

Pin on disc wear investigation of nitrocarburised H13 tool steel

P. C. King^{*1}, R. W. Reynoldson², A. Brownrigg¹ and J. M. Long¹

Nitrocarburised H13 disks were tested in dry, sliding wear against a stationary ruby ball (pin). Three different 4 h nitrocarburising treatments were compared, using $N_2/NH_3/CO_2$, N_2/NH_3 /natural gas and N_2/NH_3 gas mixtures, resulting in compound layers of varying thickness, hardness, porosity and oxide morphology. During mild, oxidative wear, with the formation of abrasive wear debris, the most brittle and oxidised surfaces performed poorly. Polishing to a bright, reflective finish greatly reduced wear. However, the $N_2/NH_3/CO_2$ sample also frequently maintained a 'very mild' wear regime, owing to the formation of a protective film between the wear surfaces, and resulting in a lowering of the friction coefficient. This treated surface was porous and covered in a complex layer of coarse oxide + ϵ -carbonitride. Nitrocarburised samples and wear tracks were characterised by optical microscopy, SEM, atomic force microscopy and stylus profilometry.

Keywords: Pin on disc, Wear testing, Nitrocarburising, Compound layer, H13, Tool steel, Oxidative wear, Friction coefficient, Fluidised bed, Cover layer, Polishing, Porosity, AFM, Profilometry, SEM

Introduction

Nitrocarburising is a common, inexpensive surface treatment that can be applied to Cr–Mo–V hot working steels such as H13, to improve their hardness and resistance to wear and fatigue. Forging dies and core pins for die casting¹ are two prime examples. H13 used for hot plastic working is successfully nitrocarburised to mitigate against abrasive wear and thermal fatigue. Nitrocarburising is used to extend the life of extrusion dies. High temperature, unlubricated sliding contact with aluminium causes wear of the die wall, which results in changes in the dimensions and surface finish of the product.²

The role of treatment parameters on the surface microstructure of nitrocarburised tool steels was discussed in a previous paper.³ Particular attention was paid to the effect of secondary, carbon bearing gas on the degree of carbon enrichment and compound layer properties. It was noted, for instance, that the choice of carbonaceous gas greatly influenced the degree of porosity and oxidation at the compound layer surface. This is important, not only because components are frequently put into service directly after nitrocarburising, but also because, if the surface is to be polished back, the amount of oxidised, porous material that needs to be removed can be an important issue. Furthermore, it was shown that on some substrates, such as H13 hot working die steel, carbon may be deeply

absorbed throughout the entire diffusion zone. The total diffusion depth, the amount of grain boundary cementite below the compound layer, and even the sharpness of the compound layer–diffusion zone interface, are all affected. Carbon may become highly concentrated in the compound layer when high levels of natural gas are used, resulting in a harder layer, or decarburisation at the surface may occur with carbon dioxide.

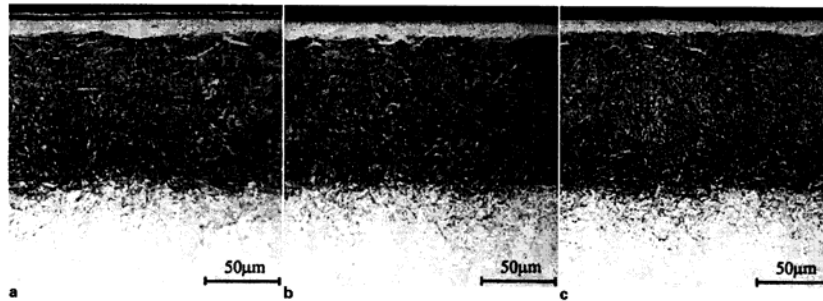
Clearly, it is possible to produce a multitude of different nitrocarburised layers by altering the treatment conditions. A variety of different commercial nitrocarburising processes are also in existence.^{4–6} And yet, there has been very little effort to understand the role of these differences in a wear situation. In this study, the effect of compound layer properties on wear behaviour was investigated. Using a pin on disc apparatus, nitrocarburised samples were tested in dry, sliding wear conditions. Porosity, hardness, layer adhesion and toughness were the dominating factors.

