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Tribofilms in Solid Lubricants

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Synonyms: Tribo-layers, Transferred layers / Films.

Definition

Tribofilm is defined as a thin solid film generated as a consequence of sliding contact, which is adhered on its parent worn surface but has different chemical composition, structure and tribological behaviour. Tribofilms are found to exist in many tribo-systems, where they work as a ‘third body’ having remarkable influence on both the friction behaviour and the wear performance. Up to date, the fundamental understanding of tribofilms is increasingly enriched, especially attributed to the instrumental advances in materials characterisation techniques. These research efforts in turn contribute to the synthesis of novel tribological materials.

A solid lubricant refers to such a functional material which can significantly decrease the friction force of a tribo-system when it is introduced to the sliding interface. However, the friction property of a solid ‘lubricant’ depends not only on the chemical composition, structure and physical properties of the solid, but also on the applied tribo-system including the counterface, applied load and sliding speed, sliding distance, temperature, and the chemical species in environment. In many circumstances, the friction behaviour of a solid lubricant is environment-dependent because of the formation of different tribofilms at varying tribological conditions.

Scientific Fundamentals

Classification of Tribofilms

Tribofilms can be classified according to their generation process, which in fact involves complex mechanical, chemical and thermal reactions of matters including not only the couple of sliding surfaces, but also the environment species. For example, Biswas described three types of tribofilms formed in metal-to-metal and metal-to-ceramic sliding interactions, namely, mechanically mixed, chemically generated and thermally activated tribofilms [1].

On the other hand, tribofilm formation is one of many important phenomena resulted from a sliding process. To distinguish tribofilms from other components of a tribo-system, the following aspects are excluded this classification:

- The gaseous and liquid adsorption films on a solid surface;
- Sliding induced plastic deformation layer without changes in the crystalline structure and or chemical composition;
- And solid particles entrapped in a sliding interface without forming a continuous film, whether they are wear debris or from the environment.

Tribofilms can be classified into the following four types.

I. Tribofilms generated from the wear of the major constituents of the sliding couple surfaces;
II. Tribofilms generated from the preferential wear of the soft or lubricious constituents of a multi-phase or composite material;
III. Tribofilms being different from the parent worn surfaces in chemical composition and or crystalline structure as a result of sliding contact;
IV. Tribofilms generated as a result of tribo-chemical reactions between the wear products (i.e. wear debris and worn surfaces) and the environmental species.

The first type of tribofilms can be found in the running-in sliding wear of metals and ceramics. Because of strong metallic, ionic or covalent bonding of these materials, tribofilms of this type usually form strong adhesive bonding to the parent worn surfaces and thereafter trigger high friction coefficient. For example, the origin of high friction coefficients in dry sliding wear of transition metal nitride coatings was found to be attributed to the formation of tribofilms [2].

The tribofilms formed in many solid lubricant materials belong to the second type. For example, grey cast iron is a multi-phase alloy, its microstructure comprising ferrous matrix and graphite. In sliding wear, preferential wear of the relatively soft graphite flakes results in a carbon based tribofilm adhering on the worn surface which breaks the adhesive joints between the ferrous asperities and thereafter leads to low friction. Free cutting steel is a special grade of ferrous alloys containing certain amount of sulphur, phosphorous, lead, or other elements to form soft inclusions in the structure. In machining, these inclusions are worn and transferred onto the tool surface as a lubricious tribofilm to reduce cutting forces. The formation of such tribofilms facilitates high machining speed.

In the third type, the tribofilm is different from the parent material due to the occurrence of either chemical reactions or phase transformation. For example, diamond and diamond-like-carbon (DLC) are known to exhibit low friction in various sliding conditions, which have been found to be attributed to a sliding induced graphitisation [3]. The graphitisation results in the generation of a nano-scale tribofilm having sp^2-type chemical bonding. More details of the graphitisation will be described in next section. Other examples of tribofilms belonging to this type may include the ‘white-etching layer’ observed on the worn surface of alloy steels after high-stress and high-speed sliding wear, and the hardened ε-martensite layer of the worn surfaces of high-carbon and high-manganese austenitic steel after severe impact wear.

