IMPROVED NANOMECHANICAL TEST TECHNIQUES FOR SURFACE ENGINEERED MATERIALS

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ABSTRACT

The development and implementation of a wide range of innovative nanomechanical test techniques to solve tribological problems in applications as diverse as biomedical and automotive are described in this review. For improved wear resistance and durability, the importance of understanding the system response rather than the coating-only properties is emphasized. There are many applications involving mechanical contact where the key to understanding the problem is to test at higher load and to combine reliable measurements taken across different length scales using both nano- and micro-indentation and related wear measurement techniques which more closely simulate contact conditions to fully understand the mechanical behaviour and hence deliver improved application performance. Results are presented with the NanoTest platform for applications for biomedical devices and surface engineering of lightweight alloys for the automotive industry. By combining results with different techniques it is possible to postulate predictive design rules – based on the elastic and plastic deformation energies involved in contact - to aid the reliable optimisation of mechanical properties in the various contact situations in the different applications.

Keywords: nanomechanics, nanoindentation, surface engineering

1. Introduction

Nanomechanics has gained in prominence with the increasing popularity of thin coatings and the realisation that their performance is intimately linked to their mechanical properties. As coatings became thinner it was often assumed that only very low load measurements were important. Applications have developed (e.g. MEMS) where decreasing coating thickness has necessitated development of enhanced test capability at lower load by improvements to instrument force and displacement resolution (e.g. NanoTest NTX). As an illustration, figure 1 shows the variation in measured hardness with contact depth for 60 nm tetrahedral amorphous carbon (ta-C), 80 nm ta-C and 150 nm MoST films deposited on Silicon wafer substrates [1]. The MoST film is clearly considerably softer than the substrate (H ~ 11.5 GPa) whilst the ta-C coatings are much harder. Unsurprisingly, as the indenter penetration approaches the order of the film thickness the measurements become increasingly dominated by the substrate properties. For these measurements, a Berkovich indenter (rather than a cube corner) indenter has been used to avoid anomalously high hardness measurements. The figure shows that reliable measurements are possible to penetration depths as low as 5 nm though care should be taken not to automatically equate the measured mean pressure under the indenter with the hardness of the film, as in this region the plastic zone is not fully developed and the contact remains elastic until larger penetration depths.

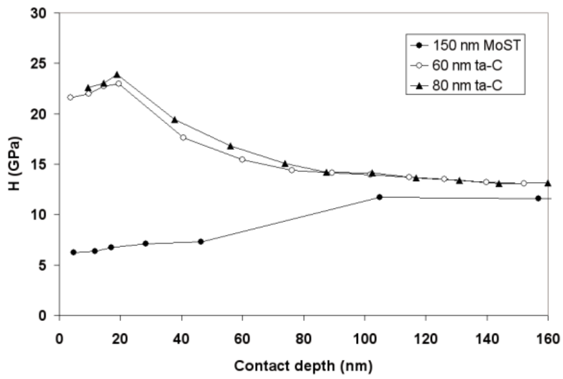

Fig.1. Variation in hardness with contact depth for 150 nm MoST, 60 nm ta-C and 80 nm ta-C on Si

However, there exist equally many applications involving mechanical contact where the key to understanding the problem is to test at higher load and to combine reliable measurements taken *across different length scales* using both nano- and micro-indentation and related techniques to fully understand the mechanical behaviour and hence deliver improved application performance. Amongst the early adopters of nanomechanics technology, Bell and co-workers in the UK in particular realised that understanding the system response – rather than the coating-only behaviour – could be the key to improving performance in actual mechanical contact applications [2-7]. To that end they pioneered the use of nanomechanical testing to assess the load-carrying capability of a wide variety of surface-engineered systems in a wide range of contact geometries. These included duplex technologies [3] and graded coatings where the aim is to combine different treatments and/or tailor composition during coating deposition to achieve a combination of desirable properties in the final surface engineered component that would be unachievable by a single-step process – i.e. synergy occurs.

In this paper we review the principles and the developments of novel nano- and micro-mechanical test methods from their inception in the late 80's to the present day. The developments are aimed at understanding the importance of the load-carrying behaviour of the system (coating(s)/surface modified layers/substrate) in controlling the behaviour in mechanical contact, initially for quasi-static nanoindentation at room temperature but more recently our nanomechanical test capability has been expanded and adapted to include the effects of shear (scratch and sliding wear [8-12]), strain rate (high strain rate and impact loading [13-16]) and environment (fluid [17], humidity or temperature [18-21]). Tests performed under these conditions often yield more useful applications data than quasi-static testing at room temperature in ambient laboratory conditions.

