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Ceramics International 26 (2000) 787–795

CERAMICS INTERNATIONAL

Review

Tribology of thin coatings

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Received 24 July 1999; received in revised form 31 August 1999; accepted 4 September 1999

Abstract

The fundamentals of coating tribology are presented in a generalised holistic approach to friction and wear mechanisms of coated surfaces in dry sliding contacts. This is based on a classification of the tribological contact process into macromechanical, micromechanical, tribochemical contact mechanisms and material transfer. The tribological contact process is dominated by the macromechanical mechanisms, which have been systematically analysed by using four main parameters: the coating-to-substrate hardness relationship, the film thickness, the surface roughnesses and the debris in the contact. The description covers both soft and hard coatings with thicknesses typically in the range 0.1–50 μm, where the interaction between the coating and the substrate is essential to the tribological behaviour. The concept is supported by experimental observations. The important influence of thin tribo- and transfer layers formed during the sliding action is shown. Optimal surface design both regarding friction and wear can be achieved by new multilayer techniques giving reduced stresses, improved adhesion to substrate, more flexible coatings and harder and smoother surfaces. The differences in 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 ball. The mechanisms of the formation of dry transfer- and tribolayers and lubricated boundary and reaction films are discussed.

Keywords: A. Films; C. Friction; C. Wear resistance; D. Carbon

Contents

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PII: S0272-8842(00)00015-8

1. Introduction

There has been a large interest in studying thin surface coatings for wear protection and friction reduction both in the scientific community and in industry. Recent advances in coatings technologies now permit the deposition of films with properties which were unachievable even a decade ago. Examples are multilayered and metastable coatings with extreme mechanical and chemical properties. The 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.

The paper presents a review of the present level of understanding of contact mechanisms, especially for thin coated surfaces. This includes an appreciation of stress states, mechanical properties and chemical influences. The possibilities opened up by using multiple layers of coatings are 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. Their behaviour in dry and lubricated conditions is discussed.

2. Tribological 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. Other input data are the energy parameters such as 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.

2.1. 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 separately analyse 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. 1. In addition there has recently been an increasing interest in studying tribological behaviour on a molecular level; i.e. nanomechanical or nanophysical effects [2].

A better and more systematic understanding of the mechanisms involved in a tribological contact is neces-

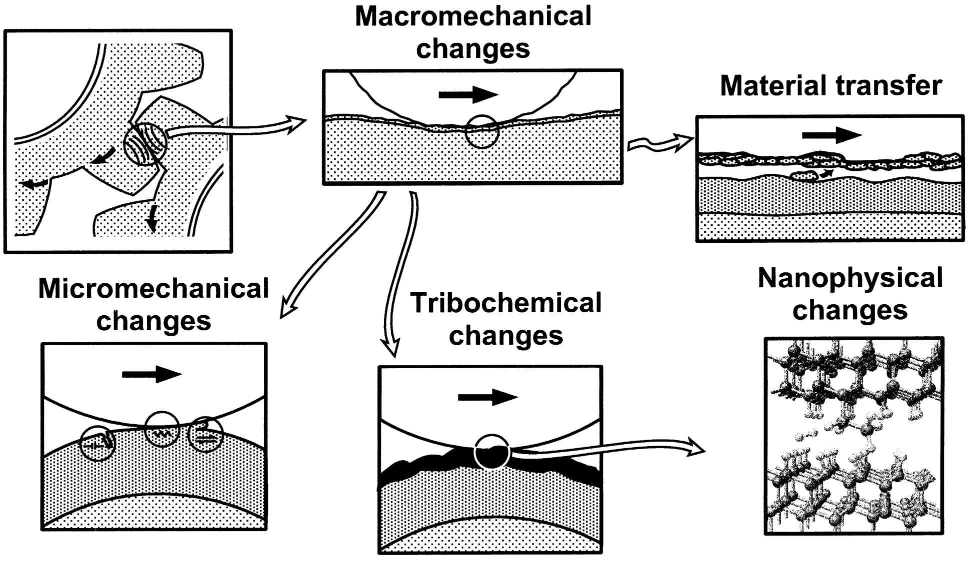

Fig. 1. Tribological contact mechanisms are related to macromechanical changes, material transfer, micromechanical, tribochemical and nanophysical changes in the contact.

sary for the 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.

2.2. 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. 2 shows, schematically, 12 such very typical tribological contacts, with different mechanisms influencing friction, when a hard spherical slider moves on a coated flat surface [5]. The corresponding wear mechanisms have been described in a similar way [6].

