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Coatings tribology—contact mechanisms and surface design

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The fundamentals of coating tribology are presented by using a generalised holistic approach to the friction and wear mechanisms of coated surfaces in dry sliding contacts. It is based on a classification of the tribological contact process into macromechanical, micromechanical, nanomechanical and tribochemical contact mechanisms, and material transfer. The important influence of thin tribo- and transfer layers formed during the sliding action is shown. Optimal surface design regarding both friction and wear can be achieved by new multi-layer techniques which can provide properties such as reduced stresses, improved adhesion to the substrate, more flexible coatings and harder and smoother surfaces. The differences between contact mechanisms in dry, water- and oil-lubricated contacts with coated surfaces is illustrated by experimental results from diamond-like coatings sliding against a steel and an alumina ball. The mechanisms of the formation of dry transfer layers, tribolayers and lubricated boundary and reaction films are discussed. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: *coatings tribology, friction mechanisms, wear mechanisms, lubricated contact, multilayer coatings*

Introduction

Recent advances in coatings technologies now permit the deposition of films with properties that were unachievable even a decade ago. Examples are multi-layered and metastable coatings with extreme mechanical and chemical properties. Plasma- and ion-based vacuum coating techniques have been at the forefront of these new developments. They allow the coating/substrate system to be designed in such a way that the combination performs in an optimal manner. This objective is further aided by improvements in our fundamental understanding of contact mechanisms between surfaces, at the macro, micro and nano level. This paper therefore begins with an overview of the present level of understanding of contact mechanisms, especially for coated surfaces. This includes an appreciation of stress states, mechanical properties such as hardness, and chemical influences such as oxidation.

The possibilities opened up by using multiple layers of coatings are then discussed; this includes the possibility to grade the functional properties from the surface to the interface between coating and substrate. Special mention is made of recent developments in carbon-based coatings which combine excellent frictional properties with good wear resistance.

Contact mechanisms

The tribology of a contact involving surfaces in relative motion can be understood as a process with certain input and output data[1]. Input data that are used as a starting point for the analysis of a tribological contact are the geometry of the contact, both on a macro and micro scale, the material properties based on the chemical composition and structure of the different parts involved, and the environmental parameters, as shown in Fig 1. Other input data are energy parameters such

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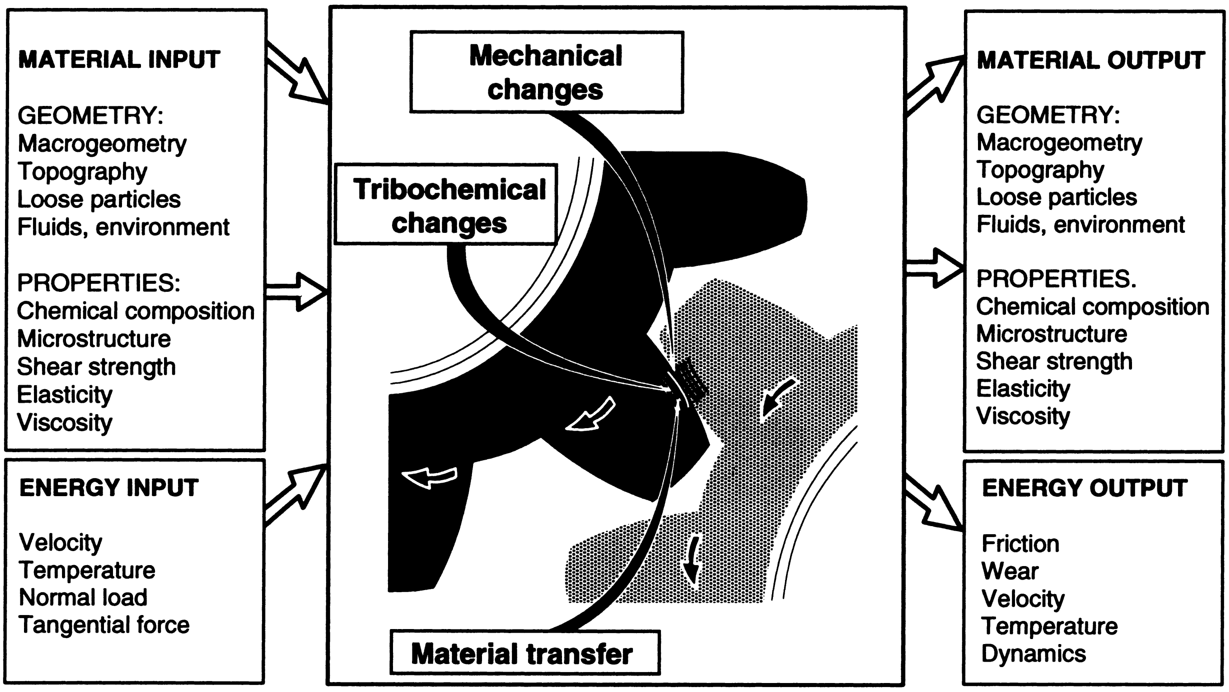

Fig. 1 The tribological process in a contact between two surfaces includes mechanical and tribochemical changes as well as material transfer

as the normal load, velocity, tangential force and temperature.

The tribological process takes place as the two surfaces are moving in relation to each other, and both physical and chemical changes occur in accordance with the physical and chemical laws with respect to the input data. As a function of time, the tribological process causes changes in both the geometry and the material composition and results in energy-related output effects: friction, wear, velocity, temperature, sound and dynamic behaviour.

Tribological contact mechanisms

The complete tribological process in a contact in relative motion is very complex because it involves simultaneously friction, wear and deformation mechanisms at different scale levels and of different types. To achieve a holistic understanding of the complete tribological process taking place and to understand the interactions, it is useful to analyse separately the tribological changes of four different types: the macro- and micro-scale mechanical effects, the chemical effects and the material transfer taking place, as shown in Fig 2. In addition, there has recently been an increasing interest in studying tribological behaviour on a molecular level; i.e. nanomechanical effects[2].

A better and more systematic understanding of the mechanisms involved in a tribological contact is necessary for optimisation of the properties of the two contacting surfaces in order to achieve the required friction and wear performance. Approaches to the tribological optimisation of surfaces have been presented by Matthews *et al.*[3] and Franklin and Dijkman[4], who introduce eight wear design rules in an expert system for assisting the selection of metallic materials, surface treatments and coatings during the initial stages of engineering design.