A wide range of laboratory techniques have been developed and applied to assess the load-carrying capability and other mechanical (hardness, yield stress, elastic modulus, creep) and tribological (friction, wear, fatigue) characteristics of coated components. These vary greatly in the severity of the mechanical contact, as controlled by indenter geometry, contact strain, applied load (and hence contact pressure), type of contact (static, or dynamic with oscillatory loading or sliding), and the presence or absence of tangential forces. Table 1 summarises the range of tests possible. As the nano- and micro-scale techniques all utilise *in situ* monitoring of the development of wear behaviour they aid the development of coatings with improved practical performance. For a specific application, a better understanding can often be built up by combining results from several of the characterisation techniques. Instrumental stability (no signal drift) is vital for quality assurance of results, particularly when the test takes some minutes as is the case for load partial unload nanoindentation and wear testing. Nanomechanics instruments with less stability have tended to perform tests more rapidly, but as ISO 14577 has shown, this can lead to problems with data reliability, particularly for nanoindentation of soft metals where creep occurs. It is necessary for this creep to occur before unloading so that the determination of the unloading stiffness is not influenced by anelastic effects.

Table 1. Ttypical forces ranges, contact geometries of different testing techniques[a]

Technique	Applied load range	Contact	Probe geometry	Load application
Nanoindentation	0-500 mN	Quasi-static	Pyramidal/spherical	Ramped
Nano-scratch	0-500 mN	Unidirectional sliding	1-10 μm end radius	Ramped
Nano-wear	0-500 mN	Unidirectional sliding	1-10 μm end radius	Constant
Nano-impact	0-200 mN	Impact	Cube corner	Dynamic
Nano-fretting	0-200 mN	Bidirectional sliding	1μm-1 mm end radius[c]	Constant
Micro-indentation	0.1-20 N	Quasi-static	Pyramidal	Ramped
Micro-scratch	0.1-20 N	Unidirectional sliding	25 μm end radius	Ramped
Micro-wear	0.1-20 N	Unidirectional sliding	25 μm end radius	Constant
Micro-impact	0.1-1 N	Contact fatigue	10 μm end radius	Dynamic
Scratch[b]	2-200 N	Unidirectional sliding	200 μm end radius (Rockwell C)	Ramped
Pin-on-disk[b]	10-100 N	Unidirectional sliding	5 mm end radius[d]	Constant

[a] Specifications taken from NanoTest system unless otherwise mentioned. Dual loading heads mounted simultaneously in NanoTest. Probe material is diamond unless otherwise specified. [b] Teer Coatings. Indenter

material is typically diamond unless otherwise specified. c sapphire for larger radii. d cemented carbide as standard, although alumina and other geometries are possible.

Whilst at the macro-scale conformal contacts can occur in tribological contact situations, at the nano- and micro- scale non-conformal test geometries are typically preferred for practical reasons. Scratch testing, for example, simulates the contact between an asperity sliding on a flat surface. In figure 2 the relative movement involved in the different test techniques is illustrated schematically for an idealised spheroconical probe. Different indenters are optimum for the different techniques. As well as altering the stress for a given applied load, changing the probe geometry directly influences the contact strain that occurs during the test, with higher contact strains promoting fracture. In nanoindentation, pyramidal (Berkovich) indenters are most popular as they have the same projected-area-to-depth ratio as Vickers indenters that are used on the macro-scale, and can induce plasticity rapidly (though not instantaneously – see figure 1). Spherical indenters allow investigation of elastic-plastic transitions and yield stress determination and are preferred for scratch testing where the sharper Berkovich indenters can suffer tip wear. Cube corner indenters are preferred for rapidly inducing fracture, in nanoindentation, and especially in nano-impact testing.

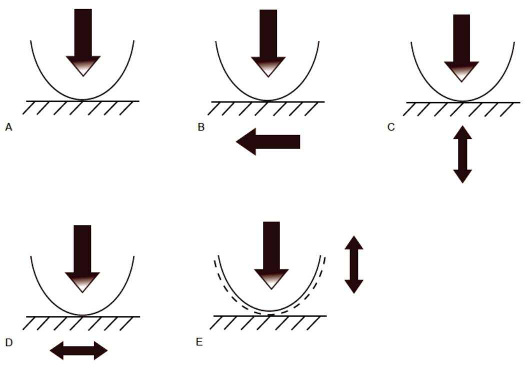

Fig. 2. Contact geometries in nanomechanical testing (a) indentation (b) scratch/wear (c) impact/contact fatigue (d) fretting and reciprocating wear (e) impulse impact

The interrelationships between the mechanical properties measurable by nanomechanical testing and nano-, micro- and macro- tribological performance are discussed in detail in the following sections. By simulating contact conditions, the nanomechanics test results have enabled reliable coatings and surface engineering design rules to be determined for a range of mechanical contact applications of differing severity. As mentioned above, close to application nanomechanical testing has become possible at a range of strain rates, environments, temperatures and contacting geometries in the NanoTest system. This closer simulation of the conditions actually occurring in specific applications allows more effective and faster optimisation of coatings and surface treatments as illustrated schematically in figure 3.

