1.06 μm respectively dominated LSE processes for a long time¹ until the kilowatt-range high-power diode laser with output wavelengths at 0.808 and 0.940 μm became commercially available a few years ago. The beams from the CO_2 and Nd-YAG lasers are circular and normally assume a Gaussian or low-

order mode power distribution. In some applications that demand a large interaction beam size or uniform power distribution across the beam profile, a beam raster unit or beam integrators are used. On the other hand, the high-power diode laser beam is normally of a rectangular shape with a top-hat power intensity. This beam can be used for wide-area application with less optical complexity than that required for CO₂ and Nd-YAG lasers. In addition, the shorter wavelength of the diode laser beam allows higher energy absorption by the cold metal surface than that of CO₂ and Nd-YAG lasers. The smaller footprint, lower investment cost, easy maintenance and preferred beam profile for surface treatment have led to the increased popularity of this type of laser for LSE.²⁻⁴

10.4 Advantages and limitations of laser surface engineering

LSE can be applied precisely to a small and specific surface area of a metal component where enhanced wear resistance is desired. Because of its high power intensity and power delivery rate at the localised region, rapid heating of a small volume of metal to the desired temperature is possible. The high heating rate also gives less heat loss to the substrate by conduction, and the total heat input to the component is small, resulting in minimum thermal residual stress and heat distortion. The latter helps to reduce the number of post-heat treatment processes that are frequently needed in many other surfacing techniques.

LSC and LSA offer the ability to tailor make the composition of the surface of interest and at the same time to form a metallurgical bond between the clad layer and the substrate. This type of bond cannot be achieved by other surfacing techniques except arc surfacing and friction cladding. However, those techniques induce a large heat-affected zone and heat distortion.

The major well-known limitation of LSE put forward by technology commentators is its slow area coverage rate. This is, in fact, a wrong impression derived from improper comparisons with other surfacing techniques. LSE should be considered for what it is good at, i.e. treating localised areas and not large areas. Also, it is often the case that, by good design of the laser treatment pattern, it is not necessary to treat the entire surface to achieve the same wear-resistant effect. A good example of this is the laser hardening of the surface of the bore of engine cylinders in which spiral hardened tracks with a wide spacing are sufficient to enhance the wear resistance of the cylinder inner surface by three to four times. Current research on wide track cladding, i.e. greater than 15 mm, using specially designed optics and/or using diode lasers has shown very promising results.⁵

Another limitation of LSE is its high capital cost. To utilize its unique property of rapid heating rate and to realise its capacity of production fully, the laser system must consist of robotic work-handling facilities which constitute the major proportion of the total equipment cost. Although the cost of the laser source alone has decreased steadily over the years, the total system cost is still relatively high compared with other surface engineering techniques. However, the advantages of LSE such as low distortion, fewer post-treatment machining steps, no environmental problems, etc., should be considered in the cost equation before the conclusion of high cost is made.

10.5 Applications on ferrous alloys

The most widely applied LSE process in industry is laser surface hardening (LSH) of ferrous alloys. Successful industrial adoption of this process dates back to as early as the mid-1970s to the hardening of ferritic malleable iron steering gear housings at Saginaw by General Motors.⁶ A large amount of literature dealing with the microstructures, heat transfer mechanisms, hardness and wear resistance improvements has been published. The technologies involved in the LSH of ferrous alloys have been more or less well established. The process involves heating a small volume of ferrous alloy to above the austenising temperature such that the carbon atoms, either from the carbide phase in pearlite or from the graphite phase in cast iron, dissolve in the austenite phase. When the laser beam is removed and rapid quenching is effected owing to the rapid heat loss by conduction to the substrate, a fine martensitic structure is formed which contributes to the increase in hardness. Because of the increase in volume of the surface layer due to the martensitic transformation, a residual compressive stress is built up at the surface and this contributes to the improvement of fatigue resistance. The increase in hardness and fatigue resistance accounts for the increase in the wear resistance of LSH components. Hence, any factor that affects carbon diffusion in the austenite during the heating period and the martensitic transformation during the quenching period will influence the hardening response of the ferrous alloys.

The effectiveness of laser hardening of different ferrous alloys can be grouped into three categories, as shown in Table 10.1.

The wear resistance of the liners of cast iron engines can be improved by 300% by using spiral laser-hardened tracks. This technology has been widely adopted by the car maintenance industry in developed countries. Other successful examples are the surface hardening of cam shafts, gears, piston rings, etc. The hardened case ranges from 0.3 to 1 mm depending on the laser material interaction time and incident power intensity.

LSM of cast iron camshafts using 6kW CO₂ lasers is being commercialised in the automobile industry. LSM of cast iron produces a thin surface

Table 10.1 LSH effect on various ferrous alloys

Excellent	Fair	Poor
0.35–0.8% C steel	0.15–0.3% C steel	<0.1% C steel
Tool steel	Annealed carbon steel	Ferritic stainless steel
Martensitic stainless steel	Spheriodised carbon steel	Austenitic stainless steel
Pearlitic cast iron (grey, malleable, nodular)	Ferritic nodular cast iron	Wrought iron
Low-alloy high-strength steel		

layer of very hard material, white cast iron, which can provide excellent wear resistance. Each cam is melted by a line focus in one step and gives a smooth surface with the same hardness. The technical and economical aspects of this treatment are superior to those of the conventional plasma arc melting method.⁷ LSM has also been applied for surface hardening of cast iron brake shoes for heavy trucks and has replaced induction surface hardening.⁸

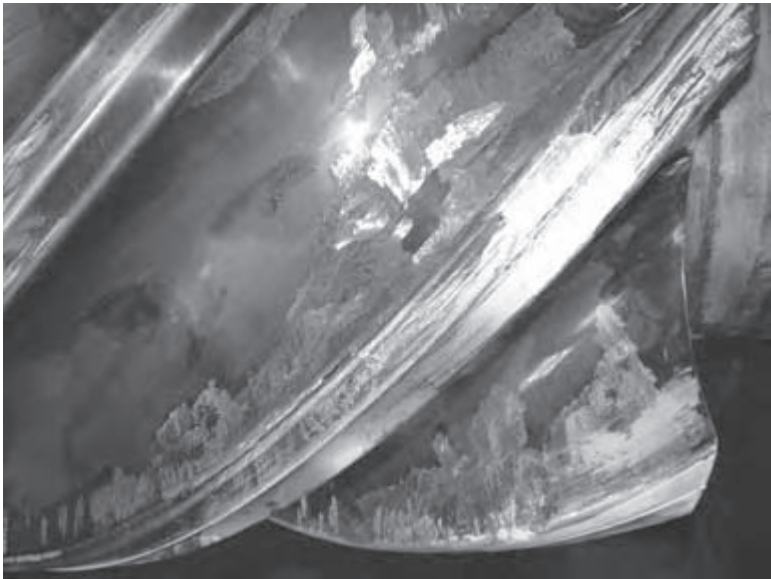
LSA of ferrous alloys is still being studied in the laboratory and industrial application is still sparse. Many interesting research results that show significant improvement in wear resistance have been published.^{9,10}

LSC, on the other hand, has been successfully adopted in the maintenance industry. Localised cladding is ideal for repairing the worn area without affecting thermally other regions of the components. LSC is used for repair of moulds, engine parts, turbine blades, shafts, gears, etc. Figure 10.3 shows the repair of costly parts by laser cladding.