Tribofilms of the fourth type are the most popular because that most tribo-systems are exposed to the environments containing chemically reactive species such as oxygen, water moisture and or others. For example, sliding wear of steels at mild loads results in the formation of an oxide film strongly adhering to the metallic worn surface reducing severe metal-to-metal adhesive contacting. In lubricated sliding contacts, some additives in the lubricating fluid may chemically adsorb on the worn surface to deposit as a protective tribofilm reducing friction and wear.

It should be pointed out that the classification of these four types of tribofilms may have exceptions due to the limited reading of literatures. Meanwhile, the continuous emerging of novel tribological materials will advance the friction and wear performance and give birth to the generation of new unknown tribofilms. Also the current understanding about tribofilms will certainly be updated when increasingly more research is spent in this area, especially with the advances of materials characterization techniques. Nevertheless, the classification can be considered as an outline of up to date understanding of tribofilm formation, while more detailed examples are given in the following section.

Mechanisms of Tribofilm Formation - in a ceramic coating

Most sliding processes start with a so-called ‘running-in’ stage. In this stage, the worn surface experiences a series of topographical, structural and chemical changes, including the generation of a tribofilm. Meanwhile, the friction coefficient undergoes a series of dynamic changes until it enters the period of steady state sliding when the friction coefficient becomes relatively stable and the sliding continues in conformal contact.

This section presents a piece of experimental study to demonstrate the mechanism of tribofilm generation in a magnetron sputtered transition metal nitride coating. Relevant research can be found in literatures [2, 4-6].

Transition metal nitride coatings grown by physical vapour deposition, such as the TiAlN/VN shown in this case, have excellent wear resistance owing to their high hardness, good chemical and thermal stability, and excellent oxidation resistance. Most coating surfaces, however, are non-flat in micro- and nano-scales subjected to the deposition conditions, Figure 1. A friction curve obtained in a ball-on-disk tribotest shows the dynamic variation of friction coefficient in the running-in sliding period of the coating, Figure 2. The tests were undertaken against an alumina ball at applied normal load 5 N, linear sliding speed 0.1 $m \cdot s^{-1}$, in air at room temperature and at relative environmental humidity 30 – 40%. Figure 2 also shows SEM images taken on the worn surfaces after different sliding cycles, including the evolution of wear debris size and the tribofilm formation.

The tribofilm was generated in the following process. Initial sliding contact took place on a limited number of surface asperities, i.e. the top points of the growth defect grains protruding upon the coating surface. The concentrated compressive and tangential loads resulted in prompt fracture of these grains leading to the generation of first wear particles, seeing one such fracture evidenced in Figure 2. This process continued until all the protruding grains inside the wear track were worn off. Meanwhile, some of the wear particles entrapped within the sliding contact zone worked as a ‘third body’ to make special contributions to the tribo-system. Firstly, the sliding and rolling motion of the wear particles resulted in high-stress abrasive wear of the coating. Secondly, these particles were further broken themselves into progressively smaller sizes. Then taking account of the increased surface to volume ratio of the wear debris and the strong ionic chemical bonding of the TiAlN/VN nitride, high compressive and shear loading as well as frictional heating in the sliding contact zone, would promote both the self agglomeration of the fine wear debris into clusters and the ionic adhesion of the clusters to the worn surface, which eventually led to the formation a continuous film to attach on the parent worn surface. Afterwards, further sliding was more restricted within the tribofilm and resulted in continuous powdering or amorphorisation. Figure 3 shows a high resolution SEM image of the tribofilm of the TiAlN/VN coating after 200,000 cycles of ball-on-disk sliding wear. Figure 4 is cross-sectional TEM observation of the tribofilm, in which the tribofilm is approximately 80 nm thick, exhibits amorphous structure and has a distinct interface with the adjacent TiAlN/VN. Tribofilms of similar amorphous structure have also been observed on the worn surfaces of other transition metal nitride coatings, such as TiN, TiAlN/CrN and TiAlCrYN.

