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An Investigation of Tribological Properties of CN and TiCN Coatings

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Today the tool industry on a worldwide basis uses hard, wear-resistant, and low-friction coatings produced by different processes such as electrochemical or electroless methods, spray technologies, thermochemical, chemical-vapor deposition (CVD), and physical vapor deposition (PVD). In the current work, two different coatings, nitrocarburized (CN) and titanium carbonitride (TiCN) on M2-grade tool steel, were prepared by commercial diffusion and PVD techniques, respectively. Properties such as thickness, roughness, and hardness were characterized using a variety of techniques, including glow-discharge optical emission spectrometry (GD-OES) and scanning electron microscopy (SEM). A crossed-cylinders wear-testing machine was used to investigate the performances of both coatings under lubrication. The effect of coatings on the performance of lubricants under a range of wear-test conditions was also examined. Degradation of lubricants during tribological testing was explored by Fourier transform infrared (FTIR) spectroscopy.

Keywords CN, coatings, crossed cylinders, lubricants, TiCN, tribology

1. Introduction

Metal forming is a very complex process that involves plastically deforming a metal workpiece into a desired shape of high dimensional accuracy and surface quality via several stages. Surface engineered coatings have primarily been used in tools for metal forming operations for wear resistance. Hard, wear-resistant, and low-friction coatings are currently produced on a worldwide basis by different processes such as electrochemical or electroless methods, spray technologies, thermochemical processes, chemical vapor deposition (CVD) and physical vapor deposition (PVD). The most commonly used coating deposition and surface treatment techniques are described in the literature.[1] PVD coatings have high purity with a fine structure and good performance and are commonly used for cutting tools, dies, drill bits, and joint replacements.[2] Diffusion coatings have been used as an effective metallurgical tool for protection and upgrading of a diverse range of metals. Alloy coatings and/or compound layers, which are produced when one element diffuses into the surface of a second element, can have excellent resistance to high-temperature oxidation and aqueous corrosion.[3]

Wear resistance is the main application of engineered surface coatings. Wear tests can be conducted to rank the wear resistance of coatings to optimize coating selection or development for specific applications.[1,4,5]

A crossed-cylinders wear test has been used by Mills et al.[6] and Wallen et al.[7] to evaluate the tribological characteristics of conventional tool materials. More recently, Sato et al.[8,9] used this test to evaluate the tribological characteristics of coatings and found it an appropriate testing method for evaluation of wear and tribological characteristics of coated metal forming tools with very thin coating layers (about 2-5 μm). This test is also used in the current study to investigate the performance of coatings and lubricants under a range of wear test conditions. The degradation of lubricants during tribological testing was also investigated by means of Fourier transform infrared spectroscopy.

2. Experimental

2.1 Preparation of Sample Materials

M2 high-speed steel (0.90 C, 4.1 Cr, 5.0 Mo, 1.8 V, 6.4 W, bal Fe) was used as a substrate material for the samples subjected to characterization and wear testing. Two different, commercially available surface treatments were used. A fluidized-bed technique was used to produce a CN diffusion layer (Quality Heat Technologies Pty Ltd, Victoria, Australia) and a TiCN coating was applied by PVD (Surface Technology Coatings, Victoria, Australia).

Three noncommercial oil-based lubricants with simplified formulations were provided by Castrol (Australia) (Table 1).

2.2 Coating Surface Quality Measurements

The hardness, roughness, and thickness of the coatings were characterized using a range of techniques (Table 2).

Table 1 Lubricants Used for the Study

Code	Lubricant Type
L1	Oil—mineral oil
L2	Oil—mineral oil, fatty additives
L3	Oil—mineral oil, chlorinated paraffin EP additive

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Table 2 The Properties of Coatings and M2 Substrate Material

Coating	Hardness, HV	Roughness (R_a), μm	Thickness, μm
M2 Substrate	820	0.05	…
CN	1220	0.40	18.7 (compound layer)
TiCN	1900	0.12	5.2

A Leitz Wetzlar (Wetzlar, Germany) microindenter tester was used for MicroVickers hardness measurements. A load of 100 g was selected and five measurements were averaged.

The surface roughness of the coatings was measured using a Taylor Hobson Surtronic 3^+ Profilometer (Leicester, UK) over a 25 mm traverse length, and the average roughness (R_a) was calculated from five traces in different directions.