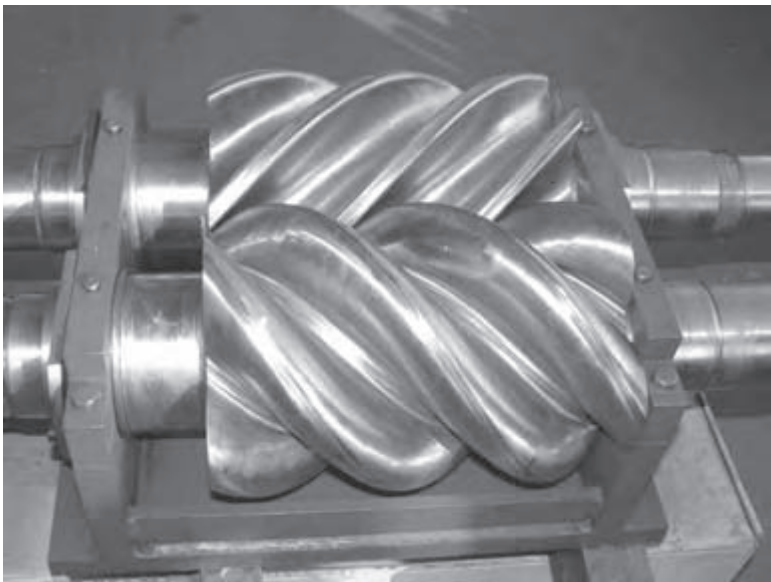
10.6 Applications on aluminium alloys

Aluminium alloys are one of the most important engineering alloys used in a wide variety of industries. Traditionally, aluminium alloys have been regarded as 'soft metal'. By alloying, and then either by rolling to a fully hard condition or by appropriate heat treatment, the strength of aluminium can be increased by up to a factor of 10. Nevertheless, the tribological properties of aluminium alloys are still much less than desired. Aluminium alloys do not have an allotropic transformation as do iron, cobalt or titanium alloys; so there is no possibility of a martensitic transformation, and hardening effects by conventional solid-state treatments are very limited.

Because of these limitations, there has been much research interest in the surface treatment of aluminium alloys. Ion implantation, chemical vapour deposition or physical vapour deposition are methods to modify the surface



(a)



(b)

10.3 Worn region of the screws are repaired by LSC: (a) before LSC repair; (b) after LSC repair. (Courtesy of Dailu Laser Co. Ltd.)

properties of aluminium alloys. However, the depth of coating offered by these methods is restricted to only a few micrometres. This is not suitable for some stress-intensive applications. Electron-beam deposition, arc welding and thermal spraying are high-energy beam treatments. Because of the high energy input from these methods, they may cause distortion of the workpiece and have limitations in coating small and deep cavities. Moreover, thermal spraying usually produces a porous coating and does not provide sufficient bonding to the substrate for many applications.

The CO₂ laser has been utilised for LSE of steel, titanium and Stellite®. However the application of this gas laser for laser surface treatment of aluminium alloys has been limited. This is because aluminium alloys have a high reflectivity to the 10.6µm radiation of a CO₂ laser. The Nd-YAG laser with a shorter wavelength (1.06µm) is more suitable for the laser treatment of metallic materials than the CO₂ laser. On the other hand, the relatively high thermal conductivity of aluminium (226.5 W m⁻¹ K⁻¹), compared with that of a 304 stainless steel (65.3 W m⁻¹ K⁻¹), creates difficulties in producing continuous tracks on its surface. Research studies on laser cladding on aluminium are much less extensive than those for steel.

In the past two decades, laser alloying, laser cladding, laser melting and laser nitriding of aluminium alloys have received immense interest because the strength, hardness and wear resistance of the surface can be improved greatly.¹¹ LSM of Al-Cu or Al-Fe systems leads to an extended solubility of the alloying elements in the matrix and this contributes to the hardness enhancement observed. However, laser melting and laser nitriding provide only a very thin coating and little improvement in hardness when compared with laser cladding.

The effects of rapid multiple surface remelting by a laser on the mechanical properties of Al-Si alloys with different alloying elements such as copper, nickel and iron have been investigated.¹² A fine dendrite arm spacing was found in the homogeneous microstructures of the remelted zone. Several workers have carried out investigations on pure aluminium and Al-Cu binary alloys to characterise the modification of the surface microstructure resulting from LSM. Resolidification of the melted layers has been shown to be epitaxial, commencing with a very thin layer of planar front growth.

LSC or LSA has been used to improve the wear resistance and hardness of aluminium alloys. Almeida and Vilar¹³ and McMahon *et al.*¹⁴ confirmed that molybdenum can mix well with an aluminium alloy and forms a homogeneous defect-free coating with high hardness. The alloying elements and compounds commonly used include cobalt, iron, copper, nickel, titanium, tungsten, chromium, molybdenum, Zr-Ni, titanium nitride (TiN), Co-Cu, Al-Ti-Ni-Fe-V, Ni-Cr-Al and other systems.¹⁵

Most studies premixed metal powder with the reinforcing ceramic particle phase to form an aluminium matrix composite on the surface of aluminium alloys. This soft and low-melting-point matrix is unable to bind the hard ceramic phase when the surface is subjected to shear stress and high temperature, such as in the case of wear.^{16–19} Various ceramic or ceramic–alloy systems, such as silicon, alumina (Al_2O_3)–titania (TiO_2), titanium carbide (TiC), tungsten carbide (WC), Silicon carbide (SiC), Zirconia (ZrO_2)–yttria (Y_2O_3), SiC –silicon nitride (Si_3N_4) and SiC – Al_2O_3 synthesised on aluminium or aluminium alloys have been studied.²⁰

LSA of silicon into 319 and 320 aluminium casting alloys as a means of improving the wear resistance of these low-silicon-content alloys for automobile industry application has been investigated.²¹

The major concern for LSA of aluminium alloys is to avoid defects such as cracking, porosity and unacceptable roughness of the clad surface. Because of the different thermal expansion coefficients of the substrate and coating and in addition the high cooling rate in laser processing, cracking is the most important problem associated with laser treatment of aluminium alloys. Preheating the substrate is usually used to eliminate the formation of cracks. Some research studies have found that adding certain chemical elements such as nickel into the coating may decrease the residual stress in the coating and prevent crack formation. Other researchers found that it is difficult to alloy iron and nickel into aluminium alloys without cracking.²² To overcome the cracking problem, both pure nickel and aluminium were used as intermediate coatings. A pure aluminium coating was found to be a better barrier layer to prevent the continuous formation of embrittlement.