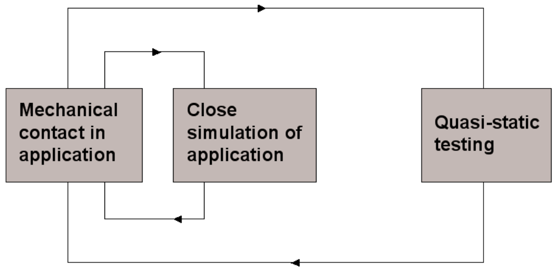

Fig. 3. Close-to-application testing improves speed and accuracy of optimisation

2. Deformation energy in mechanical contact: link to H/E

The dimensionless ratio between material hardness and stiffness (H/E) provides a link with energy-based approaches to indentation that involve plasticity indices. Before the technique of depth-sensing indentation was developed, plasticity indices were proposed (e.g. by Greenwood and Williamson as shown in Eqn. 1 [22]) that related the deformation in rough contacts to the ratio of E_r/H multiplied by a geometric factor:

$$\psi = E_r/H(\sigma/R)^{1/2} \quad (1)$$

where E_r is the reduced elastic modulus, ψ = a plasticity index, σ = standard deviation of the height of the contacting asperities and R = their average radius. When this plasticity index is much greater than 1 the deformation of asperities is predominantly plastic whilst if it is less than 0.6 it is largely elastic. Inverting the E_r/H ratio gives H/E_r, where the larger this ratio the more elastic the material behaves in rough contacts. A similar approach is applied to the deformation that occurs in nanoindentation. The ratio of plastic work done to total work done in indentation, $W_{(pl)}/W_{(total)}$, is another plasticity index, that can be obtained directly from nanoindentation data. For an elastoplastic contact:

Plasticity Index (PI) = plastic work/(elastic work and plastic work) (2)

With the support of finite element analysis (FEA) Cheng and Cheng proposed that for an ideal pyramidal Berkovich geometry (equivalent conical angle 70.3°) indenting bulk materials the plasticity index should be related to the H/E ratio according to:

$$W_{(pl)}/W_{(total)} \approx 1 - x(H/E_r) \quad (3)$$

With x being ~5 [23-24]. Although experiments have later shown that for metals which exhibit pile-up higher values (~7) are found in practice [25], nevertheless the link between the H/E ratio and the energy of deformation in the indentation process is now well established. Materials with high H/E show low plasticity and low values of the ratio of residual depth to maximum depth in indentation (h_r/h_m). In principle PI, h_r/h_m and H/E can be used interchangeably. Of these three parameters, the PI has the potential advantages of

(i) negating the requirement for the indenter area function (since H and E are not being determined)
(ii) using the entire indentation curve rather than only the unloading segment
(iii) easier to determine the areas accurately than the exact residual displacement
(iv) it is a direct measurement of the energies involved in the indentation process.

Since it is not (yet) common to report PI or deformation energies during indentation the H/E_r ratio will be referred to throughout the remainder of this review. H/E appears to have fundamental importance to the wear resistance in contact, and this review focuses on its measurement and optimisation for a variety of different applications.

3. Nanoindentation for optimisation of hip joint prostheses

Total joint replacement protheses need to function effectively over extended periods (ideally 25 years or more) [26-33]. Premature failure leads to painful revision surgery and the likelihood of subsequent joints being less durable. Along with skill of the surgeon and high quality post-operative care, the mechanical integrity and wear resistance of long-term implantable devices are vital to their continuing success *in-vivo*. Despite many different biomaterials being used over the last 40 years, including polymers (notably UHMWPE), metals/alloys (CoCr, Ti6Al4V) and ceramics (alumina and zirconia), all the tribo-couples have been found to have deficiencies that can limit the ultimate joint lifetime in practice, particularly for younger and more active patients [27]. Analysis of retrieved protheses has determined that the primary failure mode for alloy-UHMWPE joints is production of sub-micron wear debris of PE which causes an immune response leading to bone cell death (osteolysis) and resorption of the bone surrounding the implant and aseptic loosening of the joint which ultimately leads to catastrophic failure of the joint if not replaced.

