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Tribological properties of unbalanced magnetron sputtered nano-scale multilayer coatings TiAlN/VN and TiAlCrYN deposited on plasma nitrided steels

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Abstract: Unbalanced magnetron sputtered multilayer coatings TiAlN/VN and TiAlCrYN grown on pulse plasma nitriding pre-treated low alloy steel P20 have been characterised by using X-ray diffraction (XRD), scanning electron microscope (SEM), micro-indentation, scratch and pin-on-disc wear tests. A 160-Å-thick nitrided case was formed on the steel surface containing a pure Fe₃N and Fe₄N compound layer and showing hardness up to 8.5 GPa, which led to improved load bearing ability and adhesion behaviour of the coating-substrate system. The coatings deposited on non-nitrided P20 showed poor adhesion and severe cracking and spalling wear. In contrast, the TiAlN/VN and TiAlCrYN deposited on nitrided substrates showed only mild polishing and oxidation wear mechanisms and extremely low wear coefficients in the scales of 10⁻¹⁷ and 10⁻¹⁶ m³ N⁻¹ m⁻¹, respectively. In drilling solution treated 304 austenite stainless steel, the TiAlN/VN-coated drills showed a lifetime 50% longer than TiAlN-coated drills. Plasma nitriding pre-treatment led to further increases of lifetime by 33%.

Key Words: Wear resistance; Wear mechanisms; Multilayer coatings; PVD; Pulsed plasma nitriding

1. Introduction

Transition metal nitride hard coatings fabricated by physical vapour deposition (PVD) have advanced from binary TiN and ternary TiAlN [1,2] to the multicomponent nitride TiAlCrYN [3,4] and nano-layer structured nitrides such as TiN/NbN and TiN/VN [5], TiAlN/VN [6–8] and TiAlN/CrN [9,10]. These technological advances have led to enhanced properties aiming at better tribological performance. For example, the incorporation of yttrium in the TiAlCrYN showed improvement in the oxidation resistance of the coating, with the onset-oxidation temperature being 950 °C [4]. The TiAlN/VN coatings, on the other hand, have doubled the hardness of the associated monolithic coatings TiAlN and VN. In particular, the TiAlN/VN has shown low friction coefficients in the range of 0.5 and low wear coefficients typically in the range of $10^{-17} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}$. However, most of previous results were obtained on the coatings deposited on cemented carbides and hardened tools. Little is known about the mechanical and tribological properties of these coatings when they are deposited on relatively soft substrates, for example, medium-carbon and low-alloyed steels.

When a hard coating is deposited on a low-alloyed and medium-carbon steel, one can expect that the coating substrate hardness compatibility should be enhanced to resist mechanical failure. This enhancement has in fact been achieved by a duplex surface engineering technique of ion nitriding or plasma nitriding and PVD hard coating, i.e. by creating a transition layer of intermediate hardness between the substrate and the hard coating [11–15]. Nitriding pretreatment has been applied to low-alloy structural steel [11,13,16], austenite stainless steel [12] and high speed steel (HSS) [13,17,18]. Scientific interests in nitrided steels have been addressed in the microstructural characterisation [19–21] and mechanical and tribological evaluation [11,13,16,18]. Previous published results were mostly on the duplex treatments including the deposition of TiN or CrN coatings. In case of duplex processes involving advanced multicomponent and multilayer coatings, however, one may expect similar improvement in both the mechanical properties and the tribological performance, whereas experimental confirmation is still necessary.

This paper presents original experimental research on the mechanical properties and wear performance of the newly developed TiAlN/VN and TiAlCrYN coatings which were deposited on a low alloy cold-mould steel P20 following a pulse plasma nitriding pre-treatment. The results are also compared to those obtained on duplex-treated high speed steel M2. Finally, the promising effect of plasma nitriding pre-treatment on the drilling performance of TiAlN/VN coated drills is reported.