During sliding wear of metals, oxide formed by frictional heating is known to prevent excessive adhesive damage to the underlying metal, resulting in mild wear. Mild wear produces fine, oxidised wear debris.⁷ Upon close metallurgical examination, many authors have noticed protective, raised patches of oxide on the worn metal surface.^{8,9} If oxide is removed faster than it is formed, severe wear results. Severe wear is characterised by a rough, torn wear surface with ploughing by hard asperities, and the formation of large, metallic debris. It has been shown by Kato *et al.*⁸ that nitriding shifts the onset of severe wear to higher loads and sliding speeds, and reduces the wear rate compared with unnitrided steel within the same wear mode.

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a $N_2/NH_3/CO_2$; b $N_2/NH_3/nat. gas$; c N_2/NH_3 ; top compound layer remained unetched apart from oxide (grey); middle diffusion zone was heavily etched, and bottom substrate was unetched

1 Micrographs of nitrocarburised samples, etched with nital

Experimental method

Discs 40 mm in diameter were machined from H13 tool steel (0.38C–4.8Cr–1.2Mo–1.1Si–0.4Mn–0.2Ni (wt-%)). The discs were quenched from 1025°C and tempered once at 580°C to a hardness of 48 HRC. A second temper was omitted, since some further tempering occurs during nitrocarburising. The flat surfaces were then precision ground to a high finish (Table 1).

Nitrocarburising was performed in an industrial 160 mm dia. fluidised bed, with 120 grit Al_2O_3 (mean diameter 100 μm) as the fluidising medium. All treatments were 4 h long, at 570°C, and a total gas flowrate of $1.5 m^3 h^{-1}$. Three different inlet gas mixtures were chosen for comparison. These were $N_2/25\%NH_3/8\%CO_2$, $N_2/25\%NH_3/20\%$ natural gas, and $N_2/25\%NH_3$. Samples were then quenched in another fluidised bed, operating at ambient temperature on N_2 flow. The topography of nitrocarburised surfaces was characterised using atomic force microscopy (AFM) on a DME Dualscope DS 45-40 non-contact instrument.

Nitrocarburised samples were wear tested in the as treated condition or with a polish after treatment. Polishing was performed on a Struers RotoSystem automatic polisher using 15 μm diamond paste and a steady 20 N force applied to the samples, rotating in a counter direction to the pad. All samples were polished, with periodic visual inspections, to a bright, reflective finish. Different times were needed to achieve this, as shown in Table 1.

Wear tests were performed using a CSEM pin on disc tribometer. The pin was a 6 mm dia. single crystal Al_2O_3 (ruby) ball. It was held down stationary on the flat face of the testpiece disc under a 20 N load. The disc was then rotated at $0.1 m s^{-1}$ relative to the pin, creating a circular wear track. Tracks were made at various diameters, but the frequency of revolution was adjusted

to maintain the same sliding speed. All tests were performed unlubricated and in air. Lateral friction force data were sampled at 1 Hz.

Cross-sectional line scans of the wear tracks were performed using the Tencor Alpha step 200 profilometer. A 12.5 μm radius stylus was moved across the surface, and data sampled at 1 μm intervals. The profilometer was also used for determining surface roughness R_a of the treated surfaces. Micrographs of the wear track area were taken by SEM using the LEICA S440 microscope on secondary electron mode at 10–20 kV.