With simulator tests of the performance of artificial joints typically taking several months to complete, it is not feasible to test each potential new material pair in development, so more rapid laboratory test techniques are invaluable tools in optimising the biomaterial performance. Although Pin-on-disk techniques have been used, these have some limitations; being (i) not depth-sensing and (ii) macro-scale tests, they are not sensitive to wear processes or mechanical homogeneity occurring on the nano- and micro- scale. In contrast, nanomechanical testing can provide valuable additional information and has been used to both characterise the mechanical behaviour of surface-engineered components and assess their likely tribological performance. During the course of several collaborative projects, Bell and co-workers and their collaborators have developed novel techniques for the surface modification of hip joint protheses. Advanced plasma-based techniques were employed to modify the mechanical and tribological properties of both the acetabular cup *and* the femoral head in the replacement hip joint.

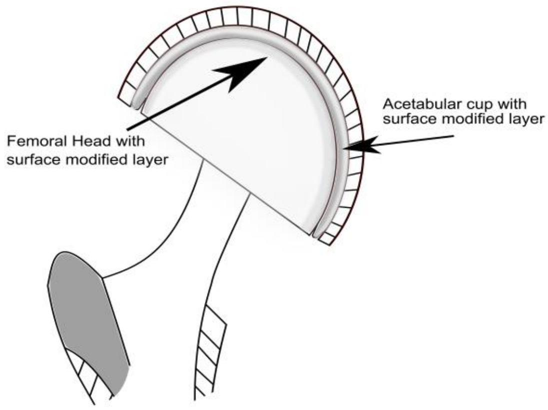

Fig. 4. Surface engineered hip joint prothesis

At first it may seem counterintuitive that hardening the harder material in the couple is necessary. However, it has been noted that retrieved austenitic steel femoral head implants show cross-scratches (third body abrasive wear) after many years implantation in the body [33]. The scratches exhibit pile-up around their edges, particularly at the crossing points, that can engage the polymer surface and machine away small fragments of polymer. Surface engineering of the femoral head to minimise scratch deformation should therefore indirectly minimise wear of the polymer counterpart. For this reason Bell and co-workers have characterised the nanomechanical and tribological behaviour of systems such as (i) Ti6Al4V alloys after thermal oxidation [3,28-29] and (ii) medical grade 316L stainless steel after carburisation for different times at varying temperatures.

Nanoindentation shows the surface treatments produce mechanically consistent behaviour as illustrated for plasma carburisation of 316L stainless steel (Table 2). It is clear from Table 2 that the treatment is effective in greatly increasing the surface hardness whilst leaving the stiffness virtually unchanged, thus resulting in a large increase in H/E, which can, depending on the contact conditions, result in a more elastic contact and a reduction in wear. Indentation mapping suggests the small variations in mechanical properties across the sample surface after the carburisation treatment are correlated with the original microstructure of the steel (large grains with consistent mechanical properties within grains but subtle variations from grain to grain).

Table 2 Nanoindentation of plasma carburised stainless steel

Sample	Indentation depth/nm	Hardness/GPa	Reduced modulus/GPa
316L	464 ± 18	3.9 ± 0.3	201 ± 11
PC 400C/30h	278 ± 6	12.5 ± 0.7	210 ± 4
PC 450C/20h	293 ± 7	11.1 ± 0.6	201 ± 4
PC 500C/15h	282 ± 4	12.2 ± 0.4	205 ± 5

Nanoindentation with a Berkovich indenter to 20 mN at 0.5 mN/s with 30s hold at peak load for creep before unloading at 0.5 mN/s. For the plasma carburisation the plasma unit was 60 kW Klöcner DC (570V, 30A/m^2) with atmosphere: 2 % CH_4 + 98 % H_2 at 4 mbar.

The load-partial unload indentation technique has been used to assess the variation in hardness, modulus and H/E with increasing indentation depth. For this technique to return accurate values it is essential that the instrument has ultra-low thermal drift. A load history was programmed (fig 5 (a)) and a typical experiment result is shown in fig 5(b). From analysis of repeat tests at different locations a picture of the variation of mechanical properties with increasing indenter penetration is determined (fig. 5(c)).

The small variation in H/E_r with increasing indenter penetration for the sample carburised at 500°C is consistent with a thicker carburised zone as confirmed by optical microscopic analysis. plasma carburising of 316L at 500°C for 15h produces a S-phase layer with corrosion and wear resistance. Carburisation at 400°C produces higher near-surface hardness but a smaller case depth as revealed by testing over wide force range.

Ion-beam and plasma techniques are effective in modifying the near surface structure of polymers to improve wear resistance, however their widespread use has been hampered by their line-of-sight nature that makes it problematic to use them to evenly coat or surface treat medical devices such as protheses with their more complex geometrical forms.