The elemental depth profile and thickness of the coatings were measured using glow-discharge optical emission spectrometry (GD-OES) and scanning electron microscopy (SEM). A Leco (Leco Grp., St. Joseph, MI) GDS-850A GD-OES spectrometer with a Grimm-type DC lamp (Carl Zeiss SMT AG, Oberkochen, Germany) and a Leo 1530 scanning electron microscope were used for this study.

2.3 Crossed-Cylinders Tribological Testing

A simple crossed-cylinders wear test was used for evaluation of tribological properties of coatings under different operating conditions (Fig. 1).

A cylindrical specimen (representing the tool) fixed at the end of a loading apparatus was forced against another cylindrical sample (representing the work material), which was rotated on a program-controlled lathe. The loading apparatus was mounted on the table of the lathe. The tool specimen was attached to the loading apparatus with a customized jig that facilitated easy removal and relocation of the specimen. A load cell with a capacity of 20 kg was used to measure friction force during the crossed-cylinders wear test. The output data from the load cell was acquired using a Portable DT9800 Datalog system with Data Translation Version 2.4 software (Marlboro, MA). The operating conditions including load, sliding speed, sample cylinders, and lubricant could be easily changed.

Friction and wear tests were carried out under both dry and lubricated conditions at room temperature, about 25 °C. The diameter of the coated tool specimen was 12 mm. The counter material was a 100 mm long steel bar with a diameter of 11.5 mm, machined from a coil of AISI 1019 steel rod (nominal composition: 0.15 C, 0.02 Cr, 0.89 Mn, 0.03 V, 0.33 Si, 0.04 Cu, 0.20 Ni, bal Fe) with a diameter of 13 mm. A load range of 35.3-88.2 N was selected, and the sliding speed between the contact surfaces was 0.23 and 0.37 m/s.

The sliding contact between the cylinders resulted in a wear scar (Fig. 2). The wear scar width was measured using an optical microscope (Olympus BX51M, Melville, NY), and then the maximum wear depth could be obtained from a geometrical calculation as follows:

$$(D/2 - \delta)^2 + A^2/4 = D^2/4 \qquad \text{(Eq 1)}$$

$$D\delta - \delta^2 = A^2/4 \qquad \text{(Eq 2)}$$

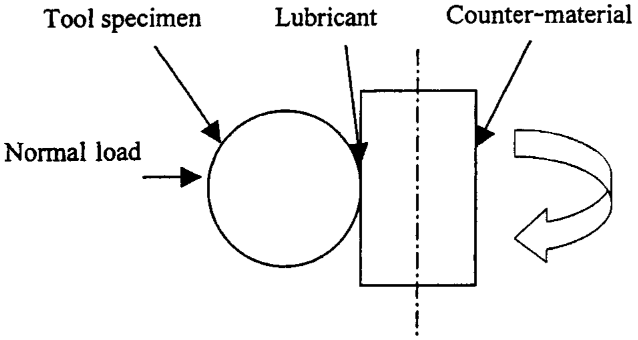

Fig. 1 Schematic view of a crossed-cylinders wear test

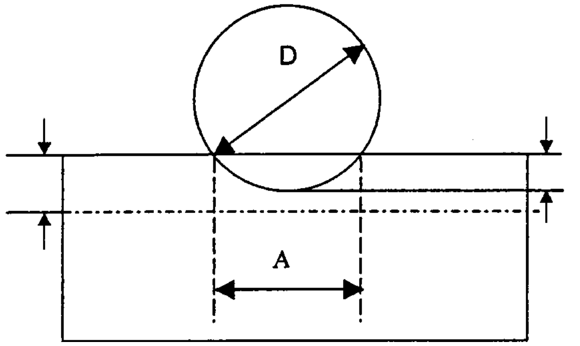

Fig. 2 Schematic of contact between cylinders and wear scar of coating. T: thickness of coating; δ: maximum wear depth; D: diameter of counter material; and A: width of wear scar

However, $\delta \ll D$, therefore, $\delta^2 \cong 0$. Thus, in Eq 2, δ^2 is negligible and becomes:

$$D\delta \cong A^2/4, \text{ rearranging gives } \delta \cong A^2/4D \qquad \text{(Eq 3)}$$

where δ is the maximum wear depth, D is diameter of the counter material, and A is the width of wear scar.

