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Fretting wear of Ti(C_xN_y) PVD coatings under variable environmental conditions

T. Liskiewicz^{a,b,*}, R. Rybiak^{a,b}, S. Fouvry^a, B. Wendler^b

^a *Laboratoire de Tribologie et Dynamique des Systèmes, CNRS UMR 5513, Ecole Centrale de Lyon, 36 Avenue Guy de Collongue, 69134 Ecully Cedex, France*

^b *Institute of Materials Engineering, Technical University of Lodz, Stefanowskiego 1, 90924 Lodz, Poland*

** current address: School of Mechanical Engineering, University of Leeds, Leeds LS2 9JT, UK*

Abstract

Fretting wear as a specific type of degradation is defined as an oscillatory motion at small amplitude between two nominally stationary solid bodies in mutual contact. Under external stresses the interface is being damaged by debris generation and its successive ejections outside the contact area. A potential protection against fretting damage by means of hard coatings is being offered by different surface engineering techniques. For this study TiC, TiN and TiCN hard coatings manufactured by a PVD method have been selected and tested against smooth polycrystalline alumina ball. A fretting test programme has been carried out at the frequency of 5Hz, 100N normal load, 100µm displacement amplitude and at three values of a relative humidity: 10, 50 and 90% at 295-298K temperature. It turned out that the intensity of wear process was depending not only on loading conditions but on environmental ones as well. A significant impact of RH on wear rate and friction behaviour of the coatings under investigation has been observed. Two different damage mechanisms have been identified and related to the phenomena of debris oxidation and debris adhesion to the counterbody surface. In the latter case the debris deposited onto the surface of the alumina ball lead to a change of stress distribution at the interface and as a result to accelerated wear. In this work experiments with variable relative humidity increasing from 10% to 90% within

a single fretting test have been completed. It follows from these experiments that there exists an intermediate value of the RH at which the friction coefficient changes rapidly. Finally a dissipated energy approach has been applied in the work in order to quantify and compare fretting wear rates of different hard coatings.

1. Introduction

Micro-displacements are always observed between two mating components of mechanical systems subjected to vibrations or thermal fields as there are no means to completely immobilize them. Consequently, damage of the solid surfaces can occur leading to the degradation of the joint. This kind of damage mechanism under small-amplitude oscillatory motion (usually tangential) is called fretting [1]. It has been identified in such diverse practical situations like riveted joints [2], electrical contacts [3], rolling bearings [4], medical implants [5] or nuclear stem generators [6]. Depending on the fretting loading conditions the surface damage can occur by crack nucleation and propagation or due to wear induced by debris formation. The former is usually related to partial slip condition in which the contact displays both stick and slip domains [7], while the latter to full sliding at the interface.

Hard coatings have been considered as a potential way to mitigate the harmful impact of fretting due to their high hardness and chemical stability [8]. Especially physical vapour deposition (PVD) techniques are widely applied due to low deposition temperature. As a matter of fact, independently on the deposition method the durability of a coated component needs to be predicted in order to avoid the catastrophic damage by exceeding the nominal lifetime of the coating [9].

A characteristic feature of the fretting phenomenon between two mated components with hard coatings is the generation of hard wear particles [10]. Formation of hard debris is of basic importance for the friction [11]. It is different for different tribo-systems and depends on the particle shape [12]. In case of fretting the third-body can be ejected outside the wear scar or

stay within and play the role of an abrasive particle. Its high hardness accelerates the wear process, particularly during the final catastrophic stage. Behaviour of wear particles is strictly related to the relative humidity (RH) level as the presence of water can promote agglomeration of debris or formation of compounds acting as lubricant within the contact area [13]. In order to realize how the RH can change in different time scales, some related meteorological data for two locations (Leeds and Lyon) is presented in Fig. 1. Over a span of two days the RH varies as much as 63% in Leeds and 52% within two weeks in Lyon. It is clear that adequate evaluation of tribological behaviour of a mechanical system requires consideration of variable environmental conditions.

Fig. 1. Evolution of air relative humidity as a function of time for two locations: Leeds (between 26.07.2005 16:00 GMT and 28.07.2005 04:00 GMT); Lyon (between 26.07.2005 and 07.08.2005) [14].

