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Fretting Wear Performance of PVD Thin Films

Brahim Tlili

Abstract

Nowadays, most surface treatments are realized through vapor deposition techniques as thin hard coatings to guarantee high surface hardness, low friction coefficient, and improve wear resistance. Several experimental investigations have led to the development of multilayer coatings in preference to the traditional TiN coating. In the current chapter, research was conducted on the fretting wear of (TiAlCN/TiAlN/TiAl) and (TiAlZrN/TiAlN/TiAl) multilayer coatings deposited by reactive DC (magnetron sputtering) of Ti-Al and Ti-Al-Zr alloys on AISI4140 steel. Fretting wear tests (20,000 cycles at 5 Hz) were conducted in ambient conditions, where the interaction between normal load and displacement amplitude determined the fretting regime. The influence of the normal load and displacement amplitude on the coefficients of instantaneous coefficient of friction and stabilized coefficient of friction is different in the two multilayer, coated steels. The PVD coating (TiAlZrN/TiAlN/TiAl) reduces the friction. The worn volume of coated AISI4140 steel is sensitive to normal load and displacement amplitude. The relation between worn volume and cumulative dissipated energy was established for the two coated steels. The energetic fretting wear coefficients were also determined. A multilayer (TiAlZrN/TiAlN/TiAl) coating has a low energetic wear coefficient.

Keywords: fretting, wear, PVD, coatings, hardness

1. Introduction

The hard coatings have been used extensively to increase the wear resistance under loading conditions in fretting wear. Various methods of coating deposition have found industrial application. One successful approach is the physical vapor deposition (PVD) technique. Presently, development of TiAlN-based multilayer and nanocomposite coatings are the most important trends in the hard coating industry [1]. The ternary coating has better resistance to oxidation and poor adherence [2]. In order to remedy these imperfections, additional constituents such as carbon or zirconium are recommended. In order to characterize the quality of a coating, evaluation of a number of properties is essential. Hardness, friction coefficient, roughness, wears, and oxidation resistance have primary importance. The addition of carbon to TiAlN provides a quaternary coating, TiAlCN, which has better resistance to oxidation, improved mechanical properties, and has good adherence with high tribological capacities [3, 4]. However, the addition of zirconium to TiAlN provides a quaternary coating, TiAlZrN. Although some studies are available on TiAlZrN layers and their behavior in terms of wear [2], data on resistance to fretting wear are not available. First, according to the intensity of the imposed

parameters (normal force, amplitude of displacement, and frequency), fretting maps were established to determine the sliding conditions and the type of damage according to the fretting conditions. The running condition fretting maps indicate when total or partial sliding conditions occur, and the material response fretting maps quantify the damages (wear, cracking). Actually, the partial slip regime (PSR) is associated with cracking as a result of a fatigue phenomenon, whereas the gross slip regime (GSR) leads to wear by debris formation [5]. The mechanical models of contact including elastoplasticity are used to delimit the boundary between the partial slip and gross slip [6]. Crack propagation is studied using efficient fatigue criteria [7, 8], while wear is studied by more or less empirical multiple quantitative approaches [9]. Second, in this step, we have to determine the tribological properties of quaternary coatings and correlate the worn volume according to the parameters of loading in fretting wear. Finally, the comprehension of fretting behavior remains sensitive as soon as the mechanical, thermal, and physical-chemical interactions [occurring in a contact associated with the role played by the interfacial layer generated by detachment of the particles during friction (third body)] need to be taken into account; when wear particles have been liberated from the surface, some of them may attach to the counterface to form a transfer layer and significantly change the tribological properties of the counterface (like forming a new counterface) [10–13]. The wear analysis performed with imposed displacements or tangential forces is based on an energetic approach [6, 14]. The wear volume increases linearly with the dissipated energy within the contact.

The PVD surface treatment process makes it possible to produce nanocomposite coatings with a metal matrix. During this process, the particles are accelerated at very high speed through a flow of inert propellant gas under pressure and are pre-heated to a temperature below the melting temperature of the materials to be sprayed [1–3]. Due to the very high speeds, the coatings thus formed are very dense [2]. Obtaining large thicknesses (several micrometers), accompanied or not by superficial oxidation, with densities close to the volume of base substrate have advantages over deposits produced by other thermal processes. The cold spraying process is also a repair method used either on new parts under development or on parts under maintenance. Certain layers are also a means of protection against corrosion, for example, for components of aeronautical parts. Reinforcement phases can be filled layers, the composition of which also varies depending on the material of the matrix [2, 4]. Solid lubricants can also be incorporated [5]. Coatings with solid lubricants are used for technical parts such as bearings or rings to reduce friction.

