1 Microtribological studies of different nanocomposite TiC/a-C:H 2 coatings using a modified nanoindentation setup

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7 Received 21 September 2003; accepted 28 May 2004

8 The microtribological behavior of different nanocomposite TiC/a-C:H coatings against 100Cr6 (AISI 52100) balls with
9 250 μm radius has been studied using a modified nanoindentation setup and was compared to the results of macroscopic pin-
10 on-disc (POD) experiments. First results reveal significant differences between macroscopic friction coefficients μ_{POD} determined
11 using (POD) tests and microscopic friction coefficients μ_{micro} . On the macroscopic scale low friction coefficients can be obtained
12 for high hardness coatings. On the microscopic scale the high hardness samples induce considerable wear on the steel counter-
13 body leading to high microscopic friction coefficients of around 0.3. For samples with lower hardness no wear has been
14 observed and low microscopic friction coefficients (<0.2) can be achieved.

15 **KEY WORDS:** microtribology, friction, hard coatings, nanoscratching, nanocomposite TiC/a-C:H

16

17 1. Introduction

18 Components with high reliability and life-time can
19 only be successfully applied in devices in motion if
20 their mechanical and tribological properties are pre-
21 cisely known. Novel types of devices on the micro-
22 scale, like micro-electromechanical systems (MEMS)
23 [1] or galvanofomed watch parts [2], demand new
24 measurement techniques to explore the tribological
25 properties. In this context, thin coatings with opti-
26 mized mechanical properties are promising candidates
27 to improve the tribological properties of such devices.
28 Classical tribological tests on the macroscopic scale,
29 like pin-on-disc (POD) experiments, are conducted on
30 components with large mass under heavily loaded con-
31 ditions (up to several N). Wear phenomena are, there-
32 fore, inevitable and the bulk properties of the involved
33 tribo-partners determine the tribological system under
34 investigation to a large extend. In devices like MEMS
35 or for mechanical watch parts, the involved masses
36 and the applied loads are small (a few μN up to sev-
37 eral mN only). As a consequence, wear phenomena
38 play an inferior role but surface properties like rough-
39 ness or interaction forces between the tribopartners are
40 expected to be important.

41 Beside much lower loads, one also has to consider
42 the small object's dimensions and instruments to inves-
43 tigate the tribological properties on the micro-scale
44 have to be able to simulate small contact areas and to

perform short movement path lengths. In addition, 45
many of the techniques applied to fabricate MEMS or 46
small watch parts do not allow an up-scaling to pro- 47
duce large samples for conventional POD tests. 48

49 There are several approaches to investigate the tribolo-
50 gical properties at small length scales. Much work has
51 been done by using the lateral deflection of the cantile-
52 ver in atomic force microscopy (AFM). This so-called
53 friction force microscopy (FFM) mode was first applied
54 by Mate *et al.* [3]. Since then, ample work has been per-
55 formed using FFM techniques (for an overview see e.g.,
56 the book of Bhushan [4] and the references therein).
57 FFM is an extremely local probe. It allows the charac-
58 terization of single asperity contacts or the study of
59 forces between the FFM tip and molecules of the inves-
60 tigated surface or of a lubrication layer. The calibration
61 routines needed to obtain a quantitative value for the
62 friction coefficient are, however, rather complex [5] and
63 several parameters with high uncertainties like the pre-
64 cise tip geometry or cantilever stiffness have to be
65 included. In addition, it has to be considered that the
66 study of single asperity contacts only describes one
67 aspect of a tribological system. The results of the work
68 presented in this paper, for example, indicate that under
69 some conditions an alternate formation and pulsing out
70 of wear debris at the contact between the tribopartner
71 determines the friction coefficient value (see Section 3).
72 Such phenomena are difficult to study using an AFM.
73 In addition, the choice of the tribopartner (the tip in the
74 case of FFM) is limited to the materials of the available
75 FFM tip surfaces.