The impact of the RH on friction and wear properties of hard coatings has been noticed and widely investigated by many authors. First developed ceramic surface treatments were Ti-based coatings and these have the greatest number of reference data in the scientific literature [15-20]. It has been established that the degradation of the TiN coating proceeds by oxidation wear, as the debris generated during the fretting wear form the layer of TiO_{2-x} and these oxides play a lubricating role within the contact area. High RH accelerates the reactions between TiN coating and the oxygen from the atmosphere during fretting and is conducive to easier formation of TiO_{2-x} which decreases the coefficient of friction (COF). Another popular surface coating in engineering practice has become the diamond-like carbon (DLC) one [21-26]. That latter exhibits a characteristic frictional behaviour as a function of the relative humidity opposite to that observed for other hard coatings, i.e. a lower friction coefficient is observed for lower RH values. This contrary behaviour has been explained by numerous

authors with use of different complex tribochemical reactions involved in friction process. Some of the authors suggest formation of an unstable oxide layer in the wet air [22]; other ones point out the increase of contact area induced by surface smoothing in an oxygen environment due to desorption of an oxidized carbon layer [23]. Still other explanations are linked to the cease of surface graphitization in humid environment [24]; sliding impediment due to debris agglomeration [25] or finally to the interaction of the wet air with counterbody material [26].

The attention of scientists has been attracted as well to tribological behaviour of other hard coatings in variable environmental conditions, e.g. CrN [20], (Ti,Al)N [27] or CN_x [13]. It should be noticed however that for all considered tribo-systems the key issue for frictional behaviour of surface treatments or coatings are tribochemical reactions at the sample/counterbody interface.

The present work focuses on the study of friction and wear behaviour under fretting of three Ti-based hard coatings in air at different RH conditions in order to identify the dominant damage mechanisms and to juxtapose them with a broad scope of surface treatments and coatings and their tribochemical degradation.

2. Experimental Section

2.1. Materials

High speed steel Vanadis23 has been selected as a substrate material for hard coatings with the following chemical composition: 1,28 wt.% C; 4,2 wt.% Cr; 5,0 wt.% Mo; 6,4 wt.% W and 3,1 wt.% V. The unique properties of the steel, like homogenous distribution of carbides, increased amount of VC-type carbides with regular MC-type elementary cells isostructural to the TiC, TiCN and TiN phases make this material especially predestined to be deposited by titanium carbide or nitride layers providing high hardness and a very good adhesion between the coating and the substrate.

Three different kinds of Ti-based hard coatings have been selected to this study: titanium carbide, titanium carbonitride and titanium nitride. TiCN and TiN coatings have been manufactured by means of classical Arc-PVD method with use of a single source device while TiC coating has been prepared with use of the indirect method [28]. The latter one consists of two stages. In the first one thin metallic Ti layer is deposited on the specimen surface by magnetron sputtering and in the second one the coated specimens are submitted to high temperature annealing in a vacuum furnace. Due to reactive outward diffusion of carbon atoms from the steel substrate activated by the high temperature the metallic (Ti) coating transforms into the carbide one (TiC).

X-Ray diffraction spectra of the hard coatings is shown in Fig 2. Monochromatic $\text{CoK}\alpha$ radiation and conventional Bragg's geometry (θ - 2θ) have been used during registration of the spectra. Due to this geometry the intensity of a diffraction peak (hkl) is related (among others) to the number of planes with suitable distance d_{hkl} and orientation parallel to the surface of the sample. One can see from Figure 2 that in case of the TiN and TiCN coatings only one diffraction peak from (111) planes has been registered and also that the angular position of the TiCN (111) peak is more near to that of the TiC (111) peak than to the respective peak of the TiN phase. This can be interpreted as a result of different concentration of carbon and nitrogen atoms in the TiCN phase: the concentration of the former is greater than that of the latter. Taking into account a rather considerable thickness of these two coatings ($4\mu\text{m}$ in case of TiN and $2.5\mu\text{m}$ in that of TiCN) as well as the fact that according to the respective powder diffraction data [29] the relative intensities of the first three peaks should amount 72:100:45 and 59:100:46 for TiN and $\text{TiC}_{0.7}\text{C}_{0.3}$ phases respectively, it is evident that the orientation of crystallographic planes in these two coatings is not fortuitous. Similar preferred orientation of (111) planes is reported in the bibliography of the arc-deposited TiN coatings [30] and can be related to greater thermodynamic stability of the first nuclei of the growing coating in the case when the most dense packed (111) planes of these nuclei are parallel to "mirror"-finished flat