The experiment also demonstrated the relation between the tribofilm formation and the friction behaviour. The friction curve shows that the coefficient of friction was less than 0.2 in the beginning prior to the tribofilm formation. Then it increased immediately to 0.3 – 0.4 in the first 20 sliding cycles due to the entrapped wear particles arising from the mechanical wear. Eventually the friction coefficient increased to 0.55 accompanying the formation of a continuous tribofilm. The high friction arose from the severe shear deformation and adhesive interaction of the tribofilms. Such adhesive interaction was attributed to the ionic bonding of the tribofilm. It is known that adhesive interaction is one of the major components forming the frictional resistance in a sliding process. The adhesive interaction depends on the inter-atomic bonding, for which strong ionic, metallic and covalent bondings result in strong adhesion whereas weak bonding, such as van de Weels inter-molecule forces, leads to weak adhesion.

Mechanisms of Tribofilm Formation - when chemical reactions are involved

In the case shown in Figures 1-4, oxygen and water moisture were naturally adsorbed on the surfaces of the tribo-system, especially the surface of the wear debris because of its high surface–to-volume ratio. The adsorbed molecules partially break the ionic bonding of the wear debris agglomerates leading to lower friction coefficient. But more importantly, tribo-heating at the sliding interface triggered chemical reactions between the adsorbents and the wear debris. In this case, the tribofilms and wear debris contained both multi-component oxides and hydroxides, which have been confirmed by EDX, EELS, Raman and FTIR analyses [7]. As an example, Figure 5 shows the electron energy loss spectrum of the tribofilm shown in Figure 4 as compared to the spectrum of the underneath TiAlN/VN, suggestive of tribo-oxidation in the former. In particular, vanadium was found to be better than other elements in capturing water moisture to form hydroxide-containing tribofilm of lower friction.

Mechanisms of Tribofilm Formation - in ductile materials

The tribofilm generation for most ductile alloys, such as metallic alloys, starts from adhesion joints and plastic yielding of initial asperity contact. Therefore, wear may take place in the mechanisms of adhesion, ploughing and abrasion, and fatigue wear following repeated deformation. Such worn surface deformation has also been observed in the wear of ceramics. The following example shows tribofilm formation in high temperature sliding wear of a nickel alloy [8].

KEY APPLICATIONS

CROSS REFERENCES (a list of entries (by title only) that may be of interest to your readers. The 'current

list of contributions' can be downloaded at http://oesys.springer.com/tribology)

REFERENCES (a list of citations to important literature (e.g., journals, conference proceedings, websites)

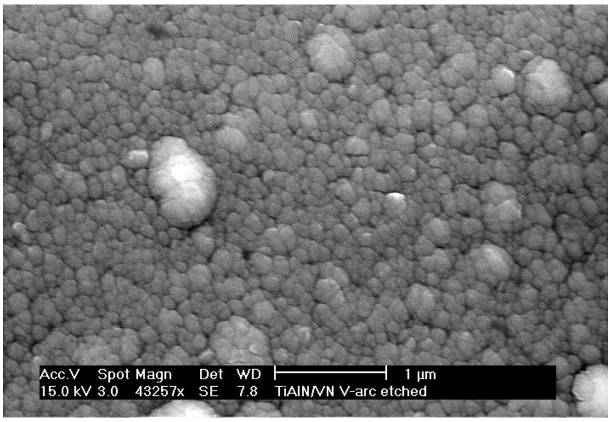

Figure 1 FEG-SEM image of the as-deposited TiAlN/VN coating surface. The coating was grown on V-ion arc-etched steel substrate by magnetron sputtering deposition at a low substrate bias of -75V. Such growth conditions resulted in a rough surface comprising large grains of arc-droplet induced growth defects protruding upon the coating surface (e.g. the large grains in bright contrast) and cellular-like front of columnar grains.

