EFFECT OF THE MICROSTRUCTURE AND THICKNESS OF NITRIDED CASES ON THE ABRASIVE WEAR RESISTANCE OF DUPLEX LAYERED PVD-TiN COATINGS

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The influence of both the microstructure and the thickness of nitrided cases on abrasive wear resistance of duplex layered PVD-TiN coatings was studied. A single layered TiN coating and various duplex layered TiN coatings, with different thicknesses and structures of nitrided case, were investigated: some with and others without a compound layer in coating-nitrided case interface. A micro-scale abrasion *test was used to evaluate the wear resistance of these coatings. For duplex laeyred coatings with thick nitrided cases, a reduction in the abrasive wear resistance is caused by the growth of coarser CrN phase in nitrided case. The presence of a black layer at the TiN/nitrided case interface also has a deleterious effect on the wear resistance. Nitrided cases of thin thickness and without compound layer or coarser CrN phase provided to the coatings the best wear resistance in micro-scale abrasive wear tests.*

Keywords*: micro-scale abrasive wear, duplex treatment, plasma nitriding, threshold nitriding potential, AISI D2 tool steel.*

1. Introduction

Duplex plasma surface-engineering technology, i.e. combined plasma nitriding and plasma assisted physical vapor deposition (PVD) of thin hard coatings, has found increasing application in industry to improve the tribological performance of various steel components [1-4]. The process consists of plasma nitriding the steel first and then depositing a thin (2-8 μm) hard titanium nitride (TiN) coating on the nitrided surface by PVD. The coating process can be carried out in the same vacuum chamber[5-10] (hybrid process) or in a different one of that used for previous plasma nitriding treatment[4] (discontinuous process). Many research institutes in Europe have developed hybrid processes and in Japan *Radical Nitriding*™ process[11] has been developed for previous surface hardening of tool steels. Considering the productivity of the processes, the first is obviously more promising because the temperatures of both plasma nitriding and PVD deposition are in the same range and the chamber has to be evacuated only once.

The combination of the as-called "duplex treatment" produces a composite with thin, hard and heat-chemical-wear resistant TiN coating supported by a thick nitrogen-hardened sub-surface, frequently referred as "duplex layered TiN coating" in literature. Figure 1 shows functional properties of a duplex-layered composite, which can be obtained through a duplex treatment. Thus properties obtained by the combination of plasma nitriding with PVD deposition allow function sharing between the core material, the hardened case and the surface, which is of special interest for application in complex stressed machine components.

It is well recognized that duplex-layered composites, containing either a white layer (compound layer) in the interface between TiN coating and nitrided case or a net of grain boundary precipitated nitrides in the nitrided case, have their tribological properties adversely affected. For substrates of low chromium steel (En40B steel) nitrided using high nitrogen contents in gas atmosphere, i.e. previously nitrided above its threshold nitriding potential curve, Sun and Bell[4] show that during PVD process compound layer was transformed in a "black" layer consisted mainly of α-Fe phase, with relatively low hardness (400-500 HV). They concluded that this "black" layer was the product of the decomposition of the outer part of the compound layer during the PVD process, which leads to the transformation of Fe_4N and $Fe_{2-3}N$ nitrides to α-Fe phase.

Nowadays, plasma nitriding in low nitrogen-containing atmospheres, during short times, is a practice currently adopted for duplex treatment of high alloying-containing tool steels. Such procedure avoids the above-mentioned problems, resulting in nitrided cases with maximum surface hardness and without compound layer. For high speed steel (HSS M2) substrates, Perillo[13] shows that the tribological properties of a duplex layered TiN coating are harmed by increasing the nitriding time due to surface softening of the nitrided case and compound layer formation. Kadléc and co-workers[14] also verified such deleterious effect. These authors observed that very short-time nitriding (30 minutes) yielded to the duplex-layered coatings high wear resistance and strong adhesion. Using nitriding times of only 30 minutes, a hardness of about 1500 HV is reached by the surface of the nitrided case, and using longer nitriding times, hardness values fall to 1050 HV. For duplex layered TiN coatings, formed on cold working tool steel (AISI D2) substrates, Höck and co-workers[9] verified a high wear resistance is attained when plasma nitriding is carried out at 510 °C and with a very low nitrogen-containing gas atmosphere. After 4 h of plasma nitriding, the surface hardness of the nitrided case reached approximately 1500HV. These researchers had also observed that nitriding at low temperatures (360 - 410 °C) for varied times was not enough for obtaining nitrided cases with the maximum surface hardness. Duplex-layered TiN coatings produced from such nitrided cases presented low abrasive wear resistance and low adhesion degrees.

One can find in literature that there is an optimum thickness value, as well as an optimum nitrided case microstructure, to obtain duplex-layered composites with high abrasive wear resistance. However, the optimum pre-nitriding conditions are not well established, varying from steel to steel, and the basic mechanisms related to a further improvement on the wear resistance of the duplex layered composites are still poorly understood.

In this work, studies were carried out to understand the mechanisms by which the wear resistance of duplex layered TiN coatings, based on cold working tool steel (AISI D2) substrates, can be improved. Additionally, both thickness and microstructure of nitrided cases that result in duplex-layered composites with high micro abrasive wear resistance are established.

