ELSEVIER

Wear 190 (1995) 204–211

WEAR

Comprehensive tribological characterization of thin TiN-based coatings

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Received 9 January 1995; accepted 31 March 1995

Abstract

Innumerable papers have been published so far describing tribological investigations of thin hard coatings based on TiN. Analysis of the presented results demonstrates a large dispersion of measured friction and wear numbers, whereas TiN-coated pieces and tools have proved their benefits in a broad area of application. Therefore an attempt was made to clarify the influences on friction and wear test results by varying the coating process, the tribological stresses due to sliding, fretting and rolling motion and by changing the surrounding medium. The results reveal that machining of substrate surfaces and type of tribological stresses due to sliding, fretting and rolling have an important influence. The formation of reaction layers is dominating the tribological behaviour in most cases.

Keywords: Tribosimulation; PTFE compounds; TiN coatings; Sliding; Rolling; Fretting

1. Introduction

Hard coatings of tribologically stressed components have demonstrated their benefits in a broad area of technical disciplines. One important reason may be that on the one side the hardness of the coatings is advantageous for the reduction of abrasive wear and on the other side the proved good properties of bulk materials remain preserved. TiN-based thin hard coatings are successfully used as resistant decorative coatings on daily goods and in respect of technological importance with more merits for material working tools improvement. Accompanied with that development innumerable papers have been published so far relating to the tribological properties of those coatings during working performance and in simulating tests [1–15]. If one compiles the results of the simulating tribo-tests the great success of TiN coatings is surprising because of the enormous scatter of test results.

Therefore an attempt was made to determine the different influences on friction and wear of TiN-based coatings by varying the coating process or the coating producer and the tribological stressing by continuous sliding, fretting or rolling motion and finally the surrounding atmosphere in pin on disc tests.

2. Imitation of wear behaviour of coated cutting tools

Coating of cutting tools with thin hard coatings for increasing working speed, tool life and also improvement of working performance is state of the art.

Nevertheless a demand exists for further improvements of cutting tools to optimise machining or surface qualities of very different materials by special coatings for adapted cutting tools and processes.

Considering the nearly innumerable types of possible coatings and coating processes for that purposes it is a difficult task to find the proper coating for each work piece material. An adequate test programme may additionally become time and money consuming if the different coatings are tested under real cutting conditions on expensive materials and if the cutting distance to life of the tools proves to be very long. Therefore the attempt has been made to simulate the working performance of indexable cutting tool inserts by means of a tribometer model wear test.

To check the results of the model wear tests for relevance in practice milling with the same coated HSS (high speed steel) tools on the same materials was performed. As far as possible the tribological system parameters of the real cutting systems have been transferred to the model tests. However, a couple of parameters and conditions remained different. First of all the direction of relative motion in the model test was opposite to the direction of cutting, so that only sliding and no cutting took place. Secondly the indexable insert was stationary, the flank of the tool continuously contacts the counterbody and it was always the same counterface material, and lower forces are applied in the model tests to limit the counterbody wear. With respect to these differences between the milling and the model wear tests no quantitative agreement can be expected. But the aim of the simulation was to

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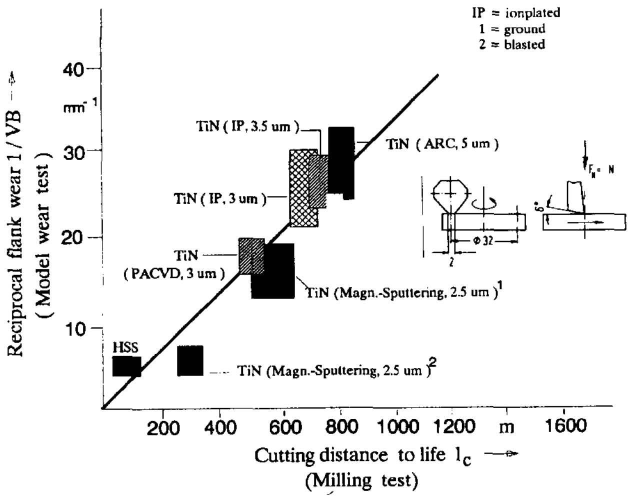

Fig. 1. Comparison of milling test and model tests of TiN-coated cutting models.

show that it is possible to preselect suitable hard coatings for milling tools in a time and money saving procedure. The results of the milling and simulating tests are compared in Fig. 1, where the reciprocal flank wear of the model tests after 1000 m sliding are plotted vs. the cutting distance to life of the milling tests.