substrate's surface [31]. In case of the third coating there are two peaks (111) and (200) registered in the X-ray spectrum of the TiC phase (the intensity of the 220 one is equal to 0) and their relative integrated intensities are 100 and 48, respectively. Taking into account that the thickness of this coating (1.6 μm) is much less than that of the the TiN and TiCN coatings, it is necessary to take this limited thickness into consideration in order to compare the relative intensities of the diffraction peaks. According to the formulas given in [32], it has been calculated (on the base of: coating thickness, mass absorption coefficient of the wavelength λ of the X-ray $\text{CoK}\alpha$ radiation by the TiC phase, the mass density of the latter and the experimental values of the diffraction angles 21.03 deg and 24.47 deg for the given wavelength λ on the (111) and (200) planes of the TiC coating, respectively) that the corrected integrated intensities of these two peaks of the TiC coating are 100 and 51,5. These two values are contradictory to the ones expected for the relative intensities of these two peaks from the ICDD diffraction standard (card No. 32-1383) for the powder specimen of the TiC phase, which are 80 and 100, respectively. These contradiction can be withdrawn once again at the assumption that there exists a strong prevalence of (111) planes at least in comparison with (200) and (220) ones with similar orientation parallel toward the substrate's surface in this TiC coating deposited by the indirect method [28]. Some micro-peaks observed on the diffraction profile of the TiCN coating come from carbides in the substrate material. The appearance of the (110) Fe peak on the diffraction spectra of the TiC and TiCN phases in Fig. 2 is due to the substrate material and gives a proof of smaller thickness of these two coatings in comparison with that of the TiN coating.

Fig. 2. X-ray diffraction patterns of the three coatings under investigation deposited onto the quenched and tempered Vanadis23 HSS steel substrate.

Polycrystalline alumina ball with a $R=12,7\text{mm}$ radius has been used in this study as a counterbody. The mechanical and surface properties of all materials employed in this work are summarized in Table 1.

Table 1. Mechanical and surface properties of the materials.

2.2. Experimental procedure

The test apparatus used in the experiments has been described elsewhere [33]. Here follows only a brief summary. Tests were carried out using an electrodynamic shaker imposing a reciprocating movement under constant frequency of 5Hz. The normal load has been kept constant, while the friction force and displacement amplitude have been recorded. A fretting test programme has been carried out under $100\mu\text{m}$ displacement amplitude and 100N normal load, which corresponds to 1350MPa Hertzian pressure for the investigated contact geometry. Gross slip condition has been maintained throughout all tests in this study.

Tests have been conducted in a closed chamber where both the ambient and relative humidity have been controlled. Three levels of RH have been considered in this work: 10% (dry air), 50% (comfort air), 90% (wet air) and the temperature has been kept at 295-298K. The PC-controlled system has been designed using LabView® software for digital measurements and control of the temperature and the relative humidity in a closed test chamber. The adequate portion of wet or dry air has been drawn from the outside of chamber in order to maintain the required humidity level. Low relative humidity level has been reached by employing the granulated silica gel to absorb the moisture in test chamber, while high RH by filling the bottom of the chamber with water.

Prior to testing and measurements, specimens were ultrasonically cleaned with acetone to remove wear debris. Experimental data have been obtained by carrying out several tests of different durations without putting the samples back in contact. The wear volume of the

fretting scars has been measured using 2D profilometry equipment and for each wear scar the profiles along the sliding direction and in the transverse one have been obtained. In order to determine the total wear volume, a simplified integration has been employed [34]. Morphology of wear tracks has been evaluated by scanning electron microscope (SEM) and 3D profilometry. Energy dispersive X-ray spectrometry (EDX) has been applied to characterize the composition of wear debris.

3. Results

3.1. Friction behaviour

Fig. 3 presents an average value of the COF for hard coatings under investigation as a function of three RH values. A running-in period has been observed for all coatings after which the friction forces stabilized and the value of COF has been calculated by deriving the average value between 3000 and 10000 fretting cycles. The error bars represent the difference between maximum and minimum value of COF recorded during this period. For each coating under investigation the value of the COF is decreasing with increase of the RH. One should note however the significant decrease of the COF value for TiC and TiCN coatings between the RH values 10% and 50% as different from very slowly decreasing COF value in the same RH interval for the TiN coating. The greatest change of the COF value has been noticed for the TiCN coating: from 0.65 at RH=10% to less than 0.2 at RH=50%.