Results and discussion

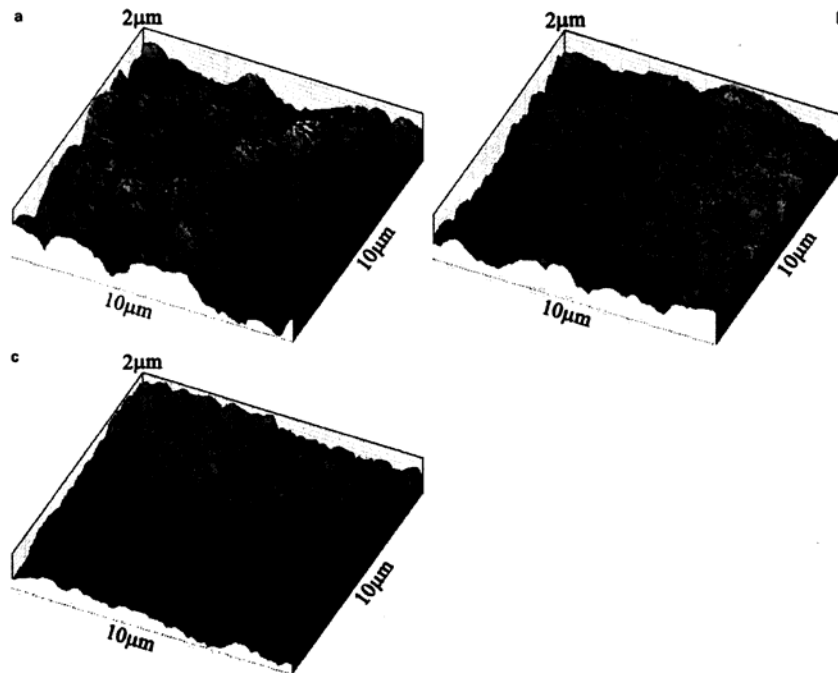
Characterisation of treated surfaces

For a detailed study of nitrocarburised tool steel, diffusion profiles and microstructures, the reader is referred to King.³ All treatments produced a hard, ϵ -carbonitride compound layer immediately below the surface, and a diffusion zone containing a heavy dispersion of alloy nitrides within the tempered martensite matrix (Fig. 1).

The $N_2/NH_3/CO_2$ treatment generated the thickest compound layer, owing to rapid development of $\epsilon-Fe_{2.3}(N,C)$ in the high oxygen potential associated with this gas mixture. The surface, which was originally bright and smooth with scratches in the grinding direction, developed a thick external Fe_3O_4 layer. As a result, the treated surface had a dull blue grey finish. It was found that this external oxide layer partially reduced back during treatment, nucleating coarse ϵ -nitride crystals above the original surface. This mixed $Fe_3O_4/Fe_{2.3}N$ layer is the so called 'cover layer' and, as a result of its nitride content, it came up white in the optical micrograph.¹⁰ The topographical investigation (Fig. 2)

Table 1 Change in surface roughness due to nitrocarburising and post-polishing procedure

	$N_2/NH_3/CO_2$	$N_2/NH_3/natural gas$	N_2/NH_3
R_a before treatment	158 ± 28 nm		
R_a after treatment	250 ± 60 nm	166 ± 21 nm	159 ± 29 nm
Compound layer	15 μm thick, porous, heavily oxidised	13 μm thick, heavily oxidised, some porosity, high carbon	9 μm thick, non-porous
Polishing time	27 min	13 min	6 min
R_a after polishing	6 ± 4 nm	18 ± 17 nm	24 ± 14 nm



a $N_2/NH_3/CO_2$; b N_2/NH_3 /natural gas; c N_2/NH_3
 2 Surface topography due to cover layer build up in various nitrocarburising atmospheres

revealed a rough, nodular surface. Gaps between nodules resulted in the cover layer being microporous.

Simultaneously, as nitrogen levels reached critical levels below the original surface, pores began to form, eventually resulting in a region of extremely fine scale porosity in the outer compound layer (porosity has been shown to be unavoidable beyond a certain layer thickness).¹¹ The fresh surface created by these pores also oxidised. The porous zone therefore appeared dull grey in the polished cross-section, owing to the 'filling in' of the pore volume by Me_3O_4 alloy oxides.