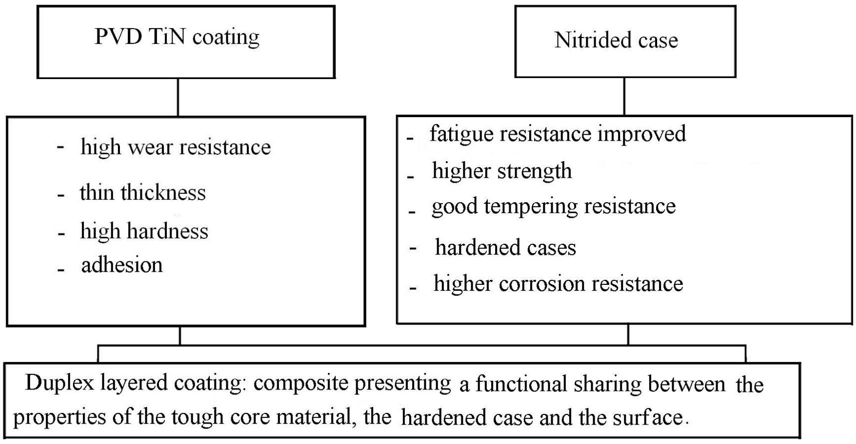


Figure 1. Functional properties of a duplex layered TiN coating obtained by means of the combination of plasma nitriding and PVD-TiN deposition, after Höck et al[12].

2.1 Abrasive wear resistance of steels coated with hard coatings

Abrasive wear resistance of a hard coating is a function of the materials used as coating and substrate, as well as their processing, according to Posti and Nieminen[15]. Improvements in adhesion and wear resistance of a hard coating with increasing the substrate hardness are associated with the increase in load-carrying capacity of the substrate [4, 16, 17].

In duplex layered composites, obtained by a combination of plasma nitriding and PVD-TiN, nitrided case has an intermediated hardness between TiN coating and unnitrided steel core, acting as a supporting zone, improving the adhesion and wear resistance of the coating deposited subsequently[5]. Researches[4,12-14,18] have demonstrated that previous processing determines the properties of the duplex-layered composite, being important that after nitriding the surface to be coated is well clean, free from oxide layer and compound layer.

Trezona and co-workers[19] studied the effect of some parameters of the micro-scale abrasion test on the wear mechanisms of both steel substrates and single layered TiN coatings. It was found that the dominant wear mechanism depends on the applied normal force, concentration of the abrasive particle in slurry, hardness of the substrate material and factors related to type, size and shape of the abrasive particles. As well as Gates[20], these researchers presented a critical analysis of the traditional classification of the abrasive wear in two-body and three-body mechanisms and consider more suitable an abrasive wear classification in two-body grooving and three-body rolling.

For tool steel quenched and tempered to a hardness of 775 HV, Figure 2 shows a map of wear mechanism by Trezona and co-workers.

A two-body grooving wear mechanism is dominant when high loads or slurries with low abrasive concentration are used. In grooving wear, abrasive particle, which acts as fixed indenter, is embedded in the surface of the testing ball. As a result, in direction of the sliding a series of parallel scars is produced.

In rolling wear, the abrasive particle rolls on the surface of the sample, producing a heavily deformed, multiply indented wear surface. In such wear mechanism, no evident surface directionality is verified. The rolling which is characteristic of the three-body abrasive wear is dominant when slurries with high SiC concentrations are used and low testing loads are applied. In such mechanism, the motion direction of the sphere on the surface of the sample is not possible to distinguish. The SiC particles roll on the sample surface, causing a great amount of indentations. Increasing testing load and abrasive concentration leads to the rolling mechanism still operate because the indentation of the sample surface for each one of abrasive particles occurs slightly.

A transition from rolling to grooving can be verified in Fig. 2. In this transition region, Trezona and co-workers show scars in center of the wear crater and indentations in its periphery. Up to loads of 1 N, the simultaneous occurrence of both wear mechanisms can be predicted by a linear equation, in which the volumetric fraction of the abrasive particles must be about seven times the applied load.

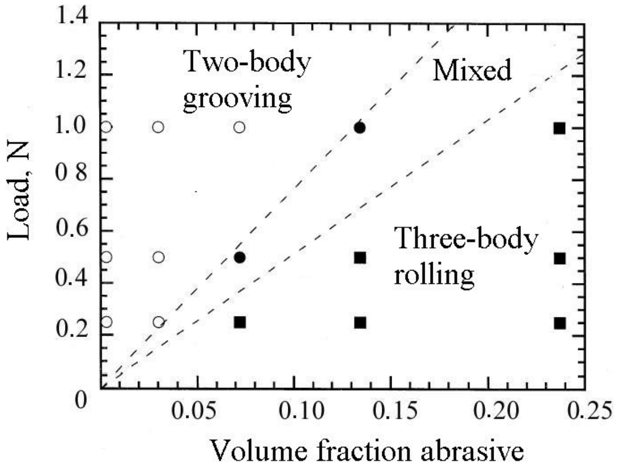


Figure 2. Wear mechanism map as a function of SiC concentration and testing load for quenched and tempered steel, after Trezona et al[19].

2.2. Abrasive Wear of TiN coating

After micro-scale abrasion tests of single layered TiN coatings, Rutherford and Hutchings[21] and Batista and co-workers[22] showed that the aspect of the inner wear surface is seemed to that produced between outer (worn coating) and inner surfaces (worn substrate). For abrasive wear controlled by grooving, the scars formed in the worn coating are narrower and less spaced than that produced in the worn substrate, indicating the scars produced through either grooving or micro cut become less deep in the coating. Batista and co-workers show that with increasing the load-carrying capacity of the substrate, which can be reached by means of a previous plasma nitriding treatment, the rolling mechanism tends to control the wear process, being observed indentations both in coating and in nitrided case. Thus plasma nitriding of the AISI H13 tool steel is effective, promoting a transition from grooving to rolling, further enhancing the wear resistance of duplex treated composites.