Successful industrial applications of laser surface modification of aluminium alloys for wear resistance are relatively sparse.

10.7 Applications on titanium alloys

Titanium alloys are characterised by their high strength-to-weight ratio, excellent corrosion resistance, good toughness, fatigue and creep resistance up to 450°C . These attractive properties have made titanium alloys widely used in the aircraft, chemical engineering and steam turbine industries. However, the poor tribological properties of titanium alloys have limited their applications in many sliding components, tools and parts that must have wear resistance. The main reasons for these limitations are the high surface friction and the low surface hardness of titanium alloys.

The most extensively studied LSE technology on titanium alloys is laser surface nitriding.²³ By the LSM of titanium alloys in a nitrogen-rich atmosphere, the molten titanium reacts with nitrogen and a thin layer of titanium nitride can be formed on the surface of the titanium alloys. The TiN layer is metallurgical bonded to the substrate and thus has a superior interfacial



(a)



(b)

10.4 LSC used to repair titanium components: (a) before LSC repair; (b) after LSC repair; (c) the repaired component. (Courtesy of Dailu Laser Co. Ltd.)



(c)

10.4 Continued

adhesion to that of nitrided layers obtained by other techniques such as physical vapour deposition. Many studies have shown that the laser-surface-nitrided layer improves the surface hardness and wear resistance of titanium alloys significantly. Other elements or compounds used for the LSA of titanium and its alloys include carbon, boron, nitrogen, aluminium, SiC, boron carbide (B_4C), TiC, boron nitride (BN), WC and Ni–Cr–Si–B. All these studies showed significant improvement in surface hardness and wear resistance. However, it seems that industry has yet to pick up these laboratory results and to apply them to real production.

On the other hand, LSC has been applied successfully for repair work on worn turbine blades. This application makes best use of the advantages of LSC, i.e. small areas clad with a minimum heat-affected zone.

Figure 10.4 and Fig. 10.5 show the repair work done on titanium components by LSC.

10.8 Conclusions

In comparison with other surface modification technologies for the enhancement of wear resistance, industrial adoption of LSE technologies has been disappointingly slow. The high capital cost of the equipment and the slow surface area coverage rate are believed to be the main factors of concern. The latest development of high-power diode lasers and techniques for wide-area surface treatment can surely help to alleviate the problems significantly. Research on arc-assisted and plasma-assisted laser cladding has also



(a)



(b)

10.5 LSC being applied for repairing titanium components: (a) before LSC repair; (b) after LSC repair. (Courtesy of Dailu Laser Co. Ltd.)

shown increased area coverage rate. It is suggested that future research on LSE should be addressed to the logistics of the technology rather than to metallurgical studies as a huge amount of knowledge on the latter has been accumulated over the last two decades already.

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Future trends in surface coatings for protection against wear

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11.1 Introduction

The ever-increasing demands for wear-resistant components and tools have led to a constant development of new coating materials and coating architectures. New systems with higher hardness, chemical stability and lower coefficient of friction are constantly being tested and theoretical models predict novel possibilities for wear-resistant coatings that may exceed by a great extent those that are currently used. However, this is only part of the ongoing research effort; much is also being developed on deposition processes that may improve our ability to deposit films free of flaws such as macroparticles, pinholes, poor adhesion, and cracking due to excessive residual stresses. The introduction of new or optimized coating processes may have as great an impact on film properties as the materials themselves.

It is a difficult task to predict future trends for wear-resistant coatings. What one might safely do is to try to extrapolate on the current available systems and carefully suggest some innovative solutions with enough merit to be pursued.

In the following sections we review some of the state of the art on coatings for wear applications that should develop into commercial products in the short to medium term.

11.2 Coating materials

11.2.1 Superhard materials

The increase in hardness is the most investigated course of action to produce wear-resistant coatings. Defined as the resistance of a material to deform plastically, the hardness of crystalline materials is, therefore, directly related to dislocation activity, and, as such, many of the coating design approaches rely on hindering dislocation motion.

The evident advantages of extremely hard coatings has led to the pursuit of the so-called ‘superhard’ materials, which present hardness values in excess of 40 GPa. This may be achieved in single compounds, either naturally occurring or synthetically obtained, such as diamond, diamond-like carbon (DLC), cubic boron nitride (c-BN) and carbon nitrides, or through the clever design of multiphase coatings. Among the former, diamond and DLC coatings show extreme hardness (Robertson, 2002) but have some limitations concerning oxidation at temperatures above 900 K and reactivity with ferrous materials. c-BN, on the other hand, does not react with iron and is chemically inert to oxidizing environments up to 1600 K (Stoessel and Bunshah, 2001) but has proven very difficult to deposit at thicknesses exceeding 0.1–0.2 μm (Sproul, 1996a; Chung and Sproul, 2003). It has been recently reported, however, that thicker c-BN films may be produced using chemical vapour deposition (CVD) techniques based on fluorine chemistries (Zhang *et al.*, 2003). The deposition of carbon nitrides, specifically $\beta\text{-C}_3\text{N}_4$, has been pursued since Liu and Cohen (1990) predicted a bulk modulus, and consequently hardness, equal to or higher than that of diamond. However, the $\beta\text{-C}_3\text{N}_4$, which should have the $\beta\text{-Si}_3\text{N}_4$ structure with carbon substituted for silicon, has been difficult to obtain (Sproul, 1996a). Nevertheless, the more easily obtained CN_x , where x varies from 0.2 to 0.3, was found to be very hard (although not as hard as diamond) and elastic, yielding interesting properties to the compound (Chung and Sproul, 2003).

Superhardness obtained through multiphase coatings is discussed in a later section of the chapter.

11.2.2 Oxidation-resistant materials in wear applications

Carbides, nitrides and borides of transition metals are natural candidate materials for wear resistance applications. They normally display high hardnesses and relatively low coefficients of friction. However, most are not suitable for operating where environmental conditions may induce oxidation or corrosion. The synergistic effect of either of these two phenomena with wear is usually more detrimental to the film than mechanical wear alone.

Ternary compounds have been found to be an interesting alternative, with possible advantages not only in oxidation–corrosion but also providing an increase in hardness, comparatively with binary systems. Titanium nitride (TiN) for instance is a very-well-known film material with a hardness of approximately 23 GPa that has been extensively used for tribological applications. Its hardness, and in some cases oxidation resistance, may be improved by the addition of a third element, such as aluminum (TiAlN), carbon (TiCN) or zirconium (TiZrN). In the case of (TiCN) the hardness may be increased above 33 GPa (Bull *et al.*, 2003). One should remember

that hardness in single-phase crystalline materials is determined by their shear modulus (which relates to the ease with which dislocations move). The introduction of a third element substituting for either titanium or nitrogen in the original structure generates localized stress fields that pin dislocation motion. In the case of the addition of aluminum to TiN, aluminum substitutes for titanium in the lattice and at high temperatures in contact with oxygen it reacts, forming a passive alumina (Al_2O_3) layer that improves the oxidation resistance of the coating.