A non-line-of-sight technique, plasma immersion ion implantation (PIII), has been developed that may overcome this limitation [7,26,30,32] and the NanoTest has been used to assess its effectiveness at modifying the hardness, modulus, scratch, impact and sliding wear resistance of PIII modified UHMWPE.

Figure 6 shows illustrative nanoindentation curves for unmodified UHMWPE and UHMWPE PIII-treated with 1 x 10^{17} N ions/cm^2 at 30 KeV. The nanoindentation data shows clear increases in hardness, H/E ratio and creep resistance after PIII treatment. In this early example a 10s hold period has been included in the nanoindentation load ramp design for viscoelastic creep to occur before unloading and the presence of a slight "bow" to the unloading curve can be observed in the curve on the unimplanted PE.

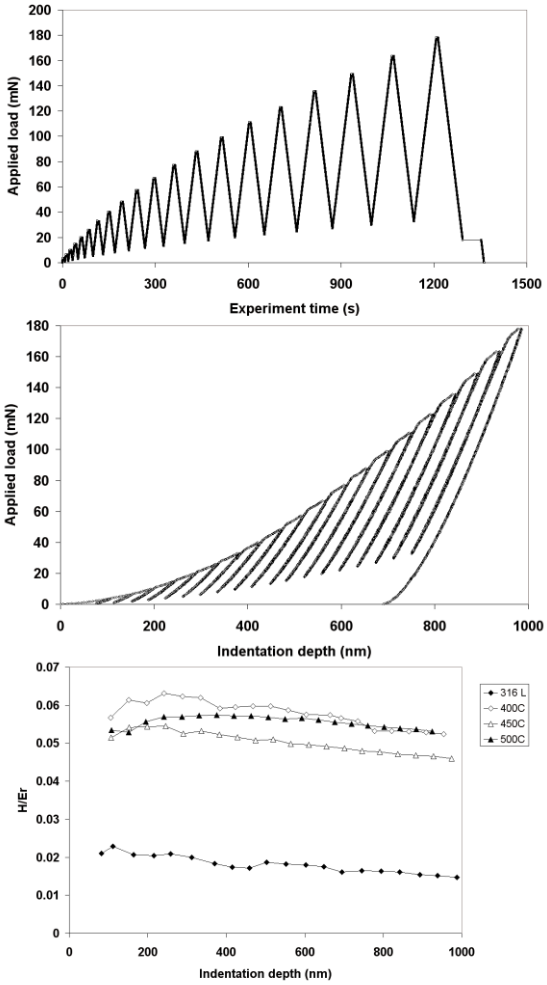

Fig. 5. (a) load vs. time for load partial unload experiment on plasma carburized steel; (b) Typical load-partial unload nanoindentation behaviour on sample plasma carburized at 500°C for 15 hr; (c) Variation in the ratio H/E_r with contact depth for untreated 316 stainless steel and samples after carburization.

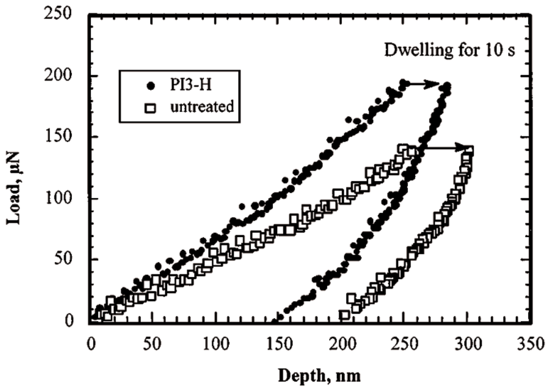

Fig. 6. Nanoindentation of UHMWPE and PIII-UHMWPE. Reprinted with permission from J. Mater. Sci. Lett. 19 (2000) 1147

Later work has shown that ideally longer hold periods (> 20s) are recommended for UHMWPE which allow more of the viscoelastic creep to occur before unloading. The PIII creates a cross-linked structure which although it has higher roughness than untreated UHMWPE, has enhanced creep resistance as shown in figure 7.

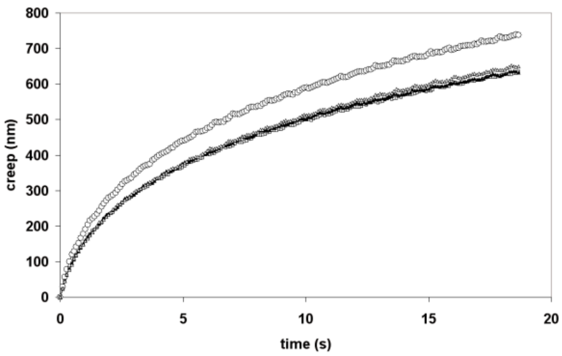

Fig. 7. Indentation creep response for UHMWPE (circles) and PIII-UHMWPE (other symbols)

Bell and co-workers showed (figure 8) a correlation between the surface hardening possible with different plasma treatments and the pin-on-disk wear rate [26]. In this example, PIII treatment resulted in greater hardness and a larger reduction in wear rate than other plasma techniques, although it should be noted that the PIII can result in a different surface sensitivity to other plasma treatments (see later). Nanoscratch testing has shown that PIII improves its tribological performance although the high roughness was detrimental to nanowear. Equally, Fisher and co-workers have reported that whilst crosslinking reduces wear on smooth UHMWPE in simulator studies, on scratched surfaces simulator wear is greater after crosslinking [34].