Rickerby and Burnett[23] show that the load-carrying capacity of single layered hard coatings and, consequently, their wear abrasive resistance can be improved by increasing the coating thickness itself. These researchers show that very thin coatings (thickness lesser than 1μm) tend to fail by micro cut or grooving that takes place during intersections between scars produced by abrasive particles. On the other hand, thicker coatings (1-3μm) support elastically the contact stresses, detaching from substrate by micro polishing or rolling mechanism without significant plastic deformation of the substrate. However, when thickness of the coating exceeds a certain value (about 3μm), these researchers show that the wear ratio tends to increase. According to Burnett and Rickerby[24], this effect is associated with the coating microstructure, as the increase in thickness of the coatings is followed either by a reduction of their density – due to an increase in porosity degree - or by an increase in grain size of the coating material. Hedenqvist and co-workers[25] also verified that dominant wear mechanism of single layered TiN coatings, deposited on ASP 30 HSS substrates, depends on the coating microstructure in terms of degree of porosity and grain size. They verified that very thin coatings tend to failure through micro cut (grooving) mechanism, while thicker coatings cohesively worn by micro polishing (rolling) and micro cut (grooving) mechanisms.

3. Experimental Procedure

3.1. Substrate Material

Cold working tool steel (AISI D2) substrates were used in the present investigation. Slices 30 mm in diameter and 2.5 mm in thickness were cut from annealed bars. These slices were machined and ground, then quenched and tempered. Table 1 shows cycles of the heat treatments modified to avoid the overtempering of the AISI D2 tool steel cores during duplex treatments.

3.2. Duplex treatment

Before nitriding, the previously quenched and tempered AISI D2 tool steel substrates were re-ground and mechanically polished to a surface roughness (Rz) of 0.12 µm, acquiring a mirror-like aspect. Additionally, they were degreased and cleaned with ethanol in an ultra-sound apparatus. A hot wall pulsed plasma nitriding unit manufactured by ELTROPULS GmbH was used for nitriding. Sputter cleaning was carried out at 400^{o}C in a pure hydrogen atmosphere at a pressure of 70 Pa, for 30 min. Table 2 shows the main plasma nitriding conditions used. A set of specimens was nitrided in a gas atmosphere containing N_2 - 5%vol. + H_2 - 95%vol. Two more series of experiments were undertaken using gas atmospheres containing N_2-vol.10% + H_2-vol. 90% and N_2 –vol.20% + H_2–vol. 80%. All specimens were cooled down to room temperature inside the vacuum chamber under a nitrogen pressure of 100 Pa.

The PVD TiN deposition was performed in a BALZERS PVD ion-plating unit with an evaporation source assisted by electrical arc. The substrate temperature was kept between 450 and 500 °C. The other conditions being: deposition time: 90 min, nitrogen pressure: 18 x 10^{-4} mbar, DCP arc current: 200 A, and the work piece negative BIAS: 50 V. Using such conditions, *TiN* coatings of about 5.0 µm in thickness were obtained.

Table 1. Heat treatment conditions.

Material	Austenization	Tempering	Resulting Hardness
Tool steel AISI H13	1020 °C, 30 min/oil	(2x2h)/600°C air	47-49 HRC
Tool steel AISI D2	1080 °C, 30 min/oil	(2x2h)/540°C air	57-58 HRC

- *All heat treatments were performed in a horizontal furnace fitted with a vacuum-tubular chamber where sample temperature was external and asymptotically controlled via thermocouples.*

Table 2. Plasma nitriding parameters.

Temperature (^{o}C)	520
Pressure (Pa)	250
Pulse duration (µs)	250
Pulse repetition (µs)	50
Voltage (V)	500

3.3. Measurements of surface hardness and thickness of the nitrided cases

To assess the surface hardness of the duplex-layered TiN coatings and respective nitrided cases, a Fischerscope *H100* depth sensing indentation apparatus, equipped with a Vickers indenter, manufactured by Helmut Fischer GmbH, was used. Indentation data were analyzed using an analytical procedure described elsewhere[26] based on an analytical approach by Oliver and Pharr[27].

Additionally, the nitriding depths (thicknesses of the nitrided cases) also were measured by Vickers depth sensing indentation technique, using testing loads of 50 mN. These measurements were established according to DIN 50.190 standard[28]. Table 3 shows the main testing conditions.

Table 3. Test conditions used for hardness determinations.

Number of indentations	20
Spacing between indentations	10 µm
Loading time, loading rate	50 s, d√P/dt
Peak load	50 mN (nitrided cases)
	30 mN (TiN coatings)
Dwell time at maximum load ("creep")	30 s
Unloading time, unloading rate	30s, d√P/dt

3.4 - Microstructural characterization of the single and duplex-layered coatings

X-ray diffraction analyses and SEM observations were used to characterize the structures of the nitrided cases, single and duplex layered coatings. The X-ray analyses were performed using a *Philips PW1810* diffractometer with CuK_α radiation, which has a shallow (3-5 μm) penetration for nitrides, carbides and iron. For microstructural characterization, slices were cut from nitrided samples, as well as from single and duplex layered coatings samples, and than mounted in Bakelite together with a thin plate of nickel so that bow-border effects during metallographic preparation were minimized. All samples were etched in 4% Nital.

Based on these analyses, threshold nitriding potential curve for AISI D2 tool steel at 520 ^{0}C was built.

3.5 - Micro-scale abrasive wear test

A “free ball” micro-abrasion tester CSEM CALOWEAR was used to assess the wear behavior of the single layered and duplex-layered coatings. Introduced in 1996 by Rutherford and Hutchings[21], micro-scale abrasion test is an alternative abrasive wear test developed for coatings, which allows evaluating simultaneously the wear resistance of both substrate and coating in a serial test.

All tests were undertaken using a hardened steel sphere 25.4 mm in diameter, with sliding speed of 0.1 ms^{-1}, normal force applied on the samples surface of 0.27 N, SiC abrasive (~4.5 μm) slurry with initial concentration of 0.75 g/ml (volumetric fraction of 0,189) and total sliding distances from 13 to 97 m.