The N_2/NH_3 /natural gas compound layer was thinner, more dense and slightly less oxidised. It contained a higher carbon content than the other compound layers and was harder as a result. However, the same processes at work in the $N_2/NH_3/CO_2$ compound layer were also beginning to alter the surface at the 4 h mark of this treatment. There was some porosity at the surface, and signs within the external oxide layer of some reduction to ϵ -nitride. In contrast, no porosity was found after the N_2/NH_3 treatment, and the layer has been shown to be more ductile as a result. The exterior surface was brighter and smoother, and scratches from the surface grinding process were still clearly visible (see roughness data in Table 1 and surface topography in Fig. 2).

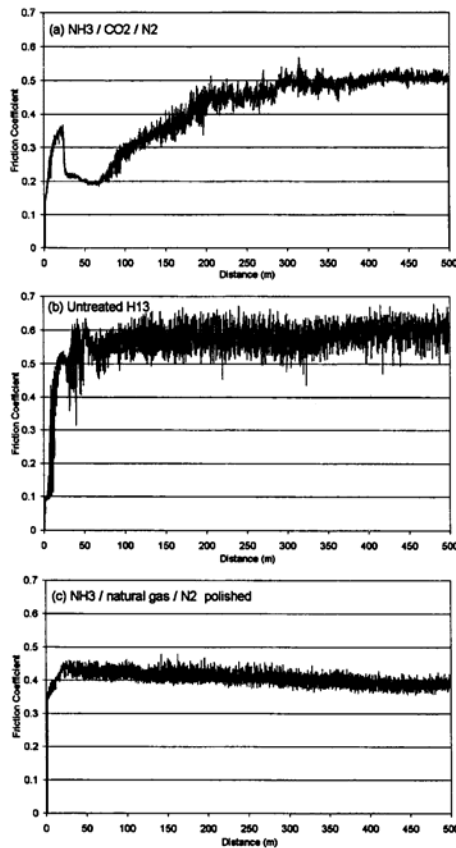
Table 1 also shows the surface roughnesses measured after polishing back the nitrocarburised surfaces. By keeping the polishing conditions strictly constant, it was found that significantly less polishing time was required for the N_2/NH_3 sample, because of the minimal surface oxidation that had occurred. Polishing only needed to remove the thin external oxide layer and expose the

original ground surface before a bright, reflective finish was achieved. Incidentally, the measured roughness of this sample after polishing was actually higher, owing to grinding marks on the original surface. For the $N_2/NH_3/CO_2$ sample, the surface remained dark until (it was assumed that) the porous zone below the original surface had also been removed. Later metallographical examination revealed that, in fact, a very small amount of porosity had remained, despite the change in appearance.

Results of pin on disc wear testing

Figure 3 shows the development of friction throughout the course of 500 m wear tests. Several phases of increasing or decreasing friction were seen between the ruby pin and the as treated CO_2 sample. Such large, sudden variations in friction behaviour were not a feature of wear testing against polished or untreated surfaces. Repeated tests on the same CO_2 sample showed some variation in the timing and shape of the features seen in Fig. 3a. While sharp drops and steady rises were common on the CO_2 sample, they were not predictable. In some cases, low friction was maintained between the two surfaces for extended periods.

Profilometer examination of the wear tracks after various test durations (Fig. 4) revealed that the CO_2 sample experienced two distinct levels of wear. Often, very little material was lost, and this corresponded to a sustained, low coefficient of friction. It seemed that, with the given test parameters, the CO_2 sample was at the threshold between two wear regimes, and that the



a $N_2/NH_3/CO_2$; b untreated H13; c $N_2/NH_3/natural\ gas$
 3 Friction coefficient during wear testing, between the ruby pin and various treated/untreated H13 substrates

occurrence of one or the other was an entirely random event. The cause may have been subtle variations in the properties of the nitrocarburised surface, which were not detected by metallographic examination (the layers appeared to be perfectly even across the treated surfaces). Changes in ambient temperature and humidity during the tests may have also played a part.