2.4 FTIR Analysis

FTIR was used to monitor the degradation of lubricants during the crossed-cylinders tribological testing. Before tribological testing, the sliding pairs were cleaned with hexane. Lubricant samples for FTIR tests were obtained by washing the wear scars of the counter cylinders (1019 steel bars) using dichloromethane then drying in air. A Perkin Elmer (Boston, MA) FTIR Spectrometer Spectrum 2000 with a KBr (Boston, MA) window was used for analysis. IR spectra of samples were recorded at 8 cm^{-1} resolution. The number of scans was set at 32 and the regular scanning range used for the samples was 400-4500 cm^{-1}.

3. Results and Discussion

3.1 GD-OES Determination and SEM Imaging

The elemental concentrations for titanium (Ti), iron (Fe), carbon (C), cobalt (Co), tungsten (W), molybdenum (Mo),

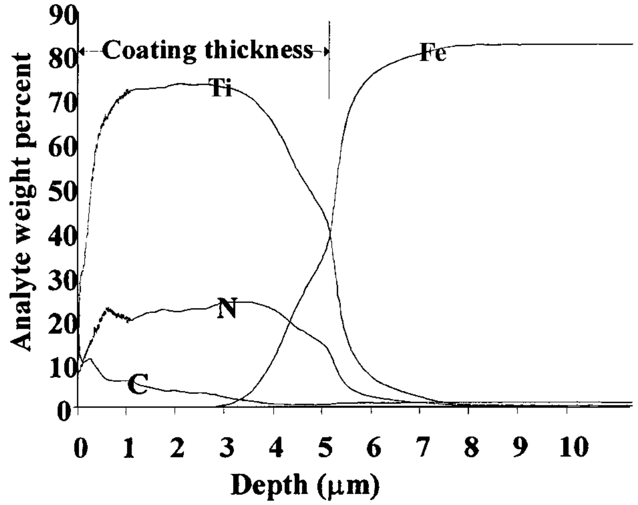

Fig. 3 The quantitative GD-OES depth-profiling results for TiCN coating on M2 tool steel

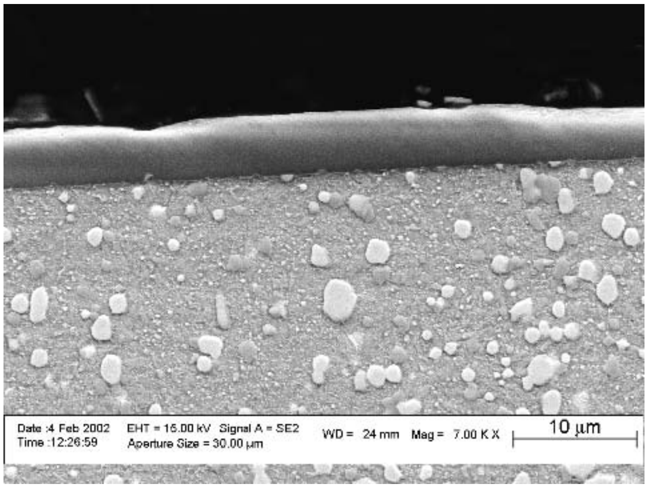

Fig. 4 SEM micrograph of TiCN coating on M2 tool steel

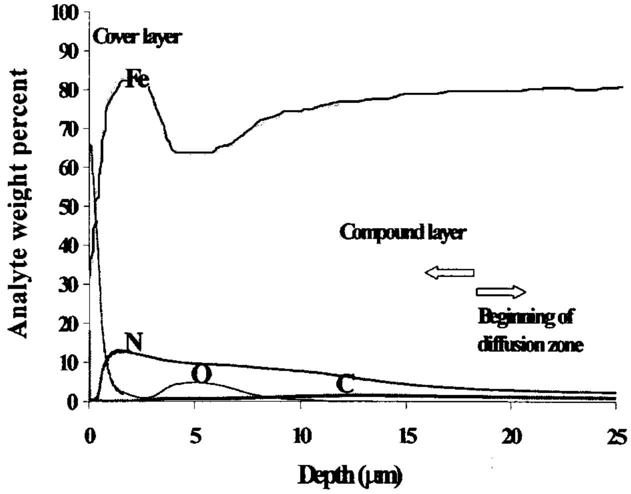

Fig. 5 The quantitative GD-OES depth-profiling results for CN coating on M2 tool steel