Stresses and strain in the surfaces

The phenomena that take place in a tribological contact are influenced by the force pressing the two surfaces together. Calculation methods for the stress fields and deformations in a coated surface have been reviewed by Holmberg and Matthews[1]. A useful approach to calculating the coating/substrate interface stresses has more recently been used by Ramalingam and Zheng[5] to assess the problems that may be encountered when hard coatings are applied on substrates with lower or higher compliance than the coating. Numerical solutions are obtained for different stress distributions on the coated surface. They show how tensile stresses in the wake of the contact tend to separate the coating from the substrate, and how this can be solved by adjusting the film thickness and choice of coating conditions to ensure that the coating-to-substrate adhesion strength can withstand the stresses.

The beneficial effect of high compressive stresses in hard and smooth diamond coatings has been shown by Gunnars and Alaheliste[6] and Gåhlin *et al.*[7]. They found that highly stressed coatings may obtain smoother surfaces and wear rates which are only 5–20% of those of the stress-free coatings. The internal stresses influenced on the crack propagation direction in diamond coatings.

Finite element methods have been applied to evaluate the stress field in a hard coating and substrate under frictional loads[8,9]. Diao and Kato[10] analysed the von Mises stress distributions in hard coatings and in elastic

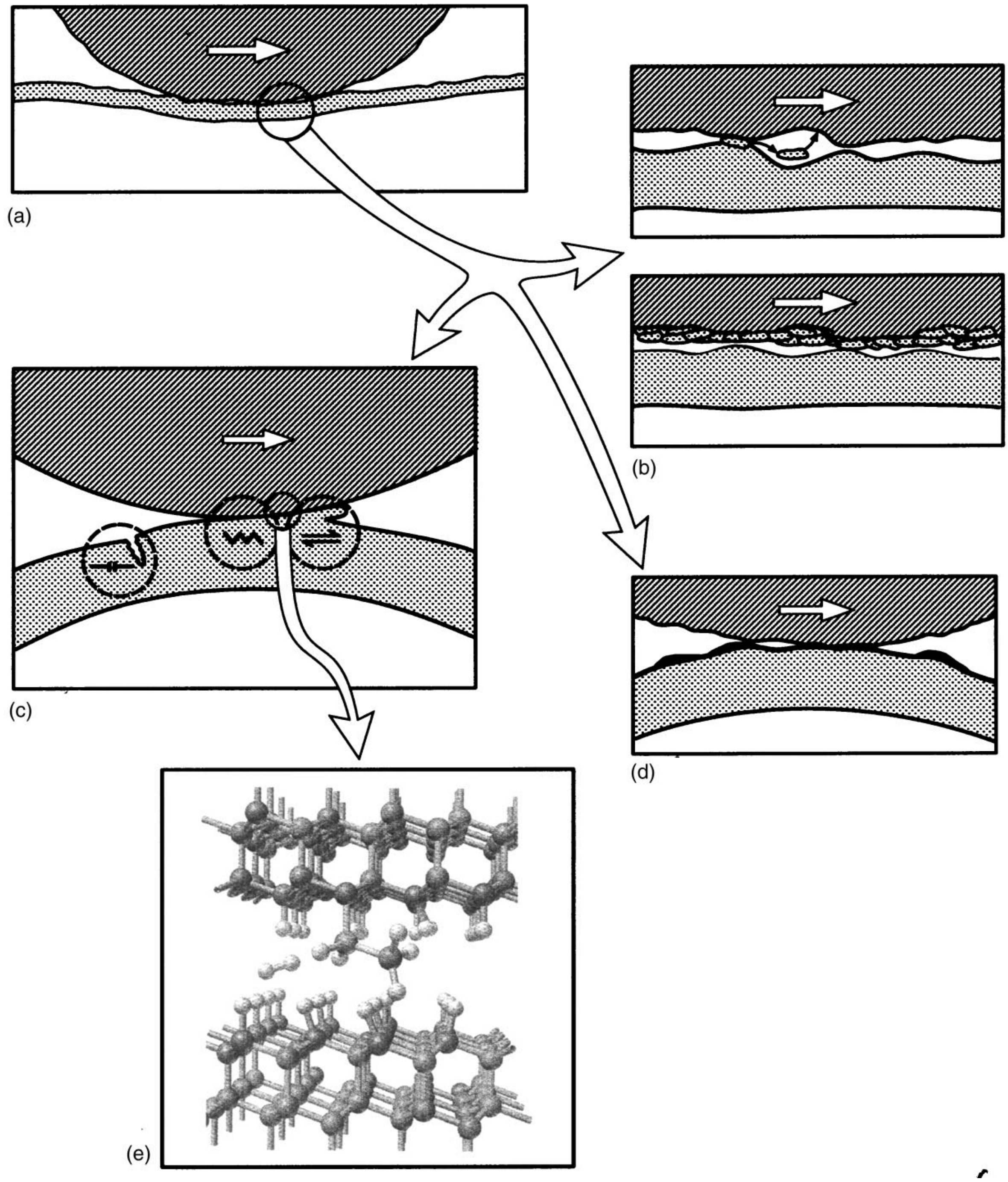

Fig. 2 Tribological contact mechanisms: (a) macromechanical, (b) material transfer, (c) micromechanical, (d) tribochemical and (e) nanomechanical contact

sliding. An elliptical distribution of normal and traction contact pressure was assumed for the analysis of von Mises stress for different coating thicknesses, friction coefficients and elastic moduli of the coating and the substrate. The position of yield could be calculated and they introduced a local yield map showing the yield strength ratio in relation to the ratio of coating thickness to contact half-width. The local yield maps showed that yield at the coating/substrate interface on the substrate side is the most common case under a wide range of contact conditions.

A new parameter for prediction of the onset of spalling of a ceramic coating under sliding contact was developed by Diao and Kato[11] and equations for calculating the critical normal load for the generation of cracks in ceramic coatings under indentation were developed by Diao *et al.*[12]. Eberhardt and Peri[13] determined the stresses near the tip of a crack by using a finite element method; their results support the use of a layer thickness with a large ratio of contact radius to layer thickness, and an appropriate lubricant to reduce friction and prevent surface crack propagation.

The surface roughness is an important parameter influencing the contact stresses, especially at the coating/substrate interface. This was first shown by Sainsot *et al.*[14], who also concluded that in hard coatings with thicknesses less than 15 μm on softer substrates, the maximum von Mises stresses both in the coating and in the substrate will be located just at their interface. This clearly points out the importance of analysing the stresses at the coating/substrate interface and comparing them with the coating adhesion strength.

More recently, Mao *et al.*[15] have developed a numerical technique including integral transform and finite element methods for solving contact problems in layered rough surfaces. They apply their numerical model[16] for the two-dimensional dry sliding contact of two elastic bodies on real rough surfaces, where an elastic body contacts with a multi-layer surface under both normal and tangential forces. Of special interest is that their model uses surface profile data recorded directly with a stylus measuring instrument. They analyse the contact pressure distribution for layers with different coefficients of friction, thicknesses and elastic moduli.