For each distance of sliding, the total wear volumes (V_t) of the single and duplex-layered coatings were determinated by means of the following equation[21]:

$$V_t \cong \frac{\pi . b^4}{32 \phi} \qquad (1)$$

where *b* is the diameter of the worn crater produced on coating surface and ϕ is the diameter of the testing sphere.

The worn surfaces were examined by optical microscopy (OM) and scanning electron microscopy (SEM).

Micro-scale abrasion tests also were used in conjunction with SEM for measuring the TiN film thicknesses of the single and duplex-layered TiN coatings.

4 - Results and discussion

4.1. Plasma nitriding response prior to coating process

4.1.1 Microstructure and thickness of the nitrided cases

Figure 3[29] shows the threshold nitriding potential curve experimentally established for AISI D2 tool steel at 520 ^{0} C. The characterization of the nitrided cases in terms of their phases and thicknesses is shown in Table 4.

When the combination of nitrogen contents (i.e. the N_2:H_2 ratio) and nitriding times is above the threshold value – represented by the curve in Fig. 3 –, a white layer (compound layer) consisting of γ- Fe_4N and ε-$Fe_{2-3}N$ iron nitrides forms on the surface of the steel, e.g. Figure 4(a). Below this threshold value, compound layer does not form on the steel surface, e.g. Figure 4(b).

As one can see in Tab. 4, plasma nitriding carried out in N_2-5% content during 42 min avoids both CrN growth and iron nitride formation.

Increasing the nitriding time promotes a disappearance of large M_7C_3 carbide on nitrided case surface. Although compound layer is not formed on surface of the steel nitrided for 3 and 6 h, X-ray diffraction analyses have shown a presence of *CrN*. Plasma nitriding treatments carried out using nitriding time of 11 h result in compound layer formation, in addition to the growth of coarser CrN phase.

Increasing the nitrogen content from 5 to 10% in gas atmosphere reduces incubation period for iron nitride formation, as one can see in Fig. 4. Compound layer formation can be also suppressed using N_2 -10% containing atmospheres and short times; however, for nitrided case produced for 42 min X-ray results pointed out *CrN* precipitates and SEM analyses shows that these nitrides are very large. Using nitriding times of 3, 6 and 11h resulted in further growth of the coarser CrN and compound layer formation.

Using 20%-N_2 in gas atmosphere leads to a sharply decrease in incubation period for compound layer formation. A surface microstructure consisting of compound layer is observed when nitriding time of only 1 h is used.

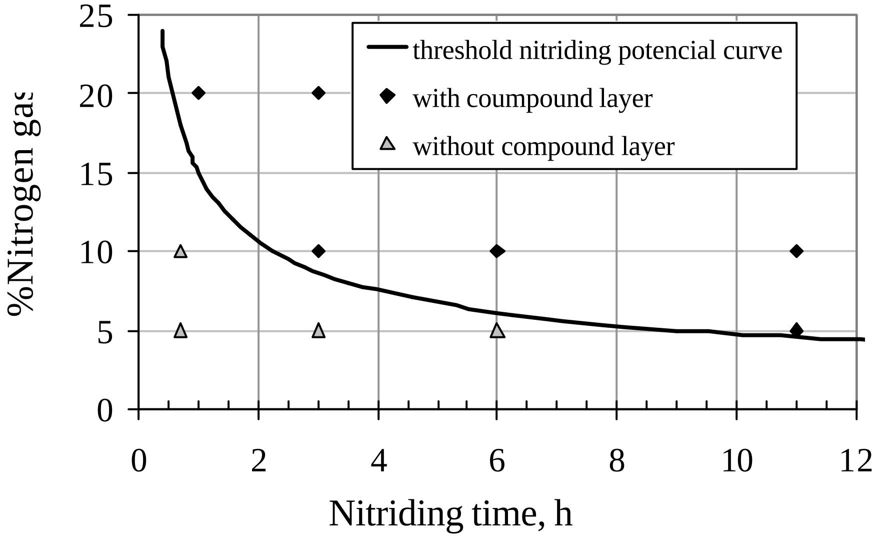


Figure 3. Threshold nitriding potential curve for AISI D2 tool steel at 520 ° C, after Franco Jr.[29]

Table 4. Microstructure and thickness of the nitrided cases obtained at 520°C as a function of the nitrogen content and nitriding time.

Nitrogen content, vol %	*Nitriding time, h*	*Microstructure of the nitrided case*	*Total thickness of the nitrided case, mm*
5	0.7 (42 min)	Fe-α(N) matrix + M_7C_3 carbide + very thin CrN (precipitated up to 800nm from surface)	23
	3 h	Fe-α(N) matrix + coarser CrN (up to 7 µm from surface)	34
	6 h	Fe-α(N) matrix + coarser CrN (up to 12 µm from surface)	57
	11 h	$Fe_{2-3}N$ + Fe_4N (very thin and irregular compound layer) + CrN (up to 30 µm from surface) + iron nitride (in grain boundary)	92
10	0.7 (42 min.)	Fe-α(N) matrix + CrN (up to 2 µm from surface)	40
	3	$Fe_{2-3}N$ + Fe_4N (irregular compound layer) + CrN(up to 30 µm from surface) iron nitrides (grain boundary)	67
	6	$Fe_{2-3}N$ + Fe_4N (compound layer) + CrN (up to 60 µm from surface) + iron nitrides (grain boundary)	93
	11	$Fe_{2-3}N$ + Fe_4N (compound layer) + CrN (up to 110 µm from surface) + iron nitrides (grain boundary)	143
20	1 h	$Fe_{2-3}N$ + Fe_4N (compound layer) + CrN (up to 35µm from surface) + iron nitrides (grain boundary)	50
	3 h	$Fe_{2-3}N$ + Fe_4N (compound layer) + CrN (up to 60µm from surface) + iron nitrides (grain boundary)	76
	6 h	$Fe_{2-3}N$ + Fe_4N (compound layer) + CrN (up to 89µm from surface) + iron nitrides (grain boundary)	103

A nitrided case with 23 µm in thickness, without coarse precipitates of the CrN phase and without iron nitrides, is obtained when N_2 5%-vol containing atmosphere and nitriding time of only 42 minutes are used. With the increase of the nitriding time to 3 h and 6 h nitrided cases with 34 and 57 µm, respectively, are produced. However, a growth of coarser CrN precipitates is observed from the surface of these nitrided cases. Nitrided cases with thicker thickness can be obtained using longer times (11h), as one can note in Tab. 4; however, under this condition, it is verified iron nitrides in its upper portion and in grain boundaries.