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The gap between POD experiments on the macroscopic scale using high loads and the simulation of the tribological properties of single asperity contacts with FFM has meanwhile been filled by custom-made [6,7] or commercially [8] available microtribometers. In the community of thin-film deposition, adhesion and fracture, as well as some microtribological properties, are often studied using the scratch mode of nanoindentation equipment. This approach has the advantage that mechanical properties (hardness, Young's modulus) as well as tribological properties can be studied using a single experimental setup. In a nanoscratch experiment, a diamond indentation tip is pushed into the sample surface and simultaneously the sample is laterally moved relative to the indenter tip. The applied load can be held constant or continuously increased with the scratch distance [9]. Typical diamond indentation tip geometries are cones with spherical tip apices and three- or four sided pyramids. Such experiments are generally used to study coating failure and adhesion [10–12]. Some instruments are equipped with sensors for lateral force measurement and can therefore be used to determine friction coefficients [13–15]. As a complication, the measured lateral force contains contributions from sliding friction and due to tip ploughing effects. Models for the extraction of the coefficient of friction from a nanoscratch experiment have been proposed [16,17], but some uncertainties like the direction of the material flow or the behavior of the material at the rear side of the indenter remain. Typical normal loads of nanoscratch devices range from a few tens of μN up to several hundred mN, the lateral range for scratches lies between a few μm up to several mm. The available loads and lateral displacements are thus well suited to study microtribological systems like MEMS or mechanical watch parts, but, as in FFM, the choice of the tribopartner (diamond indentation tips) is restricted.

In this work, we tried to overcome the shortcomings of nanoscratch experiments for the determination of the friction coefficient by using a modified nanoscratch setup. Instead of the standard diamond indentation bodies, we used 100Cr6 (AISI 52100) spheres with a radius of 250 μm and performed so-called linear oscillating tests. Using this modified setup, we investigated several nanocomposite TiC/a-C:H coatings on steel substrates. We have selected these samples because they reveal, depending on the exact composition, a wide range of mechanical properties. The 100Cr6 in tribological contact with such a thin hard coating is one of the most used combinations in machine elements, for example ball bearings. Therefore, we have chosen 100Cr6 as counter material. Furthermore, the identical set of samples has also been measured by conventional POD tests. From our experience, results obtained by using a rotational system (POD) and by using a linearly oscillating system are comparable as

long as the same contact pressures and the same average velocities are used. There may be of course differences in the running-in periods. We, therefore, are confident that a comparison between macroscopic POD tests and microscopic oscillating tests as presented in this paper is possible.

2. Experimental Setup

2.1. Samples

Thin films of nanocomposite titanium carbide and amorphous hydrogenated carbon (nc-TiC/a-C:H) at various compositions have been deposited by unbalanced reactive magnetron sputtering from a metallic titanium target in the presence of argon and acetylene. Detailed information about the coating deposition can be found in [18]. The films have been grown to a thickness of 1.5–2.0 μm on hardened steel substrates for mechanical tests and on single crystal Si(100) wafers for structural and chemical characterization. An interlayer of metallic titanium of approximately 200 nm has been deposited prior to film coating to improve the adhesion of the films on the steel substrates. The chemical composition of the TiC/a-C:H samples was determined by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics Quantum 2000 ESCA system with monochromatized Al $K\alpha$ radiation. The samples have been ion sputter cleaned (4 keV Ar^+) in order to liberate the surface from adventitious contamination corresponding to about 2 nm of carbon. Note that this treatment lowered the oxygen content by a factor of approximately 5. Details about the XPS measurements as well as spectra are given in [18]. The 12 samples used for the microtribology study have TiC concentrations ranging from 21 up to 100 atomic percent (at%) and corresponding a-C:H concentrations from 74 down to 0 at%, respectively (see table 1).

Table 1.

TiC and a-C:H concentration, hardness H and Young's modulus E of the investigated TiC/a-C:H coatings deposited on steel substrates. For samples where the sum of the TiC and a-C:H concentration is below 100%, the sample contains some oxygen.