The tribological circuit in general describes the different flow rates of the third body capable of being activated in an elementary contact in two dimensions [6, 7]. The internal source flow corresponds to the detachment of particles, due to surface tribological transformations (TTSs) [8, 9], cracking, and adhesion. It leads to the formation of the third natural body. The external source flow comes from the introduction of a third artificial body into the contact. The internal flow is the flow of the third body which circulates between the first bodies. The external flow is the flow of the third body which escapes from the contact. It is divided into a recirculation flow and a wear flow. The recirculation flow consists of the third body which, when reintroduced into contact, driven for example by one of the first bodies, will again contribute to speed accommodation. On the other hand, the wear flow is made up of the third body which, when definitively ejected from contact, will never again participate in speed accommodation. The debits will be estimated on a relative qualitative scale from very low (*) to very high (*****).

The rheology of the third solid body is characterized relatively on the basis of its cohesion and its ductility [7]. These two properties are determined from the morphology and texture of the third body obtained by observations and analyses after

tests. The cohesion translates a third body more or less compacted or pulverulent. Ductility reflects the ease with which the third body spreads in contact.

In this chapter, the multilayer coatings' behavior under various loading parameters in the fretting wear is presented.

2. Experimental procedures

2.1 Substrate

Specimens used in this work were machined from steel trade AISI4140 hardness 420 HV0.05, with surfaces of $(10 \times 10) \text{ mm}^2$ and $(10 \times 12) \text{ mm}^2$. These samples were divided into two sets; the first set was coated by TiAlCN/TiAlN/TiAl and the second round by TiAlZrN/TiAlN/TiAl. Before PVD treatment, all samples were cleaned and polished with trichloroethylene, acetone, and alcohol in an ultrasonic cleaner.

2.2 Deposition

The multilayer coatings were deposited on the steel AISI4140 by the process of spraying DC magnetron mode, using target compounds TiAl ($50^\circ/\text{Ti}$, $50^\circ/\text{Al}$) [3] and Al-Ti-Zr ($19^\circ/\text{Ti}$, $21^\circ/\text{Al}$, $10^\circ/\text{Zr}$, $50^\circ/\text{N}$) of high purity (99.9999%).

The samples were mounted on a continued rotating satellite inside the vacuum plasma chamber. The atmosphere was chosen to produce successively under a layer of TiAl, a buffer layer of TiAlN, and then a layer of TiAlCN or TiAlZrN. Indeed, the thin films of TiAl and TiAlN aim to improve the adhesion layers TiAlCN [2, 3] and TiAlZrN [10] with steel. The optimum conditions for filing as the bias voltage targets, temperature, and time of deposition were determined and optimized in previous studies; **Table 1** shows in detail the optimal conditions for verification. In addition, Argon, acetylene, and nitrogen gas which are of very high purity (99.9999%) were introduced into the vacuum chamber. The basic pressure in the room was 5.10^{-5} Pa , which grew to 0.1 Pa for the deposition of desired layers. The distance between the target and the substrate surface was 35 mm. Before the deposition, the surface of the substrate was cleaned by argon ion bombardment at the end to eliminate all these antagonists.

2.3 Characterization of the coatings

The multilayer coatings prepared in this work and their mechanical properties are shown in **Table 2**.

Unit	Traget power (K _w)	Bias (V)	Temper (°C)	Rotation velocity (rpm)	Time (mn)	Ar	Gas flow N ₂ SCCM	C ₂ H ₂
TiAl	6	-300	250	0.7	22	400	–	–
TiAlN	7.5	-200	150	0.6	17	770–800	90–150	–
TiAlCN	7.5	-200	100	0.6	42	950	150–135	20–135
TiAlZrN	7.5	-200	100	0.6	42	950	150–135	20–135

Table 1.
Deposition conditions.

	Hardness (GPa)	Young's modulus (GPa)
TiAlCN/TiAlN/TiAl [3]	15	260
TiAlZrN/TiAlN/TiAl	28	310
AISI4140 steel	42	210

Table 2.
Mechanical properties of coating layer and substrate.