To help understand the influence of the PIII modification on the near-surface properties of the UHMWPE it is useful to investigate individual indentation responses as shown in fig 9.

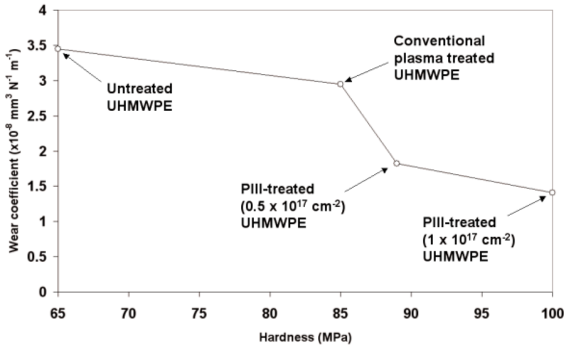

Fig. 8. Correlation between the wear rate (pin-on-disk tribometer) and hardness for UHMWPE after various plasma treatments

The He-PIII UHMWPE is harder and stiffer but more brittle and occasionally shows clear yield events during loading, such as the one occurring at ~ 900 nm indentation depth in figure 9. The decrease in indentation depth after 90% unloading is a result of extensive creep recovery occurring during a 60 s hold period rather than instrumental drift. Depending on the applied load, these creep recovery rates are typically x 50-100 greater than any underlying thermal drift (<0.01 nm/s) in the instrument. The occurrence of these yield events during loading is greatly reduced compared to other plasma and ion beam modifications.

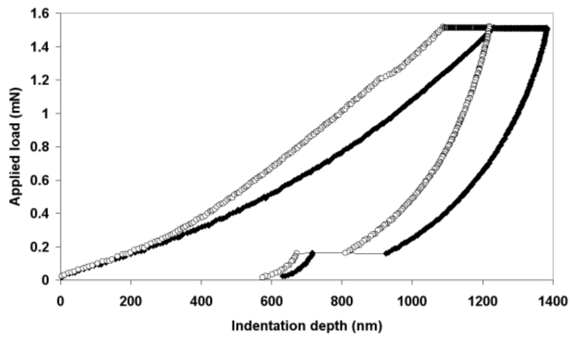

Fig. 9. Nanoindentation of UHMWPE (triangles) and He-modified UHMWPE (circles)

Another potential advantage of the PIII treatment in comparison with other plasma treatments is in its depth of surface modification. Shi, Dong and Bell showed that whilst conventional N_2 ion implantation resulted in dramatic increases in hardness for shallow indentations, for indentations to greater depths (1-2 µm) there was little difference over the unimplanted UHMWPE [32]. Although not predicted by TRIM (transport of ions in matter) simulations, cross-sectional TEM confirmed the presence of a dark modified region extending 400 nm from the polymer surface. The authors showed that the hard and tough layer produced by PIII could partially support the load whilst the indentation depth was several times the layer thickness. PIII can produce a more gradual surface treatment than other plasma treatments [32];

it is capable of more effective load support than a harder but embrittled more near-surface layer. Kondyurin and co-workers have reported PIII on LDPE does not lead to formation of a carbonised layer in the same way as ion beam modification at the same ion dose [35]. On UHMWPE, we have found that whilst N_2-PIII increases the near surface hardness and elastic modulus of UHMWPE by only around 20%, but this improvement in mechanical properties can extend even further into the material than reported in the Shi et al study. This is illustrated in figure 10. All three PIII treatments (He, H_2 and N_2-plasma) treatments result in enhanced hardness, stiffness and creep resistance even when the applied indentation load was increased to 100 mN (~10 µm indentation depth).