Similar work has been carried out for the contact of gear teeth by Varadi *et al.*[17]. They analyse the contact of spur gears, taking into account real surface topography, by using numerical algorithms. The contact pressure distribution and contact area are calculated for different types of gear surface resulting from shaping, grinding or milling. They also evaluate the sub-surface stresses for different pressure distributions by a finite element method.

Macromechanical friction and wear mechanisms

The macromechanical tribological mechanisms describe the friction and wear phenomena by considering the stress and strain distribution in the whole contact, the total elastic and plastic deformations they result in, and the total wear particle formation process and its dynamics. In contacts between two surfaces of which one or both are coated, four main parameters can be defined which control the tribological contact behaviour. They are the coating-to-substrate hardness relationship, the thickness of the coating, the surface roughness, and the size and hardness of any debris in the contact which may originate from external sources or be produced by the surface wear interactions themselves.

The relationship between these four parameters will result in a number of different contact conditions characterised by specific tribological contact mechanisms. Fig 3 shows schematically 12 such very typical tribological contacts, with different mechanisms influencing friction, when a hard spherical slider moves on a coated flat surface[18]. The corresponding wear mechanisms have been described in a similar way[19].

Hardness of the coating

An important parameter is the coating hardness and its relationship to the substrate hardness. It is common to consider hard coatings and soft coatings separately[5,20,21]. The advantages of using a soft coating to reduce friction are well known, owing to the work of Bowden and Tabor[22] and others. Soft coatings such as silver and gold may also have the function of reducing sliding-originated surface tensile stresses, which contribute to undesirable subsurface cracking and subsequently to severe wear[23]. A hard coating on a softer substrate can decrease friction and wear by preventing ploughing both on a macro scale and a micro scale[19,24–26]. These coatings typically exhibit residual compressive stresses which can prevent the likelihood of tensile forces occurring.

Further decreases in friction and wear can be achieved by improving the load support, that is by increasing the hardness of the substrate to inhibit deflections and ploughing resulting from counterpart load. This effect has been shown for hard coatings on polymers[27] but, in particular, the multi-layer or gradient-layer structures offer excellent possibilities in this respect[28–30]. Hard coatings are thus particularly useful in abrasive environments. Low friction can be achieved with hard coatings if a low shear strength microfilm is formed on the top of the coating. Thus the shear takes place within the microfilm and the load is well supported by the hard coating. This mechanism is discussed in more detail in Section 2.5.

Thickness of the coating and roughness of the surfaces

For soft coatings the thickness of the coating influences the ploughing component of friction, while for rough surfaces it affects the degree of asperity penetration through the coating into the substrate as shown in (a), (b), (e) and (f) in Fig 3[23,31–34]. A thick, hard coating can assist a softer substrate in carrying the load and thus decrease the contact area and the friction. Thin hard coatings on soft substrates are susceptible to coating fracture because of stresses caused by substrate deformation. Rough surfaces will reduce the real contact area, although the asperities may be subject to abrasive or fatigue wear, as shown in (c), (d), (g) and (h) in Fig 3[20,26,35–41].

Debris at the interface

Loose particles or debris are quite often present in sliding contacts. They can either originate from the surrounding environment or be generated by different wear mechanisms. Their influence on friction and wear may be considerable in some contact conditions, depending on the particle diameter, the coating thickness and surface roughness relationship, and the particle, coating and substrate hardness relationship. Particle embedding, entrapping, hiding and crushing represent typical contact conditions involving the influence of debris, as shown in parts (i) to (l) of Fig 3[18].

Micromechanical tribological mechanisms

The origin of the friction and wear phenomena that we observe on the macro level is found in the mechanisms that take place at the micro level. The micromechanical tribological mechanisms describe the stress and strain formation at an asperity-to-asperity level, the crack generation and propagation, material

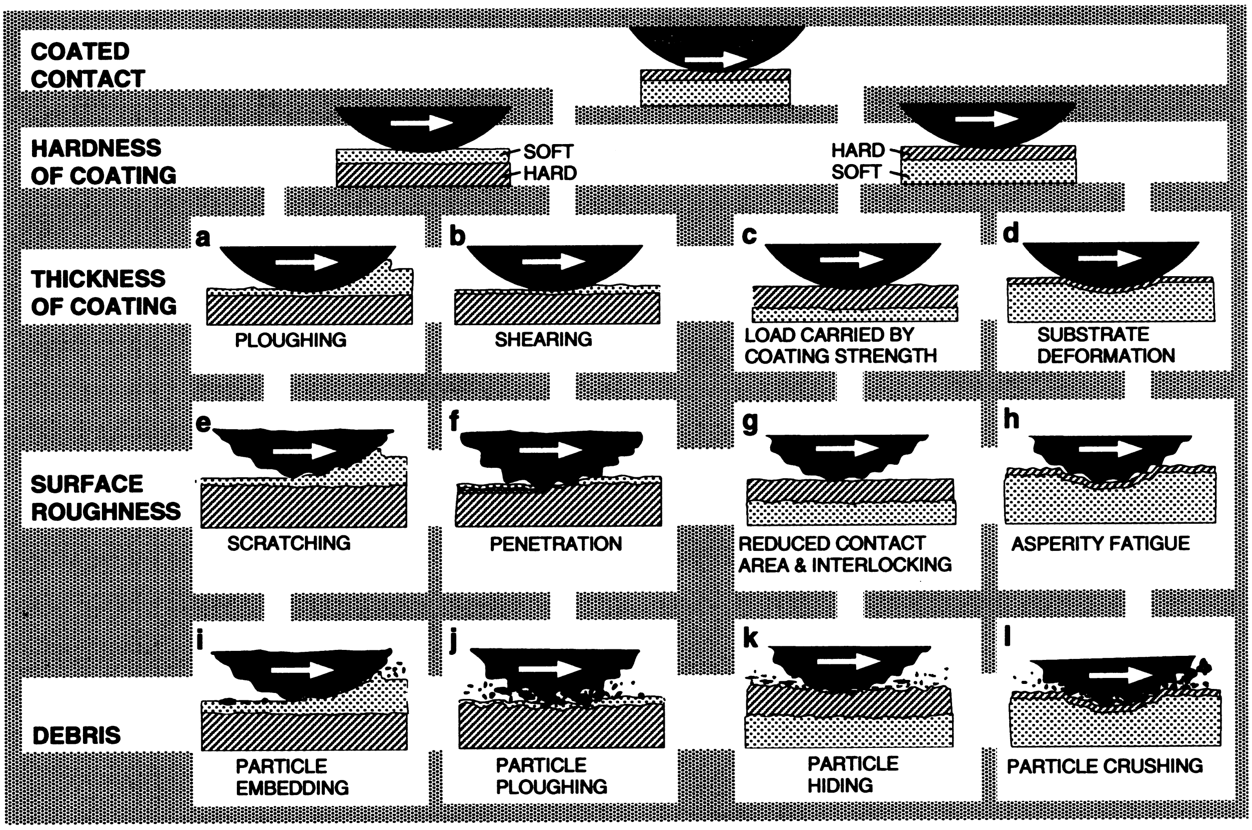

Fig. 3 Macromechanical contact conditions for different mechanisms that influence friction when a hard spherical slider moves on a coated flat surface

liberation and particle formation. In typical engineering contacts these phenomena are at a size level of about 1 μm or less down to the nanometre range.