For an explanation of this behaviour, the wear surfaces were examined following each test. Figure 5 shows optical micrographs of the wear scars (bright circular and elliptical patches) on the ruby ball after various stages in the test and on different substrates. The ball was wiped with ethanol prior to optical examination to remove any loose, powdery debris. These micrographs can be matched with SEM images of the opposing wear tracks on the H13 discs (Fig. 6) The sliding direction was from left to right in Fig. 5 and from top to bottom in Fig. 6.

During the very early stages of the test, a shiny film developed on the surface of the ruby ball (Fig. 5a). There was also a smooth layer on the H13 disc (Fig. 6a). These micrographs were taken after testing of the as

treated CO_2 sample was stopped following a sharp drop of the friction coefficient to 0.25. Gaps in the film in Fig. 6a reveal patches of the original, ground surface. Machining marks at an oblique angle to the sliding direction were clearly visible. The nodular covering layer had fractured and exfoliated in these areas. Other gaps in the film reveal only the oxide layer of the treated surface.

After longer wear distances, the film on the ruby ball (Fig. 5b) and the H13 disc (Fig. 6b) became heavily scored. However, scratches in the gaps in Fig. 6b were in the grinding direction only. Apart from removal of the covering layer, the nitrocarburised surface was undamaged at this point. These micrographs were taken during the low friction regime.

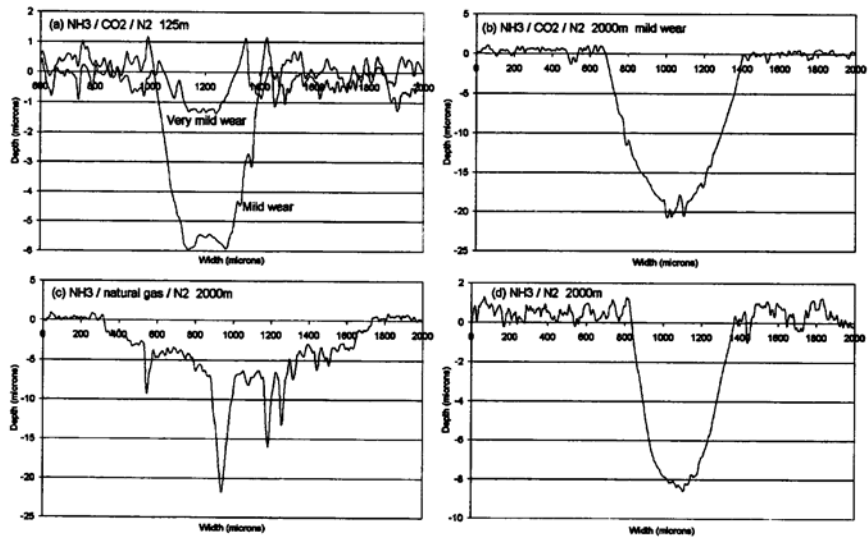
If, in contrast, the friction coefficient experienced a steady upturn, wear tracks revealed material from deeper below the surface. In Fig. 6c, the protective film had been squeezed out to the sides of the wear track, owing to the pressure beneath the ruby ball. Throughout the majority of the wear track area, the film was absent, as were the machining marks of the original surface.

Deeper wear was also accompanied by the appearance of fine, powdery red wear debris. This usually adhered to the ball, behind the wear scar, as in Fig. 5d and e, and could not be wiped off easily. Powdery debris that accumulated adjacent to the wear track was collected, and X-ray diffraction examination showed it to be largely Fe_2O_3 . Therefore, during the faster wearing mode of the as treated CO_2 sample, and in all wear tests of the other nitrocarburised samples, an abrasive mechanism took place. It appears that removal of the protective oxide film was related to the appearance of wear debris.