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 [7,8]. The advantages of using a soft coating to reduce friction are well known, owing to the work of Bowden and Tabor [9] and others. Soft coatings such as Ag and Au may also have the function of reducing sliding-originated surface tensile stresses, that contribute to undesirable subsurface cracking and subsequently to severe wear [10]. A hard coating on a softer substrate can decrease friction and wear by preventing ploughing both on a macro scale and a micro scale [6,11–13]. 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 due to counterpart load.

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. 2 [10,14,15]. 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,

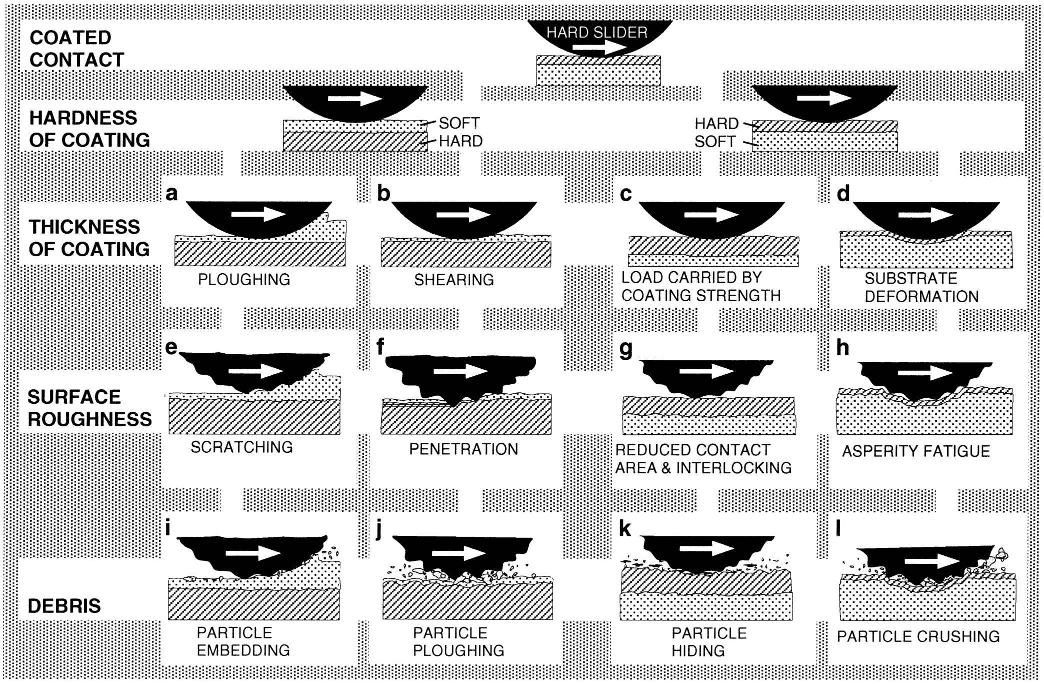

Fig. 2. Macromechanical contact conditions for different mechanisms which influence friction when a hard spherical slider moves on a coated flat surface.

although the asperities may be subject to abrasive or fatigue wear [7,13,16–19].

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, 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 Fig. 2 (i)–(l) [5].

2.3. 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 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 as shown in Fig. 1.

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 formation of a wear scar and a wear particle. These mechanisms have been discussed by for example Argon [20] and Suh [7], 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. [21].

2.4. 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 [22]. 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.

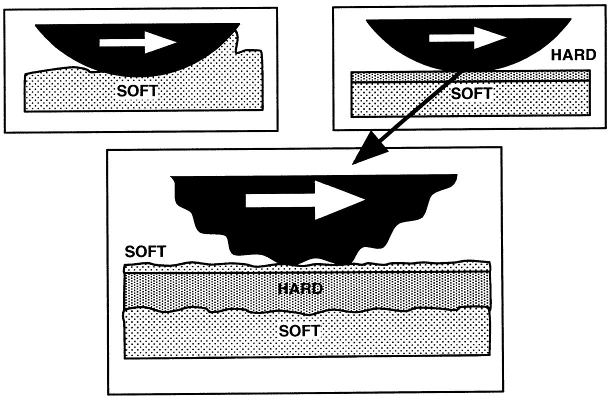

Fig. 3. A hard coating on a soft substrate inhibits ploughing and a soft microfilm on the hard coating results in decreased friction.

2.5. Formation of thin microfilms on hard coatings

Very low coefficients of friction (down to $\mu = 0.1$) have been reported for a hard titanium nitride coating sliding against itself [23] and even lower values (down to about $\mu = 0.01$ but more typically 0.05) have been measured for diamond-like hard carbon (DLC) coatings sliding against different counter materials (reviewed by Donnet [8]) and diamond coatings sliding against diamond and ceramics [13,16,24,25]. 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, as shown in Fig. 3. 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.

A transfer layer is soon built up on the counterface when a steel or ceramic surface slides against a diamond-like hard carbon coating [26,27]. 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 [28].