The fretting wear behavior of multilayer TiAlCN/TiAlN/TiAl has been carried out in previous studies [3]. Indeed, a special focus in this chapter was given to the characterization and the study of the behavior of fretting wear coating of multilayer TiAlZrN/TiAlN/TiAl. The total thickness of the coating is determined by the electronic scanning microscope (SEM) after a major fracture in vertical section, followed an analysis of the chemical composition by energy dispersive spectroscopy (EDS). The morphology of the coating TiAlZrN is being reviewed by an atomic force microscope (AFM). The microstructural characterization of this coating is investigated by X-ray diffraction (Philips X'pert system). Scans were carried out in the grazing angle mode with an incident beam angle of 3° and the normal θ -2 θ method classically used in the same situation. Young's modulus and hardness were measured by nanoindentation tests with a nanoindenter MTS-XP. The indentation was performed using a triangular Berkovich diamond pyramid. SEM and AFM observations allowed determination of the global coating thickness and the morphology of the surface, respectively. The multilayered TiAlZrN/TiAlN/TiAl coatings had a mean thickness of 800 nm, distributed in three layers as shown in **Figure 1**. The surface was globally uniform with some domes and tiny craters spread all over the area **Figure 2**.

Dimensional measurements showed that the domes had a mean diameter of about 25 nm and the craters a maximum depth of 16 nm. The crystallographic structure and orientation of the coatings were determined by X-ray diffraction. Phase identification for multilayer coatings TiAlZrN/TiAlN/TiAl revealed the presence of reflection peaks corresponding to stripes (100) and exhibited a weak intensity peak at $2\theta = 2.83^\circ$ (44.74 Å) (**Figure 3**). It can be seen that the as-coated state already has a crystalline structure of AlZr_3 . The presence of crystallographic structure is linked to the columnar morphology of the layers observed by SEM on a cross section **Figure 4**. The chemical composition of multilayered coatings is shown in **Figure 5**. The measurements of nanoindentation carried out on a depth exceeding the thickness of the coating made it possible to determine the average hardness and average Young modulus in this multilayer TiAlZrN/TiAlN/TiAl. The results are presented in **Table 2**.

Figure 1.
Distribution and thickness of the layers in the multilayers coating: (a) TiAlZrN/TiAlN/TiAl and (b) TiAlCN/TiAlN/TiAl.

Figure 2.
AFM morphologies of the surface layer of TiAlZrN.

Figure 3.
XRD diffractogram of the TiAlZrN/TiAlN/TiAl multilayer.

2.4 Fretting tests

Fretting wear, which is considered a nuisance in several branches of industry such as aeronautics, nuclear industry, etc., refers to the degradation of the contact surface resulting from wear, which requires an overhaul or replacement of the machine components. It is defined as the wear that takes place during a low amplitude oscillatory movement between two apparently immobile solids under a load normal to the contact surface. Such a phenomenon is observed especially in assemblies subjected to vibrations. To simulate the industrial process, a test bench was developed within the laboratory and subsequently installed on a fatigue machine (MTS).

The fretting tests were carried out on an MTS tension compression hydraulic machine. A sphere-on plane configuration was employed as shown in **Figure 6(a)**. The counter-body was a polycrystalline alumina ball with 24 mm diameter, a Young's modulus of 310 GPa, and a hardness of 2300 Hv0.05. The flat coating alloy (10 mm × 10 mm × 12 mm) specimens were manufactured from a cast bar of

Figure 4.
Scanning electron micrograph of a cross section of multilayered TiAlZrN/TiAlN/TiAl coating as made by fractography.

Figure 5.
Energy dispersive spectroscopy (EDS) of multilayered TiAlZrN/TiAlN/TiAl coatings.

AISI4140 steel. During the test, the instantaneous displacement, the normal force, and the tangential force were monitored and recorded for every cycle.

The fretting tests were conducted with displacement control, using an extensometer as a displacement transducer. When it is possible to plot the hysteresis loops of the fretting-wear stresses from the instantaneous measurement of the tangential force as a

Figure 6.
Illustration of the experimental fretting wear approach: (a) fretting log of one fretting cycle and test bench, (b) full slip fretting loop, and (c) 3D wear trace, obtained by optical profilometer.

function of the sliding distance for normal force values between 50 and 750 N and the sliding ranges from $\pm 20 \mu\text{m}$ to $\pm 100 \mu\text{m}$ [3, 5, 15–17]. The area of the fretting loop corresponds to the dissipated energy during the fretting cycle (E_d), whereas the residual opening of the cycle (i.e., the residual displacement when $Q = 0$) is related to the full sliding amplitude (δ_g) (**Figure 6(b)**). All tests were performed at 20×10^3 cycles and the frequency was set at 5 Hz [3, 5, 15, 18].