More thickness values can be attained using higher nitrogen contents; e.g. the use of nitrogen contents of 5% leads to the formation of a nitrided case with 23 µm in thickness, while nitrogen contents of 10% produce a nitride case with 40 µm. As seen in Tab. 4, CrN precipitates also reach more depths. These precipitates are found up to 800 nm from surface of the steel treated with 5% nitrogen for 42 min while for the steel treated with 10% nitrogen for 42 min, the growth attains up to 2 µm in depth. Further increasing in thickness of nitriding case is possible to obtain when longer nitriding times are used. However, as one can see in Fig. 3, incubation period for growing iron nitrides on nitrided surface is reduced, resulting in a nitrided case with compound layer and grain boundary precipitates.

The greatest thickness of nitrided case is reached when 20% nitrogen is used. However, together with CrN precipitates, both a compound layer and a net of iron nitride grow in nitrided case microstructure, in a very short time of nitriding. This is verified after only 1h of treatment. Therefore, increasing nitrogen contents result in very thick compound layers because the incubation period to form iron nitrides becomes very short when high nitrogen-containing atmospheres are used.

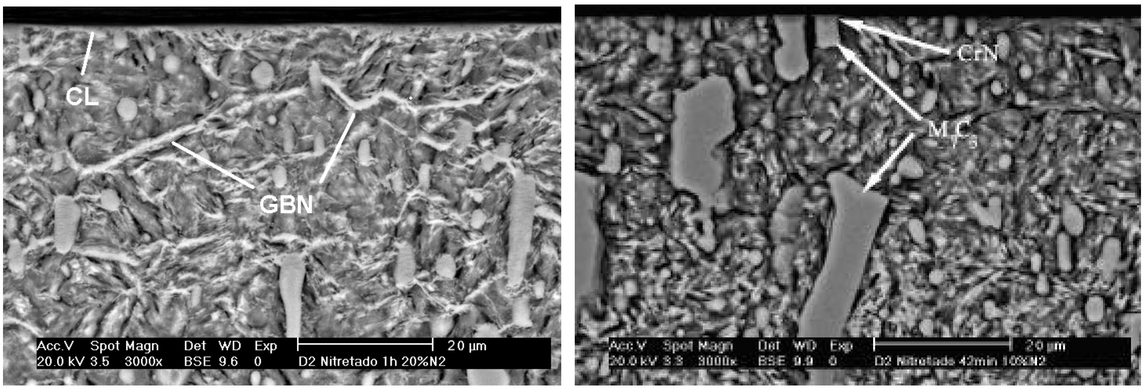


Figure 4. (a) Nitrided case obtained above threshold nitriding potential curve; note a compound layer (CL) on surface of the steel and a net of iron nitride in grain boundary (GBN). (b) Nitrided case obtained below threshold nitriding potential curve; an absence of iron nitride as well as grain boundary precipitate, can be noted in nitride case; however, coarser CrN phase can grow in upper portion of the nitrided layer by increasing the time of nitriding.

4.1.2 – Surface Hardness

Figure 5 shows the surface hardness of nitrided cases obtained as a function of nitriding time, using 5, 10 and 20%-vol N_2 containing gas atmospheres. Clearly, high surface hardness can be acquired using short-time nitriding and low nitrogen contents in gas atmosphere.

One can note that for low nitrogen content (5%N_2) in gas mixture and a short time (42 min) of nitriding, a thin nitrided case (23 µm) with maximum surface hardness (1400 HV) can be produced. After 3 h and 6 h, relatively thick nitrided cases, with hardness values of 1068 HV and 1081 HV, respectively, are produced. Thus increasing nitriding times lead to a significant drop in the hardening effect. Even though low nitrogen contents in gas atmosphere are used, increases in the thickness of the nitrided cases are followed by a surface softening, which is associated with coarser CrN growth, as pointed out X-ray and microscopy analyses. According to Lightfood and Jack[30], the growth of coarser CrN has a non-hardening effect on the nitrided chromium alloys. During treatment the steel matrix loses chromium and the growth of the *CrN*–phase renders larger carbides (M_7C_3) unstable, resulting in softening of the nitride case.

For longer nitriding times (more than 11 h), raising the surface hardness (to 1171 HV) is again verified due to the formation on nitride case surface of a compound layer with a very irregular thickness.

As one can note in Fig. 5, the increase of the nitrogen content to 10%, after 42 min results in nitrided case with surface hardness relatively minor than that produced using 5% nitrogen in gas atmosphere (1325 HV against 1400 HV). Increasing nitriding times result in nitrided cases with surface hardness of 1200HV. This value tends to keep constant. It means that both intervals for softening related to the growth of CrN phase and for formation iron nitrides are very short, when 10% N_2 containing-gas mixtures are used.

Fig. 5 also shows that a surface hardness of 1200 HV can be attained by using 20%N_2-containing atmospheres and very short nitriding times, due to the presence of a compound layer of considerable thickness on the surface of the steel.

Therefore, increasing nitrogen contents result in a marked displacement of the initial portion of the surface hardness curves downwards because the growth kinetics of coarser *CrN* phases, together with the compound layer, increase very rapidly.