nickel (Ni), chromium (Cr), vanadium (V), nitrogen (N), silicon (Si), zinc (Zn), and oxygen (O) were measured for the TiCN coating. The changes in concentrations of the main elements Ti, Fe, C, and N show that the transition between coating and substrate occurs between 5 and 6 μm. The thickness of the TiCN coating is about 5.2 μm (Fig. 3). A SEM image of the TiCN coating shows that a uniform coating has been formed on the substrate M2 steel surface and also confirms the coating thickness obtained from GD-OES determination (Fig. 4).

For the CN coating, the elemental concentrations for Fe, C, W, Mo, Cr, V, N, and O were measured. From the plots of the main elements (Fig. 5), the compound layer (white layer) and the beginning of the diffusion zone can be seen. At ~4-7 μm there is a broad O peak. This is the porous region of the compound layer. The greater surface area here allows a higher volume fraction of surface oxides to grow. The Fe and N peaks directly above the porous region (1-4 μm) presents an iron carbonitride "cover layer." There is also a broad C peak deeper within the compound layer (10-20 μm). The surface of ~1 μm is scale, formed during treatment due to the O potential of the treatment atmosphere. The percentages of all other elements decrease here because the amount of O is so high. From the SEM image of the CN coating (Fig. 6), the white layer and the beginning of the diffusion zone can be clearly observed, and the thickness of the white layer is around 18.7 μm. The SEM result of CN coating is in good agreement with the GD-OES measurement of the layer thicknesses.

3.2 Influence of Normal Load on Friction and Wear

These experiments were carried out with a range of loads under both dry and lubricated conditions. The sliding speed was 0.23 m/s.

It is clear that there are significant changes in the friction force under different normal loads (Fig. 7). Each curve has an obvious turning point, after which the friction force suddenly increases to a higher level. The curves also become noisier when compared with the earlier friction forces. The sudden increase in friction force is caused by lubricant breakdown, which can be defined as the lubricant no longer being effective.

Variation of friction and wear of the TiCN/1019 steel pairs with load was measured (Fig. 8, 9). Each test had a sliding distance of 138 m under the selected load. The friction coefficient for lubricated tests was obtained prior to lubricant breakdown. It can be seen that, under both dry and lubricated conditions, the friction coefficient remains constant when the load is raised. The depth of wear scar, however, increases with load. There is a sudden increase in the depth of wear scar under dry conditions when load is raised to 70.6 N. The sudden increase in the depth of wear scar under dry conditions is likely caused by the coating being worn through. The depth of the wear scar grows gradually in the presence of lubrication with the values for both the friction coefficient and depth of wear scar being much lower.

The generation of wear debris could be observed during both dry and lubricated tests, indicating material transfer be-

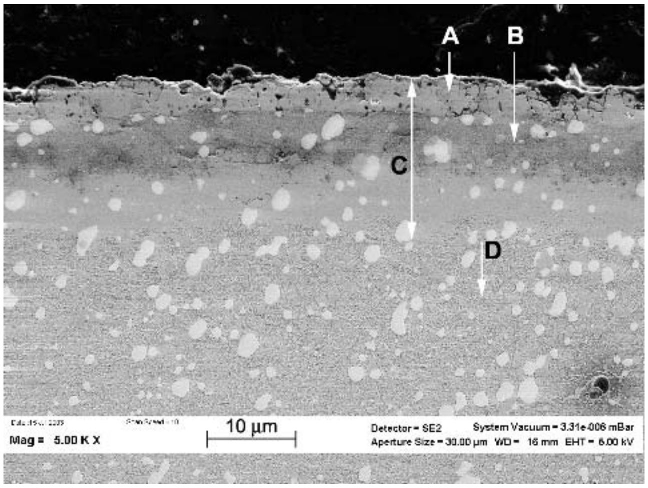

Fig. 6 SEM micrograph of CN coating on M2 tool steel: **(a)** cover layer; **(b)** porous zone; **(c)** compound layer; **(d)** the beginning of the diffusion zone