2. Experimental details

2.1. Sample preparation

Metallographically polished coupons of P20 steel (C 0.32%, Mn 0.80%, Cr 1.60%, Mo 0.40%, and balance Fe) and M2 steel (C 0.8–0.9%, W 6–6.75%, Mo 4.75–5.5%, Cr 3.75–4.5%, V 1.75–2.05%, and Fe in balance) were used as substrates. Nitriding pre-treatment of the

coupons was conducted in an industrial pulse plasma nitriding unit at a process temperature 520 °C for 5 h. Parameters applied to the nitriding processes were: sputtering clean time 120 min and temperature 490 °C, N/H ratio 1:1 and total pressure 300 Pa, bias voltage -470 V, pulse duration 50 μs and pulse repetition 150 μs.

The TiAlCrYN and TiAlN/VN coatings were deposited in an industrially sized Hauzer HTC 1000-4 ABS coater [6–8]. Deposition procedures included surface cleaning, metal ion etching in steered cathodic arc mode, UBM (unbalanced magnetron) sputtering deposition of a nitride base layer, and UBM deposition of multilayer component and multilayer coatings. Both the as-polished and pre-nitrided coupons were cleaned and dried in an industrial cleaning line, using alkali detergents and deionised water, before they were mounted into the deposition chamber. In the metal ion etching stage, V⁺ or Cr⁺ metal ion flux was generated by a steered arc discharge and accelerated towards the substrate surface by a negative substrate bias voltage $U_b = -1200$ V such that the metal ion bombardment resulted in good adhesion due to intensive sputter cleaning and ion implantation of the evaporated species Refs [6,22]. After that, a thin (0.3–0.5 μm) base layer (TiAlN for the TiAlCrYN and VN for the TiAlN/VN, respectively) was deposited by reactive UBM sputtering in a mixed N₂ and Ar atmosphere in total pressure control mode. In the final stage of deposition of TiAlN/VN, all the four cathodes were operated in UBM sputtering mode to grow multilayer structured TiAlN/VN. Measurements by means of cross-sectional transmission electron microscopy (TEM) and low-angle X-ray diffraction (XRD) have determined the TiAlN/VN bi-layer thickness to be between 3.0 and 3.5 nm. Thus, the 3-μm-thick TiAlN/VN multilayer comprised up to 1000 nano-scale sub-layers of TiAlN/VN. In the deposition of TiAlCrYN, the Cr target was operated at 0.5 kW and the yttrium was contained in one of the TiAl targets only. The Cr and Y therefore were incorporated into a layered structure (multilayer period 1.6–1.8 nm determined by low-angle XRD) although the coating exhibits a monolithically grown structure. More details of the nanoscale structure of the TiAlN/VN and TiAlCrYN coating have been published elsewhere [6–8].

2.2. Materials characterisation and tribological evaluation

The sample surfaces were analysed by glancing angle XRD (Cu-Kα radiation), Knoop (and Vicker's) indentation (Mitutoyo HVK-2 micro-hardness tester, load 0.025 or 0.05 kg), and laser surface profilometer to determine the phase composition, surface roughness and hardness, respectively. The microstructure of nitrided cases was observed on chemically etched (5% nital) cross-section using a SEM (scanning electron microscope, Philips XL40).

Coating adhesion was evaluated using a CSEM scratch tester in which a diamond stylus with tip radius 0.02 mm slides on the coated surface at a linearly increasing load (1 N increment per millimetre). The critical scratch load L_c was defined as the load leading to the first occurrence of coating adhesion failure which was observed on the attached optical microscope. Typical scratch failures were examined using SEM. Scratch-induced deformation in the coated surfaces was quantified using the laser surface profiler.

Dry sliding wear tests were conducted in air and at relative humidity 30–35% using a CSEM pin-on-disc tribometer, in which a 6-mm alumina ball slides on the coated disc surface at sliding

speed 0.1 ms^{-1} using normal loads of 5 and 10 N. After each test, the cleaned wear track was scanned using the laser profiler to determine the coefficient of wear. The wear coefficient of the counterpart ball was determined directly by measuring the volume loss by optical microscopy. The worn surfaces were examined by SEM.