The counterbody work piece was a Ni–Fe alloy (Mumetal). The indexable cutting tool inserts consisted of high speed steel coated with TiN produced by different coating processes and partially after different surface machining of the base materials.

The parameters for the model wear test have been: load 3 N, sliding velocity 1.5 m s^{-1}, sliding distance 1000 m (the other conditions are given in detail by Habig and Meier zu Köcker [16]).

The comparison shows a satisfying agreement in the wear ranking of the different TiN coatings evaluated from model tests and milling tests. It can be clearly seen that the coating process has an important influence on the wear behaviour of the coatings. TiN coatings produced by ion planting (IP) and by an arc deposition (ARC) are superior to coatings made by magnetron sputtering or plasma assisted CVD (PACVD).

The wear properties of TiN coatings produced by magnetron sputtering depend on the surface machining of the base material. The coatings on blasted surfaces are less wear resistant than those on ground surfaces.

A similar good agreement of the wear ranking by simulation and real cutting was found for SAE 1045 and copper [16].

3. Influence of substrate surface on the wear behaviour of TiN

The influence of substrate pretreatment on the wear behaviour of TiN coatings was investigated in more detail in another simulation. The conditions for these test were: body 1 = CVD TiN and PVD TiN on steel SAE 1045; body 2 = steel 100Cr6H; lubricant = paraffin, load = 600 N; p-Hertz ≈ 850 N mm^{-2}; sliding velocity = 1 m s^{-1}; sliding distance = 10 000 m.

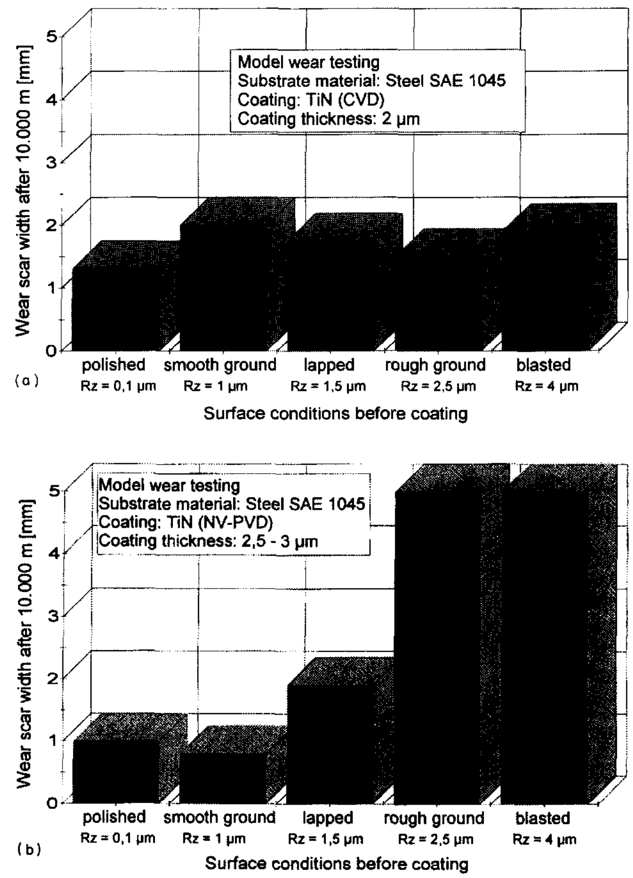

Fig. 2. (a) Wear of CVD-TiN-coatings (thickness ≈ 2 µm) on steel related to substrate surface treatment. (b) Wear of PVD-TiN-coatings (thickness ≈ 2.5-3.0 µm) on steel related to substrate surface treatment.

Fig. 2 gives the wear scar width of the TiN CVD and TiN PVD coatings on differently machined substrate surfaces. The PVD TiN coatings show a great reduction of wear resistance for substrate roughness higher than 2 µm R_z, whereas the wear of the CVD coatings is nearly independent of the substrate pretreatment.

The reason for the difference in behaviour with respect to surface roughness may be the higher coating process temperature and the inherent directional uniformity of CVD process.