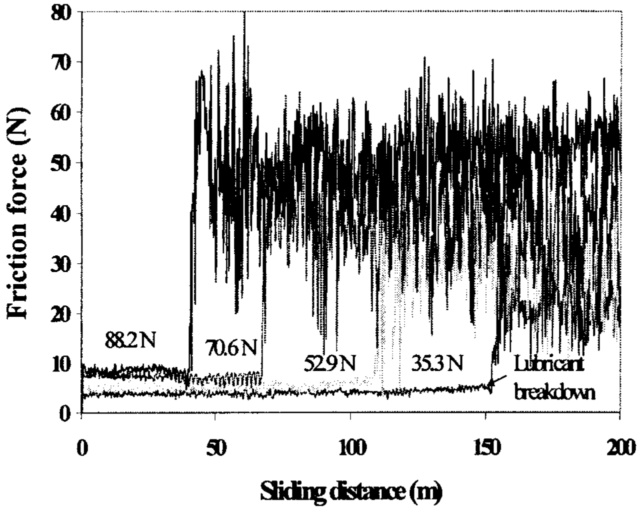

Fig. 7 Normal load dependence of the friction force for the M2/1019 steel pairs with lubricant L1 and a sliding speed of 0.23 m/s

tween the counter surfaces.[10] The greatest amount of material transfer was found under dry conditions, giving rise to the higher friction coefficient and wear depth. The lubricant can prevent adhesion and material transfer, especially at lower loads, thus reducing both the friction coefficient and wear depth.

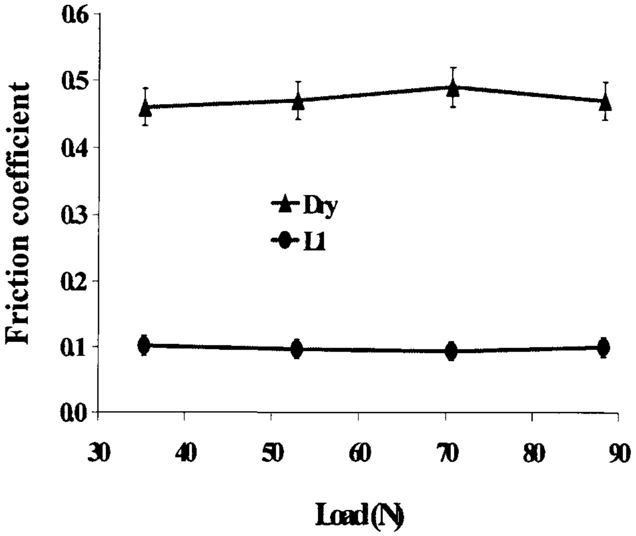

Fig. 8 Variation of friction coefficient with load for the TiCN/1019 steel pairs, unlubricated (dry) and with lubricant L1. Sliding speed, 0.23 m/s; sliding distance, 138 m. The friction coefficient for lubricated conditions was obtained prior to lubricant breakdown.

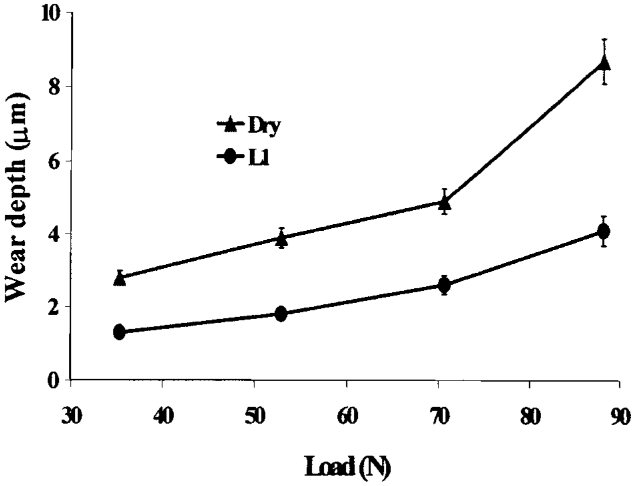

Fig. 9 Variation of wear-scar depth with load for the TiCN/1019 steel pairs, unlubricated (dry) and with lubricant L1. Sliding speed, 0.23 m/s; sliding distance, 138 m.