Shear and fracture are two basic mechanisms for the first nucleation of a crack and for its propagation, until it results in material liberation and the formation of a wear scar and a wear particle. These mechanisms have been discussed by, for example, Argon[42] and Suh[20], but still today there is only a very poor understanding of these quite fundamental phenomena. Another approach is to study the tribological micromechanical mechanisms by using the velocity accommodation mode concept developed by Berthier *et al.*[43].

Recent studies of the stress intensity factor at the tip of a surface-breaking crack in a layered surface indicate that compressive stresses may tend to prevent crack propagation[13]. The crack pattern of ceramic coatings in indentation have been analysed and correlated to coating thickness and load, and the critical normal loads have been estimated by considering the deformation of the substrate[12]. There is a strong influence on both the fracture load and the fracture pattern of the mismatch between elastic properties of the layer and the substrate[44]. Variations in coating properties and coating thickness may change the fracture loads by up to a factor of 10.

Tribochemical mechanisms of coated surfaces

The chemical reactions taking place at the surfaces during sliding contact, and also during the periods between repeated contacts, change the composition of the outermost surface layer and its mechanical properties. This has a considerable influence on both friction and wear because they are determined to a great extent by the properties of the surface, where phenomena such as shear, cracking and asperity ploughing take place[45]. The chemical reactions on the surfaces are strongly influenced by the high local pressures and the flash temperatures, which can be over 1000°C, at spots where asperities collide.

Formation of thin microfilms on hard coatings

Very low coefficients of friction (down to μ = 0·1) have been reported for a hard titanium nitride coating sliding against itself[46] and even lower values (down to about μ = 0·01 but more typically 0·05) have been measured for diamond-like hard carbon (DLC) coatings sliding against different counter materials (reviewed by Donnet[21]) and diamond coatings sliding against diamond and ceramics[26,37,47,48]. This can be explained by the formation of low-shear microfilms on the hard coating or perhaps only on the asperity tips of the coating. Thus, if we consider the contact on a micro scale, there is effectively a soft coating on a hard substrate, although now the coating (e.g. diamond) plays the role of hard substrate and the soft microfilm formed plays the role of a coating. It is obviously advantageous if the substrate under the hard coating is as hard as possible, to avoid fracture of the brittle coating by deformation, to improve the load support and to decrease the real area of contact. The very low coefficients of friction of polished diamond and diamond-like coatings are further explained by the extreme smoothness of the surface excluding effects such as interlocking and asperity ploughing, as well as of the hard coating reducing the ploughing component of friction.

It has been shown that when a ceramic counterface slides against a titanium nitride coating an oxide layer is often formed. The wear rate and the friction are highly affected by this reaction product. This process has been described in an oscillating fretting wear contact by Schouterden *et al.*[49], Fouvry *et al.*[50] and Mohrbacher *et al.*[51] and in rotational sliding by Vancoille *et al.*[52].

A transfer layer is soon built up on the conterface when a steel or ceramic surface slides against a diamond-like hard carbon coating[53,54]. The explanation for the low shear strength between the two surfaces is, however, the formation of an extremely slippery microfilm between the surfaces. Different explanations for the structure of the microfilms have been presented and it is very difficult to analyse them conclusively[55].

Recently, Erdemir *et al.*[56,57], Liu *et al.*[58] and Schouterden *et al.*[49] have published convincing evidence in the form of Raman spectra of the surfaces and the wear products which indicate that graphitization is taking place and a low-shear-strength graphitic microfilm is formed between the surfaces. Perhaps the difficulty in finding the low-shear-strength film is associated with it occurring mainly in the form of graphitic wear products or third bodies present in the moment of sliding but partly disappearing thereafter. Erdemir *et al.*[56] showed that long-term sliding is needed before a more distinct graphitic layer can be detected and they measured coefficients of friction as low as $\mu = 0{\cdot}02$. The low friction and low wear behaviour of DLC coatings have been confirmed by several authors[24,48,59–64]. The lowest value for the coefficient of friction, $\mu = 0{\cdot}006$, has been measured by Donnet *et al.*[64] for a diamond-like carbon film deposited on a silicon wafer sliding against a steel sphere in vacuum below 10^{-1} Pa. Higher sliding velocities and loads improve the graphitization process and result in decreased friction and wear[53,58]. The DLC coatings can afford the low friction in temperatures up to 300°C[65]. Decreased friction and wear properties are generally reported for decreasing environmental humidity[21,64,66,67].

The friction and wear behaviour of polycrystalline diamond films, as influenced by complex physical and chemical effects, has been reviewed by Gardos[55]. The triboconditions under which one of the controlling factors dominates over the others are not yet clearly understood. In experiments carried out in dry N_2 with ceramic surfaces sliding on diamond coatings, Erdemir *et al.*[26] have shown that micrographitization takes place and results in extremely low friction down to $\mu = 0{\cdot}04$[47,68]. In open air, evidence on interface graphitization has not yet been found. Experimental results have been reported for aluminium oxide sliding against a diamond coating where lower humidity results in decreased wear but increased friction[69]. The coefficient of friction of a spheroidal fullerene C_{70} surface in the form of a pure C_{70} film on silicon sliding against different pin materials such as alumina and stainless steel is high[70], in the range of $\mu = 0{\cdot}5$–$0{\cdot}9$.

Oxidation of soft coatings

In environments containing oxygen, such as air, a thin (about 1–10 nm thick) oxide layer is formed very quickly on most metal surfaces. Some oxide layers, like copper oxide, are sheared more easily than the metal, while others, such as aluminium oxide, form a very hard layer. Improved lubricity caused by oxidation of the top layer of the coating has been observed for lead coatings[31] and for molybdenum disulfide coatings[71–73]. When sliding molybdenum disulfide coatings, a low-shear transfer film is rapidly built up on the counterface which can result in ultra-low coefficients of friction down to $\mu = 0{\cdot}002$ ([54,74]). Low friction and wear properties are achieved in vacuum or a dry environment while increased air pressure or humidity results in increased friction[21,54,75].