4. Influence of surrounding atmosphere

To get information about the influence of surrounding medium on tribological behaviour of TiN coatings tests were performed using TiN-coated balls, which were loaded with 3 N against a rotating disc also TiN-coated. The sliding velocity was 0.3 m s^{-1} and the surrounding medium was varied from dry air (2% RH) to humid air (98% RH) and dry nitrogen. The results are shown in Fig. 3 together with the

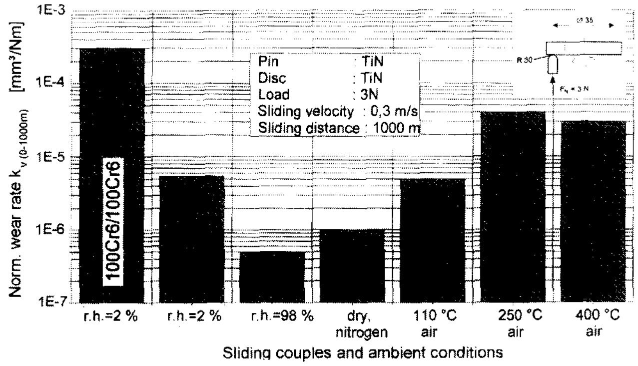

Fig. 3. Relation of wear coefficient of TiN-coatings to temperature and surrounding medium. Test temperature was 23 °C if not other stated, surrounding medium for high temperature tests was dry air.

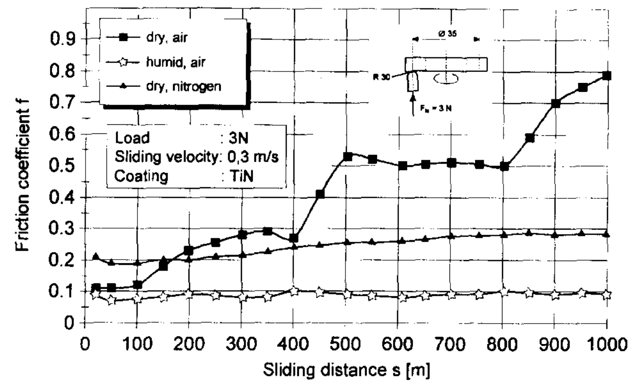

Fig. 4. Friction coefficient as a function of sliding distance and relation to atmosphere for TiN-TiN couples.

wear of an uncoated 100Cr6 couple. Additionally the results of high temperature wear tests on TiN couples are given which reveal, that at temperatures above 100 °C the wear rate is that of experiments under dry air conditions and an increase of the wear rate was found for temperatures of 250 °C and 400 °C. The wear of TiN-coated 100Cr6 couples is reduced by an order of magnitude compared with that of uncoated couples. In humid air (RH ≈ 98%) the wear rate for TiN–TiN couples is again reduced by more than an order of magnitude to the very low rate of 5×10^{-7} mm^{3} $^{-1}$ m^{-1}.

However, not only the humidity of the air has an influence on the wear of TiN as the result of a test under dry nitrogen demonstrates. The test was done because it is known that TiN layers consist on the top surface not only of TiN but also TiO_2.

Those TiO_2 layers are cited by Keller et al. [17] to have hydrophillic properties, which result by the reaction with the water vapour of the humid air in a lubricating and wear reducing layer. Those processes can not take place in dry nitrogen, nevertheless the wear rate under that condition was again one order of magnitude lower than in dry air. Therefore another wear reducing mechanism must exist in dry nitrogen atmosphere.

Robinson and Sherwood [18] have reported that an interlayer of TiO_xN_y exists between the TiO_2 surface layer and the TiN coating.

Possibly a layer like this can also reduce friction and wear and will be stable or growing again continuously in pure nitrogen atmosphere.

Fig. 4 indicates that the reduced wear for humid and nitrogen atmosphere are correlated with low friction regimes in these cases.

The development of friction with the sliding distance for the three different atmospheres supports a model of TiN surface structure described in the literature [19] which states that the structure consists of a $TiO_x \cdot H_2O$ top layer and a TiO_xN_y interlayer above the real TiN coating. According to that model the explanation of the development of the friction coefficient under dry atmosphere would be as follows.

At the start of the experiment up to a sliding distance of 100 m the friction is very low with a coefficient of 0.1 owing to the interacting $TiO_x \cdot H_2O$ layers. The layers have formed during the storage of the coated samples in normal humid air (RH ≈ 50%). This low friction coefficient corresponds to that found under humid atmosphere (RH ≈ 98%). In this case the friction remains low till the end of the test at 1000 m sliding distance. In the case of dry air after a sliding distance of 100–150 m the H_2O containing layer is worn out and the friction increases to a friction coefficient in the range 0.2–0.3. Measurements after different storage times of the samples before the start show that the sliding distance until the friction transition occurs depends in an exponential way on the storage duration in humid environment.