TiC (at%)	a-C:H (at%)	H (GPa)	E (GPa)
21	74	13.4	132
28	71	17.4	164
48	50	13.7	142
57	39	16.5	185
74	17	33.4	341
77	20	29.1	314
84	9	26.2	283
85	10	34.7	353
86	11	31.7	350
87	9	20.4	245
90	5	15.5	216
100	0	11.0	176

This type of coatings is both of scientific and commercial interest because hardness-enhancement is attained for a composition of TiC/a-C:H in the range of 90:10 to about 80:20. Between 5 at% and 10 at% a-C:H the macroscopic friction coefficient drops from about 0.6 to 0.3. It is thus possible to produce hardness-enhanced coatings with low macroscopic friction coefficients.

The coating hardness and the Young's modulus have been measured by nanoindentation with a MTS Nanoindenter XP[®] using the Continuous Stiffness Measurement technique [19]; these values are also summarized in table 1.

2.2. POD experiments

The macroscopic friction coefficients μ_{POD} were determined using a POD Tribometer from CSEM. All measurements were done in 60% relative humidity, 5 N normal load and with a sliding velocity of 0.1 m/sec, the values were taken after 700 m of total displacement. The friction counterparts were 100Cr6 balls with 6 mm in diameter, which were ultrasonically cleaned in ethanol before each measurement. The typical R_a roughness value of these balls is 250 nm.

In order to calculate the real contact pressure between the steel ball and the sample, one would need to take into account the Young's modulus values of the thin coating and the substrate. Furthermore, plastic deformations of the substrate may play a role. As this paper is mainly focusing on the microtribological study, we applied the limiting case of Hertz' theory [20,21] using only the Young's modulus of the coating. We assumed for both, coating and 100Cr6 ball, a Poisson ratio of 0.3 and 200 GPa for the Young's modulus of steel. Because the Young's modulus values of the coatings determined by nanoindentation experiments varied from 132 to 353 GPa (see table 1), the initial contact radii and the mean initial contact pressure are different for each ball-coating combination. For the investigated coatings the initial contact radii range between 50.6 and 43.2 μm , the initial mean contact pressures range from 633 to 853 MPa.

2.3. Microtribology experiments

The microtribology experiments were performed using a MTS Nanoindenter XP[®] equipped with the lateral force measurement option for nanoscratch experiments [22]. Instead of using the standard diamond indentation bodies, 100Cr6 spheres with a radius of 250 μm were glued to modified MTS tip holders. The R_a roughness value of these balls is about 230 nm, thus comparable to the roughness of the balls used in the macroscopic POD tests. Each test was performed using a new ball and its surface was examined by optical

microscopy to check for glue particles within the contact region. The standard measurement routine (used to perform one single scratch with a pre-profiling at low loads to correct for a possible slight sample tilt) has been modified such that oscillating movements (i.e., multiple forward and backward cycles) are possible. Our approach is an extension of a popular nanoindentation/nanoscratch apparatus that allows the measurement of mechanical (hardness, Young's modulus) and tribological properties in one device. The software of the device can be modified such that arbitrary trajectories can be programmed. This is an advantage for tests on complicated geometries, for example parts for MEMS.

To obtain similar initial mean contact pressures in the microtribological tests as for the POD experiments, the normal load was set to a nominal value of 30 mN. As for the macroscopic POD setup, the mean initial contact pressure was different for each ball-coating combination due to the differences in the Young's modulus values of the different coatings (see table 1) and ranged from 594 to 814 MPa. The initial contact radius for the microtribological tests was about 4 μm (values for POD setup: around 50 μm). Two-hundred and fifty forward and backward cycles have been performed with a sliding velocity of 200 $\mu\text{m}/\text{sec}$ and a stroke amplitude of 1 mm. The total sliding distance was 500 mm. Velocity and stroke have been arbitrarily chosen for these first experiments; it is supposed that in every case these quantities should be adjusted for each specific problem under investigation. The calibration of the Nanoindenter is done to perform scans in one direction during an experiment and not for forward and backward movements as done in the oscillating tests performed here. For all results presented in the following, we considered, therefore, only the values measured during the forward part of each of the 250 cycles. To check the reproducibility, two tests for each sample have been performed. The results are presented and discussed in the following sections.