Fig. 3. Average COF value of the hard coatings under investigation as a function of RH.

In order to refer to the real environmental conditions, where components can be subjected to significant humidity variations within a short time, we have designed the unique fretting experiment, where during a single fretting test RH was increased stepwise from 10% to 90% as shown in Fig. 4. During each humidity increase the fretting test was suspended for a time

interval as short as possible – usually less than 5 minutes – in order to adjust a new RH value in a closed chamber. These short detention intervals seem to be responsible for the characteristic discontinuities in COF evolution, which can be easily observed e.g. for TiC coating at 30% RH. These variations deform the overall COF evolution and suggest that rather continuous change of the RH during the fretting test should be applied. Nevertheless, this kind of test provides a very promising procedure for evaluation of the dynamic response of the system to variable environmental conditions. For TiC and TiN coatings the coefficient of friction is decreasing rather evenly whereas a sudden drop is observed for TiCN coating during the fretting interval at 50% RH. A critical value of coefficient of friction can be defined ($\text{COF}_{\text{cr}} \approx 0.5$), which separates the low and high friction regimes. One can see from Fig. 4 that the COF tends steeply to a value lower than the critical one immediately after switching the RH level from 30% to 50%, which suggests that the critical RH level has a value between 30% and 50% RH. Determination of an exact value of the relative humidity (RH_{cr}) requires additional detailed fretting tests in this critical range of the relative humidity.

Fig. 4. Evolution of friction coefficient as a function of variable relative humidity and the number of fretting cycles for (a) TiC, (b) TiCN and (c) TiN coatings.

3.2. Wear rates

Although the most common wear model proposed in tribology is the Archard's one [35], it has been found in a great number of works that for the same friction couple the wear coefficient K and friction coefficient strongly depend on the parameters like contact geometry, wear mode or displacement amplitude. It has been demonstrated that the Archard's wear coefficient increases to a great extent when the elastic limit is crossed over and that in order to quantify the fretting wear rate the coefficient of friction has to be integrated [36].

Hence, in this study the attention is paid to evaluate the resistance of the coatings to wear by means of the dissipated energy approach. In this approach the wear volume (W_v) of the degraded material is related to the shear work (i.e. dissipated energy) in the contact area [16,37-40]. Cumulated dissipated energy is obtained by summing up the energy dissipated during each fretting cycle over the whole test duration. When the wear volume of the removed material becomes a function of the cumulated dissipated energy (ΣE_d), the resistance of the material to wear can be expressed by the energy wear coefficient:

$$\alpha = \frac{W_v}{\sum E_d} \text{ (}\mu\text{m}^3\text{/J)} \quad (1)$$

The energy wear coefficient allows to synthesise wear resistance of a friction couple combining the sliding distance, the normal force and the friction coefficient influences. However, it is shown to strongly depends on the relative humidity as illustrated in Fig. 5. Linear approximations passing through the origin have been considered to fit the different experimental wear kinetics. The corresponding energy wear coefficients (α) as well the associated regression coefficients (R^2) have been compiled in Table 2. Except for one condition (TiN / RH=90%) the regression coefficients are systematically superior to 0.9. It basically confirms the stability of the given energy wear approach to capture the wear kinetic for a given relative humidity. Independently of the applied relative humidity it can be outlined that the best wear resistance (i.e. the smallest energy wear coefficient) is observed for the TiC, then the TiCN and finally the TiN coating.

Resistance of the titanium carbide coating to fretting wear is increasing with the RH value, which is rather an usual phenomenon for hard coatings as previously presented in section one of the paper. Wear behaviour of the titanium carbonitride and titanium nitride coatings is quite different with significantly lower wear rates obtained at 10% RH. There is however a difference in the resistance to wear between the TiCN and TiN coatings as the smallest resistance to wear in case of the TiCN coating has been observed at 90% RH while of the TiN

one at 50%. In general however the wear tendency of these two coatings is similar with higher resistance to wear in dry air.

Fig 5. Evolution of the wear volume as a function of cumulated dissipated energy for (a) TiC, (b) TiCN and (c) TiN coating.

Table 2. Energy wear factor extracted from the fretting wear analysis.