Drilling tests were performed on a 15-mm-thick plate of solution-treated austenite stainless steel AISI 304, at spindle speed 1313 rpm (cutting speed 33 m/min), feed rate 0.14 mm/rev, and with 6% emulsion lubricant. TiAlN/VN-coated M2 drills, with and without plasma nitriding pre-treatment, were tested and compared to some commercially available coated (TiCN and TiAlN) drills and uncoated M2 drills. For each coating or the uncoated surface condition, two drills were tested. The lifetime of each drill was quantified by the number of holes drilled.

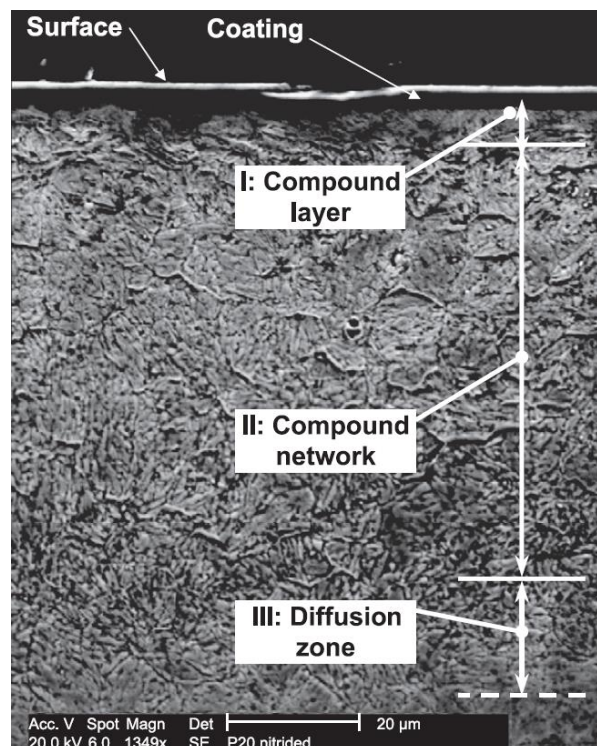


Fig. 1. A SEM micrograph showing the cross-section microstructure of nitrided case formed on P20 surface. Note the subsurface compound layer and the compound network along the P20 austenite grain boundaries.

3. Results and discussions

3.1. Characterisation of nitrided steels

Cross-section SEM observation revealed three zones in the P20 nitrided case: (I) compound layer; (II) compound network; and (III) pure diffusion zone, Fig. 1. The 6.5- μm -thick compound layer on the top of the nitride case was composed purely of $\epsilon\text{-Fe}_3\text{N}$ and $\gamma\text{-Fe}_4\text{N}$ iron nitrides, see Fig. 2. The formation of a pure compound layer was consistent with the literatures [11,16,17,19]. While SEM observation only showed uniform fibre-like morphology of the compound layer (Fig. 1), no further detailed resolution of the microstructure was available. However, it has been reported in the literature [17] that $\gamma\text{-Fe}_4\text{N}$ may cohesively distribute in a $\epsilon\text{-Fe}_2\text{-3N}$ matrix twin grains. In the sub-surface zone, grain boundary networks of iron nitride

compounds were distributed along prior austenite grain boundaries, Fig. 1. In particular, some of the grain boundary

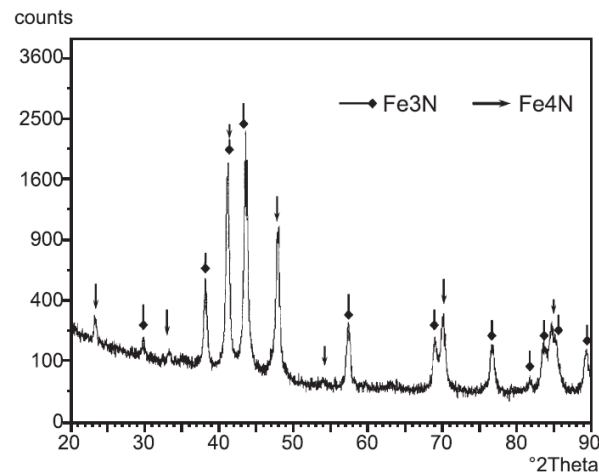


Fig. 2. Glancing angle (18 incidence) X-ray diffraction spectrum of nitrided P20 steel showing both q-Fe₃N and g-Fe₄N iron nitrides. No trace of ferrite phase (α-Fe) was found suggestive of a top compound layer.

networks developed directly from the surface compound layer. The compound network was seen up to a depth of 70 Am.