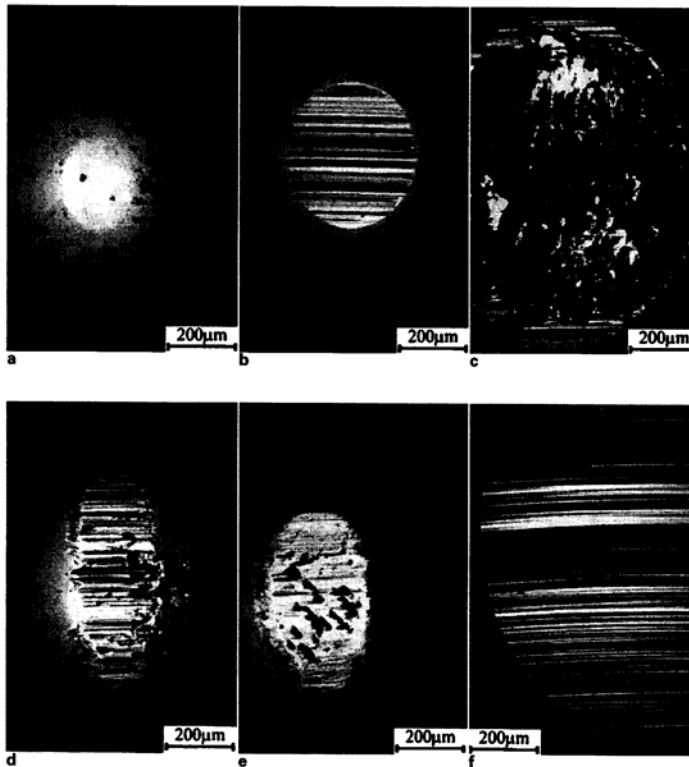
The two types of behaviour discussed so far are referred to here as 'mild' (abrasive) and 'very mild' (non-abrasive) wear. Mild wear corresponded to the oxidative process described by many authors for the sliding wear of metals. However, the formation of a protective oxide plateau, which almost eliminated wear of the underlying surface, is a new observation for nitrocarburised steels. Severe, adhesive wear and the generation of large, metallic wear particles were not seen on any of the nitrocarburised samples under the given conditions.

During deep penetration, broad ridges and grooves developed on both mating surfaces. Fragmented, compacted wear debris was found lodged within grooves, as seen in Whittle and Scott.¹² The CO_2 sample, after 2000 m of wear showed this clearly (Fig. 6d) However, it was the natural gas sample that developed the deepest groove patterns of all the samples, possibly because of the harder compound layer, and associated harder wear debris produced during testing of this sample. Figure 4c shows the dramatic peaks and valleys following a 2000 m test of the natural gas sample, whose deepest troughs penetrated well into the diffusion zone. Profiles of the NH_3 only and CO_2 samples were comparatively rounder (Fig. 4b and d). The wear scar on the ruby ball following testing of the hard, natural gas sample was much larger than the others, caused by hard debris lodged firmly within the deep grooves (Fig. 5f).