Nanomechanical contact mechanisms

Recently emerging technologies such as the atomic force microscope and the surface force apparatus[76] have opened the possibility to study friction and wear phenomena on a molecular scale and to measure frictional forces between contacting molecules at the nano Newton level. Increased computational power has made it possible to study friction and associated phenomena by molecular dynamic simulations of sliding surfaces and to investigate the atomic-scale contact mechanisms. The friction that arises from slippage between solid-to-solid interfaces[77] and between closely packed films in sliding contact[78] have been investigated. The atomic-scale mechanisms of friction when two hydrogen-terminated diamond surfaces are in sliding contact have been studied and the dependence of the coefficient of friction on load, crystallographic sliding direction and roughness have been investigated[79]. In another study the effect of atomic-scale roughness on friction when two diamond surfaces are placed in sliding contact was examined[80].

The increased understanding of the origin of friction at the atomic scale and even why friction exists has resulted in an examination of the relationship between the commonly used laws of friction at a macro scale and the molecular frictional behaviour on a nano scale. There have been suggestions that friction arises from atomic lattice vibrations occurring when atoms close to one surface are set into motion by the sliding action of atoms in the opposing surface. Thus some of the mechanical energy needed to slide one surface over the other would be converted to sound energy, which is then eventually transformed into heat[81]. Today we are only at the very beginning of understanding the nanomechanical tribological contact effects that explain the origin of friction and wear, and there is no doubt that in the near future many new theories and explanations for the origin of tribological phenomena will become available.

The scaling up of the nanomechanical explanations of contact mechanisms to practically useful conclusions on a macro scale is a most challenging and complex task and will take many years. Already there are practical applications on a nano scale where the increasing knowledge of tribological nanomechansims can be used. This has resulted in the development of Micro Electro Mechanical Systems (MEMS) such as motors, transducers, gears and bearings of sizes in the micrometre range. For these extremely small components silicon has been used in the early applications for production reasons but studies have shown that tribological improvements can be achieved by using polycrystalline diamond, MoS_2 thin coatings or hydrogenated diamond-like carbon coatings[54,82,83].

Mechanisms of material transfer

When a wear particle has been liberated from the surface, it can influence the tribological behaviour of the contacts in two ways. Loose wear debris in the contact may influence friction and wear as discussed above, although the wear debris may also attach to the counterface to form a transfer layer on it which changes significantly the tribological properties of the counterface. It can be said that a new counterface is formed, resulting in a new material pair.

Observations of the considerable influence of transfer films on the tribological behaviour of the contact have been reported, for example, for polytetrafluorethylene and polyimide coatings[84], titanium nitride coatings[38,85,86], diamond-like carbon coatings[53,54,56,57,60], diamond coatings[87] and for molybdenum disulfide coatings[54,88].

Multilayer and multi-component coatings

Multilayer coatings

In recent years, the use of multilayers has often been cited as the way forward to improve the mechanical, tribological and chemical properties of coatings. This has been argued from a number of standpoints. Firstly, taking the CVD coating industry as a guide, the move there has been to use many layers of different ceramics (e.g. [89–91]). Each layer can impart a specific property, such as the ability to act as a thermal barrier or diffusion barrier, or to impart abrasion resistance in metal cutting. Each layer in the coatings then has a discrete functional purpose. It has also been found that multilayer CVD coatings can enhance the life of punch tools and injection moulding dies[92].

In the PVD coating sector, multilayering work was carried out in the late 1970s and early 1980s by researchers at the Los Alamos laboratories in the USA[93,94]. They attempted to build on the earlier models of Koehler[95] which predicted that high-yield-strength materials could be fabricated by alternating thin layers of high-shear-modulus material with thin layers of low shear modulus. The model was based on inhibition of dislocation formation and mobility. The Los Alamos work investigated Al/Al_xO_y films deposited by a pulsed gas process in an electron beam gun system, and showed that a Hall–Petch type relationship was obeyed for yield stress, based on the layer spacings. Bunshah and co-workers also deposited microlaminate coatings by evaporation techniques; both metal/metal[96] and metal/ceramic[97] couples being studied. In general, an improvement in mechanical properties was observed for decreasing layer thicknesses.

In recent years, the literature and, at a certain level, the theoretical understanding of multilayer films has grown, in particular with regard to compositionally modulated 'superlattice' thin films (e.g. [98,99]). However, many of the theories developed are applicable to highly epitaxial or single-crystal layers, and whilst considerable progress has been made in understanding the theoretical aspects of superlattice hardening and strengthening mechanisms, their value in practical tribological systems is somewhat limited.

A more practical approach is to consider how the requirements of a surface differ at different locations within it—i.e. at the interface with the substrate, within the coating itself and at its surface as shown by Fig 4. Multilayer coatings offer a possibility to design the surface according to such requirements[1,100–102].

Holleck tended to use multilayers of different ceramic materials, such as TiC and TiB_2, selected on the basis of their dominant bonding mechanism, i.e. metallic, covalent or ionic. He demonstrated improvements in hardness, indentation toughness, adhesion and wear performance under optimised layer thickness conditions[103]. He attributes this, in part, to the crack deflection and stress relaxation mechanisms for the TiC/TiB_2 system.

This will pertain to many kinds of contact, especially where cyclic, fatigue-inducing, conditions prevail. Note that the benefits are no longer defined in terms of the early Koehler-type arguments based on the maximisation of yield strength. Rather they relate to the macro behaviour of the multilayer stack. However, the concept of the alternation of high- and low-shear-modulus layers does seem to provide benefits beyond those

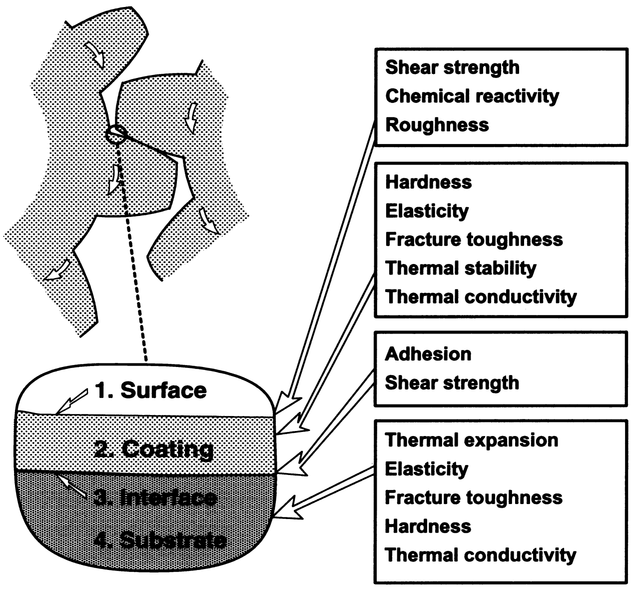

Fig. 4 Tribologically important properties in different zones of the coated surface