2.4. Validation of the microtribology experimental setup

As an illustrative example, we will first discuss in detail one measurement performed on the sample with a low TiC concentration of 21 at%. Figure 1(a) shows the measured load as a function of the cycle number. The data points indicate the mean value of all measured data points during each cycle. The nominal load has been set to 30 mN. The graph indicates that the system is very stable during the whole test. For each performed experiment, it has been checked that the applied normal load has been close to the nominal value and remained constant during all the 250 cycles. We observed, however, that within each cycle the load systematically increased as it is illustrated for cycle 1 and cycle 250 in figure 1(b),

Figure 1. Typical behavior of the applied normal load during the oscillating tests. Mean loads for each cycle (a) and load behavior during single cycles shown for cycles 1 and 250 (b).

Figure 2. Microscopic friction coefficient values measured in the forward sliding direction for the sample with 21 at% TiC concentration. The raw data are shown in (a), in (b) the data points measured during the acceleration and deceleration periods have been excluded (see text).

but this is within the accuracy of the POD control during sliding. The mean applied load in the forward direction during the complete test was equal to 30.10 mN with a standard deviation of 0.06 mN; the load varied between 30.00 and 30.19 mN.

Figure 2(a) shows the friction coefficient values measured during the forward direction as a function of the cycle number. The friction coefficient remains relatively constant with a prominent cluster point at a value of about 0.11 and several outliers with values down to zero. These data points are measured during the acceleration and deceleration phases at the beginning and the end of each single stroke. To avoid these influences, the measured friction coefficients for sliding distances below 200 μm and above 800 μm for each single 1000 μm stroke have been excluded. The remaining data is displayed in figure 2(b). It is obvious that the friction coefficient remains constant after a short "run-in period" during the first 25 cycles. For this specific test, we took as microscopic friction coefficient μ_{micro} the mean value for the data between the cycles 26 and 250 and obtained $\mu_{\text{micro}} = 0.11$ with a standard deviation of 0.01. An inspection of the sample and the ball after the test with

an optical microscope revealed no indications of a wear track or of abrasive particles.

For each of the 12 different coatings 2 measurements have been performed and the same data treatment steps have been applied. The results of each single experiment are summarized in table 2 (μ_{micro} Test 1, μ_{micro} Test 2) together with the mean values from both tests (μ_{micro}).

3. Experimental Results and Discussion

As in the case of the sample with a TiC concentration of 21 at%, a constant friction coefficient up to 250 cycles after a short "run-in period" has also been observed for the samples with TiC concentrations below 48 at%, above 87 at% and for 77 at% TiC. The corresponding friction coefficient values are listed in table 2. No or only insignificant wear traces or abrasive particles have been observed for these samples.

Table 2.

Microscopic (μ_{micro}) and macroscopic (μ_{POD}) friction coefficients for the different TiC/a-C:H samples against 100Cr6 steel. The μ_{micro} values represent the average of the two tests performed for each sample (μ_{micro} Test 1 and Test 2). The error on the friction coefficient values is about 10%. In the last column, the R_a roughness of the coatings are indicated. As can be deduced from these values there is no significant correlation between the observed friction coefficients and the sample roughness. The ball roughness is similar for all tests (R_a between 230 and 250 nm).

TiC (at%)	μ_{micro} Test 1(-)	μ_{micro} Test 2(-)	μ_{micro} (-)	μ_{POD} (-)	R_a (nm)
21	0.11	0.09	0.10	0.11	23.3
28	0.14	0.14	0.14	0.10	16.7
48	0.12	0.11	0.12	0.27	40.0
57	0.28	0.28	0.28	0.29	36.7
74	0.33	0.36	0.35	0.26	23.3
77	0.18	0.18	0.18	0.28	23.3
84	0.31	0.39	0.35	0.27	30.0
85	0.34	0.30	0.32	0.29	30.0
86	0.31	0.33	0.32	0.28	16.7
87	0.13	0.16	0.15	0.32	26.7
90	0.20	0.14	0.17	0.59	33.3
100	0.19	0.13	0.16	0.51	20.0