The use of oxides as primary film materials for wear application has not been as extensive as the above-mentioned nitrides, carbides and borides especially owing to the low toughness normally observed in oxides, coupled with some early difficulties in depositing such materials. The deposition of Al_2O_3 on cemented carbides using CVD has been reported since the mid-1970s. However, because of the high deposition temperatures, 800–1100 °C (Kathrein *et al.*, 2003) for CVD and 500–700 °C for plasma-assisted chemical vapor deposition (PACVD) (Täschner *et al.*, 1998), most tool steels would have their tempering temperatures exceeded during deposition with consequent loss of hardness. Physical vapor deposition (PVD) processes normally operate at lower temperatures, but initially the production of the electrically insulating Al_2O_3 film was only possible with radio-frequency (RF)-powered systems, which generally produced amorphous films at a very low deposition rate. This limitation has been mostly overcome with the development of pulsed magnetron sputtering (Fietzke *et al.*, 1996; Sproul, 1996a; Kelly *et al.*, 2000), but better process control is necessary in order to generate reproducible high-quality films. To hold the target at a constant oxidation level is rather challenging owing to hysteresis effects (Schütze and Quinto, 2003). When this problem is solved, Al_2O_3 may become largely employed for applications where hardness and high oxidation resistance and or corrosion resistance are necessary. Tough zirconia (ZrO_2) coatings (Koski *et al.*, 1999) and the very hard chromia (Cr_2O_3) (up to 32 GPa) (Hones *et al.*, 1999) are also attractive candidate materials that have been investigated and should gain interest as deposition processes allow better control over microstructure with higher deposition rates.

11.3 Coating architectures

In order to optimize the properties provided by the above-mentioned materials, one may have to engineer their deposition in such a way as to produce the desired characteristics in a cohesive adherent film. This ‘tailoring’ of coatings to meet specific application requirements may lead to the generation of complex microstructures where the phases present have a controlled volume fraction, distribution, crystallite size and crystallographic orienta-

tion. The clever assembly of these features may be described as the *coating architecture*.

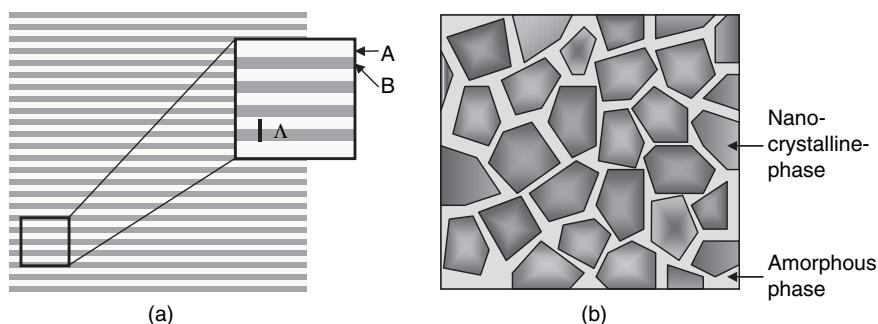
The architecture of a successful coating may follow different approaches, such as the alternate deposition of selected materials (either in the micrometer or nanometer range), the co-deposition of immiscible phases yielding nanocomposites or the deposition of materials with a gradient in composition. These architectures bring solutions to wear, oxidation and corrosion issues either by improving the intrinsic properties of the film or by providing the film with a self-healing capability.

Two of the most promising approaches to thin film design, nanocomposites and functionally graded coatings (FGCs), are presented below.

11.3.1 Nanocomposite films

Nanocomposite coatings are structures that contain nanosized features such as precipitates or film layers. In these cases, the high hardness observed is generally explained in terms of the resistance to dislocation glide across interfaces, the Hall–Petch strengthening and the so-called ‘supermodulus effect’ (Yashar *et al.*, 1998; Vepřek, 1999; Ducros *et al.*, 2003). Within the general denomination of nanocomposites, one may include nanolaminates, nanocrystalline–amorphous systems and nanocrystalline biphasic systems.

Nanolaminate or *Superlattice coatings* consist of nanometer-scale multilayers of two different alternating materials with a period Λ in the nanometer range (Fig. 11.1(a)). Entirely new properties and characteristics not directly related to the individual layered constituents can be expected for superlattice coatings. The materials selected for this architecture should conform to the following requirements.



11.1 Schematic representation of microstructures of (a) nanolaminates (superlattices) and (b) isotropic nanocomposites.

1. There should be a large difference between the shear moduli of the two materials.
2. The materials should be immiscible.
3. The interfaces should be coherent, with a small lattice mismatch between the constituent layers.

Increased hardness and strength are generally observed for superlattice coatings. In the case of transition-metal nitrides, superlattices have been effective in increasing hardness to over 50 GPa, well above the values of approximately 20–30 GPa normally observed for either individual nitride (Sproul, 1996b; Yashar *et al.*, 1998).

Since the publication by Helmersson *et al.* (1987) of work on a TiN/VN strained-layer superlattice, many papers have been published on the deposition and characterization of nanometer-scale multilayered coatings of metal nitrides. Some of these investigations report the deposition of VN, NbN, TaN, MoN, TiAlN and CrN with TiN (Nordin *et al.*, 1998; Chu *et al.*, 1999; Zeng, 1999; Yang *et al.*, 2002), mostly with the formation of an NaCl cubic structure. The superlattice of TiN/CrN, for instance, has been obtained with a hardness of about 35 GPa, which is 75% higher than predicted by the rule of mixtures, overcoming the primary limitation of low hardness of CrN coatings while retaining their excellent adhesion and oxidation resistance (Yashar *et al.*, 1998). The practical question of using these superhard superlattices as wear-resistant coatings raises other issues, namely the hot hardness of the coating and the temperature threshold for interdiffusion between the nanolayers, which would destroy the periodic nanoscale structure. In spite of this limitation, the industrial scale manufacture of superlattice hard PVD coatings has been under investigation (Münz *et al.*, 2001).

Isotropically nanostructured coatings differ from the superlattice coatings with respect to the distribution of the phases. In this case, instead of a two-dimensional laminate structure, the nanocomposite will normally be formed by interwoven phases in three dimensions (Fig. 11.1(b)). The same principle of hardness enhancement by suppression of dislocation activity applies in this case as long as the frequencies of occurrence of phase boundaries are the same in all directions. Moreover, mechanisms of strengthening and possibly toughening are most probably active simultaneously which results in a multiplication of strengthening and toughening effects. These nanocomposites are usually formed from ternary or higher-order systems and consist of two nanocrystalline phases or, more commonly, an amorphous phase surrounding nanosize crystallites of a secondary phase.

Some requirements to achieve the desired microstructure and properties are as follows.

1. Materials must be immiscible at deposition conditions.
2. The cohesive energy at the interface between phases must be high.
3. The second phase (amorphous or crystalline) must possess high structural flexibility in order to accommodate the coherency strain without forming dangling bonds, voids or other flaws (Vepřek, 1999; Vepřek and Argon, 2002).