The nitrided case on M2 steel was only 25 Am thick and was free from compound layer, Fig. 3. The thinner nitride case was related to the higher carbon content of the steel, which led to slower rate of nitrogen diffusion [11]. XRD analysis (not shown here) indicated small quantity of nitride compounds Fe₃N and Fe₄N compared to the predominant amount of the M2 carbides (FeWMo)₆C and VC. The distribution of carbide particles remained uniform as compared between the nitride case and the non-nitrided core. This was indicative of little influence by the plasma nitriding. The hardness depth profiles of the nitrided P20 and M2 steels are shown in Fig. 4. Compared to the core hardness of P20 (4.7 GPa) and M2 (7.9 GPa), the nitrided P20 exhibited hardness values higher than 8.5 GPa in a depth of 50 Am. This is believed to be associated with the formation of nitride compound network, Fig. 1. Following that, a linear slope of hardness from 8.5 to 5 GPa was measured from 50 to 160 Am. According to the measured hardening profile, the nitrided case thickness was ~160 Am. On the surface of the M2, the nitrided case showed hardness over 9 GPa to a depth of 50 Am.

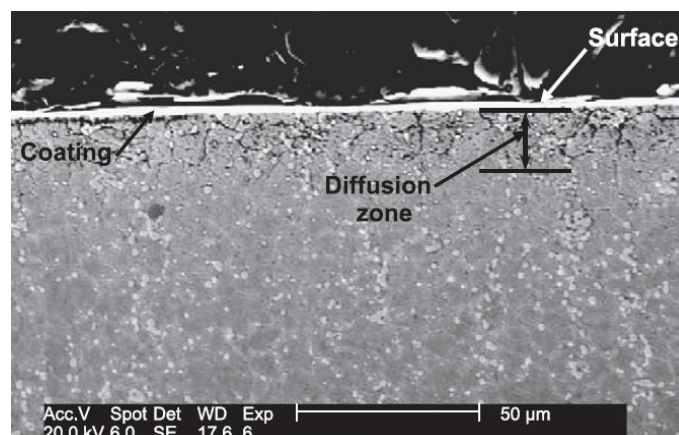


Fig. 3. A SEM micrograph showing the cross-section microstructure of nitrided M2 steel. Note that it contained no compound top layer.

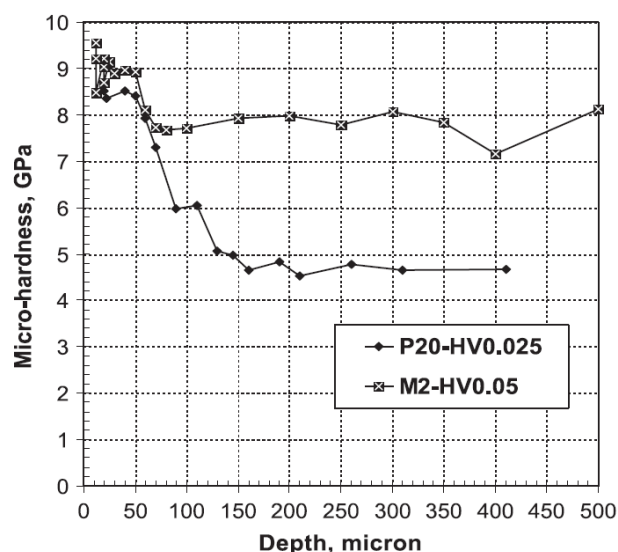


Fig. 4. Micro-hardness depth profile measured in the nitrided case of the P20 steel.