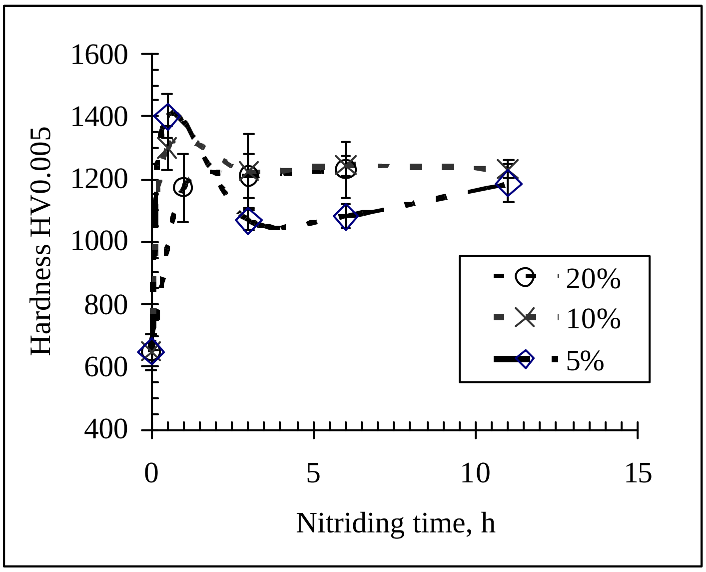


Figure 5. Effect of the nitrogen content and nitriding time on surface hardness of the nitrided cases.

4.2 - Microstructure and hardness of the duplex layered coatings

For nitrided cases obtained below threshold nitriding potential curve, i.e. without compound layer formation, the microstructures and the depths of nitride cases shown in Tab. 1 kept unchanged after PVD coating process.

However, significant changes are verified in microstructures of the duplex-layered coatings produced from nitrided cases with greater thicknesses of compound layers. It was verified that the thicker the compound layer, thicker is black layer produced and greater volume wear. An example of nitride case that has such characteristics is shown in Figure 6, prior and after coating process. One can see that the black layer forms next to the interface with the coating.

For nitrided cases produced in substrates of low chromium steel, Sun and Bell[4] show that sputtering cleaning carried out in the PVD vacuum chamber produces this type of layer. This is due to iron nitrides Fe_4N and $Fe_{2-3}N$ have low chemical stability at 500 ^{o}C during ion bombardment, resulting in transformation of the outer part of the compound layer in a α-Fe phase of low hardness.

Figure 7 shows hardness profiles for the nitrided case shown in Figure 6. As expected, compound layer resulted in an interlayer (black layer) with low hardness.

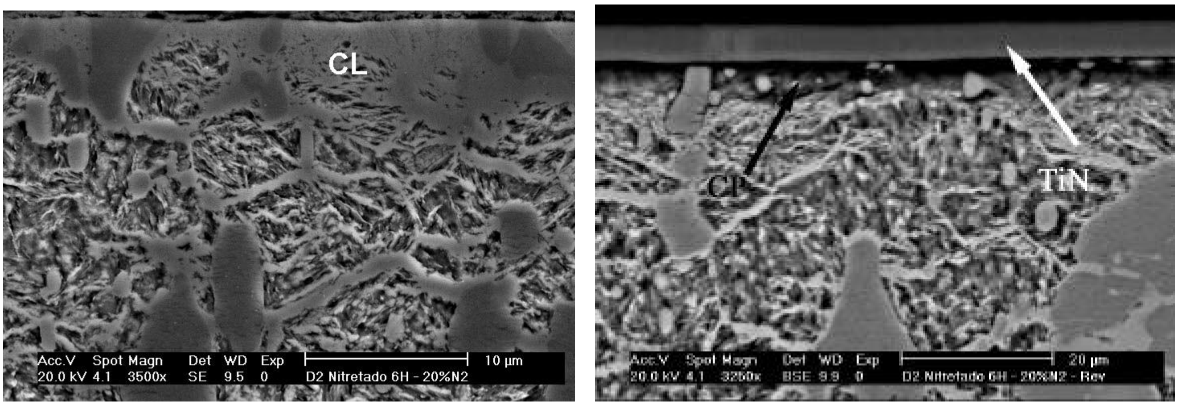


Figure 6. (a) Microstructure of a nitrided case produced above threshold nitriding potential curve, i.e., with compound layer (CL): (a) prior to the TiN coating process; and (b) after the coating process. Note upper portion of the compound layer was transformed in "black layer" (CP).

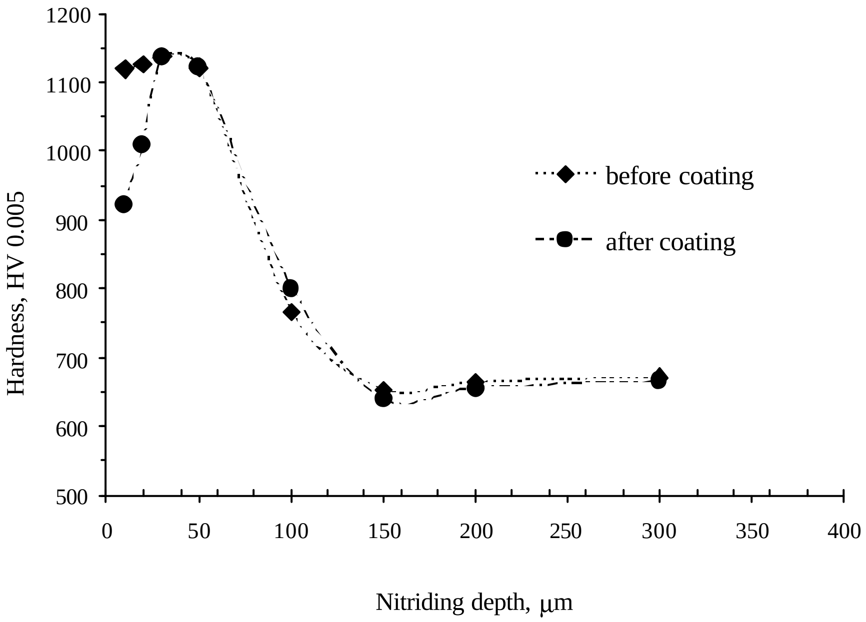


Figure 7. Hardness profiles of the nitrided case produced above threshold nitriding potential curve (20%N_2 and 6h): (a) prior (b) and after the PVD coating process.