Additionally, for nanocrystalline–amorphous systems, according to Patscheider (2003), to achieve a high hardness the particle size of the crystalline phase should be less than 10 nm and the thickness of the amorphous phase separating the nanocrystals should be only a few atomic bond lengths. In nanocrystalline–amorphous nanocomposites, the chemistry operating in these systems not only determines the constituent phases but also stabilizes their nanostructure and makes it fairly free of flaws. Therefore, there are critical values for the crystallite size and the relative amounts of nanocrystalline phases that control the interaction between the nanocrystallites and amorphous phase and thus determine the properties and performance of the nanocomposite.

Some hard nanocomposite coatings are nc- M_n N/a- Si_3N_4 (where nc indicates nanocrystalline, M is a transition metal and a- Si_3N_4 is amorphous silicon nitride) (Vepřek, 1999), nc-TiN/a-BN and nc-TiN/a- TiB_x /a-BN (Karvankova *et al.*, 2003) as examples of nanocrystalline/amorphous nanocomposites, and nc-TiN/ TiB_2 and nc-TiN/BN are examples of crystalline nanocomposite films (Vepřek, 1999).

Tribological films where a low coefficient of friction is required may be obtained by producing nanocomposite coatings with a mix of hard and lubricating phases. Transition-metal dichalcogenides (MoS_2 , WS_2 , $NbSe_2$, etc) and carbon normally constitute the low-friction phase. TiB_2 -based composites with carbon or $MoSi_2$ (Gilmore *et al.*, 1998a) and TiN/ $MoSi_2$ composite coatings (Gilmore *et al.*, 1998b) have been investigated and have good potential for tool applications. Similar systems have been investigated for aerospace applications; WC/DLC/ WS_2 nanocomposite coatings have demonstrated a desirable combination of hardness, good wear resistance and low friction in humid air, dry nitrogen and vacuum (Voevodin *et al.*, 1999).

11.3.2 Functionally graded coatings

In FGCs the composition and/or the microstructure of the coating system gradually change over the volume (i.e. throughout its thickness) to produce different characteristics at each end without generating abrupt interfaces within the film, resulting in corresponding changes in the properties of the coating system. The most familiar FGC is compositionally graded from a

refractory ceramic to a metal. Using such an FGC architecture, incompatible functions such as high temperature, wear and oxidation resistance of ceramics can be combined with high toughness, high strength and bonding capability of metals without severe internal stress. Pores are also important structures in FGCs. Grading pore size and distribution from the interior to the surface of the coating can impart many properties such as mechanical shock resistance, thermal insulation, catalytic efficiency and stress relaxation. In general, this type of system is a multilayered multicomponent coating system with a graded arrangement of phases to provide different synergistic properties and functions that are tailored for problem-specific applications. This approach is particularly useful when trying to incorporate good adhesion, high hardness and good oxidation–corrosion resistance in a film without generating excessive residual stresses.

The FGC architecture is very versatile and offers great potential with respect to the development of a coating system for protection and more favorable performance under extreme and complex environmental ‘loading’ conditions. It is unlikely that a monolithic coating would provide the optimum system for any specific application which has complex requirements for the physical, chemical and mechanical properties of the coating material. The FGC concept is applicable to many fields. For instance, coating systems that incorporate specifically engineered graded-coating architectures have been developed by the Advanced Coatings and Surface Engineering Laboratory at the Colorado School of Mines for coating dies used for material forming applications, e.g. metal stamping, glass molding and aluminum pressure die casting (Peters *et al.*, 1999; Zhong *et al.*, 2002, 2003). A schematic diagram of such an optimized coating architecture is presented in Fig. 11.2. The conceptual design of such an optimized ‘coating system’ incorporates four sections of the total coating architecture from the substrate to the top layer as follows:



11.2 A schematic diagram of an optimized coating architecture for coating dies used for material forming applications, e.g. metal stamping, glass molding and aluminum pressure die casting.

1. Surface modification of the substrate, e.g., plasma nitriding or ferritic nitrocarburizing.
2. A thin (50–100nm) adhesion interlayer, e.g. titanium or chromium, between the substrate (e.g. H13) and the coating system.
3. An intermediate layer (compositionally graded) that facilitates ‘accommodation’ of thermal and residual stresses, as predicted using finite element modeling (Zhong *et al.*, 2001; Carrera *et al.*, 2002).
4. An outer ‘working’ layer that exhibits acceptable properties to meet the application requirements, such as low wettability with the material being formed, e.g. liquid aluminum or glass, coupled to high wear and corrosion–oxidation resistance.

Thus, each layer of the coating’s architecture will provide a specific function, and the success of the coating system lies in the synergy of the properties and functions of each layer.

A functioning and robust finite-element model (FEM) has also been developed in the above-mentioned work that is capable of predicting suitable intermediate layers that are efficient in accommodating the thermal and mechanical stresses that arise from the short cycling process. An important role played by the FEM is to minimize the ‘trial-and-error’ experiments in the identification of suitable intermediate layers and coating architectures.

Because of lattice and coefficient of thermal expansion (CTE) mismatch effects, ceramic coatings on metal substrates generally have various defects such as cracking within the ceramic coating layer, plastic deformation in metal and delamination at the interface between the coating and substrate. Besides the FEM (Stephens *et al.*, 2000; Zhong *et al.*, 2001), other numerical analysis methods, such as the boundary element method (Saizonou *et al.*, 2002), solutions based on Laplace transform (Jin, 2003) and even a simple elastic lamination-type analytical approach (Teixeira, 2001) have been developed to predict resulting stresses and failure behavior in FGCs under various mechanical and thermal load conditions. Each of these numerical analyses indicates that the discontinuities in the stress distributions in a coating system as a result of the CTE mismatch can be eliminated or reduced if both the thickness and the compositional profile of the graded zone between the bonding layer and the ceramic top layer are properly designed. In addition, the deposition stress can be incorporated into the numerical analysis when an advanced FEM is used (Zhong *et al.*, 2001; Carrera *et al.*, 2002).

11.4 Smart systems

Smart coatings are systems that respond in a selective way to external stimuli such as temperature, stress, strain or environment (Nicholls, 1996).

'Smartness' results from careful selection and combination of coating materials with distinctive intrinsic properties. The approach to produce such coatings may vary; one may achieve this goal by changing the composition of a single-phase material or by producing multilayer or graded films.