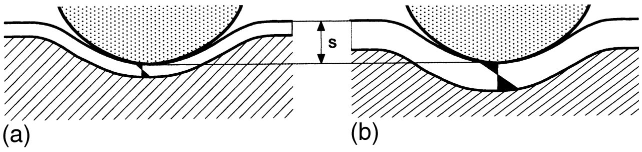

Fig. 5 (a) Thin hard coatings on a soft substrate generate lower stresses in the coating and at the coating/substrate interface compared with (b) thick hard coatings with the same deflection

described even by Holleck. We can cite, for example, the considerable benefits exhibited by multilayer diamond-like carbon and metal carbide films[104] or the multilayer TiN/Ti films[105–107]. In these cases a different argument has to be developed in order to fully explain the benefits observed.

One way to consider the behaviour of these films is to model the coating under a normal force which can be a point or distributed load, causing the coating to deflect. This will be accompanied by deformation of the substrate, which ideally should remain elastic.

If we consider the bending stresses induced in the coating under such a normal load, the level of maximum stress will increase with thickness for a given deflection and radius of curvature, see Fig 5. The diagram is highly schematic, and treats the coating in two dimensions as a beam, taking no account of the influence of the substrate on the stress distribution. Nevertheless it is illustrative since it shows that many multilayers, if bent to a similar radius, would individually see a much lower stress than one thick layer. This concept only works if the layers can effectively slide over each other, i.e. in the manner of a sheaf of paper or a paperback book being bent. In effect, we see another benefit of multilayer coatings, i.e. that the role of one of the sets of alternate layers can be to offer a shear zone to permit the harder (more brittle) layers to deflect under load without fracture. Thus a straight line scribed on such a cross-section would deflect as shown in Fig 6. This ensures that each of the hard layers will be subject to a much lower maximum bending stress than would be the case for a thick film bent to the same radius, although clearly the deflection under the same load would be greater, due to the lower ‘stiffness’ of the surface coating. That is not necessarily an issue, since for many tribological contacts with thin surface coatings it is the substrate which provides the main load support; the coating is present to provide a hard, low friction outer layer to reduce abrasive and/or adhesive wear.

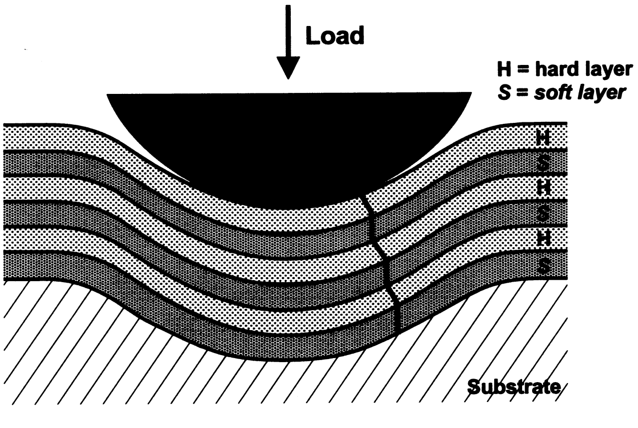

Fig. 6 A multilayer coating with alternate hard and soft layers can allow deflection to occur under load without yielding of the hard layers. They effectively slide over each other, with shear occurring in the soft layer. The pattern of shear is illustrated by the line through the film, which was initially straight in the unloaded condition

Thus we can now see why coatings based on DLC/WC and Ti/TiN, for example, have proved successful in many practical contact conditions. The former are now used on gears and bearing surfaces which see cyclic contact conditions[104], whilst the latter have shown promise in erosive conditions[99]. Since this concept is relatively new, the development of models to permit layer optimisation in terms of relative thickness and mechanical properties has been limited. The constraint on both the hard and soft layers may be that the elastic limit should not be exceeded, although this criterion seems more important for the hard layers, since if they yielded then rapid fracture would ensue.

The softer layers will be present to give an easy shear, i.e. they should have a low shear modulus, which equates to a low elastic modulus. Also these layers should have a long elastic strain to failure, meaning that yield should not occur. Although in this case plastic yielding is to be avoided, especially in contacts subject to cyclic loading and fatigue, the main purpose will be to prevent the harder layers from exceeding their yield stress. There are some interdependent variables in the optimisation of layer thicknesses. For example, since the layers also carry a load normal to the surface, they will be subject to compressive stresses, which will tend to squash the layers and in particular the softer ones. This will have the effect of limiting their minimum thickness—otherwise they may collapse and provide inadequate support for the harder layers within the coating. Note that whilst an increase in the thickness of the layers will increase the relative sliding distance of one hard layer over another, it will not necessarily increase the shear strain—which is a ratio between the sliding distance of one hard layer over the next and the thickness. The ideal seems to be to incorporate a large number of thin layers, thereby ensuring that the load support is not compromised. In the case of DLC/WC coatings produced commercially, layer thicknesses of 20 nm are typical for sliding and rolling contacts whilst for Ti/TiN films, layers 1 μm and 2 μm thick have proved effective in erosion conditions. The optimisation of layer thickness will thus depend on the application and the loading conditions. In erosive or abrasive contacts, for example, a greater overall coating thickness is often needed, especially for coarse and hard third bodies.

The benefits of the multilayering of relatively hard and relatively elastic layers has recently been demonstrated in a specially developed cyclic impact test[108,109]. In that work, a relatively soft substrate (316 stainless steel) was used. This deformed plastically under repeated loads of 900 N applied at a frequency of 8 Hz by a 6 mm diameter tungsten carbide ball, while coatings comprising multilayer stacks of Ti, TiN, TiCN, TiC, Ti/DLC, TiC, Ti/DLC showed good wear performance, though not optimised for adhesion. Further tests using machines such as this, which apply the kinds of impact load often encountered in industry, will allow the full benefit of multilayered coatings to be achieved through further optimisation.

In effect, the above represents a functionally graded coating designed to utilise specific layers for the provision of distinct properties (Fig 7)[25,101,110]. Such a concept can even be achieved with just two layers; for example, an electroless nickel coating can be used as a load supporting layer for a hard PVD TiN or CrN coating, to improve the abrasive wear performance and enhance the corrosion resistance[111,112]. It is even possible to include within this approach the concept of pretreating a substrate surface, to produce a hardened outer layer, which can then support the coating more effectively. Such approaches have been termed hybrid or duplex coatings[113–115].