4.3 - Abrasive wear resistance of the duplex- layered coatings

The wear volume as a function of sliding distance is shown in Figure 8 for AISI D2 substrate, single layered TiN coating and three duplex layered TiN coatings. A notable reduction on wear volume can be reached when TiN coatings are applied on surface substrate of AISI D2 tool steel, as one can note.

Comparing the AISI D2 substrate with single layered TiN coating, one can note that the wear resistance can be improved markedly with the application of the single layered TiN coating. After a sliding wear of 97 m, wear volume falls from 0.0340 mm^3 to 0.0318 mm^3.

Further increasing in the wear resistance of the composite can be reached when a duplex-layered composite with thin thickness of nitrided case is produced. A relatively thin nitrided case with 23 µm in thickness, with maximum hardness of 1400 HV, is sufficient to yield high abrasive wear resistance, as wear volume is of only 0.0299 mm^3. This indicates that the nitrided case of this composite has a high load-carrying capacity.

Even though the thicknesses of nitrided case are increased to 34 or 57 µm, a slight lost on wear resistance is verified (0.0315 mm^3 or 0.0312 mm^3, respectively). This decrease in wear resistance is related to *in situ* heterogeneous precipitation of coarse *CrN* on the sample surfaces, which reduces the surface hardness of the nitrided case to about 1070 HV.

The wear volume progressively increases when thickness of the nitrided case is increased to 92 µm. This nitrided case has grain-boundary nitrides and a white layer containing both ε and γ' phases, while nitrided case with 23 µm in thickness has a structure with no traces of white layer, coarse CrN precipitates or grain-boundary nitrides. As shown in Fig. 8, the duplex-layered composite having the latter structure in interface presented the lowest wear resistance (0,032 mm^3).

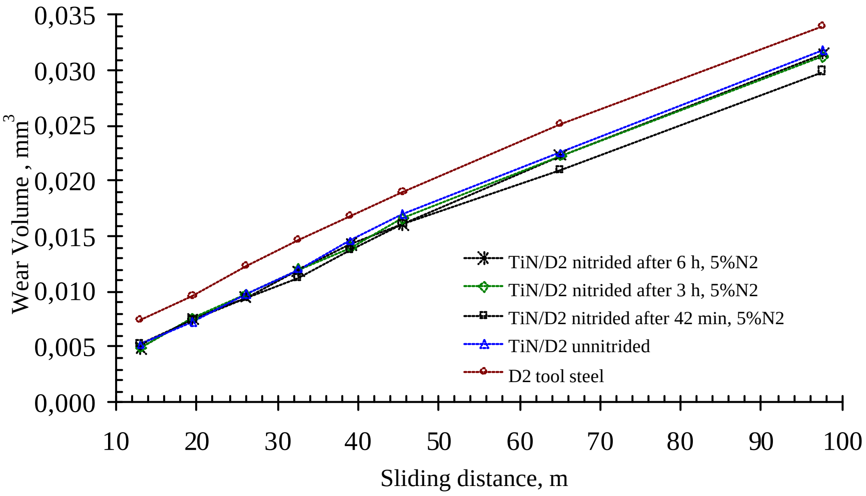


Figure 8. Wear volume of duplex layered TiN coatings deposited on AISI D2 tool steels nitrided during 42 min, 3 h, 6 h and 11 h, in 5% N_2, at 520°C.

Increasing nitrogen contents in gas mixture lead to the formation of nitrided cases with more thickness. However, the increase in thickness is followed by the decrease in surface hardness due to growth of coarser CrN or formation of iron nitrides, which transform in black layer during PVD process. As a result, a duplex-layered composite with low load-carrying capacity and low wear resistance is produced.

These results are in accordance with those reported by Kadlec et al.[14] and Höck et al.[9]. They show that TiN coatings deposited on top of pre-nitrided tool steels, at 500-520 °C, for short-times of nitriding, in low nitrogen containing gas atmospheres have their tribological properties optimized. Nitrided cases with the maximum surface hardness (1400-1550 HV) were produced during short times. Increasing times of nitriding or nitrogen contents in the gas mixtures resulted in duplex-layered composites with inferior tribological properties.

Therefore, increasing thickness of the nitriding case is not a good choice to further improve the wear resistance of duplex layered TiN composites formed on AISI D2 tool steel. Microstructures of these nitrided cases can be consisted of either coarser CrN precipitates or grain boundary nitrides or white layer, which is transformed in black layer during PVD process, reducing significantly loading carrying capacity of the coatings, as a result, their tribological properties.