The fretting tests were conducted in dry conditions at an ambient temperature of 25°C and a relative humidity of 60%. Prior to the fretting test, the specimen and counter-body were cleaned with acetone and alcohol. Hundred to 2000 fretting cycles were performed. The tests were stopped in two different ways: once the displacement was stopped abruptly after the last fretting cycle, and once the displacement amplitude was reduced to zero during several cycles. However, to quantify the wear volume, a specific 3D surface profilometry methodology, fully developed in reference, [15] is applied. It consists of determining the wear volume below the reference surface (V^-) and the transfer volume above the reference surface (V^+). This analysis is performed both on sphere and plane fretting scars. A system wear volume is then deduced from the following relationship:

$$V_{\text{system}} = (V^- - V^+)_{\text{plane}} + (V^- - V^+)_{\text{orb}} \quad (1)$$

However, other conditions have been tested to investigate the effect of certain parameters suspected of having a dominant role in the wear mechanism. These conditions will be given in due course. Furthermore, optical observations are coupled with scanning electron microscopy to examine posttest fretting scars.

3. Test results and discussion

3.1 Fretting wear

Preliminary work was carried out to determine the fretting running map of PVD multilayered coatings in contact with alumina sphere. The tangential force (Q) and displacement (δ) amplitudes are determined for each cycle, and each sliding rate is reported on a 2D map of the fretting displacement and friction force. After a certain number of cycles, the partial slip regime (PSR) is manifested as a change in the hysteresis loop form, whereas the gross slip regime (GSR) maintains the buckle form with a variation of tangential force [3]. Running condition fretting maps (RCFMs) can then be determined from this map [15]. **Figure 7** shows the boundary lines of both sliding rates for different multilayered TiAlCN/TiAlN/TiAl and TiAlZrN/TiAlN/TiAl coatings. It can be seen that the gross slip regime region of the PVD-coated AISI4140 steel is enlarged due to the presence of the TiAlZrN, then the TiAlCN layers. From a phenomenological consideration, the gross slip regime corresponds to wear, and in the partial slip regime, the wear is associated with cracking, and the contribution of TiAlZrN/TiAlN/TiAl-reducing coatings should be interpreted positively. Indeed, in such a situation, wear is favored with the cracking of the covered part, which makes it possible to sacrifice the surface in order to protect the volume of the part [3].

The TiAlZrN coating thus reduces the partial slip regime field, which is the most detrimental for fretting. However, sliding amplitudes are rather large and seen to be related more to the reciprocating condition. However, it is fundamental to relate the displacement value to the contact dimension. The boundary between the fretting and reciprocating conditions can be related to the ratio between the displacement amplitude and the contact radius, $e = d/a$ [19]. It transpires that when e remains little than 1, a nonexposed surface exists and grosses slip fretting conditions prevail, whereas if e is above 1, the whole surface is exposed to the

Figure 7.
Effect of multilayered coatings (TiAlZrN/TiAlN/TiAl) on the running condition.

ambient and the contact is under reciprocating conditions [18]. The maximum e value calculated for all performed test situations remains lower 0.5, which implies gross slip fretting conditions.

3.2 Tribological properties

Figure 8 shows the evolution of the coefficient of friction as a function of the total number of cycles for the two multilayered PVD coatings under same loading parameters. The first cycle systematically presents a low friction coefficient around 0.11, and the incipient low friction coefficients can be explained by the presence of surface oxides. During the test, the friction coefficient increases progressively toward a level known as the stabilized friction coefficient. Such a difference of friction behavior between the two antagonists (TiAlZrN and TiAlCN) is clearly illustrated in the graph of evolution of the friction versus the fretting cycles. It confirms the previous fretting cycle analysis and outlines the difference of friction kinetics between the two antagonists. The transition period is systematically longer in the presence of the TiAlZrN coating. In the case of the PVD layer, De wit [20] showed that the transition period corresponds to the formation of debris made of amorphous retiles and nanocrystallines. Beyond this transition, the amorphous phase is transformed into a crystalline phase and contributes to further wear. Depending on the loading condition, the film of TiAlCN or TiAlZrN can be eliminated, thus favoring a significant increase of the friction coefficient **Figure 9**. It explains the influence of the pressure and displacement amplitude on the evolution of the friction coefficient on a coated specimen, taking into account a slight surface degradation at low friction, which must be introduced into the friction cycle [21, 22]. It can be seen that by increasing the displacement amplitude or the pressure, the wear depth will grow faster and the elimination of surface porosity will be accelerated. As soon as the surface porosity and the aluminum oxide, which plays the role of a solid lubricant, are removed, low friction conditions can no longer be maintained and high metal/metal interactions with high friction coefficients in the range of 0.5–0.6 are observed, indicating that the PVD film has been breached. When a microarc oxidation coating was used, the fretting friction coefficient of modified PVD coatings alloy under higher loading condition remains as high as about 0.6; however,