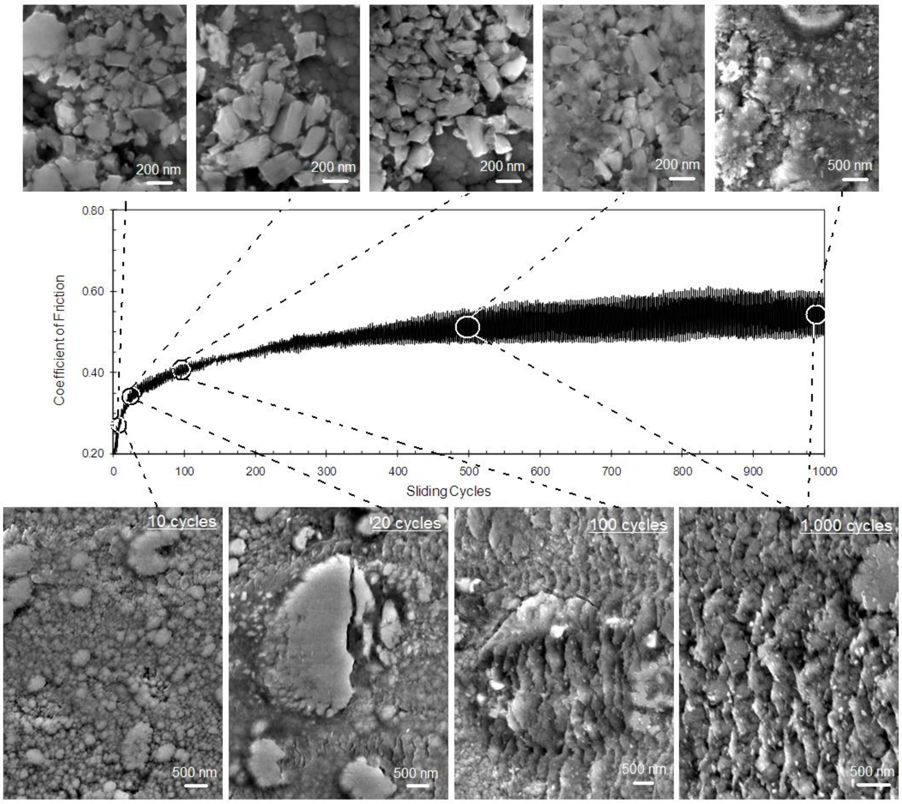

Figure 2 Demonstration of tribofilm formation in the running-in sliding wear of a magnetron sputtered TiAlN/VN coating. The running-in friction curve is in the middle showing progressive increase of friction coefficient. The SEM images in the upper row show wear particles generated in initial wear of the coating and their subsequent fragmentation with increasing sliding cycles. The SEM images in the lower row show evolution of the worn surface towards the formation of a tribofilm.

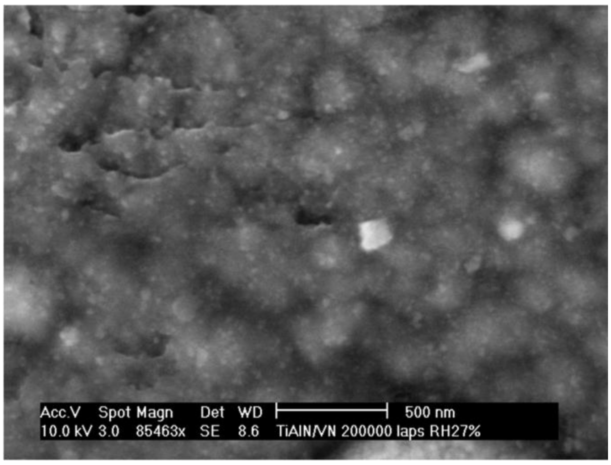

Figure 3 A high resolution SEM image of the TiAlN/VN worn surface.