Cleaning the test samples with alcohol immediately before the start of the experiment reduced the low friction regime to a very small sliding distance.

The region with a friction coefficient between 0.2 and 0.3 in the sliding distance range from 150 to about 400 m could be attributed to the contact of the TiO_xN_y, an explanation which is supported by the friction test in dry pure nitrogen atmosphere with samples cleaned immediately before the test. Under those conditions the friction coefficient is 0.2 from the beginning and remains below 0.3 until the end of the test after 1000 m sliding distance.

Tests in dry air atmosphere on the other side show again an increase of the friction coefficient to about 0.5 after 500 m sliding distance. That friction level holds to a distance of about 800 m and may be attributable to real TiN–TiN sliding contacts.

The further rise of the friction after 800 m sliding distance in dry air is caused by wear down of the TiN coating at the ball and the friction coefficient of 0.8 corresponds to steel–TiN contact. That value is in agreement with test results found for those couples and was also confirmed by microscopical examination of the worn balls after test.

Some tests with different sliding velocities under normal air conditions (RH ≈ 40–60%) indicate that the friction transition for TiN–TiN couples occurs after shorter sliding distances if the velocity was higher. But an unambiguous functional relation was not found.

Results of pin on disc wear measurements of TiN-coated couples in dry, normal and humid atmospheres, constant load

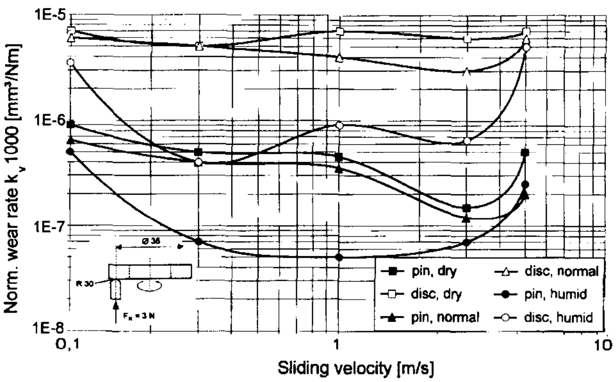

Fig. 5. Wear of TiN-coated couples as a function of sliding velocity.

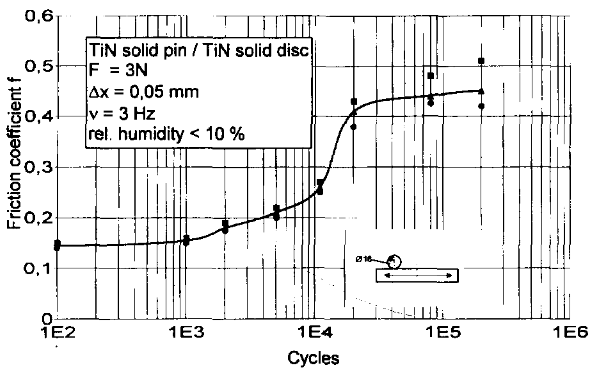

Fig. 6. Friction of solid TiN bodies under fretting conditions.

3 N, and for different sliding velocities (Fig. 5) reveal, preferentially at high humidity, lower wear rates for medium sliding velocities and the wear rates of the pins are under all conditions lower than those of the discs.

The periodic stressing of the disc coating may be responsible for that difference in the wear rate of pins and discs. It seems that in humid atmosphere an optimal velocity of sliding for the given contact conditions exist. For the used geometry, velocity and load the reaction of TiN with the surrounding O and H_2O vapour and the tribological destruction of the continuously built layers in the sliding velocity range of 0.3 m s^{-1} to 3 m s^{-1} produce optimal conditions for low friction and therefore lower wear owing to lower stress concentrations in the coating. Under high sliding velocity the destruction rate of reaction layer by tribological stressing exceeds the production rate due to physicochemical reaction with the surrounding atmosphere.

At low sliding velocities the reaction layer becomes too thick leading to higher wear and friction. This explanation at the time is a hypothetical, but the analysis of wear scars and wear particles of stressed TiN layers reveal that tribo-oxidation is a main wear mechanism because as well by ESCA as by Raman spectroscopy mainly TiO_x in differing phases and Ti/O ratios are found. The proof of the H_2O reactions with the surfaces is quite difficult because the analytical methods introduce vacuum and energy on the surface area to be analysed.