For instance, films that operate at moderate- or high-temperature oxidation can be designed to produce protective layers of either Cr_2O_3 or Al_2O_3 depending on the environment. Al_2O_3 scales offer the best protection under high-temperature conditions while Cr_2O_3 is more resistant to hot corrosion (Nicholls *et al.*, 2002). TiAlN is an example of a very basic smart coating since it reacts to the presence of oxygen at high temperatures producing a protective Al_2O_3 layer that prevents further deterioration of the film by oxidation. Tribological coatings for aerospace applications may have to deal with broad ranges of environmental conditions such as air humidity, air pressure and temperature while maintaining low friction and good wear resistance. Adaptative nanocomposite coatings such as WC/DLC/WS_2 (Voevodin *et al.*, 1999) and nanocrystalline yttria-stabilized ZrO_2 (YSZ) in an amorphous YSZ/Au matrix (Voevodin *et al.*, 2001) may present different friction mechanisms depending on the operating conditions. In the former case for instance, a change in humidity triggers a reversible modification of the composition of the transfer film between WS_2 and graphite while in operation.

A more sophisticated type of coating that could be defined as 'smart' is that of films with imbedded sensors and/or actuators. Little work has been conducted in this area with still limited results, but the possible products of this research would be extremely valuable. The use of strain sensors alone could be beneficial on critical applications for monitoring stress in films. In the die-casting industry for instance, molds are subjected to wear, corrosion, and thermal and mechanical cycling. The ability to monitor stress in the film could help to optimize casting parameters and mold design (geometry and placement of cooling channels) and to provide a more efficient program for maintenance and replacement of the die.

An even more ambitious goal would be the use of both sensors and actuators, where the latter, triggered by the former, would relieve some of the stress imposed to the coating at peak conditions during thermal or mechanical cycling of mechanical parts or tools.

Work by Kim and Lee (2001) on coatings containing piezoelectric materials and shape memory alloys investigates the possibility of combining the fast response to strain provided by piezoelectricity with the large force-displacement produced by the martensite-to-austenite transformation in the TiNi shape memory alloy. The application of such systems may still be some years ahead but the concept is certainly worth investigating.

11.5 New processes

CVD was the first process used commercially to produce wear-resistant coatings for carbide cutting tools. Because of the high temperatures necessary, tool steels could not be coated by such processes. The development of plasma-enhanced chemical vapor deposition (PECVD) and PVD processes, normally operating at much lower substrate temperatures, permitted the deposition of a variety of different coatings on several types of substrate, including carbides, metals and even plastics. In 1996, Sproul (1996a) reviewed the PVD processes used for hard-coating deposition and found that the most important techniques for producing wear-resistant coatings were low-voltage electron beam evaporation, cathodic arc deposition, triode high-voltage electron beam evaporation and unbalanced magnetron sputtering.

While the fundamentals have not changed much, the industry has grown enormously in the last decade. Cost-effectiveness coupled with major processing technological advances have been the major driving forces for innovative process development. Because of the highly competitive nature of the coating industry, novel process improvement and invention have generally been considered as proprietary information and kept secret. As such, it is a very difficult task to elaborate on all process innovations. Nevertheless, an outlook is given here on some technological advances based upon current and potential developments of coating processes reported in the literature. Although there is a wide variety of emerging processes for surface engineering, the criteria for the selection of an appropriate deposition process for a specific engineering application, i.e. the surface coating method, should be based on its ability to achieve the following:

1. The method should deposit the required type of coating and thickness.
2. It should not affect or impair the properties of the substrate materials.
3. It should deposit the engineering components uniformly with respect to both size and shape.
4. It should be cost effective in terms of coating technique, minimum equipment downtime, and improved quality and performance of the coating.

Plasma-assisted vapor deposition processes are very important and extensively utilized for the deposition of compounds and novel technological materials, but their full potential has yet to be exploited. Over the past few decades, substantial progress has been made in the design, research and development of various types of plasma source to obtain coatings and surfaces with desired properties. Three important research and development

areas are pulsed plasma processing, utilization of high-density plasma sources and hybrid processes. These are also the topics of the following overview, with emphasis on pulsed plasma processing since it has the potential to revolutionize some of the established deposition processes. Note that other deposition processes, such as thermal or plasma spray, diffusion, laser ablating and non-vacuum-based CVD, are not covered in this chapter, but it does not mean that they do not have their advantages and are out of date. These techniques are still widely used in industry and subjected to active research programs.

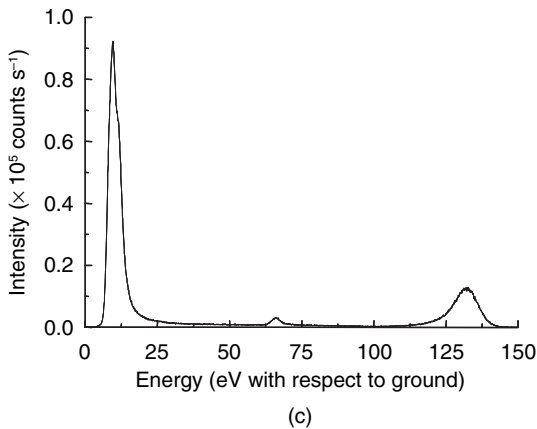
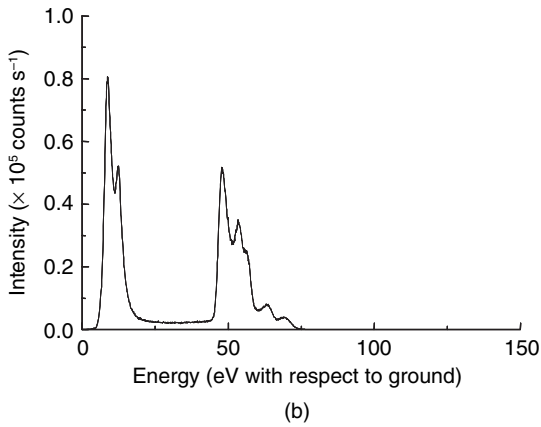
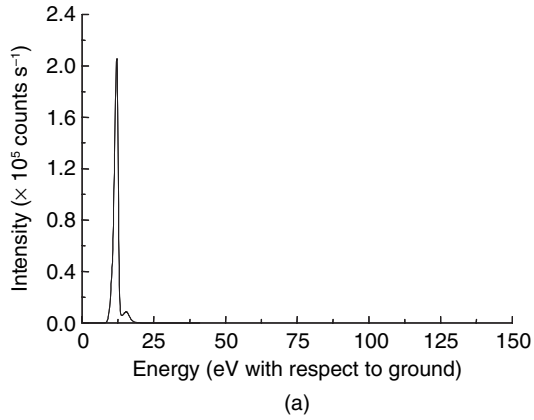
11.5.1 Pulsed plasma processing

Pulsed plasma processing is one of the state-of-the-art technologies implemented into PVD, CVD, surface modification, surface pretreatment and cleaning processes such as pulsed magnetron sputtering (Kelly and Arnell, 2000), pulsed PECVD (Das *et al.*, 2002; Fedosenko *et al.*, 2002), pulsed plasma nitriding (Panjan *et al.*, 2002; Feugeas *et al.*, 2003) and pulsed ion beam treatment (Akamatsu *et al.*, 2001; Kondyurin *et al.*, 2002; Bayazitov *et al.*, 2003). The recent development of pulsed plasma processing technologies opens an avenue for altering plasma chemistry and physics (Samukawa and Furuoya 1993; Sugai *et al.*, 1995; Schneider *et al.*, 1999; Ehiasarian *et al.*, 2002; Gudmundsson *et al.*, 2002) and thus for activating and energizing condensing particles, enhancing surface mobility of adatoms, and, in turn, improving the microstructure and properties of deposited films (Bartzsch *et al.*, 2000; Cremer *et al.*, 2003; Fenske *et al.*, 2003). As an example, when pulsed power is applied to a growing dielectric film during magnetron sputtering, ion bombardment of the surface is enhanced, thus promoting denser crystalline film growth at lower substrate temperatures (Cremer *et al.*, 1999; Schütze and Quinto, 2003). Pulsed sputtering at very high rates and stable conditions over long production runs can be obtained for a variety of materials such as Al_2O_3 , silica (SiO_2) and titania (TiO_2).