3.3 Influence of Lubricants on Friction and Wear

Experiments were carried out to evaluate the performance of the lubricants. The selected load and sliding speed were 70.6 N and 0.37 m/s, respectively. The sliding distance for each test was 222 m. It was found that the values of both friction coefficient and wear depth under lubricated conditions were much lower compared with those of the unlubricated condition (Fig. 10). The tested lubricants have similar values of the friction coefficient; however, the lowest value of wear depth was achieved when the lubricant L3 (mineral oil with EP additive) was used. This may be attributed to the use of EP additive, which can improve the performance of lubricant under higher contact pressure. The breakdown of lubricants L1 and L2 was clearly observed during the early stage of wear testing (around 180 m sliding distance), while lubricant L3 did not appear to break down during testing.

3.4 Wear Performance of Coatings

A load of 70.6 N and a sliding speed of 0.23 m/s were selected to compare wear performance of the coatings when

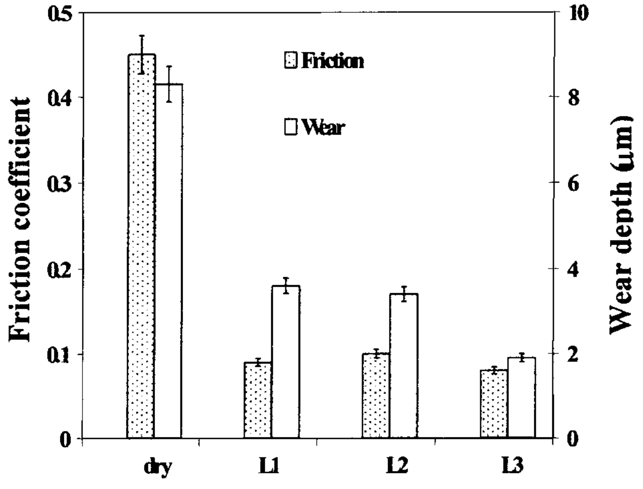

Fig. 10 Wear depth on CN coating and friction coefficient for the CN/1019 steel pairs. Load, 70.6 N; sliding speed, 0.37 m/s; sliding distance, 222 m. The friction coefficient was obtained prior to lubricant breakdown.

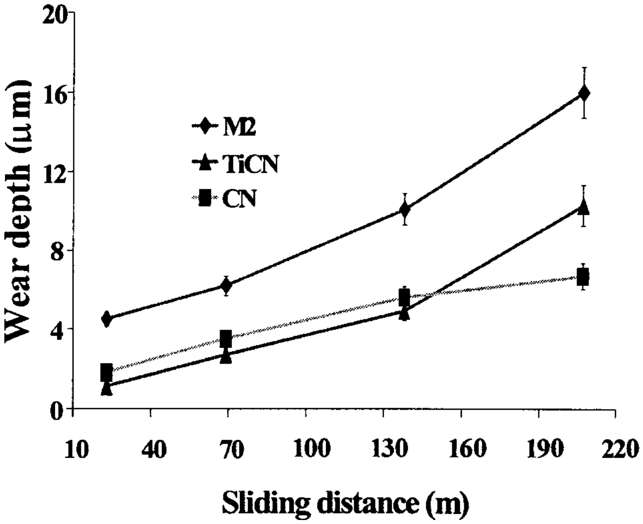

Fig. 11 Variation of wear scar depth on different tool surfaces with sliding distance under unlubricated conditions. Load, 70.6 N; sliding speed, 0.23 m/s; counter material, AISI 1019 steel.

sliding against AISI 1019 steel. It is clear that the wear depth of both TiCN and CN coatings is much less than the M2 substrate (Fig. 11). This indicates that the surface coatings can significantly improve wear resistance. The wear depth of both coatings increases gradually to a sliding distance of 140 m with the TiCN coating wearing slightly more slowly than the CN coating. This may be attributed to the harder surface of the TiCN coating. However, there is a significant increase in the wear depth of the TiCN coating when the testing continues after a sliding distance of 140 m. This is very likely to be caused by the coating being worn through. The compound layer of the CN coating is much thicker than the TiCN coating and good wear resistance persists to a greater wear scar depth.