Recently Erdemir et al. [29,30], Liu et al. [31] and Schouterden et al. [32] 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.

2.6. Nanophysical contact mechanisms

Recently emerging technologies such as the atomic force microscope and the surface force apparatus [33] 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 [34] and between closely packed films in sliding contact [35] 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 [36]. In another study the atomic scale roughness effect on friction when two diamond surfaces are placed in sliding contact was examined [37].

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 [38]. Today we are only at the very beginning of the understanding of 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 nanophysical 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 micrometer 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 or MoS_2 thin coatings or hydrogenated diamond-like carbon coatings [27,39,40].

2.7. *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 [41], titanium nitride coatings [42,43], diamond-like carbon coatings [26,27,29], diamond coatings and for molybdenum disulphide coatings [44,27,45].

3. Multilayer and multicomponent coatings

3.1. *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. A 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.

By using multilayer coatings it is possible to improve the tribological properties by increasing the coating/substrate adhesion, by improving the load support, by reducing the surface stresses and by improving the resistance for crack propagation as shown in Fig. 5. 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 [46], whilst the latter have shown promise in erosive conditions.

The benefits of the multi-layering of relatively hard and relatively elastic layers has recently been demonstrated in a specially developed cyclic impact test [47,48]. In that work a relatively soft substrate (316 stainless steel) was used. This deformed plastically under repeated loads of 900N applied at a frequency of 8 Hz by a 6 mm diameter tungsten carbide ball, 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 loads often encountered in industry, will allow the full benefit of multi-layered coatings to be achieved through further optimisation.

Although the multilayer films are all effectively "multicomponent", 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 [49–51], TiCN [51–53], Ti,B,N [54,55] and others, e.g. [56,57]. 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.

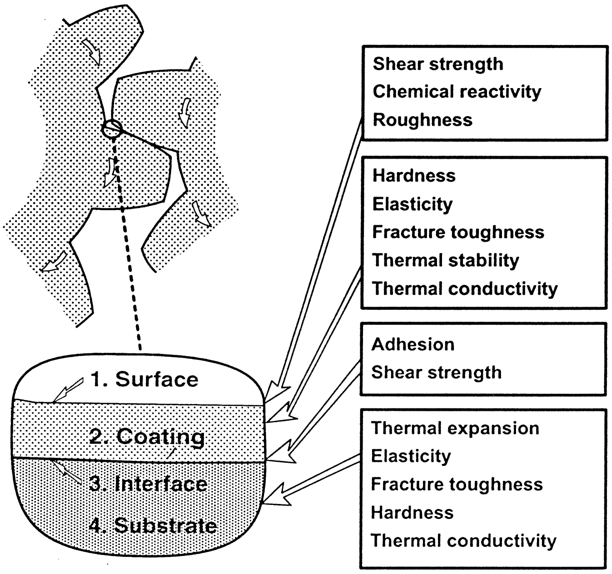

Fig. 4. Tribologically important properties in different zones of the coated surface.

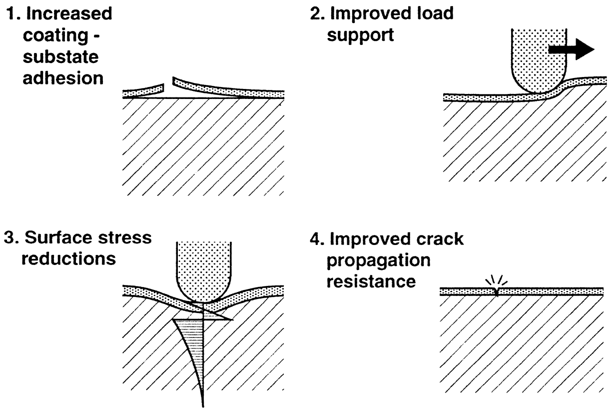

Fig. 5. A multilayer coating can improve the tribological properties of the surface by increasing the coating/substrate adhesion, improving the load support, reducing the surface stresses and improving the resistance to crack propagation.

Hard coatings can be further improved if a relatively low shear strength film 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 [8], 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 700C and above are already under test [58,59].

With developments such as those described above, advanced coating processes are now allowing tribologists to exactly specify the optimised surface properties which they need as shown in Table 1.