Substrate bias has been used extensively in variants of plasma processes. It is usually of negative polarity to attract positive ions from the processing plasma either to pretreat the substrate for coating or to improve the coating by ion bombardment. In the last 10 years, pulsed biasing of the substrate has become popular for several reasons. One reason is the likelihood of the elimination of arcing and enhanced process stability when using a substrate bias with short pulses. Other reasons are associated with the nature of pulsing. Applying a pulsed bias at the substrate has a profound effect on the energy and flux of particles incident on the substrate (Kelly *et al.*, 2001). This can both improve the effectiveness of pre-cleaning and the quality of subsequent coatings which benefit from improved adhesion, uniformity, lower stress and suppression of columnar growth morphology.

Emerging technologies of pulsed plasma in PVD and CVD processes provide a new set of process parameters, such as pulse frequency, pulse duration, duty cycle and pulse amplitude. For instance, during direct-current (DC) reactive magnetron sputtering of titanium oxide thin films, ion energies (with respect to ground) increased from approximately 12 eV for a continuous mode to much higher values (50–150 eV) by midfrequency pulsing, and increased with decreased reverse time (Fig. 11.3) (Muratore *et al.*, 2003a). Through controlling these pulsing parameters, a pulsed plasma process can provide momentary high power, leading to more high-energy and ionized particles in the plasma. High kinetic energy in pulsed processing allows film growth to occur much further from thermodynamic equilibrium than with continuous processing. Temporal development of the plasma composition in pulsed processing allows film growth under an environment unachievable in continuous processing. Consequently, superior films can be deposited. To illustrate the application of pulsed plasma processing, selected examples that have attracted increasing interest recently are briefly presented as follows.

Pulsed sputtering processes can be grouped into two categories: midfrequency ‘medium’-power pulsed sputtering and low-frequency high-power pulsed sputtering. Midfrequency ‘medium’-power pulsed sputtering was developed in the 1990s. A unipolar or bipolar pulsed DC was used at typical frequencies from 10 to 350 kHz and for a high-duty cycle. Typical values of the pulsed power and current density are at the level of a few (3–10) watts per square centimeter and several milliamperes per square centimeter respectively. Midfrequency ‘medium’-power pulsed reactive sputtering has been successfully used to deposit various dielectric coatings such as Al_2O_3 (Cremer *et al.*, 2003; Schütze and Quinto, 2003). Note that pulsed DC sputtering is used when a simple one-magnetron system is preferred and, unfortunately, such an approach does not solve the ‘disappearing’-anode problem suffered in reactive sputtering of dielectrics. The disappearing-anode and arcing problems are solved simultaneously using midfrequency (20–100 kHz) alternating-current-powered dual-anode or dual-magnetron systems. In contrast, high-power pulsed sputtering, which was introduced in late 1990s, uses a low-frequency (less than 1 kHz) low-duty cycle, but very high peak power and current densities (several thousands of watts per square centimeter and several thousands of milliamperes per square centimeter respectively). By increasing the power density to a magnetron by orders of magnitude, appreciable ionization of the sputtered metal can be obtained (Kouznetsov *et al.*, 1999). A significant change in the slope of the voltage–current characteristics was observed by Ehiasarian *et al.* (2002) when the current density at a chromium target exceeded 600 mA cm^{-2} , which is a sign for the transition to a fully ionized plasma. This method has been demonstrated as an extremely promising PVD technique suitable



11.3 Argon ion energy distributions determined by a Hiden EQP mass spectrometer–energy analyzer are shown for reactive magnetron sputter deposition of titanium oxide films with (a) a continuous DC discharge, (b) a 60kHz pulsed discharge with 6 μ s reverse time, or 64% duty cycle, and (c) a 60kHz pulsed discharge with 1 μ s reverse time, or 94% duty cycle.

for both substrate pretreatment and coating deposition (Ehiasarian *et al.*, 2003).

Pulsed glow discharge plasma immersion ion processing (PIIP) is a non-line-of-sight technique for depositing uniform coatings over large areas and can also be viewed as one kind of pulsed PACVD, which was proposed at Los Alamos National Laboratory, USA (Nastasi *et al.*, 2001). A pulsed plasma sheath is realized by applying a high negative pulsed bias to the substrate and is utilized to attract ions from the plasma for high-energy condensation at the substrate surface and to accelerate secondary electrons in the sheath for plasma generation. Typical precursors utilized in PIIP are carbon-containing gases (e.g. C_2H_2) for DLC films (Walter and Nastasi, 2002), or gas mixtures leading to doped DLC films (He *et al.*, 2002), or metallo-organic precursors for TiCN coating (Peters and Nastasi, 2002).

Metal plasma immersion ion implantation and deposition utilize both pulsed plasma and pulsed bias. The techniques can be viewed as hybrid systems of ion plating with pulsed bias. Anders (2002) presented an excellent overview on the principles and trends of this method. By synchronizing pulsed plasma generation and pulsed high-voltage bias, metal ion implantation without film formation is possible. This technique has been successfully demonstrated for wear-resistant surface modification (Mändl *et al.*, 2003), for thin-film deposition (Huber *et al.*, 2003) and for minimization of intrinsic stress in coatings (Lim *et al.*, 2003).

11.5.2 High-density plasma sources

High-density plasma sources with higher ionization efficiency are indispensable for large-scale plasma and ion beam technology. Such plasmas are generated in discharges excited at higher RF (including microwave) frequencies, or in discharges employing power-coupling schemes which are more efficient than capacitive coupling, or by utilizing confinement and resonant effects of a static magnetic field generated by external means (coils or permanent magnets). It is impossible to include in this chapter all novel high-density plasma sources which are suitable for low-pressure plasma processing. Two examples are given below.