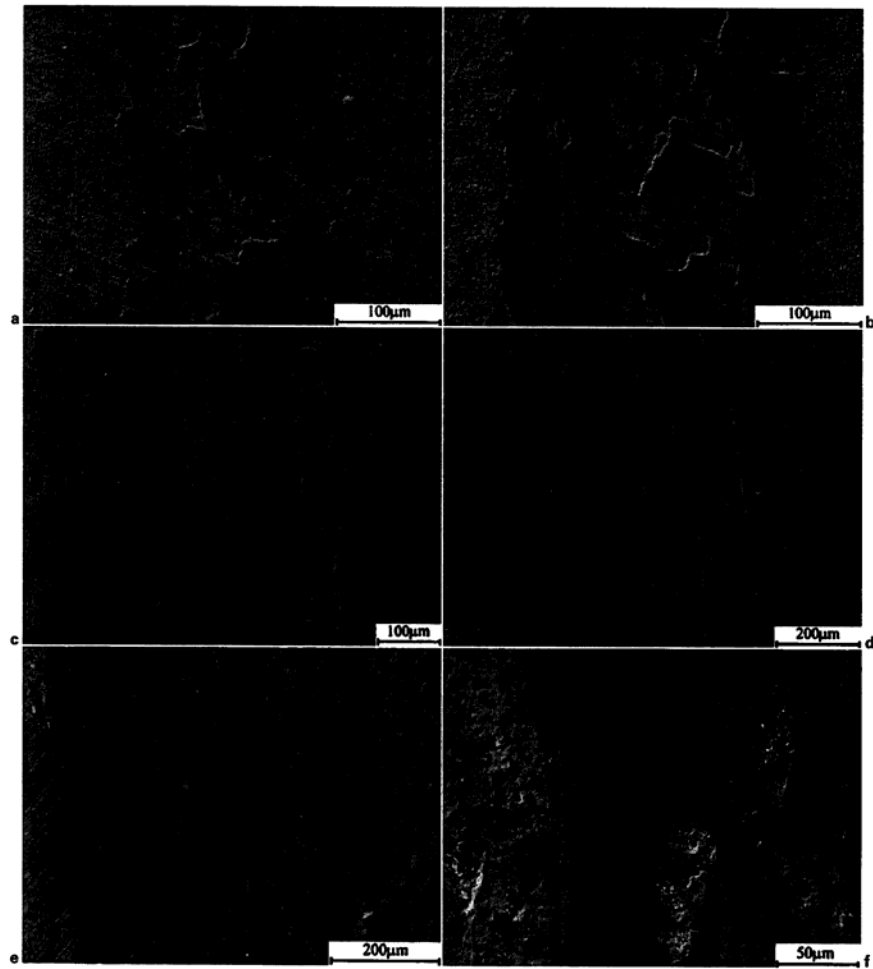
Wear tracks on the NH_3 only and natural gas samples were also covered in a dark film, which showed signs of heavy shearing and plastic flow. Many places were bare, while in others the film was peeling off (Fig. 6e).



a $N_2/NH_3/CO_2$ 125 m; b $N_2/NH_3/CO_2$ 200 m, mild wear; c N_2/NH_3 /natural gas 200m; d N_2/NH_3 200m
 4 Wear track cross-sectional profiles after various wear distances and substrate treatments



a CO_2 22 m; b CO_2 125 m, very mild wear; c untreated H13 500 m; d CO_2 2000 m, mild wear; e NH_3 only 2000 m; f natural gas 2000 m
 5 Optical micrographs of worn area on surface of ruby ball



a CO₂ sample 22 m; b CO₂ sample 125 m, very mild wear; c CO₂ sample 125 m, mild wear; d CO₂ sample 2000 m, mild wear; e N₂/NH₃ 2000 m; f untreated 500 m

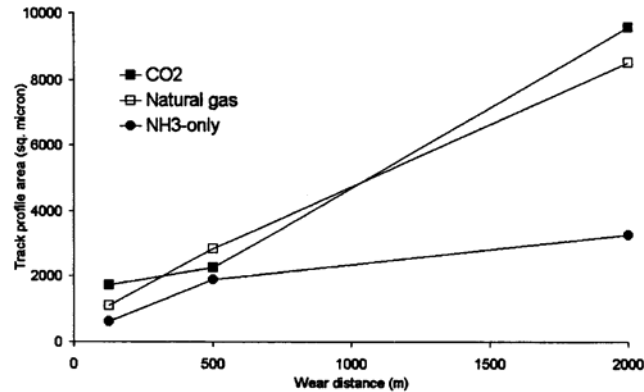
6 SEM micrographs of wear tracks on H13 discs

However, despite these obvious signs of oxidation, only raised film formed on the CO₂ sample was of high enough integrity to result in very mild wear.

The ability of the CO₂ sample to maintain a protective film without the formation of abrasive debris should be related to the covering layer and/or underlying porous region, as these were the features that distinguished this sample from the others. Similar situations, where reduced wear has come as a result of an oxide layer as part of a hardened surface microstructure, have been reported in the literature. For instance, it has been found that post-oxidation of plasma nitrided AISI 5140 steel resulted in a reduction in friction coefficient and wear rate compared with plasma nitrided only samples in an unlubricated pin on disc wear test against WC-Co. Wear debris was absent from the wear tracks of the post-oxidised specimens.¹³ Other systems where metal oxides act as solid lubricants are well documented.