4. Water and oil lubricated DLC coated sliding contacts

The diamond-like carbon coatings are of special interest because of their considerably lower deposition temperature compared to 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 the hydrogen-free hard carbon (a-C) films in dry, unlubricated conditions was studied [60–62]. The results verify the low friction and high wear resistance properties of a-C:H and a-C coatings referred to by several

Table 1
Properties of different layers in multilayer coatings

Required property	Type of coating	Coating material examples	Typical coating thicknesses, μm
Wear resistance	Hard coatings	TiN, TiC, Al_2O_3, diamond	0.5–5
Low friction (shear)	Soft or layered coatings	Pb, PTFE, MoS_2, diamond	0.5–5
Lubricity	Liquid coatings	Perfluoropolyether	0.001–0.05
Corrosion resistance	Dense, inert coatings	Au,Zn, Cd, Al_2O_3	3–20
Adhesion to substrate	Soluble or bonding coatings	Ti, Cr, Si_2N_3	0.01–1
Diffusion barrier	Dense, inert coatings	Ni, NiAl, Al_2O_3	1–30
Thermal barrier	Insulating coatings	ZrO_2,PSZ	50–250
Magnetic	Metallic coatings	γ-Fe_2O_3, Ci–Ni, Co-P	0.02–5
Electrical conductivity	Noble or pure metal coatings	Au, Cu	1–10

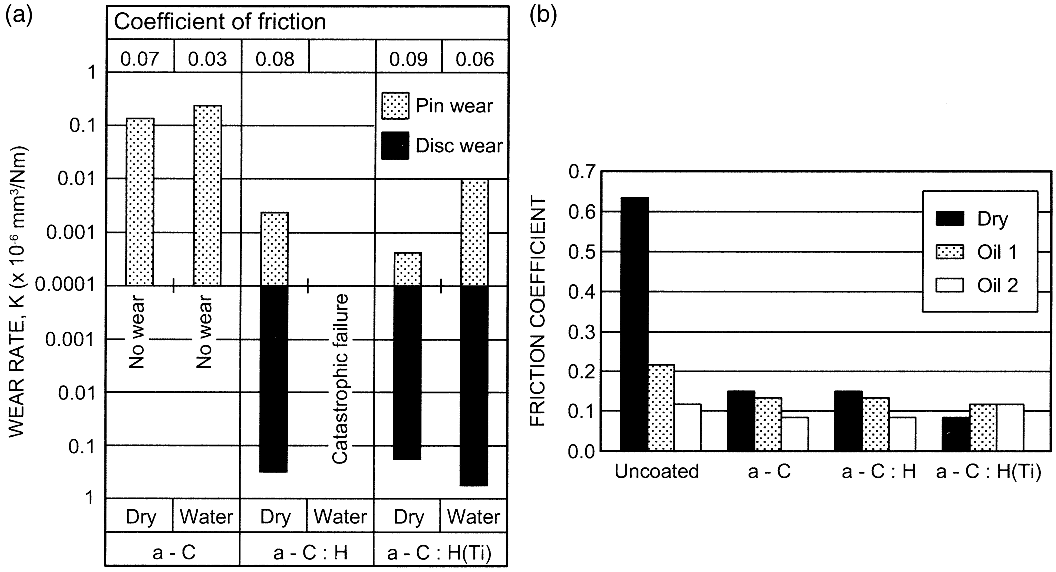

Fig. 6. (a). Friction and wear results from dry and water lubricated reciprocating sliding tests. The counterface material was an alumina ball with 10 mm diameter. Sliding speed 4 mm/s and normal load 5 N. (b). The coefficient of friction from oil lubricated reciprocating sliding tests. The counterface material was a steel ball with 10 mm diameter. Sliding speed 4 mm/s and normal load 10 N.

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 [63].

As a general trend the hydrogen free hard carbon coatings, deposited by vacuum arc, are more wear resistant compared to hydrogenated carbon films deposited in a capacitively coupled r.f. plasma, shown in Fig. 6. On the other hand the counter parts sliding against a-C films suffer from more severe wear compared to counter parts sliding against the a-C:H films. The coefficient of friction is also generally lower for the a-C films.

4.1. 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 [63]. The coating is peeled off in an early stage of the test, after only about 1.5 h sliding. The same type of behaviour has also been reported by Drees et al. [64] 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, shown in Fig. 6a. Since titanium alloying of the a-C:H coating improves the performance of the coating in the 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 to a-C:H coatings 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.

4.2. The effect of oil lubrication

The 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 the hydraulic oil with EP additives (oil 2), has a greater effect on the friction coefficient, as shown in Fig. 6b [63]. 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) 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. [46,65,66].

By the addition of oil the formation of the tribolayer on a-C:H(Ti) 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 the coefficient of friction 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 e.g. poorly lubricated conditions.

5. Conclusions

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 nanophysical 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. In dry sliding the friction of diamond and diamond-like hard carbon coatings can be extremely low with a coefficient of friction less than 0.01 and a wear resistance more than one order of magnitude better than for any other hard coating. The hydrogen-free diamond-like carbon coatings can be used with good tribological performance in oil or water lubricated conditions.

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