4. Discussion

Results presented in part 3 depict the significant role of the relative humidity conditions and complexity of the tribochemical reactions involved in the fretting wear process. It is evident that the effect of the environmental conditions should be considered separately for each superficial layer, as the reaction of each coating at different RH values is unique. Another variable that can change the tribological properties of a system to a great extent is the counterbody material. Steel has been found to be chemically active in contact with TiN and DLC [15,19,41] coatings, which causes unstable frictional behaviour. To avoid this situation and limit impact of tribochemical interactions at the interface, chemically non-active but also rare in engineering practice, materials like alumina [40,42], sapphire [26,43] or corundum [27] are applied. For this study, alumina ball has been selected as a counterbody, which allowed us to exclude one variable from a complex tribo-system controlled by changeable environmental conditions and as a result focus on fretting wear mechanism under different RH conditions.

The expected tribological behaviour, for which an increase of friction forces leads to increase of wear rates, has not been observed for TiCN and TiN coatings in this study. This unexpected result suggests that not only the mechanical damage is involved in the overall degradation process of the coating.

The differences in terms of wear energy rates which are illustrated in Fig. 5 are very interesting regarding the stability of the energy wear approach. The approach includes the friction coefficient through its formulation and for a given stable wear regime, relation of the wear volume and cumulated dissipated energy should be expressed by a single, unique energy wear coefficient. This fretting wear behaviour has been observed under significantly lower normal load of 1N for a TiN coating tested against alumina ball at different relative humidities [27]. The very different wear regimes observed in this study suggest that humidity not only interacts on the friction behaviour but also on the corresponding wear mechanism. Energy wear approach is stable only for constant RH conditions and can not be directly extrapolated for variable RH conditions, as it doesn't take into account different tribochemical response of a system.

An analysis of fretting scars surrounded by debris using SEM has been undertaken in order to examine the distribution and morphology of wear particles. Similar scar and debris morphology has been observed for TiCN and TiN coatings, therefore representative results for only two coatings (TiC and TiCN) are given in Fig. 6. It follows from these results that with increase of the RH value greater debris agglomerates have been formed, so the content of moisture in the surrounding atmosphere has a significant impact on the formation mechanism of debris in the contact area. It has been established that in situ formation of a tribofilm can reduce the wear rate and decrease the coefficient of friction of Ti-based coatings and that the Magneli-type oxides Ti_nO_{2n-1} have been identified as a lubricating agent responsible for an improvement of tribological properties [44]. In this study the EDX technique has been used, to characterize the composition of wear debris, however there was no evidence for oxides in the wear debris. For further investigation of the chemical composition rather more sensitive methods should be applied, like the spectrometry of the energy of the Auger electrons, spectroscopy of Raman shifts or the X-ray photoelectron spectroscopy (XPS).

An interesting evolution of wear particles distribution has been established in the present work (Fig. 6). Similar amount of debris has been observed for all the three values of the RH in case of TiC coating, while in case of TiCN and TiN coatings the quantity of debris is lower for higher values of the RH.

Fig. 6. SEM images of wear scars and debris created during fretting wear; (a,b) TiC at 10%RH; (c,d) TiC at 50%RH; (e,f) TiC at 90%RH; (g,h) TiCN at 10%RH; (i,j) TiCN at 50%RH; (k,l) TiCN at 90%RH. Scale bare length = 200 μm (for the Figs. a, c, e, g, i, k); scale bare length = 10 μm (for the Figs. b, d, f, h, j, l).

The 3D surface morphology analysis of wear scars as well as of the alumina ball surface allowed to establish that the missing wear particles in case of TiCN and TiN coatings are transferred onto the ball surface. With increasing number of fretting cycles an annular spatial structure is being formed on the surface of the counterbody (Fig. 7d). In contrast to this finding similar transfer of the debris is not observed in case of the TiC coating (Fig. 7b).

To estimate the volume of the TiN coating transferred onto the surface of the alumina ball, a separation procedure has been carried out using Surfscan® software. For the 15000 of fretting cycles this volume was equal to $1.011 \cdot 10^6 \mu\text{m}^3$. If we compare it with the wear volume of the scar ($1.859 \cdot 10^6 \mu\text{m}^3$), the ratio of the material transfer can be calculated as 0.54. Hence, it is clear that approximately half of the removed material is transformed in this case into the debris and ejected outside the contact area, while the second half is transferred onto the counterbody surface. However, it should be indicated that this calculation has been done for a given test duration and the ratio of the material transfer should be treated as a demonstrative value as it can evolve as a function of applied fretting cycles.