Table 1 Effect of pre-nitriding treatment on surface roughness, adhesion and hardness of coatings

Coating—Substrate	<i>TiAlN/VN</i>				<i>TiAlCrYN</i>			
	R_a [μm]	R_z [μm]	L_c [N]	$HK_{0.025}$ [GPa]	R_a [μm]	R_z [μm]	L_c [N]	$HK_{0.025}$ [GPa]
Nitrided P20	0.341	3.213	55.6 ± 3.1	28.3 ± 1.4	0.378	3.343	73.0 ± 3.6	27.2 ± 3.5
Non-nitrided P20	0.067	1.243	30.0 ± 1.7	22.2 ± 1.0	0.198	2.163	20.7 ± 3.5	26.6 ± 2.5
Non-nitrided M2			46.8 ± 2.1	25.7 ± 1.8			42.3 ± 1.1	23.0 ± 1.6
Nitrided M2							60.4 ± 4.6	28.0 ± 2.1

3.2. Characterisation of the *TiAlN/VN* and *TiAlCrYN* coatings

Table 1 summarises data for the surface roughness, hardness and adhesion of *TiAlN/VN* and *TiAlCrYN* coatings deposited on pre-nitrided and non-nitrided P20. It is interesting to note that the coatings deposited on pre-nitrided soft steel P20 could exhibit equivalent hardness values as compared to those deposited on M2 indicating excellent support of the coating by the nitrided case. Higher hardness values were measured in the *TiAlN/VN* (28.3 GPa) and *TiAlCrYN* (27.2 GPa) deposited on pre-nitrided surfaces than those deposited on non-nitrided surfaces, Table 1. In contrast, the hardness values of the coatings deposited on non-nitrided P20 were 22.2 and 26.6 GPa, respectively. Similar hardening effect was also found in the nitrided M2 steel.

Higher roughness values R_a and R_z were measured on the coatings deposited on pre-nitrided surfaces as a result of preferential ion etching during the plasma nitriding, e.g. 0.341 μm (R_a) and 3.213 μm (R_z) for the *TiAlN/VN* compared to the values of 0.067 and 1.243 μm on the non nitrided sample. Moreover, the *TiAlCrYN* exhibited rougher surfaces than the *TiAlN/VN*. This was attributed to the Cr etching which generated more growth defects than the V etching [23].

The TiAlCrYN and TiAlN/VN deposited on non-nitrided P20 showed poor adhesion with critical adhesion loads being 20.7 and 30 N, respectively, Table 1. In contrast, excellent adhesion

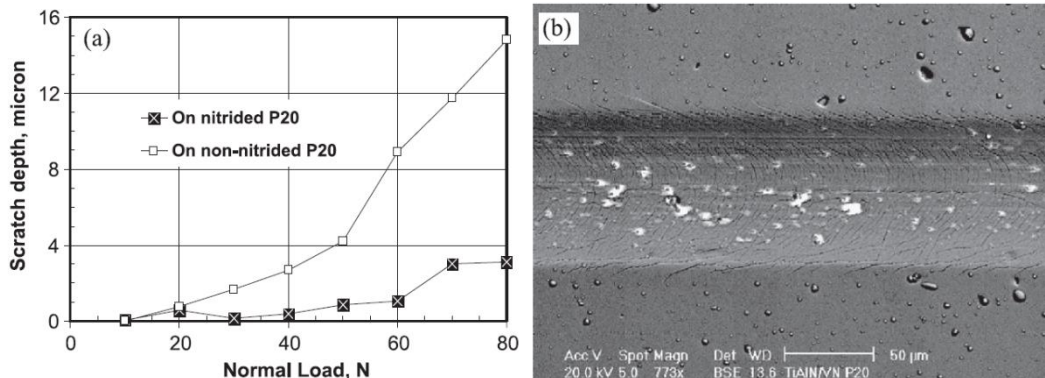


Fig. 5. (a) Scratch-induced plastic deformation in the TiAlN/VN-coated P20 steels plotted against applied normal scratch load. The scratch depth was determined by laser profiling. Note the high load bearing ability of the prenitrided steel. (b) Typical deformation and cracks in the scratch track of TiAlN/VN-coated non-nitrided P20.

has been achieved when the coatings were deposited on pre-nitrided P20, e.g. 73 and 55.6 N for the TiAlCrYN and TiAlN/VN, respectively.