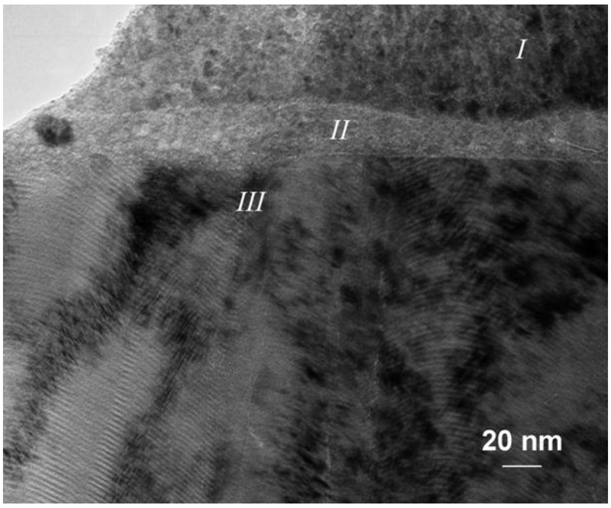

Figure 4 A cross-sectional TEM bright field image showing a tribofilm (region II) attached on the worn surface of TiAlN/VN (Region III). Region I is a copper layer deposited during the ion-beam sputter-thinning of the TEM foil. Note the amorphous structure of the tribofilm in contrast to the multilayer TiAlN/VN columnar grains.

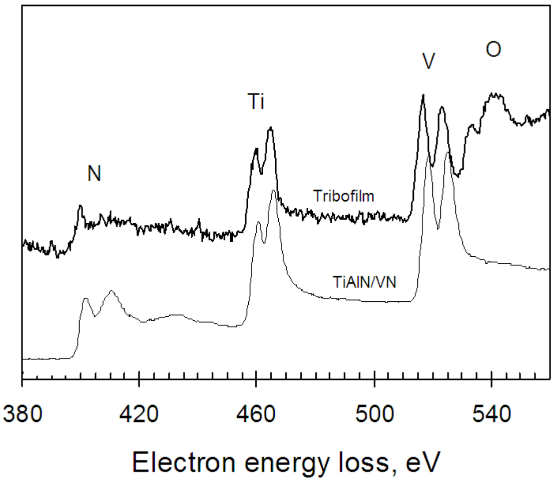

Figure 5 TEM electron energy loss spectroscopy of TiAlN/VN nitride coating and the associated tribofilm. Note the sub-stoichiomatric nitrogen content and substantial oxygen content in the tribofilm.