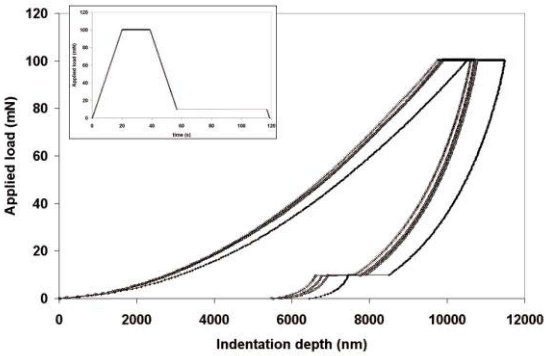

Fig. 10. Nanoindentation to 100 mN on UHMWPE (filled) and PIII-UHMWPE (other symbols). The insert shows the load history with hold periods at 100% of peak load (for creep assessment) and at 90% unloading (to assess creep recovery)

Nanomechanical testing has highlighted some of the potential advantages and disadvantages of the surface treatment approach being developed. The surface treatment of the femoral head by plasma carburisation can successfully produce a deep modified layer with higher hardness and load bearing capacity though it is advisable to subsequently re-polish the implant to reduce its roughness, possibly with subsequent coating deposition. A complementary approach involves the use of ceramic femoral heads to minimise third body damage that CoCr can be susceptible [27]. For surface engineering of the acetabular cup, PIII treatment can coat complex geometries and produce a graded enhancement of mechanical properties and improved load bearing capability without the brittleness that other plasma and ion beam techniques introduce, though here also care must be taken to optimise (minimise) the surface roughness.

The results presented above are consistent with other studies – recently reviewed by Clarke and co-workers [27] - that clearly show that crosslinking UHMWPE leads to a reduction in wear. Short-term (3-5 year) clinical studies have demonstrated benefits *in vivo* but also highlighted the much higher sensitivity of cross-linked UHMWPE under averse wear conditions that may reduce its potential benefits. In future work, closer simulation of the complexities *in vivo* could be beneficial. It has been suggested that a reduction of the size of PE debris after wearing crosslinked UHMWPE could actually lead to increased osteolysis but as yet the links between crosslinking, PE wear debris and osteolysis via macrophage response are insufficiently understood [27]. Typically hip replacement joints do not wear out but fail through loosening brought on by the formation of wear debris so over-reliance on wear rates during pin-on-disk or hip simulators may be dangerous. Nanomechanical characterisation has been useful thus far in understanding the advantages and potential limitations of the various surface treatment approaches. Closer simulation of the actual contact situation is now required; given that nanoindentation at 37°C in saline solution is now possible and novel techniques such as nano-fretting and reciprocating nano-wear (see figure 2(d)) may also be useful in simulating the boundary lubrication regime during running in there is considerable potential for future optimisation.

4. Surface engineering of lightweight intermetallics for automotive applications

The wear resistance of lightweight intermetallics such as FeAl is not as high as most stainless steels which may limit its suitability for applications involving tribo-contact, such as valves in automotive engines. Enhancements to both hot hardness and post-test nanoscratch and wear resistance were observed in the elevated temperature nanoindentation testing of Fe-40 at.% Al alloy. During heating to 400°C and subsequent testing a mixed thin Fe_2O_3 and Al_2O_3 oxide layer formed on the FeAl surface [36]. Whilst it is possible to avoid formation of this oxide by deposition of a very thin (5-10 nm) and dense passivation layer of Pt prior to heating, its presence suggested that thermal oxidation (TO) might be a viable route to modifying its surface properties whilst leaving the bulk FeAl properties unchanged. Accordingly, to improve its tribological properties Bell and co-workers applied a higher temperature controlled TO treatment (air-circulating furnace at 1000°C for 30-150 hr) to FeAl alloy [4]. After the TO treatment the mechanical properties were assessed by cross-sectional scanning electron microscopy (SEM), nanoindentation, and the nano-/micro-tribological behaviour (simulating non-reciprocating sliding contacts) with nanoscratch and nanowear tests. The cross-sectional SEM showed the oxide layer was sufficiently thin (~ 1 µm thick after 60 hr treatment, with a varying microstructure through its thickness) to necessitate the use of nano-scratch testing rather than higher load testing [4].

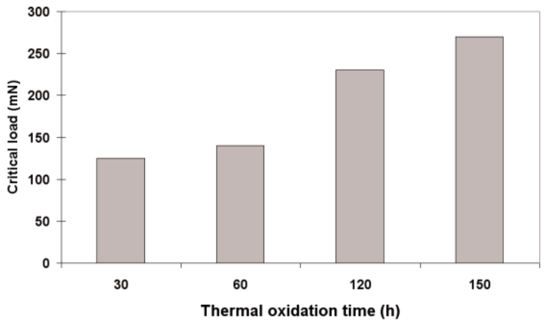

Fig. 11. Variation in critical load with thermal treatment time for thermal oxidation of FeAl.