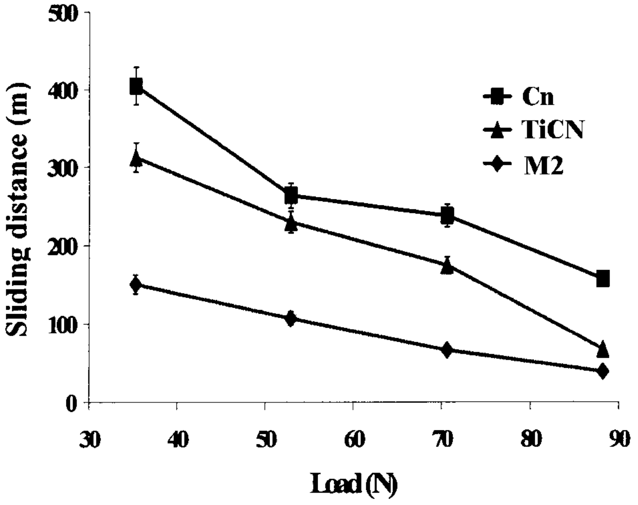

Fig. 12 Sliding distance before lubricant breakdown for different coatings and M2 steel in contact with AISI 1019 steel and lubricated with L1, at a sliding speed of 0.23 m/s

3.5 Influence of Coatings on Sliding Distance

As discussed earlier, at some point during each test, the friction force suddenly increased due to lubricant breakdown (Fig. 7). The sliding distance before lubricant breakdown for different contact pairs was compared. L1 was used as a lubricant and a sliding speed of 0.23 m/s was selected. It was found that in all systems tested, the sliding distance before lubricant breakdown reduced with an increase in normal load. This indicates that all contact pairs can slide a longer distance before lubricant breakdown when a lower load is used. Under all tested loads, coated tool/1019 steel pairs can slide a much longer distance before lubricant breakdown than the M2/1019 steel pair, and the CN coating achieves the best performance among the tests (Fig. 12). It is possible that the longer sliding distance before lubricant breakdown with the CN coating can be attributed to the porous zone of the coating. The porosity reduces the hardness of the coating, but sometimes benefits the coating due to lubricant retention and, thus, enhances the tribological properties under lubricated conditions.[11]

3.6 Degradation of Lubricants During Tribological Testing

Degradation of oil lubricants usually involves oxidation of hydrocarbon molecules to functional groups, such as alcohol, hydroperoxide, carboxylic acid, ester, aldehyde, and ketone, that provide characteristic FTIR spectral bands. The FTIR spectra for the products generated from oil oxidation usually appear in three regions: O–H (3600-2500 cm^{-1}), C=O (1900-1600 cm^{-1}), and C–O (1500-900 cm^{-1}).[12]

For both the original and used lubricant L3, no significant changes are observed in C–H bands. A number of strong bands in the spectra represent these (Fig. 13), the C–H stretch bands for the $-CH_3$ group are at around 2955 cm^{-1} while the $-CH_2$ groups are at about 2921 and 2854 cm^{-1}. The bands for C–H asymmetric deformation in $-CH_2$ groups and $-CH_3$ groups, and for the $-CH_2$ chain rocking, are at approximately 1460, 1377, and 722 cm^{-1}, respectively.[12]

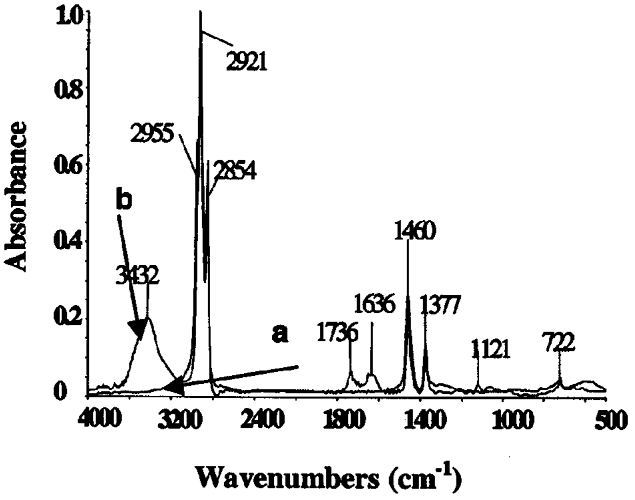

Fig. 13 FTIR spectra of lubricant L3: **(a)** unused; **(b)** used for tribological testing on the M2/1019 steel pairs with a load of 35.3 N and a sliding speed of 0.23 m/s