Figure 8.
Evolution of the friction coefficient for the TiAlZrN/TiAlN/TiAl and the TiAlCN/TiAlN/TiAl ($F_N = 50\text{ N}$, $\delta = 20\text{ }\mu\text{m}$).

Figure 9. Stabilized friction coefficient as a function of normal load and slip amplitude of PVD multilayered coating. (a) TiAlCN/TiAlN/TiAl [3] and (b) TiAlZrN/TiAlN/TiAl.

the cracking domain and severe adhesive nature was limited. Under low loading condition, the friction coefficient was significantly reduced and remained favorable stable at 0.4–0.3 in the long term, which indicates that the multilayered coatings lowered the shear and adhesive stresses between contact surfaces, consequently alleviating the possibility of initiation and propagation of cracks in the inner layer of multilayered coatings.

3.3 Wear properties

In every tribological application, the extent of the damage or surface deterioration is of interest. There are several methods of evaluating the wear volume/loss, which can be roughly classified into three methods: weight measurement, topographical analysis, and 2D analysis by means of empirical equations. In tribological research, where many specimens need to be analyzed, a simple and fast procedure is desirable for wear volume/loss determination. Moreover, the effect of different material combinations, slip amplitude, normal force, and the energy dissipated during sliding are also presented.

3.3.1 Prediction of the wear volume evolution

The linearity of the variation of fretting wear with normal load and displacement obtained by the two multilayered TiAlCN/TiAlN/TiAl- and TiAlZrN/TiAlN/TiAl-coated specimens are used to impose the same definition as Archard's equation, namely, a quasi-linear function. The wear volume evolution of the two coated steels is shown in **Figure 10**, as a function of slip amplitude and normal force. For all specimens, the beneficial effects of the coating on wear volume diminished with the increasing normal force and fretting stroke. The latter observation is consistent with the work of Santner et al. [23], who reported that TiN was much more effective at suppressing wear under sliding wear conditions. For the steel substrate, the coating TiAlCN or TiAlZrN had no good effect on the fretting wear for sliding amplitudes larger than 50 μm , regardless of the applied normal forces out of 500 N. The wear transition is attributed to the higher variation of both normal load and sliding amplitude. However, for all fretting wear tests, the behavior evolution of wear volume versus displacement is the same. This means in all tests, wear volumes remain constant and are not greatly influenced by the low normal load or sliding distance. In fact, it is only the wear amplitude which changes according to the displacement and high normal load. In every case, there is a constant wear volume which precedes the establishment of the high wear regime. Three suppositions can be made to synthesize all the results presented above. Wear volumes are similar for all loading conditions and consist of two phases. The first one corresponds to the elimination of the contamination layer and the native oxides. Thus, alumina to PVD coatings contact will be established. As a result, the adhesion phenomenon is favored as regards the miscibility antagonists by plastic deformation, which increases the micro-junction density by crushing asperities. Hence, adhesive wear appears by creating transfer of the softer material (PVD coatings) on the harder

Figure 10. Wear volume as a function of parameters loading multilayered coatings: (Zr) TiAlZrN/TiAlN/TiAl, (C) TiAlCN/TiAlN/TiAl.

material (alumina). This phase will be followed by a transitional stage: wear of transferred PVD coatings. The second phase (high wear regime) happens as soon as the trapped debris are oxidized. Gradually, wear is accentuated on both sides of contact (on PVD coatings and alumina ball). For larger displacements ($\delta > 50 \mu\text{m}$) and a high normal load, fatigue wear induced by multicracks has been detected **Figure 11**. One hypothesis is that the generated plastic strain leads to a brittle layer, which can be associated to the tribologically transformed structure (TTS) [24, 25]. Enduring cyclic loading, multicracks are activated which induce debris formation and wear. De Wit [16] showed that the transition period corresponds, in the case of the PVD layer, to the formation of debris made up of amorphous rutiles and nanocrystallines. Beyond this transition, the amorphous phase is transformed into a crystalline phase and contributes to further wear. SEM observations showed that the debris appeared on this TiAlCN/TiAlN/TiAl multilayer coating during the first cycles, in the form of particles less than $1 \mu\text{m}$ in size [3].