The enhanced adhesion property of the coatings deposited on pre-nitrided steel was correlated to the load bearing ability of the coating-substrate combination. In Fig. 5 (a), the scratch deformation for the TiAlN/VN on non-nitrided P20 showed a linear increase from negligible value at 10 N to 4.2 Am at 50 N. The penetration depth was doubled as the load was increased to 60 N. The critical scratch load in this case was 30 N, which corresponded to a penetration depth of 1.7 Am. Such large amount of deformation resulted in the formation of a dense network of cracks in the coating as observed by SEM, Fig. 5(b). In contrast, the scratch depth was less than 1 Am at a load of 60 N for the TiAlN/VN deposited on pre-nitrided P20. Adhesive failure of the TiAlN/VN coating occurred at 55.6 N where the penetration was only ~0.95 Am. SEM observation revealed no substantial cracking except delamination of large pieces of the coating. The results presented in Fig. 5 confirm that loadbearing ability is a critical factor to the adhesion of the coating-substrate combination [11]. The poor load bearing ability of the non-nitrided P20 substrate cannot provide sufficient mechanical support to the coating. Because the fracture of hard coatings as a brittle material follows the strain model, cracks were generated at relatively low scratch load. As a result of the formation of a hardened layer on the pre-nitrided sample, Fig. 4, the load bearing ability has been dramatically increased which consequently led to higher adhesion. This conclusion is in agreement with Refs.[13,16].

3.3. Sliding wear behaviours of coated P20 steels

The friction and wear behaviour of the tested samples at loads 5 and 10 N are summarised in Table 2. At the load 5 N, the friction coefficient of TiAlN/VN was in the range of 0.4 which was lower than the TiAlCrYN.

The TiAlN/VN coatings showed low coefficients of wear in the range of $10^{-17} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}$. The coefficients of wear for the TiAlCrYN coatings were in the range of $10^{-16} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}$. These data were in good agreement to our previous work [6,7]. The nitrided samples showed slightly higher

Table 2 Wear and friction properties of TiAlN/VN and TiAlCrYN coated P20 samples at load 5N and sliding speed 0.1 ms^{-1}

Coatings	TiAlN/VN		TiAlCrYN	
	Nitrided	Non-nitrided	Nitrided	Non-nitrided
<i>Load=5 N</i>				
Coefficient of friction	0.48	0.43	0.61	0.66
$K_{\text{coat}} [\times 10^{-17} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}]$	8.5	2.3	37.3	24.4
$K_{\text{ball}} [\times 10^{-18} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}]$	2.0	0.4	20.1	3.8
<i>Load=10 N</i>				
Coefficient of friction	0.55	0.52	0.73	0.70
$K_{\text{coat}} [\times 10^{-17} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}]$	7.1	4.6 (8.2)*	17.0	17.5
$K_{\text{ball}} [\times 10^{-18} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}]$	1.92	1.41	28.8	6.7

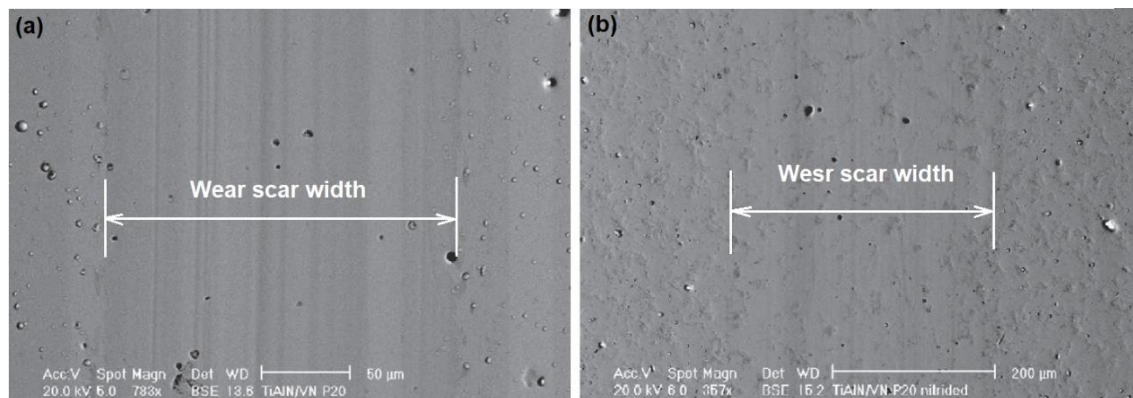


Fig. 6. Worn surfaces of TiAlN/VN coatings tested at 5N: (a) on non-nitrided P20, (b) on pre-nitrided P20.

friction coefficient by 0.05 than the non-nitrided ones owing to the increased surface roughness, Table 1. Correspondingly, the rougher nitrided surfaces resulted in more wear of the counterpart ball by a factor of 5.