Tribo-oxidation of WC-Co is known to produce oxides which lower the friction parameters. In tests of WC-Co against various hard counterface materials, it has been shown that abrasive wear debris can break down the protective oxide film, resulting in increased friction coefficient.¹⁴ Metal oxide 'plateaus' or 'islands' have also been found to lower friction and wear of Fe-5%Cr⁹ as well as titanium sliding against Al₂O₃(sapphire).¹⁵

In tests where the CO₂ sample behaved according to the mild, abrasive wear regime, the differences between the various treatments followed a more recognisable pattern. The more oxidised, porous and brittle surfaces wore at a faster rate (Fig. 7). The advantage of the harder compound layer on the natural gas sample was apparently nil (apart from considerably greater wear of the counterface material; Fig. 5f). Nitrocarburising resulted in a reduced wear rate compared with the untreated material (Fig. 8). SEM examination of the



7 Wear track area measured by profilometry

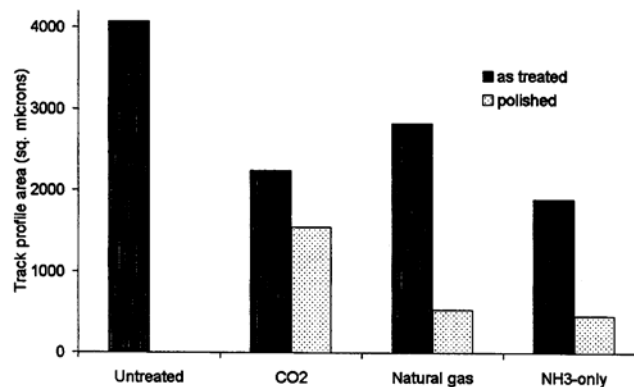
worn surface of untreated H13 (Fig. 6f) showed rough, oxidised sections and smoother areas with scratches running in the sliding direction. Some deep ploughing had occurred. The wear scar on the ruby ball was covered in well adhered wear debris (Fig. 5c). Therefore, there were features of severe, adhesive wear that were not seen on the nitrocarburised samples. Polishing after nitrocarburising further improved the wear resistance. There was little difference between the natural gas and NH₃ only samples, once the surfaces were fully polished. However, wear of the CO₂ sample was still significant, owing to a small amount of porosity that was not removed by polishing, despite the significantly longer polishing period and the bright, shiny finish achieved.

The response of the as treated N₂/NH₃/CO₂ specimen to the given wear conditions was, at worst, unpredictable and, at best, frequently superior to the others. Heavy oxidation is common with many commercial nitrocarburising (oxynitrocarburising) processes, and is not usually seen as detrimental for many applications. However, in some cases brittleness must be avoided, such as in extrusion dies, where debris from excessively thick compound layers is known to cause downtime.¹⁶ A smooth surface is often required for die components to ensure a high surface finish on the product. It was seen

here that, if nitrocarburised parts are to be polished following treatment, a non-porous, less oxidised surface is a better starting point. These microstructural features can be more influential than other, more often discussed details, such as the compound layer hardness.

Conclusion

It has been shown that the porous and highly oxidised surface produced during nitrocarburising under a high oxygen potential may behave very differently from more dense layers under the given wear conditions. While this sample wore faster during oxidative, abrasive wear, it was also prone to switch to a very mild wear regime. Very mild wear was characterised by a sudden lowering of the friction coefficient, the persistence of a protective film between the wear surfaces, and a lack of wear debris. Future work could investigate a broader range of conditions (force, sliding speed, counterface material) under which very mild wear is likely or certain to occur. The controlled engineering of an oxide layer, such as is done commonly using steam or oxidising treatment following nitrocarburising for corrosion resistance,^{6,17-19} offers an opportunity to exploit this behaviour for tribological purposes. However, it has been shown here



8 Influence of polishing/treatment conditions on wear track area, measured by profilometry

that a single step 'oxynitrocarburising' process is also effective.

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