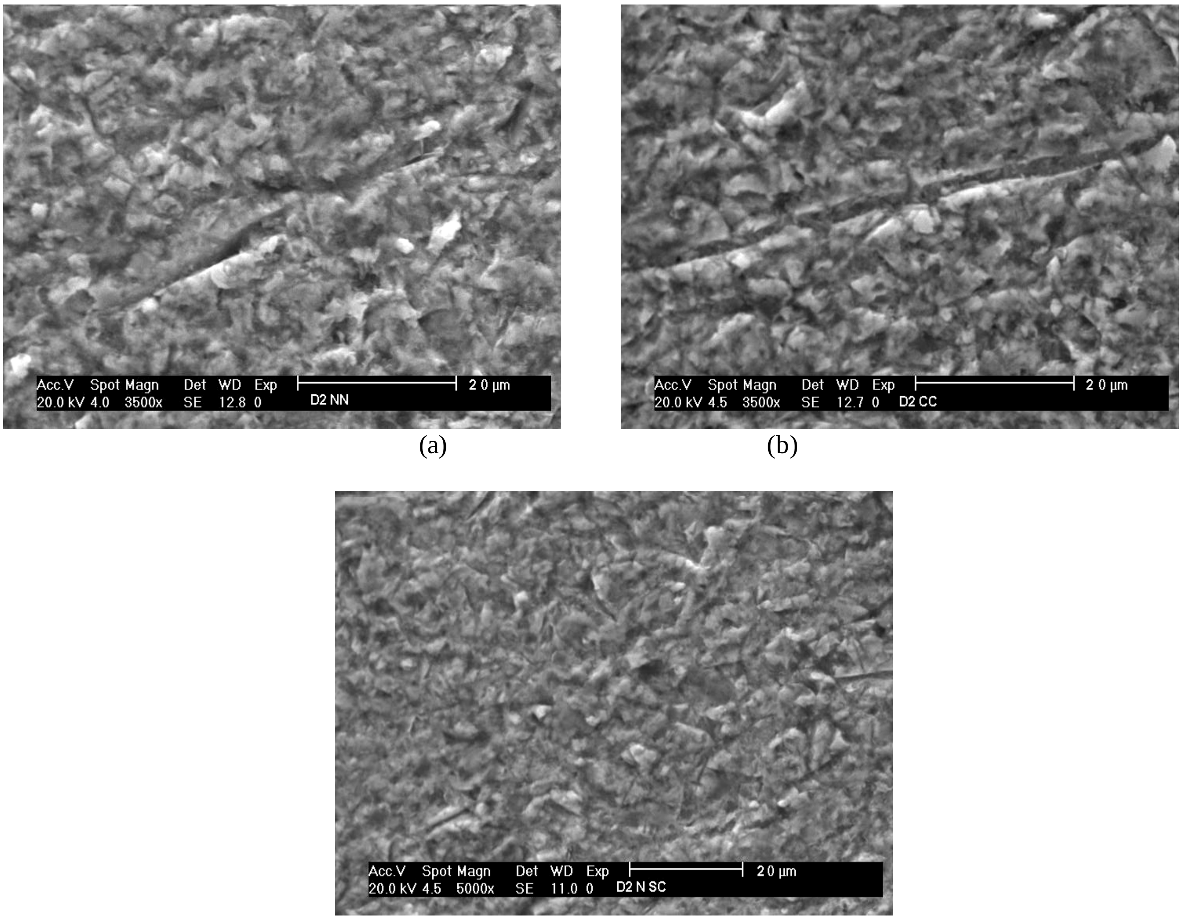
4.5 - Wear mechanisms of the coatings

Figure 9(a) shows the worn surfaces produced after a sliding distance of 195 m, in the substrate of a single layered TiN coating and Figure 9(b) and 9(c) shows the worn surfaces produced in the nitrided cases of duplex layered composites, with and without a black layer, respectively.

For the single layered TiN coating, one can note that sliding direction of testing sphere on the worn surface is not completely evidenced. Some scars in some directions are observed, as well as a great amount of indentations. Therefore, abrasive wear mechanism is controlled simultaneously by rolling and grooving. This behavior is typical for abrasive wear occurring within a transition region where both grooving two-body and rolling three-body mechanisms are acting. It was observed that this surface is very similar as compared with that produced in outer worn surface (worn coating). However, the scars formed in the worn coating are narrower and less spaced than that produced in the worn substrate, indicating the scars produced through either grooving or micro cut become less deep in the coating.

For duplex-layered coating without black layer, rolling is the mechanism that controls the wear process because, in contrast to the great amount of indentations, very small scars can be seen in Figure 9(c).

For duplex-layered TiN coating with black layer, in Figure 9(b) one can see that the scars produced by the abrasive particles are similar to those produced in Figure 9(a). This indicates that the duplex layered coating with black layer in interface is grooved by abrasive particles in the same extension and, consequently, resulting in a wear volume very close to that of single layered coating. For single layered TiN coating, therefore, using testing load of 0,29N and slurry SiC concentrations of 0,75 g.cm^{-3} (volume fraction of 0,189), both wear mechanisms (transition region in Figure 2) will take place.



(a) (b)

(c)

Figure 9. Worn surfaces of the: (a) AISI D2 substrates coated with a single layered TiN coating, (b) duplex layered coating with a black layer) (c) duplex layered coating without black layer).

5 - Conclusion

- Nitrided cases with thin thickness (23 µm), which can be produced using short times and low nitrogen contents, are sufficient to guarantee a high wear abrasive resistance to duplex *layered TiN coating*.
- A duplex-layered composite with a nitrided case presenting high surface hardness has its load-carrying capacity improved. This composite tends to suffer wear by the rolling (micro polishing) wear mechanism.
- For duplex-layered composites with nitrided case of greater thickness, the decreases of the load carrying capacity and, as a result, of the wear resistance are due to microstructural changes that take place on nitrided case during either nitriding or coating process.
- The drop in surface hardness of the nitride case due to growth of coarser CrN precipitates leads to a decreasing of the load carrying capacity of the nitride case, in spite of its greater thickness. The produced composites tend to be worn through the mechanisms of two-body grooving and three-body rolling.
- The presence of a black layer in the nitrided case, independent on its thickness, causes a sharply decrease in surface hardness of this nitrided case, lowering the load carrying capacity of the duplex layered composite in the interface *TiN* coating/nitrided case.

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