The main wear mechanism of the TiAlZrN-coated AISI4140 steel was the brittle cracks of TiAlZrN, before destroying the coating. After destroying the TiAlZrN coating, the main wear mechanism was cracks due to a low normal force and high slip amplitude and cumulated plastic flow on the edge of the fretting scar and adhesive and abrasive wear at high slip amplitude. Oxidation was observed on most the worn surface.

Moreover, the effect of surface roughness before deposition on the wear behavior of multilayer coatings deposited on an AISI 4041 steel substrate. After deposition, the surface roughness of the coating was approximately half of the original substrate surface roughness. While the frictional behavior was not apparently affected, the wear rate of the coatings increased significantly with increase in the substrate surface roughness. Wear rate increased rapidly when the substrate surface roughness exceeded $R_a 1 \mu\text{m}$. Above this substrate roughness, the dominant wear mechanism also changed from adhesion to chip/flake formation and fragmentation of the coatings. Chipping/flaking of the coatings initially occurred mainly at the tops of asperities of the surface texture. The Archard's specific wear

Figure 11.
Fretting wear scar morphology of multilayered TiAlZrN/TiAlN/TiAl coating (gross slip regime), $F_N = 200 \text{ N}$.
 $\delta = \pm 100 \mu\text{m}$.

rate increased with the increase in total load for coatings on the rough substrate surfaces; however, this was almost invariant with the increase in load for coatings on the smoother substrate surfaces, nominally following the Archard's wear law. Contact pressure distributions over the real area of contact between the ball and the rough coating surfaces have been analyzed by applying the elastic foundation model of contact mechanics. It has been shown that the contact pressures increase significantly with the increase in surface roughness of the coatings. Plastic yielding is highly possible in the coatings deposited on rough substrate surfaces above $R_a\ 1\ \mu\text{m}$. The observed apparent effect of surface roughness on wear and wear mechanism transitions of the multilayer coatings can be explained according to the contact mechanics analysis results.

3.3.2 Prediction energy wear coefficient

Investigations at various loads and slip amplitudes confirm that there exists a correlation between the wear volume extension of the TiAlZrN/TiAlN/TiAl multilayer coating and dissipated energy. For all the different loading conditions previously defined in Section 2.4, **Figure 12** shows the rates of the wear volume as a function of the dissipated energy. The used volume is measured using a 3D optical profilometer, and the dissipated energy is estimated directly by the area of the fretting loop for each cycle. As a separate form of this behavior, when the energy approach is applied, all of the test parameters are represented by the one and only linear equation from which a single overall energy wear coefficient (α = slope of the curve) can be detreminated for each antagonist. In fact, the energy coefficient represents the slope of the straight line which connects the lost volume and the energy dissipated by friction: $V_{\text{Lost}} = \alpha E_d$. In the case under consideration, $\alpha_{\text{TiAlZrN}} = 104\ \mu\text{m}^3/\text{J}$, and TiAlCN coating provides an energetic wear coefficient of $\alpha_{\text{TiAlCN}} = 23.103\ \mu\text{m}^3/\text{J}$ [3].

Figure 12.
Fretting wear scar morphology of multilayer TiAlZrN/TiAlN/TiAl coating (partial slip regime).