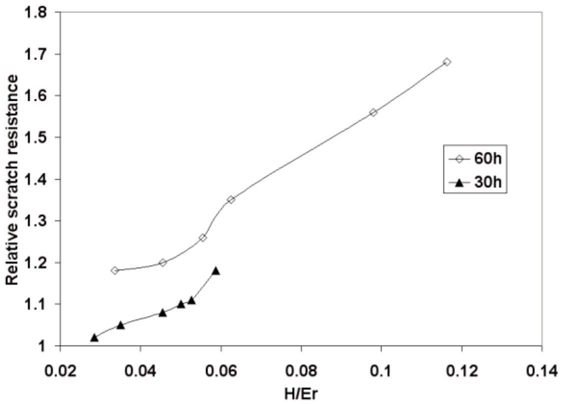

Fig. 12. Variation in the relative wear resistance with H/E_r for 30 and 60h thermal oxidation treatment FeAl.

The critical load for buckling and chipping of this oxide layer increased with oxidation time as shown in figure 11. Although for this system the exact relationship between tribological performance and H/E is a complex function due to differing thickness and through-thickness microstructural changes, nevertheless, it is clear that increasing the H/E ratio by the thermal treatment improved the scratch (figure 11) and wear resistance of the intermetallic alloy (fig. 12).

5. Towards design rules

It is clear from the examples above that the nanomechanical test results are closely correlated with the actual performance in a range of mechanical contact applications. Therefore it could be possible to propose a robust set of design rules for the required mechanical properties that the surface engineering of a component should aim for *in a given application*. In particular it is clear that increasing the H/E ratio can enable contact to remain elastic at higher load and contact pressure. This applies equally to coatings and surface treatments; increasing the hardness of the coating or substrate increases the load bearing capability of the surface in loaded contact.

Since the correlation between H/E and wear resistance is good for a wide range of contact situations it is vital to understand its limitations - i.e. when and why high H/E does not lead to a dramatic reduction in wear. In the examples above, surface treatment and coatings can greatly enhance the load bearing capacity of relatively low modulus substrates (Ti alloys and steels) resulting in increased scratch resistance and higher critical load. These substrates are relatively ductile and the coating can deform elastically with substrate without cracking.

When the substrate is more brittle (silicon) and/or higher modulus (cemented carbide) increasing H/E is only successful up to a point. It appears that on these substrates the H/E ratio should not be very high for highly loaded applications. For coating deposition conditions resulting in very high H/E, actual performance can be acceptable only provided the contact stress remains below critical values. Above these values – exceeding the elastic limit - limited plasticity in the contact can result in fracture and dramatic delamination and uncontrolled wear. The problem appears particularly acute on brittle substrates. In high speed machining applications, such as the high load stamping wear of carbide punches, the correlation between high H/E and improved wear resistance breaks down completely. Cemented carbides with higher H/E are more susceptible to fracture and ultimately much greater rates of tool wear than carbides microstructurally designed to have greater plasticity (lower H/E) [37].

Deposition of coatings with very high H/E can result in high intrinsic stresses (when sufficiently thick) and subsequently in poor adhesion when the contact-induced stresses are added. It has been found that for coatings such as TiSiN and a-C there exists an optimum H/E [11-12]. Typically, above H/E_r ~0.85 the critical load in the scratch tests can decrease in combination with a transition to a different failure mechanism. Repetitive nano- and micro-wear tests can reveal stress and adhesion problems more clearly than single ramped load scratch tests. Lower load fatigue tests (such as the nano-impact, nano-fretting or nano-wear) can often correspond to more realistic contact pressures than in overload tests such as the ramped scratch test. For these (and more severe) conditions, coatings deposited with slightly lower hardness and H/E such as Teer Coatings Graphit-iC (graded a-C) possess an optimum balance of hardness and toughness for impact fracture resistance and so can outperform more standard DLC coatings that have H/E > 0.1. For optimisation of a-C:H films enhanced load bearing capability in beneficial. Multilayering appears to be an encouraging way to enhance H/E and load support without introducing too high internal stress, so thicker DLC coatings can be deposited. Duplex approaches, i.e.

multilayering or grading in conjunction with substrate pre-treatment, may be required for other applications.

6. Conclusions

The development and implementation of a wide range of nanomechanical test techniques in the NanoTest to solve tribological problems in applications as diverse as MEMS, biomedical and automotive have been described. Dramatic improvements to component durability are now becoming possible with the possibility to tailor the surface engineering approaches towards optimum mechanical properties in the envisaged application. By considering the system response rather than just the coating-only mechanical properties it is shown that surface engineering to increase H/E can be beneficial in a range of applications. However, care should be taken that (1) it be done without introducing too high intrinsic stress or stress discontinuities in loading or (2) the severity of the application is such that it is impossible for stresses to remain anywhere close to elastic and there is a requirement for some plasticity in contact to avoid fracture.

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