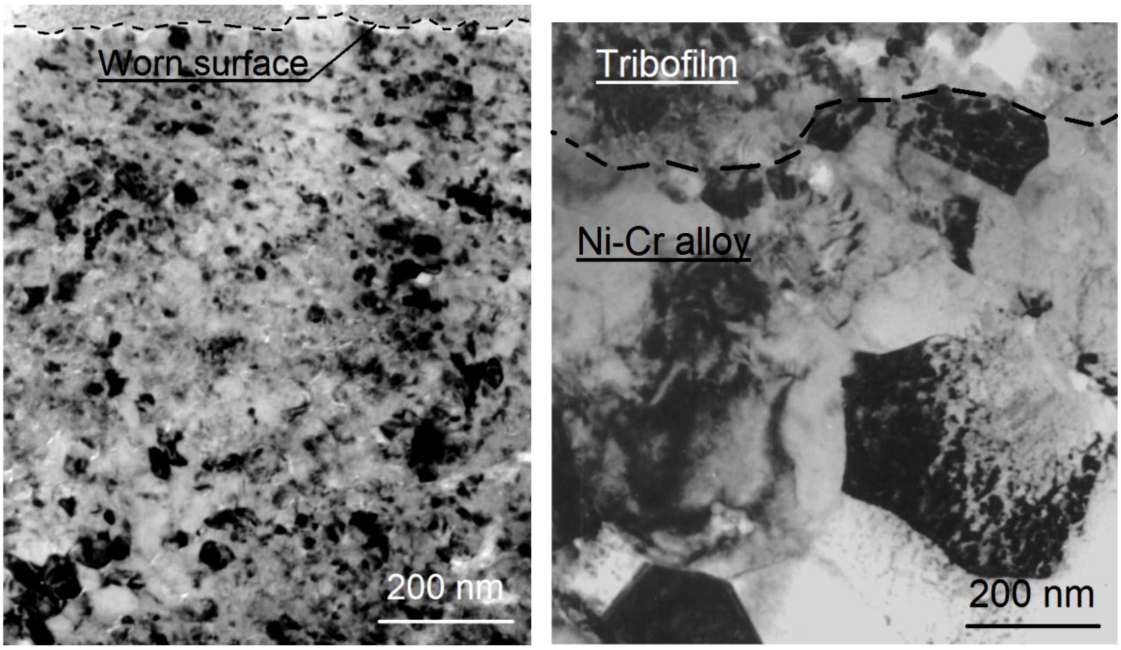

Figure 6 Cross-section TEM bright field images of the top ‘glaze layer’ of nano-crystalline tribofilm (left) as compared to the subsurface coarse Ni-Cr alloy (right).

A Nimonic 80A alloy (Ni 75.8, Cr 19.4 plus Ti and Al, in wt%) was subjected to reciprocating sliding contact against a Stellite 6 counterpart (Co 60%, Cr 27% plus W, Ni and Fe) at 750 ^{0}C and linear sliding speed of 0.3 $m{\cdot}s^{-1}$. The sliding process maintained a relatively stable friction coefficient of 0.5 – 0.6 and slight mass gain instead of loss attributing to the formation of a densely packed smooth surface layer with metal shining, the so-called ‘glaze layer’. It has been repeatedly found that as soon as such a glaze layer was form, the wear rate was extremely low. Cross-sectional TEM imaging, electron diffraction and EDX chemical analysis suggested that the glaze layer is a tribofilm closely adhering to the plastically deformed NiCr alloy worn surface. The tribofilm and the deformed alloy underneath are shown in Figure 6 respectively. The tribofilm shows equiaxial nano-crystalline structure as compared to the coarse structure of the Ni-Cr alloy. TEM-SAD and EDX analyses indicated that the tribofilm is a mixture of Ni based metallic phase and multicomponent oxide $CoCr_2O_4$, resulting from the wear of both the Ni-Cr and Co-Cr surfaces. In this case, initial adhesive wear happened in the Ni-Cr and Co-Cr surfaces. The generated wear particles were mixed together, adhered on the worn surface, and underwent severe plastic deformation. Because the tests were undertaken in air, it triggered preferential oxidation of the Cr as well as Co components. Meanwhile, repeated plastic deformation was accompanied by a continuous dynamic recrystalisation process since the testing temperature was higher than the recrystalline temperature ($0.4T_m$ at approximately 400 ^{0}C). The dynamic recrystallisation made the tribofilm progressively approached to and maintained at a minimum grain size. Thus, sliding induced shearing deformation at the contact interface was restricted within the nanocrystalline tribofilm by means of viscous flow of the grain boundaries. Consequently further wear of the Ni-Cr alloy was prohibited.

3.4 Tribofilm generation in diamond-like carbon

As the last example, this section reports recent studies of tribofilm formation in the sliding wear of diamond and diamond-like carbon (DLC) films [9-11]. Carbon, known as No.6 element, has two electrons in its inner orbit and four electrons in its outer orbit, and therefore is capable of forming up to four covalent bonds. In Diamond, each carbon atom is bonded to four carbon atoms with strong covalent bonds to form the sp^3 structure. Similar sp^3 bonded structure also exists in many artificially made amorphous DLC films. Diamond is the hardest solid found in nature, and therfore is widely used as a tooling material to machine other less hard materials. More interestingly, diamond is also found to exhibit much lower friction coefficient in dry sliding than other super-hard materials. This phenomenon has recently been explained by the formation of a lubricious tribofilm.