The remaining samples with intermediate TiC concentrations (57, 74, 84, 85 and 86 at% TiC, respectively) revealed a rather different behavior. As an illustrative example, the friction coefficient as a function of the cycle number for the sample with a TiC concentration of 57 at% is presented in figure 3. The same data treatment as described above (only forward direction, only values between traveled distance 200 and 800 μm) has been applied to the raw data set. A short “run-in period” (from cycle 1 to 30, region I in figure 3) is followed by a period where μ_{micro} remains constant (between cycles 31 to 130, region II in figure 3). After that, a sudden drop of the friction coefficient is observed and the μ_{micro} values show a kind of erratic behavior for the remaining cycles (cycle 130–250, region III in figure 3) of the experiment. This behavior has also been observed for the samples with TiC concentrations of 74, 84, 85 and 86 at%, respectively. The only differences have been slightly different

Figure 3. Microscopic friction coefficient values measured in the forward sliding direction for a sample with 57 at% TiC concentration. The data points measured during the acceleration and deceleration periods have been excluded. The three different regimes (I, II, and III) are discussed in the text.

“run-in periods” and the cycle where the sudden drop of the friction coefficient occurs. The friction coefficient values indicated in table 2 for these samples have always been evaluated in “region II” following the “run-in period”. For the example shown in figure 3, a friction coefficient of 0.28 (standard deviation 0.01) has been determined for region II between cycles 31 and 130.

An inspection by optical microscopy of the sample surface and the 100Cr6 ball revealed for all samples with intermediate TiC concentrations a clear track on the sample surface (figure 4(a)) after the test as well as a prominent wear mark on the ball (figure 4(b)). The track width (i.e., the distance within the two wear debris lines) on the sample is about 36 μm and agrees well with the diameter of the modified section of the ball. After cleaning with ethanol, no marks remained visible on the sample surface and on the ball only an approximate circular wear mark remains (figure 4(c)). Note that the images of the ball (b) and (c) may be slightly distorted due to the recording conditions using an optical microscope. From this we conclude that the wear debris originated from the 100Cr6 ball and was partially transferred to the sample surface. To check whether this wear observation is linked to the sudden drop of the μ_{micro} values (see figure 3, transition from region II to III) we performed an additional test on the sample with 57 at% TiC, but only up to 75 cycles, i.e., the test was stopped before the sudden drop of the μ_{micro} values has been reached. The μ_{micro} value for region II of this test is 0.27 (standard deviation 0.01) and agrees well with the value determined for the test presented in figure 3. The prominent wear marks on sample and ball are however already present after 75 cycles. We therefore conclude that the wear formation starts immediately or during the “run-in period” where significantly higher friction coefficient values are measured (up to 0.4 for the test in shown in figure 3).

Figure 4. Optical micrographs made after the test with the sample having a TiC concentration of 57 at%. The corresponding friction coefficient values are shown in figure 3. (a): Steel wear particles deposited on the sample, the visible track width is about 36 μm . (b) Wear marks and particles on the ball. The wear particles can be easily removed from sample and ball (c) with ethanol. Note that the images of the ball (b) and (c) may be slightly distorted due to the recording conditions using an optical microscope.

Figure 5. Macroscopic (μ_{POD}) and microscopic (μ_{micro}) friction coefficients for the different TiC/a-C:H samples as a function of the TiC concentration. The error on the friction coefficient values is about 10%. The lines between the points are drawn as guide to the eye.

for intermediate TiC concentrations the macroscopic friction coefficient is between 0.2 and 0.3, for TiC concentrations above 90 at% the μ_{POD} values are higher than 0.5. This is not the case on the microscopic scale. The difference is especially significant for TiC concentrations above 90 at% where μ_{POD} is high (>0.5) but values below 0.2 have been found for μ_{micro} . Zehnder and Patscheider explained the high μ_{POD} values for samples with elevated TiC concentrations with insufficient amounts of a-C:H that can be transformed into lubricant graphitic carbon, which is often encountered on the transfer films formed on diamond-like Carbon under wearing conditions and, therefore, self-lubrication is no more possible for these samples [18]. On the microscopic scale, we can basically distinguish two categories of samples having friction coefficient values below 0.2 (typical behavior shown in figure 2) and around 0.3 (typical behavior shown in figure 3). The high friction coefficients are always accompanied with considerable wear on the steel ball. The friction properties on the microscopic scale are therefore correlated with the wear behavior.