SEM observations indicated micro-abrasion and oxidation on the smooth worn surfaces of the TiAlN/VN coating containing an attached thin oxide film and loose oxide wear debris, Fig. 6. Similar wear features were also observed on the worn surfaces of the TiAlCrYN coating. The worn surface showed neither crack nor delamination wear. The thin oxide tribofilm was similar to that of the TEM studies reported previously [24,25] which contained amorphous or nanocrystalline oxides of multi-metals. However, the coatings deposited on non-nitrided P20 showed more pronounced wear than those on nitrided P20. In the test condition, the latter showed only partial polishing of the surface asperity. In addition, the SEM micrographs

supported the roughness measurements in Table 1 demonstrating that the plasma nitriding treatment led to rougher surfaces.

At the load 10 N, the coatings deposited on nitrided P20 showed slightly higher friction coefficients and more counterpart wear than the non-nitrided sample. The TiAlN/VN and TiAlCrYN

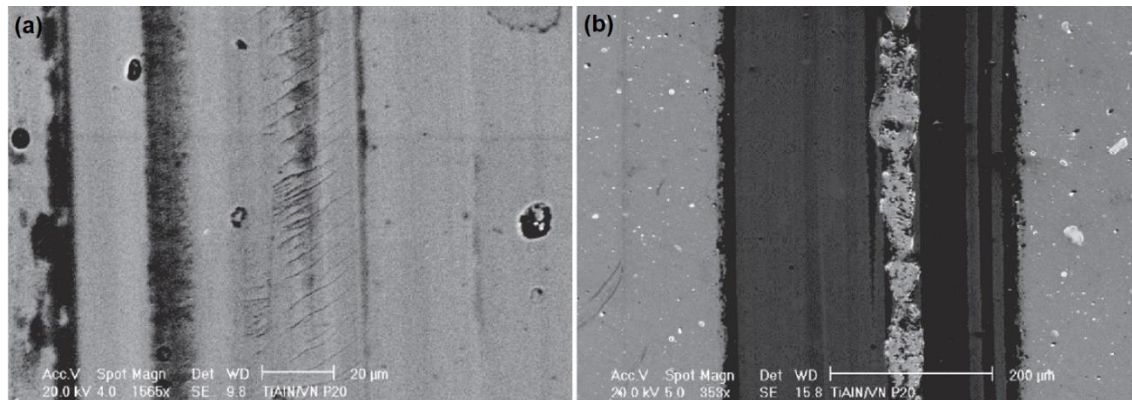


Fig. 7. Worn surface micrographs of TiAlN/VN deposited on non-nitrided P20 and tested at 10N showing (a) cracks and (b) spalling wear due to the low load bearing ability.

showed mild wear with wear coefficients of 7.1×10^{-17} and $1.7 \times 10^{-16} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}$, respectively. The worn surfaces were almost feature-less except for some micro-abrasion traces.