However, there are significant changes in the O–H, C=O, and C–O spectral regions between the original and used lubricant L3. For used lubricant, a new broad band with maxima at around 3432 cm^{-1} may suggest the presence of alcoholic O–H groups.[12] It appears that the C=O spectral region contains a spectral band with maxima at 1736 cm^{-1}, which is usually associated with esters[13,14] and absorptions at around 1635 cm^{-1}, possibly representing conjugated carbonyl species.[13] The peak at 1121 cm^{-1} is likely to be due to the presence of low to medium molecular weight aliphatic esters.[13,14]

FTIR spectra of used lubricant L1 (mineral oil) used in sliding tests with both M2/1019 steel and CN/1019 steel contact pairs were obtained (Fig. 14). A load of 35.3 N and a sliding speed of 0.23 m/s were used. It can be seen that there are some differences for the absorptions in the carbonyl region (1900-1600 cm^{-1}) between two spectra. The results for L1 used for M2/1019 steel contact pairs are similar to those for used lubricant L3 reported in Fig. 13. However, the FTIR spectrum for L1 used for the CN/1019 steel pair shows a strong peak at 1712 cm^{-1}, which usually represents carboxylic acids. The minor peak at 1768 cm^{-1} indicates the possible formation of a five-membered ring lactone.[13] No absorption appears at around 1735 cm^{-1}, which is usually associated with esters. Bowman et al.[15] have reported that the formation of carboxylic acids from the oxidation of oil lubricant can absorb on the contacting surfaces and protect the surfaces against scuffing failure. Our results show that the lubricants have better performance when used with the CN coating. This may relate to the formation of carboxylic acids from the degradation of oil lubricants during the tribological testing.

4. Conclusions

From this study, the following conclusions can be drawn:

- The wear depth of TiCN coating in the TiCN/1019 steel sliding pairs varies with the loads. Higher loads give greater wear scar depths.
- The friction-reducing effect of lubricants minimizes adhesion between the contact surfaces and thus reduces the wear. The performance of lubricants is affected by the coating used. Lubricant L1 lasted longer before breakdown when used with the CN coating. This may be attributed not only to the porous zone of the CN coating, but also to the formation of carboxylic acids during the oxidative degradation of oil lubricants.
- Engineered surface coatings can significantly improve wear resistance of the tool surface. The sliding wear performance of coatings strongly depends on the type, thickness, and hardness of the coating.
- On the whole, the methodology based on the crossed-cylinders wear rig, as described previously, is reliable and could be used as an inexpensive laboratory technique to prescreen new lubricant formulations and aid in materials selections.
- It is evident that FTIR is a useful technique for determining the degree of degradation of lubricants during tribological testing.

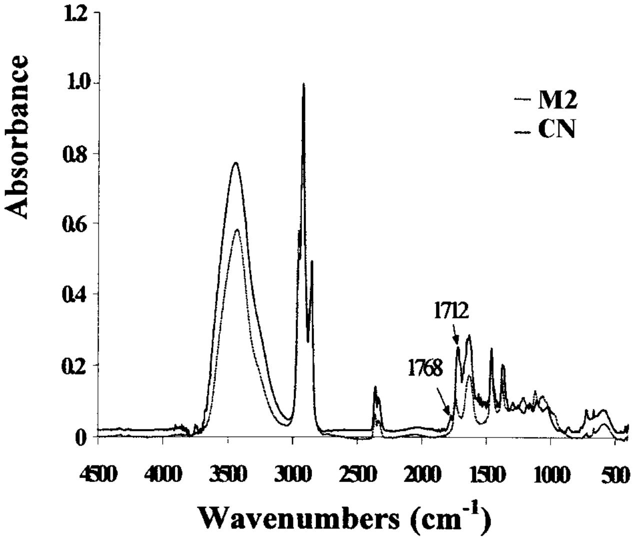

Fig. 14 FTIR spectra of used lubricant L1 in contact with CN coating and M2 steel. Load, 35.3 N; sliding speed, 0.23 m/s; sliding distance 69 m.

Acknowledgments

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