5. Fretting behaviour of solid TiN

Sintered solid bodies of TiN have been tested under fretting conditions in dry air, to check whether the found behaviour is special for thin coatings or is a common one of TiN. Fig. 6 gives the friction coefficient developing with the sliding distance expressed in stroke cycles. The stroke was 0.050 mm, the load 3 N and the fretting frequency 3 Hz.

The friction coefficient at the beginning of the test was 0.15 and increases finally to 0.5 what is comparable with the results found for continuous sliding tests of TiN coatings before they were worn out. But the sliding distance until the friction transition point was only 1–2 m under fretting conditions compared with 500 m for continuous sliding pin on disc measurements (Fig. 4). That different behaviour may be a consequence of the structure differences of sintered TiN and TiN coatings and as well of the special conditions of

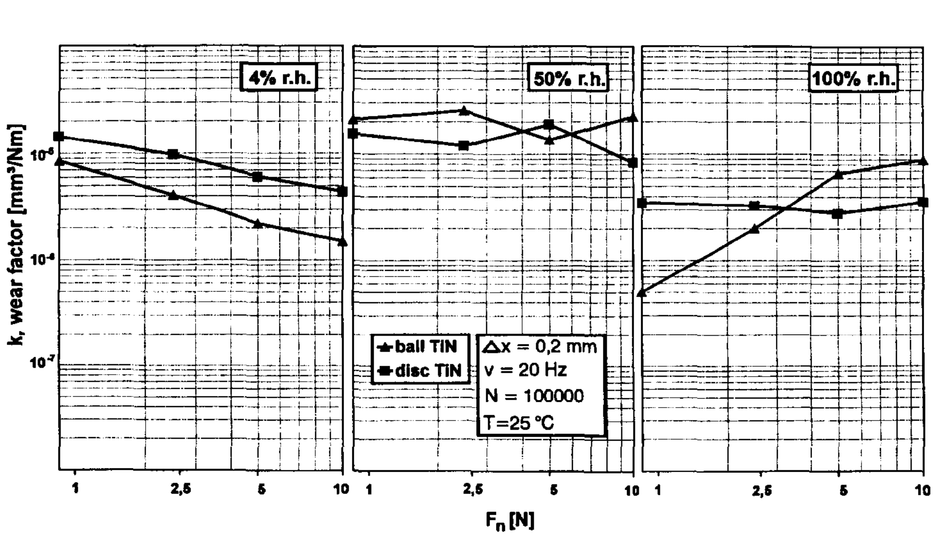

Fig. 7. Wear rates of TiN-TiN-couples under fretting conditions.

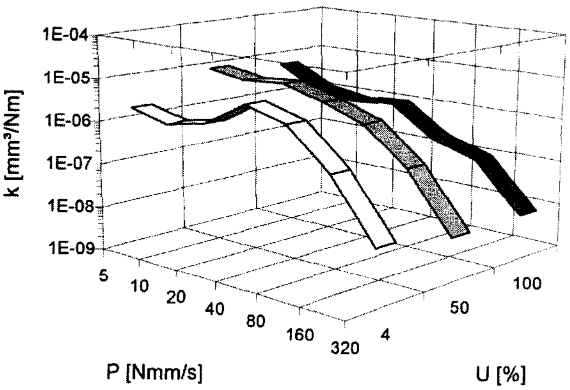

Fig. 8. Normalized wear rates k of TiN discs as a function of power parameter P (N mm s^{-1}) and relative humidity U.

fretting stresses with stroke length in the range of the contact dimension.

Fretting wear tests with TiN-coated steel balls and discs (100Cr6) with 0.2 mm stroke, 20 Hz frequency, load variation from 1 to 10 N in air humidities of 4% RH, 50% RH and nearly 100% RH at room temperature were performed to characterize the wear behaviour of TiN coatings in comparison with the continuous sliding tests. In Fig. 7 the wear rates as a function of load are composed. The wear is increasing with load nearly linearly. The increase of wear is most pronounced under humid conditions. Only under dry conditions the discs show an unambiguous higher wear rate than the pins.

Compared with of the pin on disc sliding tests the wear rates lie an order of magnitude higher.

The lowest wear rates are found for low loads under high humidity. That means the reaction layers built with the H_2O vapour can bear only low loads.

This explanation is in accordance with the friction and wear development of 100Cr6 balls fretting against TiN-coated discs. In that experiments the friction coefficient drops from 0.8 to 0.2 after a distinct sliding distance and the wear rate becomes nearly unmeasurable small after this point. The wear at this sliding distance has enlarged the contact area to an amount that the contact pressure lies below 4 MPa. The sliding distance necessary for this transition depends on the load, the higher the load the longer the necessary sliding distance.