Electron cyclotron resonance (ECR) plasma sources have proven to be very useful for plasma processing applications, primarily by exploiting their ability to operate at low pressure and high density (a few 10^{12} cm^{-3}) in a wave-supported electrodeless mode, which allows the plasma to be generated remotely from tool surfaces. It is widely used in sputtering (Tokai *et al.*, 2003) and CVD (Li *et al.*, 2001) for fabrication of highly wear-durable coatings. The electron temperature of the ECR sources is generally higher than that of the other plasma sources because of its heating mechanism,

resulting in plasma-induced substrate damage. Accordingly, much effort has been made to decrease the electron temperature, for instance, by a mirror magnetic field configuration (Itagaki *et al.*, 2001) or pulse modulation (Itagaki *et al.*, 2000).

Electron-beam-generated plasmas have several important attributes for processing applications including high plasma generation efficiency, independent control of ion and radical fluxes, decoupling of plasma production from chamber walls, scalability to large area (square meters) and low electron temperature. The Naval Research Laboratory has developed a number of hollow cathodes to generate sheets of electrons culminating in a 'large-area plasma processing system' (LAPPS) based on the electron beam ionization process (Fernsler *et al.*, 1998; Meger *et al.*, 2001). The LAPPS uses a sheet electron beam (2–10 kV; 10–20 mA cm⁻²) confined by a 100–200 G magnetic field, to produce a plasma of density about 10¹² cm⁻³ in a neutral gas nearly independent of composition (oxygen, argon, neon or other gas mixtures), over a few square meters of area within centimeters of a surface. It can be operated in pulsed or continuous mode depending on the application. This process has demonstrated considerable flexibility for materials-processing applications, although only a few of the attributes have been investigated so far (Leonhardt *et al.*, 2003).

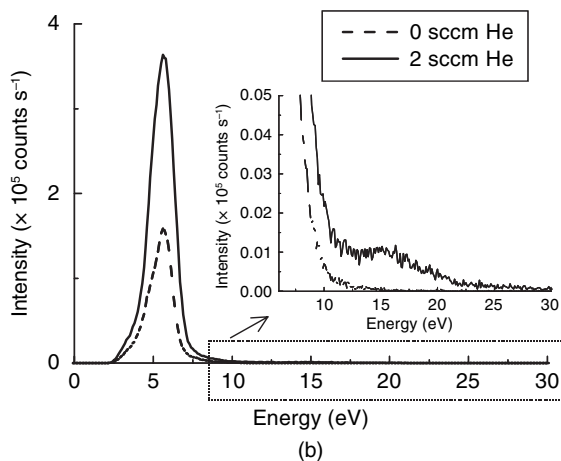
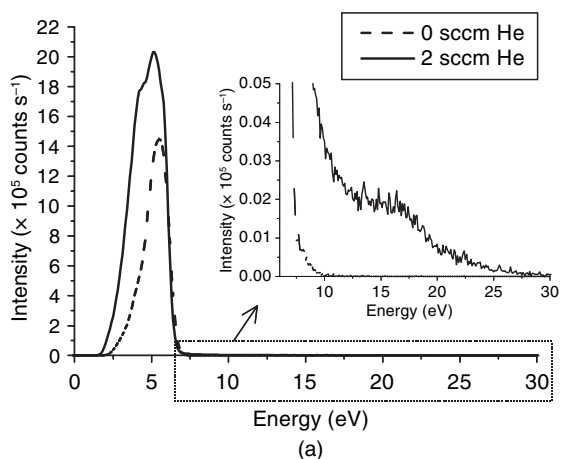
11.5.3 Hybrid processes

Another area subjected to extensive research and development and that has shown great promise is that of hybrid processes, in which different deposition techniques have been combined to extend the processing capabilities and to overcome the limitations of each of the individual techniques. The general thrust is directed towards the following:

1. Separation of the various parts of the process so as to exert independent control over each part and avoid complications due to overlap between the parts.
2. Use of substrate/film bombardment with different species of controlled energy in contrast with a spectrum of energies.

There are numerous examples of such hybrid techniques in the literature, such as ion-beam-assisted sputtering, microwave- or ECR-assisted PECVD, and hybrid systems of magnetron sputtering and filtered vacuum arc ion plating. These are generally innovations of effective plasma deposition processes by manipulating the processing discharges and then controlling the effects of ion bombardment on resultant coatings. For instance, plasma chemistry was successfully manipulated by the addition of helium in an ion-beam-assisted reactive sputtering process. Helium was mixed with nitrogen in an inductively coupled plasma (ICP) reactor (Muratore *et al.*,

2003b). Figure 11.4 shows the effect of a 2 sccm helium gas addition on the nitrogen ion density in an ICP–magnetron plasma. Comparison of the integrated areas under the ion energy distributions shows that the introduction of helium increased the number density of N_2^+ and N^+ ions by 200% and 250% respectively. Using a combination of electrostatic measurements, it was determined that the fraction of nitrogen species constituting the total ion flux to the substrate increased from 24% to 37%. Helium addition resulted in an increase of approximately four times in the grain size, a 22%



11.4 (a) N_2^+ and (b) N^+ ion energy distributions measured in ICP–magnetron plasmas. Other processing parameters were as follows: DC power to titanium magnetron, 11.84 W cm^{-2} ; ICP power, 1.9 kW ; argon flow rate, 15 standard cubic centimetres per minute (sccm); nitrogen flow rate, 7 sccm.

increase in surface smoothness, and a 44% increase in hardness of the deposited TiN films (Muratore *et al.*, 2003b).

Besides some hybrid processes discussed in the previous sections, novel hybrid processes of combining pulsed arc or pulsed laser ablation with molecular beam deposition are presented here as examples.

Laser-assisted molecular beam deposition (DeLeon *et al.*, 1998) and pulsed-arc molecular beam deposition (Rexer *et al.*, 2000) have been developed at AMBP Tech Corporation, USA, a spin-off company of the State University of New York at Buffalo. These techniques are hybrid systems of pressurized-chemical-reactor and pulsed-laser or arc ablation, which utilize a train of gas pulses to control precisely the chemistry and transport of species to be deposited on a substrate. These techniques have been used to grow a variety of films (e.g. oxides and DLC) on a variety of substrates.

11.6 Conclusions

There have been some considerable advances in the development of wear-resistant coatings over the past decade. These advances have come through radical new ideas and approaches that have included coating architecture and design as well as advanced plasma processing concepts. The development of 'adaptive' coatings that can respond to a changing or cyclic environment, such as high and low temperatures, humidities and oxidizing atmospheres, is gaining some considerable momentum, while the concept of 'smart' coatings is a little farther into the future. Nevertheless, the time is rapidly approaching when both of these concepts will be combined to produce a 'smart' and 'adaptive' coating system that first senses a problem in the coating, such as a sudden and critical increase in stress or corrosion-oxidation, and the coating system subsequently responds to this sensing to provide a cure for that problem.

There is no doubt that there will be considerable improvements and developments of new deposition processes in the near future that will provide increased control over the structure and properties of the coating and provide more cost-effective processing techniques. The most realizable of the current approaches will be a further development in the use of controlled energy plasma sources and synergistic hybrid combinations of the currently used deposition systems.

There is an exciting future ahead for engineering radically new coating systems that will substantially improve the wear resistance of surfaces.

11.7 References

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