We assume that for the coating-ball combinations showing wear, the tribosystem consists of the TiC sample, the steel ball and the steel particles acting as third body. Friction coefficients lying between the values for steel on TiC samples without wear (below 0.2, see figure 2) and for steel sliding against steel (between 0.5 and 0.6) seem, therefore, to be reasonable. A comparison of the μ_{micro} values with the sample hardness (see tables 1 and 2) reveals that for most samples the wear seems to be correlated with a high sample hardness. It can, therefore, be assumed that for our microtribological setup, TiC/a-C:H samples with high hardness induce considerable wear on the 100Cr6 balls which leads to the higher μ_{micro} values compared to the samples with lower hardness where no wear has been

The friction coefficient values for all investigated samples measured by macroscopic POD tests (friction coefficient μ_{POD}) and by microtribology experiments using the modified nanoindenter setup (friction coefficients μ_{micro}) are summarized in table 2 and in figure 5.

As a first important conclusion, we would like to emphasize that the macroscopic and microscopic friction coefficients are different. On the macroscopic scale, the friction coefficient of the investigated samples can be divided into three groups: For low TiC concentrations a low friction coefficient (about 0.1) is found,

observed. To check whether the observed μ_{micro} values depend on the roughness of the investigated coatings, R_a values have been determined using an optical profilometer. The values are given in table 2. The R_a roughness of the 100Cr6 balls was comparable for both types of tribological tests (250 nm for the macroscopic POD, 230 nm for the experiments done with the nano-indentation setup). As can be deduced from the values indicated in table 2, there is no significant correlation of the friction coefficients with the coatings roughness. Especially the low μ_{micro} value observed for the sample with a TiC concentration of 77 at% cannot be explained by an unusual sample roughness. The oxygen content, as measured by XPS after removal of surface oxides, amounted to 4 ± 2 at%. There was no systematic dependence of the oxygen content from experimental parameters or from the phase composition. From this, we conclude that the influence of the a-C:H content has a much more pronounced influence on the friction coefficient than the O content.

Finally, we would like to comment on the sudden drop in the microscopic friction coefficient observed for samples where we observed wear on the steel ball (see figure 3, transition between region II and III). The reason for this sudden drop will be the subject of further investigations but we assume that it could be related with the steel wear debris transferred to the contact area between ball and sample surface. The sudden drop could be the result of pulsing wear debris out of the contact such that afterwards the steel ball is mainly in contact with the sample surface. This would explain the decrease of the μ_{micro} value down to values comparable to μ_{micro} values found for the samples without wear. The sliding steel ball on the hard sample causes then again the formation of steel wear debris and the friction coefficient remounts to a value around 0.3. As can be observed in figure 3, the system ends in a kind of oscillating state with friction coefficients between 0.2 and 0.3, resulting from the alternate formation and pulsing out of steel wear debris. The present results indicate that a detailed study of the wear surfaces and the wear debris is necessary for a complete understanding of the microtribological behavior of the investigated coatings, but this will be the subject of future work.

4. Summary

In this work, we studied the microtribological behavior of different nanocomposite TiC/a-C:H coatings against steel using a modified nanoindentation setup. Our experiments showed that reproducible microtribological measurements are possible by replacing the standard diamond indentation tips by 100Cr6 balls

and by adapting the standard measurement routines for nanoscratch experiments.

The results of the first experiments performed on different nanocomposite TiC/a-C:H coatings revealed that for high TiC concentrations the macroscopic friction coefficient is different from the microscopic one and that the high hardness samples induce considerable wear on the steel counterbody leading to high microscopic friction coefficients around 0.3. For samples with lower hardness no wear has been observed and low microscopic friction coefficients (< 0.2) can be achieved.

Acknowledgments

The authors would like to thank M. Diserens for performing the nanoindentation experiments for the determination of hardness and Young's modulus, J.-L. Bucaille for his help and stimulating discussions concerning nanoscratch experiments, T. Zehnder for his work in the deposition of the TiC/a-C:H samples, and M. Hadad for critical reading of the manuscript.

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