The TiAlN/VN deposited on non-nitrided P20 showed mild wear, with a wear depth of 0.28 μm and low wear coefficient $4.6 \times 10^{-17} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}$, in the major length of the wear track. Similarly, the TiAlCrYN deposited on non-nitrided P20 showed a wear coefficient $1.75 \times 10^{-16} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}$. However, cracks had formed in the smooth worn surface, Fig. 7(a). In fact, severe mechanical wear had occurred in a length of 5 mm in the wear track where the spalling wear was about 50 μm wide giving an average wear depth 0.50 μm and coefficient of wear $8.2 \times 10^{-17} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}$. The spalling wear feature is shown in Fig. 7(b). Our previous cross-section SEM and TEM work has confirmed that such cracks were formed due to the inferior mechanical support of the substrate under heavy load [26]. Literature [13] also reported similar observations. In summary, because cracking and deformation did not occur under the applied load of 5 N, the TiAlN/VN and TiAlCrYN coatings exhibited typical mild wear by micro abrasion and oxidation. In this regime, the wear resistance is predominantly dependent upon the coating itself instead of on the substrate [26]. On applying heavier loads, however, hard coatings require strong support from the nitrided substrate to resist deformation and spalling. As a result of the pre-nitriding treatment, the TiAlN/VN and TiAlCrYN coatings were able to show excellent wear resistance.

3.4. Lifetime of TiAlN/VN-coated drills in drilling stainless steel

Fig. 8 shows the lifetime of several PVD-coated and uncoated M2 drills in drilling austenite stainless steel, which was quantified by the number of holes drilled by each individual drill. Two data were obtained on each material condition. The two TiAlN/VN-coated drills achieved lifetimes of 107 and 116 holes, which were even better than the TiAlN (by 50%) or TiCN (by 20%). The longest lifetimes were obtained in the TiAlN/VN-coated and nitriding pretreated drills,

which had 33% longer lifetimes than those of the drills TiAlN/VN-coated only and six times longer than those of the uncoated drills.

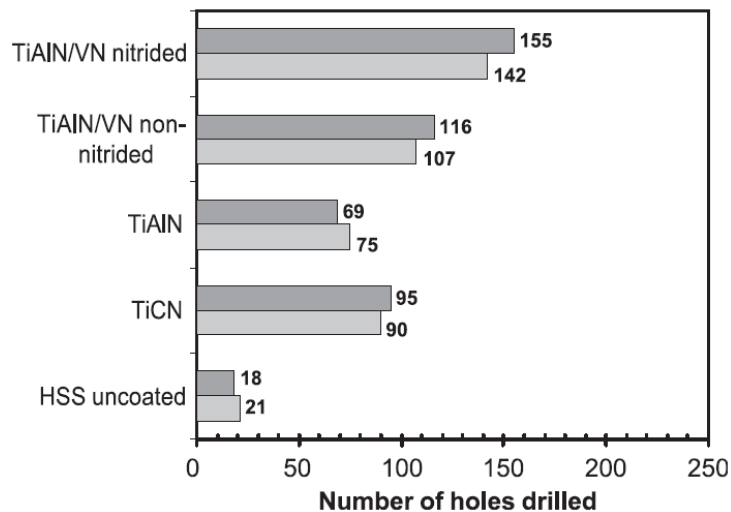


Fig. 8. Performance of coated HSS drills in drilling austenite stainless steel AISI304. Note the lifetime of TiAlN/VN-coated drills outperforming all the other cutters.

4. Conclusions

- 1) Nano-structured multilayer TiAlN/VN coatings showed excellent wear resistance both in dry sliding wear and in drilling austenite stainless steel AISI 304. It exhibited friction coefficients between 0.43 and 0.55 depending on the applied load and wear coefficients in the region of $10^{-17} \text{ m}^3\text{N}^{-1}\text{m}^{-1}$, which are significantly lower than those of the monolithically grown TiAlCrYN.
- 2) Pulsed plasma nitriding treatment of P20 steel resulted in a nitrided case having a hardness value of 8.5 GPa in a thickness of 50 Am and containing a surface compound layer containing both $\epsilon\text{-Fe}_3\text{N}$ and $\gamma\text{-Fe}_4\text{N}$. The pre-treatment increased significantly the adhesion of the PVD coatings, and resulted in excellent wear resistance at the higher applied load, whereas the coatings deposited on non-nitrided P20 showed limited wear resistance due to their poor load bearing ability.
- 3) In drilling austenite stainless steel, the TiAlN/VN-coated drills showed a lifetime 50% longer than TiAlN, 20% longer than TiCN, and six times longer than the uncoated drills, respectively. Plasma nitriding pre-treatment further prolonged the lifetime of the TiAlN/VN-coated drills by 33%.

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