A series of fretting experiments with TiN-coated S6-2-5 steel discs against 100Cr6 balls under variation of load, stroke, frequency and relative humidity of surrounding air was performed to establish wear maps for those couples. The results are composed in Fig. 8 as a function of a power parameter.

The primary conclusion from this figure would be that, the higher the power introduced in the contacts, the lower the wear rate. This is a very surprising effect from a physical point of view. But that first glance conclusion disregards that the wear coefficient is the volumetric wear rate divided by the load which is one factor of the power parameter. Secondly at the higher stroke amplitudes the contact stresses of the discs are spread over a greater surface area than at small stroke amplitudes.

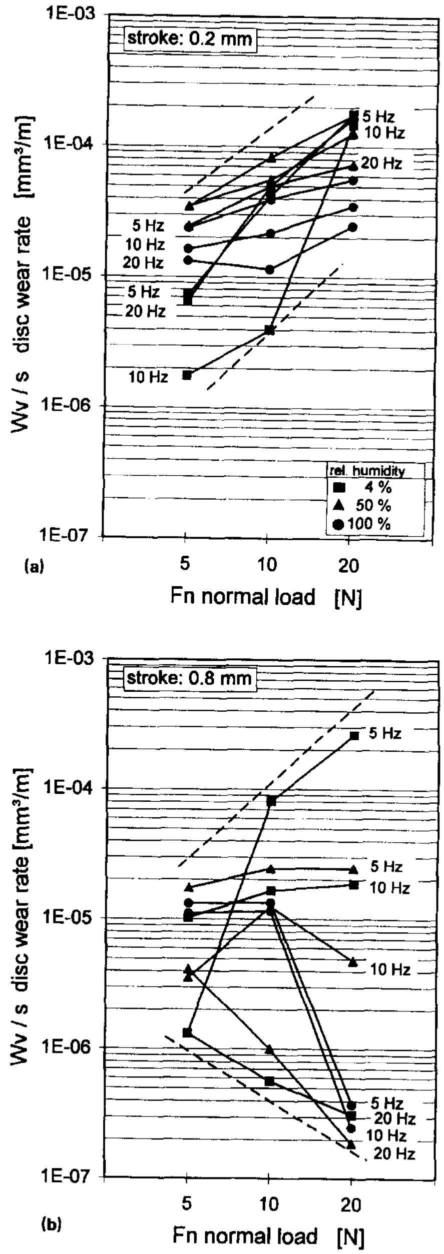

Fig. 9. (a) Wear rates of TiN-discs as a function of load under fretting of 100Cr6 with stroke 0.2 mm at different humidities and frequencies (□, 4%; △, 50%; ○, 100%). (b) Wear rates of TiN-discs as a function of load under fretting of 100Cr6 with stroke 0.8 mm at different humidities and frequencies (□, 4%; △, 50%; ○, 100%).

The presentation of wear rates over the load in Fig. 9 leads to a more satisfying result from a physical point of view, especially for the small stroke condition. The wear rate increases with the load for all other parameters.

This increase with load is more pronounced for tests in dry air and less for those in humid air, what is in contradiction to the findings of TiN–TiN couples (Fig. 7) and must be a consequence of the steel pin in this case.

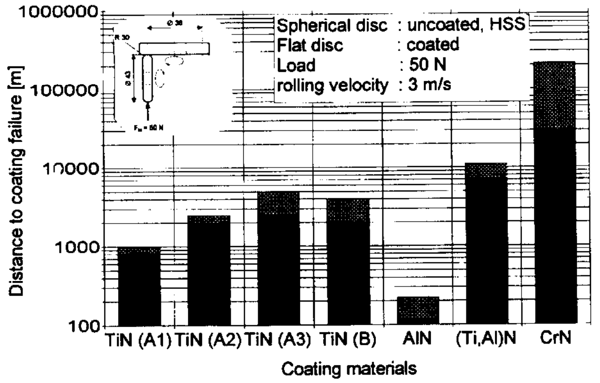

Fig. 10. Rolling distance to coating failure of different coatings and different coating processes.

The great spread of wear rates at different frequencies and humidities for high stroke and higher loads (Fig. 9(b)) can not be explained at the time but should perhaps be caused by different reaction mechanisms at higher stroke amplitudes. The very low wear rates of the TiN coated discs at high loads only found for high strokes may again be a consequence of the formation of a reaction layer which is able to carry the load brought up through a larger contact area of the worn 100Cr6 ball under these conditions.