Multi-component coatings

Although the multilayer films are all effectively ‘multi-component’, this title is usually reserved for coatings in which there is a mixing of phases but not in a layered sense. For many years it has been known, for example, that mixed phases of ceramics such as HfN and TiN could exhibit higher hardnesses than each phase on its own. Now there is intense research being carried out into other mixed ceramics, especially TiAlN[116–118], TiCN[118–120], Ti,B,N[121,122] and others (e.g. [123,124]). These coatings can exhibit much improved properties—e.g. in terms of high-temperature hardness and oxidation resistance or suitability for interrupted cutting applications due to improved impact resistance. In some processes these mixed phases are deposited using an approach which is identical to that for multilayered films—e.g. by rotating samples in front of two or more sources or targets of each material. Whether this leads to multilayering or complete mixing depends largely on the speed of rotation and/or the degree of scattering and mixing of the vapour. The boundary between the definitions of multilayered and multicomponent is thus somewhat blurred. Subramanian and Strafford[91] add further types: ‘multi-phase’ and ‘composite’, depending upon the size and distribution of any secondary phase(s) in the primary matrix. Terminology thus presents a further complication, and there is no doubt that, on these definitions, even many multilayered coatings could be defined as composites, or at least as mixed multilayer/composite structures. In a sense this illustrates the enormous potential of these coatings; at the same time the requirement to coat complex shapes in a controlled way with such ‘fine-tuned’ coatings can present problems[125].

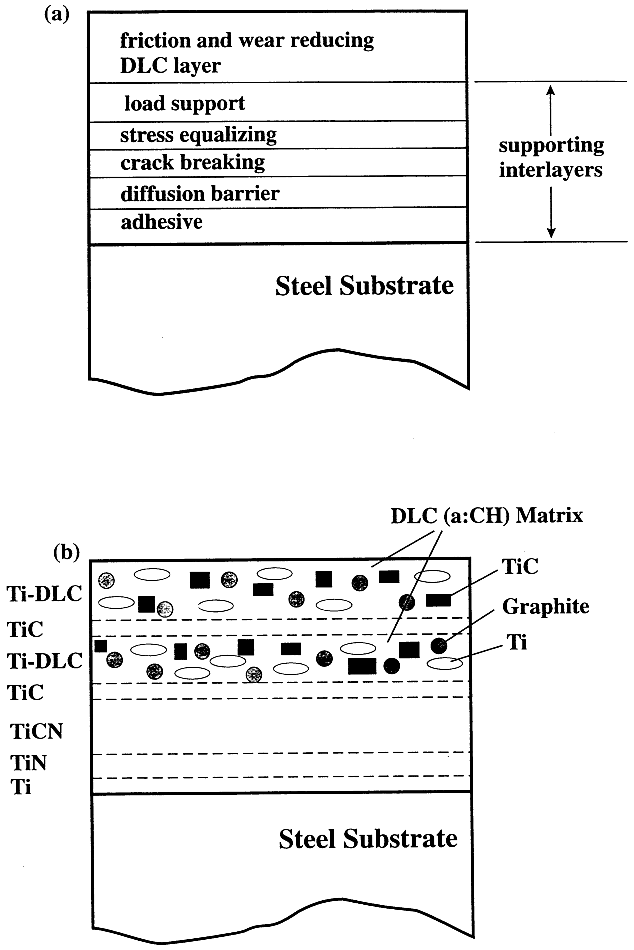

Fig. 7 (a) A functionally graded multilayer coating design to utilise specific layers for distinct properties. (b) A particular multilayer coating tested by Voevodin et al.[25]

As mentioned in Section 2, hard coatings can be further improved if a film with relatively low shear strength is deposited at the outer surface. This represents a further modification to the multilayering concept. In effect, the gradient coatings described above, with DLC as the outer layer, are an example of this approach. Another suitable low-friction layer is MoS$_2$ ([21]), although at the present time the greatest research interest lies in carbon-based layers. As explained in the next section, when suitably deposited, these can even provide benefits in lubricated contacts, thus providing a wider range of operating conditions. It is likely that further developments will see other solid lubricant outer layers being developed for specific applications—for example, films for high-temperature sliding at 700°C and above are already under test[126,127].

With developments such as those described above, advanced coating processes are now allowing tribologists to specify exactly the optimised surface properties they need.

Lubricated coated surfaces

We have seen that thin diamond and diamond-like carbon coatings deposited in low-pressure conditions, such as with the PVD and CVD techniques, can provide excellent low-friction and wear-protection properties in dry sliding conditions[1]. The typical coefficients of friction values measured against steel are lower than typical values for boundary-lubricated sliding with good oil lubrication and thus considerably lower than for any other hard coated surfaces in dry sliding conditions. Only thin MoS$_2$ coatings can provide a similarly low friction. But, at the same time, the diamond and diamond-like carbon coatings also provide an excellent wear resistance of about one order of magnitude lower wear than for any other wear-resistant coatings. The diamond-like carbon coatings are of special interest because of their considerably lower deposition temperature compared with diamond films, which enables a larger variety of substrate materials to be coated.

The excellent tribological properties of diamond-like carbon coatings have been verified in many tests in dry conditions. However, the tribological performance of coatings in industrial applications may also be influenced by water or oil from the surrounding environment. In practical applications the coatings will at least be exposed to humidity. Earlier, the tribological performance of amorphous hydrogenated carbon films (a-C:H) and hydrogen-free hard carbon (a-C) films in dry, unlubricated conditions was studied[63,128,129]. The results verify the low-friction and high wear-resistance properties of a-C:H and a-C coatings referred to by several authors. To ensure the functionality of a-C:H and a-C coatings in water and oil environments, their tribological performance was studied in such lubricated conditions[130].

As a general trend, the hydrogen-free hard carbon coatings, deposited by vacuum arc, are more wear-resistant than hydrogenated carbon films deposited in a capacitively coupled RF plasma. On the other hand, the counter parts sliding against a-C films suffer from more severe wear compared with counter parts sliding against the a-C:H films. The coefficient of friction is also generally lower for the a-C films.

The effect of water lubrication

When the coatings are exposed to water lubrication, the water is a very aggressive medium for the a-C:H coatings and causes catastrophic failure of the coating[129]. The coating is peeled off in an early stage of the test, after only about 1·5 h of sliding. The same type of behaviour has also been reported by Drees *et al.*[131]. The a-C:H(Ti) film, with a titanium-alloyed surface layer, endures the test even though the water lubrication increases the wear of the coating (Fig 8). Since titanium alloying of the a-C:H coating improves the performance of the coating in water, it is suggested that the hydrogenated structure itself is vulnerable in a water environment. Conversely, the a-C coating performed well with water lubrication, since no measurable wear could be detected even after 21 h of sliding in the pin-on-disc test. Obviously the hydrogen-free structure of the a-C coatings is preferable compared with a-C:H coatings for providing lower wear and friction, even when water is introduced to the system.