A hydrogenated DLC film fabricated by chemical vapour deposition in a hydrogen rich medium was found to exhibit extraordinarily low friction coefficient of 0.001 – 0.005 and extremely low wear rate. This phenomenon was firstly explained by using a mechanistic model that a layer of hydrogen atoms distributing on the outer surface terminates the bonding to the counterpart surface, and thereafter causes little or no physical and chemical interactions during a sliding contact. More recently, the low friction was found to be related to a sliding induced graphitisation of the diamond surface, i.e. a structural transformation from sp^3 to sp^2 bonding. After the transformation, the sp^2 bonded surface is worn and transferred to adhere on the counterface to lead to a self-mating sliding contact between sp^2-bonded graphite surfaces. This transformation was in the first recognised by Raman spectroscopic and EELS analyses of the resultant tribofilms, and then ‘more directly’ observed by in-situ TEM imaging and EELS analysis although at an environmental condition different from the previously performed tribo-tests [11]. In the TEM vacuum chamber, a sp^3 bonded condensed carbon film was conducted to reciprocating slid against a tungsten nano-tip. With increasing cycles of the reciprocating sliding, the EEL spectrum of the sliding contact zone showed increasingly higher π-resonant peak. As the π-resonant peak is a fingerprint feature of the sp^2 bonding, the EELS results indicated sliding induced transformation from sp3 diamond structure to sp^2 graphite structure. The sliding activated $sp^3 \rightarrow sp^2$ transformation was also revealed in molecule dynamic modelling [11].

More examples of tribofilm generation can be found in literatures of tribologg research. In particular, the understanding in this issue will be more comprehensive with further technical advances in surface characterization.

4. Tribofilm characterisation

Since tribofilms differ from their parent worn surfaces in terms of morphology, microstructure, chemical composition, and the elastic and plastic properties, the characterization of tribofilms aims to reveal these differences. In fact, many instrumental techniques of material characterization and surface analysis have been used in tribofilm characterisation, as shown in Table 1. Readers interested in this issue can read more in literatures [11, 12-16].

A tribofilm usually has different elastic and plastic responses to the applied sliding loads as compared to its parent worn surface. Micro Vicker’s and Knoop indentations are available to quantify the wear induced surface hardening or softening. This measurement can be more accurate if the obtained indents are measured precisely, e.g. using high resolution SEM or AFM. Recently, the development of depth sensitive indentation instrumentation makes it possible to measure both the elastic modulus and plastic hardness of nano-scale surface films. This technique has been employed to study the mechanical properties of coatings and thin films, whereas little research is reported on characterisation of tribofilms and worn surfaces.

Scanning electron microscopy (SEM) is perhaps the most widely used tool of materials characterisation in terms of their microstructure, topography and chemical composition. In the latest field emission gun SEM, the spatial resolution in low-KV secondary electron imaging mode is high enough to show nanometre scale features. Other analytical tools having the function of surface topography analysis include contact and non-contact profilometers, and atomic force microscopy (AFM). In addition, SEM based electron backscatter diffraction (EBSD) technique can be used to study the crystallographic properties of a solid surface, which is expected to find applications in tribofilm study. Other SEM based techniques, including back scattered electron imaging and energy dispersive X-ray spectroscopy (EDX or EDS), are available to reveal chemical compositions for the elements heavier than boron. The chemical compositions and chemical structures of triboflms can also be analysed using various other techniques such as Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR). For example, the high energy resolution XPS analysis provides not only qualitative and quantitative chemical compositions, but also the profile of the binding energies of a particular element. The quantified binding energies help determine the types of chemical compounds. Raman spectroscopy and FTIR have been used to analyse the oxide and hydroxide tribofilms of transition metal nitride coatings.