6. TiN coatings under rolling stresses

Tribological stresses under rolling motion mainly lead to surface fatigue. With respect to this, rolling of coated samples should give information about the adhesion behaviour of different coatings to the substrates. To examine the potentiality of this method, which should deliver more realistic information about adhesion of coatings in tribologically stressed machine elements, rolling experiments with different coatings have been performed. The principle of test geometry is a rotating disc which drives by the friction force in the contact another one. First results gives Fig. 10, which shows the

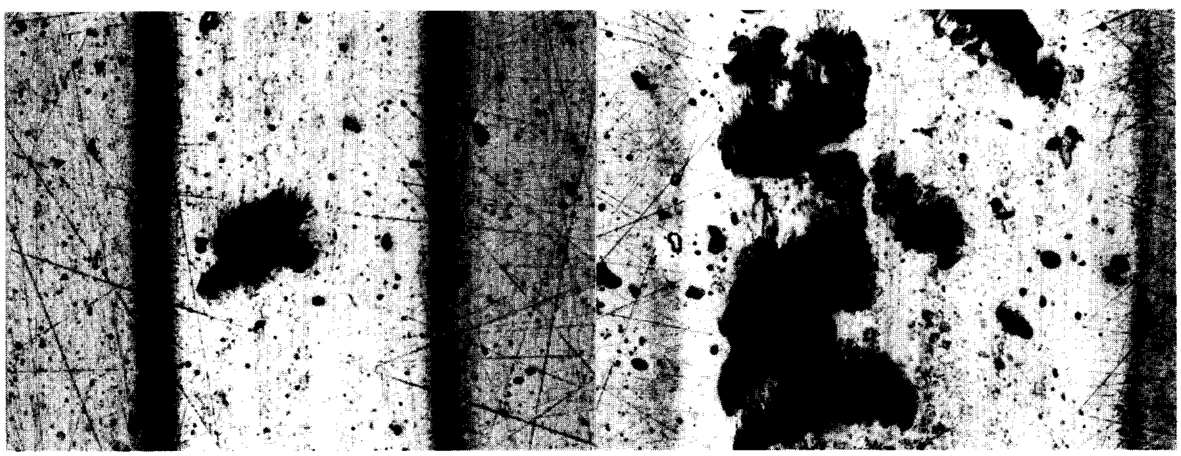

Fig. 11. Wear scar of TiN coatings after 10 000 rolling cycles (left) and 25 000 cycles (right).

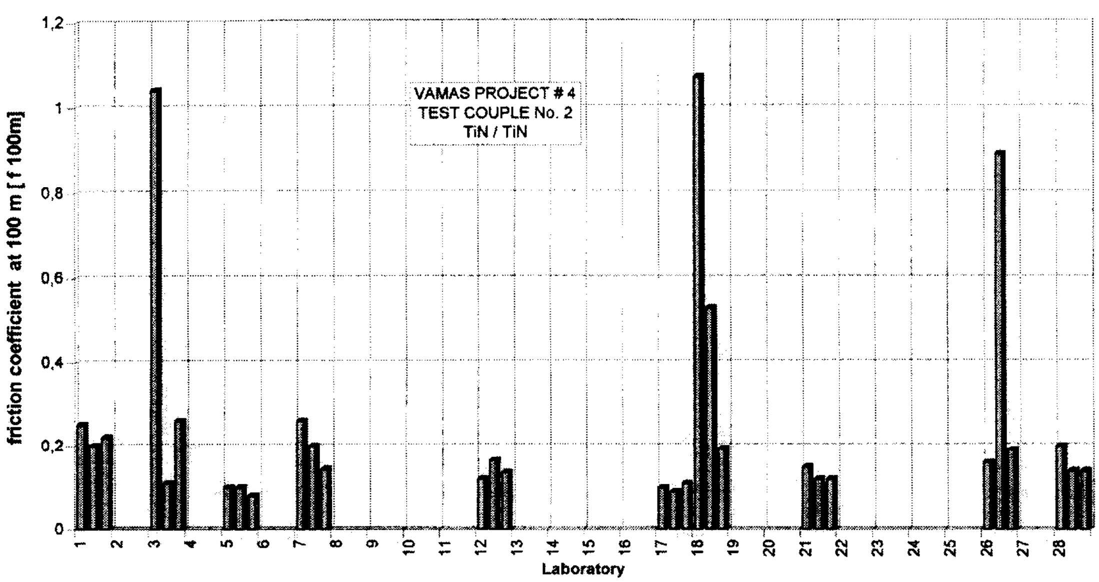

Fig. 12. Friction coefficients of TiN-TiN-couples measured by different laboratories under identical conditions (VAMAS project).

rolling distance to coating failure. The failure of the coatings was identified by optical observation and by the changes of friction and wear signals. Typical wear scar images are given in Fig. 11 demonstrating the delamination type of wear damage.