This result shows that the TiAlZrN coating improves its higher capacity to wear in fretting. The principal factors favoring this tendency are generally related to the presence of compression residual stress, the decrease of friction coefficient, the increase of superficial hardness, and the roughness effect of the surface [20]. Without measuring the residual stress, the contribution of the reduction of friction coefficient and the increase in hardness are confirmed in this study. One can notice as in **Figure 13** that hard coatings quickly give rise to particle detachment and prevent the partial slip regime by accommodating the displacement in the powder bed, and favor debris formation. A large amount of debris has been observed during fretting tests, and coatings are damaged by material transfer due to adhesion and/or abrasion. It can be seen that a small amount of debris remains within the contact area, while a large amount of debris is ejected outside and located near to the border of the fretting scar. However, fretting scars have three characteristic regions, which are clearly visible for the multilayered TiAlZrN/TiAlN/TiAl coating; central convex region with slight abrasion traces, outer annular region covered with debris, and transition region where the abrasion traces parallel to the sliding direction can be easily identified. **Figure 14** compares the energetic wear coefficients with those reported in the literature [3, 20, 21]. Magnetron-sputtered TiAlZrN coatings in the as-deposited condition possess a better fretting wear resistance ($104 \mu\text{m}^3/\text{J}$) than TiAlCN coatings ($23 \mu\text{m}^3/\text{J}$) for tests performed in ambient air. According to energetic considerations, the multilayered TiAlZrN coatings improve the resistance to fretting wear by a factor 6.5, compared with non-coated steel [3]. But the TiAlCN multilayer has a lower performance as it improves the resistance only by a factor of 2.8. This result is acceptable since the addition of Al, Zr forms stable oxides, especially Zr, which forms a very thin oxide layer similar to Al_2O_3 [2, 21, 22, 26] that strongly influences the energetic wear coefficient and provides good tribological properties [2].

Figure 13.
Wear volume as a function of cumulated dissipated energy.

Figure 14.
Energy wear rates of different substrates and hard coatings in fretting wear tests [27].

4. Conclusion

In this work, we reviewed the deposition parameters and properties of titanium and titanium-aluminum-based quaternary coatings. It is found that the effect of the individual as well as multiple alloying elements are manifested in further modifying the properties of (Ti, Al) N coatings. Research and developments on simple binary and ternary coatings in previous studies are discussed. This was followed by the investigations on quaternary multicomponent coatings (TiAlZrN/TiAlN/TiAl and TiAlCN/TiAlN/TiAl); the behaviors in these coatings in fretting wear are compared. The main conclusions are the following. The local card solicitation obtained for the two layers of quaternary studied shows the delimitation of both sliding rates. It is shown that the gross slip regime region (GSR) of the coated AISI4140 steel is extended by the presence of the TiAlZrN layer in comparison with the TiAlZrN layer. These results are being very useful in the tribology. Indeed, the GSR is always associated to wear, but the partial slip regime (PSR) is accompanied to a crack that can be disastrous and leads to the failure. To reduce the instantaneous friction coefficient and stabilized friction coefficient, it is necessary to choose the coating-based zirconium coating instead of the coating-based carbon. In general, the stability of the coefficient of friction observed under the fretting conditions tested for a PVD coating was linked to the presence of a third multilayer body: a first layer consisting of particles mainly of submicron size; a second, discontinuous lamellar layer; and a third layer consisting of particles having a microstructure with ultrafine grains (refinement). In steady state, the third body formed easily remains trapped in contact. The third body, less than 50 μm thick, protects the surface (reduced wear) and is stable.

However, the gap between these two coatings is governed by the amplitude of the loading parameters. The thin coatings formed by physical vapor deposition may provide an initial friction reduction but it is not sufficiently durable for this application. However, the beneficial effect of the PVD coatings on fretting wear diminishes with increasing normal force and decreasing fretting stroke. In this chapter, the worn volume of the two quaternary layers is very influenced by loading conditions. Therefore, special attention should be given to better distinguish the effect of zirconium. Adding Zr improves the wear resistance of Al-Ti-N coating. Zr stabilizes Ti-Al-N lattice and also forms a very thin stable oxide layer similar to Al_2O_3 . These two effects together enhance the wear resistance of the Ti-Al-Zr-N coatings. The

stability of the energy approach is used to predict the wear kinetics in a volume of tribo-systems: $W_v = \alpha \times E_d \Sigma$, where, α is the energetic coefficient, W_v is the worn volume, and E_d is the dissipated cumulated energy. The multilayered TiAlZrN/TiAlN/TiAl coatings improve the resistance to the fretting wear of AISI4140 steel by twice as much as the multilayered TiAlCN/TiAlN/TiAl coatings.

In the light of various experimental investigations, the study of the wear mechanisms of the different films was carried out. It follows that the advantages of a multilayer coating over a single-layer coating are mainly presented in three points:

- multilayer coatings are multifunctional,
- good resistance to wear, and
- reduce friction.

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