The pin wear rates increased against both a-C and a-C:H(Ti) coatings in water-lubricated conditions. The tribolayers formed on the wear surfaces in dry sliding conditions usually reduce the pin wear and the friction coefficient. In a water environment the formation of protective tribolayers is prohibited and thus the pin wear is increased. However, the coefficient of friction is significantly lower for the water-lubricated coatings, particularly for the a-C coating.

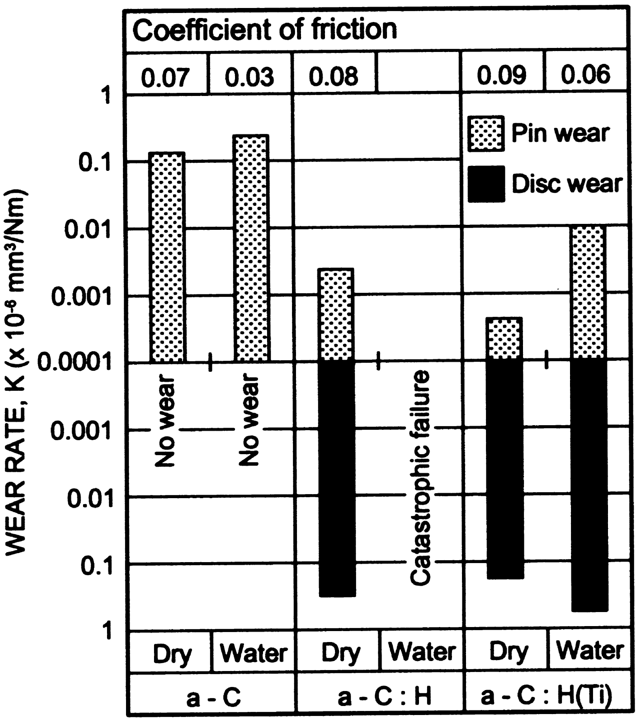

Fig. 8 The friction and wear results of water-lubricated reciprocating wear tests. The counterface material was an alumina ball with 10 mm diameter. The sliding speed was 4 mm s^{-1} and the normal load was 5 N

The effect of oil lubrication

Oil lubrication reduces the friction coefficients in uncoated, as well as in coated tribosystems. The mineral base oil (oil 1) has only a minor effect on friction behaviour of a-C and a-C:H coatings, but hydraulic oil with EP additives has a greater effect on the friction coefficient as shown in Fig 9[129]. For the titanium-alloyed a-C:H(Ti) coating the friction coefficient is increased when oil is introduced in the contact. This shows that in dry conditions a tribologically beneficial tribolayer formed on the wear surfaces, which provides a low coefficient of friction. Actually the a-C:H(Ti)

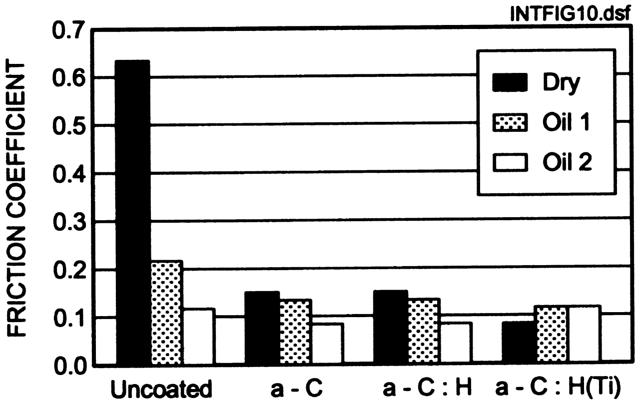

Fig. 9 The coefficient of friction from oil-lubricated reciprocating sliding tests. The counterface material was a steel ball with 10 mm diameter. The sliding speed was 4 mm s^{-1} and the normal load was 10 N

coating shows a lower friction coefficient in dry conditions than the uncoated contacts in oil-lubricated conditions. This low-friction behaviour of alloyed a-C:H films has been reported also by several other authors (e.g. [104,132,133]). By the addition of oil the formation of this tribolayer is prevented, thus causing an increase in the friction coefficient. The frictional behaviour of the coatings in oil-lubricated conditions is governed by the lubricative properties of the oil, particularly when the oil with EP additives is used. Surprisingly, in tests with oil containing EP additives, the a-C coated contacts had the lowest friction, which suggests that the hydrogen-free coating can have a beneficial effect when used with EP additives. No coating wear of the a-C and a-C:H coating is detected when oil lubrication is used. However, the oil lubrication prevented the formation of the tribolayer on the pin wear surface in the same manner as the water lubrication, which increased the pin wear rates to some extent.

The lubricated tests showed that the DLC coatings give low friction and high wear-resistance performance in dry conditions, which can still be improved with oil lubrication. The a-C coatings operated well also in water-lubricated conditions, but for the a-C:H coating the water-lubricated conditions were detrimental. Considering the utilisation of DLC films in practical components, it is suggested that a-C coated components can be used also in lubricated conditions to give additional safety for friction and wear control in, for example, poorly lubricated conditions.

Conclusions

The fast development of a large variety of different advanced surface modification and coating deposition techniques during the last few decades offers remarkable possibilities to improve the tribological properties of surfaces and thus improve the functional reliability and lifetime of tools, components and other surfaces in sliding contact. Full advantage of these developments can only be achieved when appropriate methods for surface design and optimisation are available. To support this, a systematic approach to the analysis of tribological coated surfaces has been outlined. It is based on a classification of the tribological contact process into macro-, micro- and nanomechanical and tribochemical contact mechanisms and material transfer.

The use of thin multilayers offers an excellent possibility for surface design to achieve the required properties at the surface. Increased coating/substrate adhesion, improved load support, surface stress reduction and improved crack propagation resistance can be achieved by different concepts of multilayer surface design.

From a tribological point of view, the diamond and diamond-like hard carbon coatings represent the most dramatic new coating concept introduced during the last few decades. In dry sliding the friction can be extremely low with a coefficient of friction of less than 0·01 and a wear resistance more than one order of magnitude better than for any other hard coating. The diamond-like coatings can also be used with good tribological performance in oil- or water-lubricated conditions with some care. For example, hydrogenated diamond-like coatings may show catastrophic failure when sliding in water environment while hydrogen-free DLC coatings perform well.

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