Fig. 7. Surface morphology of coated specimens and alumina counterbody after fretting test:

(a) TiC coating; (b) alumina ball; (c) TiN coating; (d) alumina ball with TiN debris.

The phenomenon of debris transfer has been observed in tribology of thin films [10], it is conducive to formation of a new counterface and as a result to evolution of loading conditions in the contact area. It has been observed, that the maximum wear depth of the TiCN and TiN coatings is situated at the border of the wear scar and a minimum at its centre (Fig. 7c). Therefore the longitudinal profile of the wear scar has a typical W-shape. It has been proved earlier [30] that this characteristic scar shape, obtained under gross slip condition, is related to a modification of the surface geometry by the generation and distribution of the third-body within the contact area. Evolution of the contact geometry leads to the shear and pressure fields modification. The maximum stress values are observed in the centre of the contact at the beginning of the test and are being translocated towards the borders of the contact during test duration. This type of damage is especially dangerous for thin films as for a relatively small wear volume a significant wear depth occurs and, at last, wear through the coating and reaching the substrate. The initial Hertzian radius for a studied contacts was around $180\mu\text{m}$, then the coating surface was subjected to progressive wear and the wear scar radius was increasing exponentially with a test duration. The schematic representation of the both damage mechanisms observed in the experiments is summarized in Fig. 8.

Fig. 8. Schematic representation of two different mechanisms of the fretting damage observed in the experiments.

5. Conclusions

The tribological behaviour of three different Ti-based hard coatings has been evaluated under variable relative humidity conditions. The following conclusions have been drawn from the present study:

- Durability of investigated hard coatings is not only a function of loading conditions but of environmental conditions as well. Strong impact of the relative humidity of the environment on the friction and wear properties of the coatings has been observed. The complex problem of thin films degradation has to be treated separately for each tribo-system, as for different coatings tribochemical reactions provoked due to environmental conditions are unique.
- For all the coatings under investigation the increase of the relative humidity leads to decrease of the friction coefficient. In case of TiC coating the increase of RH is conducive also to decrease of wear rates, while for TiCN and TiN coatings lower wear rates have been observed in lower RH.
- SEM analyses of the mating surfaces and 3D analyses of the wear scars have shown that approximately 50% of wear particles in case of TiN (TiCN) coating are transferred onto the counterbody surface, for a given test duration, in contrast to the TiC coating for which all the debris are ejected outside the contact area.
- Two different damage mechanisms have been observed for the hard coatings under investigation based on the phenomenon of debris adhesion to the counterbody surface. Evolution of the interface shape leads to the shear and pressure fields modification in the contact area in case of TiCN and TiN coatings.
- Energy wear approach doesn't take into account different tribochemical reactions, is stable only for constant RH conditions and can not be directly extrapolated for variable RH conditions.
- Unique experiments with variable relative humidity within one fretting test have been completed. It is a promising procedure for evaluation of dynamic response of a system to

variable environmental conditions as well as for elucidation of the critical value of the relative humidity which separates the low and high friction regimes of a fretting test.

This study leaves some open questions and interesting aspects worth additional work. More attention is required to explain the mechanism of wear debris transfer observed for TiCN and TiN coatings. Is this phenomenon due to different deposition techniques used in the work or rather to the presence of nitrogen atoms in the coating? Also the test concept with variable relative humidity values should be studied accurately as it gives the potential mean for accurate modelling of real environmental conditions.

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	Thickness	Hardness	Young's modulus	Poisson ratio	Surface roughness
	t (μm)	H	E (GPa)	ν	Ra (μm)
Vanadis23	-	64 HRC	230	0.3	0.2
Alumina	-	2300 Hv _{0.1}	370	0.27	0.01
TiC	1.6	1250 Hv _{0.05}	510	0.2	0.2
TiCN	2.5	1700 Hv _{0.05}	550	0.25	0.2
TiN	4.0	2000 Hv _{0.05}	600	0.25	0.2

	α ($\mu\text{m}^3/\text{J}$) // R^2		
	RH=10 %	RH=50%	RH=90%
TiC	488 // 0.95	385 // 0.98	242 // 0.95
TiCN	1080 // 0.96	1668 // 0.99	2205 // 0.97
TiN	1574 // 0.93	6753 // 0.97	5397 // 0.87