7. First results of round robin exercise on tribological behaviour of TiN coatings

With respect to the great scatter of friction and wear results for coatings an interlaboratory comparison was started under VAMAS (Versailles Project on Advanced Materials and Standards) coordination. Twenty six laboratories from twelve different countries were supplied with test samples of the same kind to perform friction and wear tests under an identical procedure. In Fig. 12 the measured friction coefficients for TiN–TiN couples are compiled. Though all laboratories had got the same kind of samples and should perform the tests under the same procedure the measured friction values scatter to a surprising amount. To come to a judgement of achievable reproducibility, and to get information about the error sources statistical treatment of the reported values and examination of the used samples for differing appearances in the stressed areas has to be done.

8. Conclusions

The tribological behaviour of TiN coatings depends in a complex way not only on the stressing parameters but also on the surrounding atmosphere during storage and tests, the production process, and producer and so on. A lot of investigations is still necessary to understand their behaviour thoroughly, but some characteristics could be clarified:

- Cutting performance of TiN coated tools can be simulated by a time and money saving laboratory test, which gives the correct ranking compared with wear behaviour under real cutting conditions. The ion plated coating are superior to magnetron sputtered ones.
- If the surface of the substrates are machined to a lower roughness, the coatings are more wear resistant. This is not found for CVD coatings indicating less sensitivity of this process for substrate pretreatment.
- The wear rate at room temperature is low in humid air or in dry nitrogen compared with that under dry air conditions.
- The friction coefficient of TiN coatings stored in normal humid air is in the range of 0.1 at the start of sliding and rises to about 0.2–0.3 for another sliding period. This friction range corresponds with the friction in dry nitrogen. Whereas the first range is proposed to be caused by reaction with H_2O vapour the second may be attributed to contact of a TiO_xN_y interlayer. The third regime with friction coefficient of 0.5 should be that of TiN–TiN contact and finally the regime of friction coefficient 0.8 corresponds to steel–TiN contact after wearing out of ball coating.
- Because tribo-oxidation of TiN to TiO_x and other tribo-reactions with the surrounding atmosphere play an important role, special combinations of load, sliding velocities and geometries can lead to optimal friction and wear behaviour as for example found for medium sliding velocities and high loads.
- Under normal fretting conditions the wear of TiN coatings is higher than under sliding pin on disc tests, but high fretting strokes can also produce low wear rates.
- Stressing of coatings by rolling motion may give realistic information about tribological relevant adhesion of coatings to the substrates.
- Better reproducibility of tribological test results can only be reached by thorough control of test circumstances and parameters, which also have to be reported for each set of results.

The presented results demonstrate, that stressing parameters like type of motion, load, velocity and also surrounding atmosphere can lead to considerable different wear and friction numbers for identical tribo-couples. Tribo-materials can only be characterised adequately by "tribo-mapping", i.e. by performing test under widely varied conditions.

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Biographies

Dieter Klaffke: is head of the laboratory "Fretting wear; Cryotribology" of BAM. He studied physics at the Technical University in Berlin and received the degree of doctor of engineering from the same university in 1978. He joined the BAM in 1970 and worked in the field of fatigue of metals. Since 1980 he has been working in the field of tribology; mainly fretting wear with special interest in ceramics and coatings.

Gerd Meier zu Köcker: received his M.Sc. (Dipl.-Ing.) and Ph.D. (Dr.-Ing.) from the Technical University of Berlin. In 1989 he joined BAM, where he is researching in the area of tribology of wear resistant coatings and ceramics.

Erich Santner: is head of the subdivision "Tribology; Wear Protection" of BAM. He studied physics at the Free University of Berlin and received and M.Sc. (Dipl.-Phys.) and a doctor's degree from the same University. He was engaged in nuclear research, radiation protection and nuclear fuel analysis at the Hahn-Meitner-Institute for nuclear research and at the BAM. In 1986 he joined the tribology group of BAM. The main working fields are tribology of polymers, coatings, development of measurement methods, microtribology and tribophysics.