Table 1 Classification of material characterization techniques in tribofilm study

Characteristics of tribofilms	Appropriate analytical techniques
Elastic and plastic properties	Depth sensitive micro/nano indentation
Surface morphology	Scanning electron microscopy (SEM); Surface profilometry; Atomic force microscopy (AFM)
Microstructure	Optical microscopy (OPM); SEM; TEM
Crystallography	X-ray diffraction (XRD); Electron diffraction (TEM-SAD)
Chemical composition	Energy dispersive X-ray spectroscopy (EDX); Electron energy loss spectroscopy (TEM-EELS); X-ray photoelectron spectroscopy (XPS)
Chemical bonding property	XPS; TEM-EELS; Raman spectroscopy; Fourier transform infrared spectroscopy (FTIR)

Compared to the analytical techniques mentioned above, transition electron microscopy (TEM) has the highest spatial resolution. The instruments equipped with latest field emission filaments and aberration correction techniques have demonstrated the highest spatial resolution in sub-Å scale. Conventional TEM instruments with tungsten or LaB_6 filaments care capable of resolving nm-scale features. These provide feasibilities in fundamental study of tribofilm structure and the friction and wear mechanisms. TEM is also a multi-functional platform to carry out microstructural, crystallographic and chemical characterisations. These analytical techniques include selected area electron diffraction and convergent bean electron diffraction for crystallographic examination of nano-scale objects, qualitative and quantitative EDX chemical analysis with much higher precision than SEM-based analysis of light elements, EELS chemical analysis at much higher energy resolution than EDX, energy loss near edge structure (ELNES) for precise analysis of the chemical state of individual element. These techniques facilitate both structural and chemical analysis at extremely fine scale in the study of the tribo-chemistry. A few examples of TEM studies of tribofilms have been cited in this article, such as cross-sectional imaging (Figures 4 and 6), EELS (Figure 5), and in-site TEM-EELS study of graphitised tribofilm in diamond-like carbon.

A special issue in the applications of TEM techniques in tribofilm study has been the preparation of representative TEM foils. For the studies of tribofilms as well as other surface features, cross-sectional TEM is more often used than plane-view. A conventional method for cross-sectional TEM foil thinning is the low-angle ion beam milling technique which is commercially available in most TEM laboratories worldwide. In practice, special care should be taken in every steps from selection of representative area, sample cutting, cross-sectional grinding and mounting, and in ion-beam polish-thinning, in order to protect the required worn surface structures against mechanical damage, chemical contamination and ion-bombarding damage. Obviously such preparation is quite challengeable to many TEM users. To overcome this barrier, a new technique dedicated for cross-sectional TEM sample preparation has emerged, i.e. the focused ion beam (FIB) technique in a specially designed dual-beam SEM instrument. This method employs the conventional SEM imaging to observe a solid surface and, after identifying a feature for cross-sectional analysis, can be converted to sputtering mode using a focused ion beam to ‘cut’ a thin foil containing the identified feature, and lifts it out for TEM investigation. The FIB-SEM technique has been increasingly used in cross-sectional TEM sample preparation of surface features, including coatings and interfaces, friction and wear, and corrosion and oxidation. In tribofilm studies, it was recently employed to prepare a cross-sectional TEM foil containing roll-like wear particles along with an oxide tribofilm generated during dry sliding wear of a multilayer transition metal nitride coating.

5. Conclusion remarks

So far, this article has classified four types of tribofilms according to their generation, namely the tribofilms generated from the major sliding components, from the low-friction phases, as a result of phase transformation, and as a result of tribo-chemical reactions. A detailed description of tribofilm formation was subsequently provided based on recent research of the dry sliding behaviour of transition metal nitride coatings. The effect of testing environment on the tribofilm characteristics was also discussed with respect to the influence on friction and wear properties. Finally, a brief overview was given on the state of the art instrumental techniques available for tribofilm characterisation, especially the application of cross-sectional and analytical transmission electron microscopy in tribofilm study.

Up to date, it is appreciable that the role of tribofilm formation in the friction and wear process has been recognised in the field of tribological research. Further understanding would be expected to achieve following more fundamental studies of tribofilms in various tribo-systems. On the other hand, it is hoped that fundamental research in tribofilms would promote the design and fabrication of solid lubricant materials with higher performance. Working for this purpose, one should take account not only the chemical composition and structure of the designed solid lubricant materials themselves, but also the compositions and structure of the tribofilms expected to form in the due tribological environment.

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