

Microstructural and tribological investigations of CrN coated, wet-stripped and recoated functional substrates used for cutting and forming tools

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Abstract

Recent breakthroughs in wet-stripping Physical Vapour Deposited (PVD) CrN coatings on standard high speed and stainless steels and on hard metal substrates are reported in this work. Validation of the stripping processes was evaluated in terms of substrate damage after exposure to the chemical agents and also in terms of the tribological properties of the PVD CrN layers before (Pristine) and after stripping and re-coating (Recoated). The investigation was focussed on the influence of the stripping process on the hardness, roughness, adherence and wear resistance of the Recoated CrN coatings deposited by electron beam PVD (e-beam) after stripping. Analysis of the chemically stripped and Recoated steel substrates showed that: (a) hardness and elastic modulus of the Recoated e-beam CrN did not change significantly compared to Pristine e-beam CrN, and (b) surface roughness of the Recoated e-beam CrN layers was greater by a factor of 50–60% than the initial. For hard-metal substrates, the surface damage and its effect on the re-deposited coating performance in terms of the chemical reactions during the stripping process were discussed. It was observed that wet-stripping in a basic solution led to depletion of tungsten and carbon at the surface of the stripped WC-Co specimens.

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1. Introduction

The recent development of plasma technologies to produce functional thin films has led to rapid expansion within many industrial niches such as machining, moulding and casting [1–3], and more recently in the automobile sector [4]. The automobile industry is seriously considering Physical Vapour Deposition (PVD) technologies as an alternative to standard electrochemical coating processes. For instance, plasma spray is now widely utilized in big production factories [4].

A major potential application of PVD coatings is the progressive substitution of highly contaminating (due to the undesired production of hexavalent Cr) hard Chromium plating procedures. The European Commission for Environmental Protection plans to restrict significantly or even prohibit the use of these treatments beyond 2007. Chromium nitride is a possible replacement, with a bright silver appearance (similar to hard-Chromium) and excellent oxidation and corrosion resistance. In addition, Physical Vapour Deposited (PVD) CrN has been demonstrated to exhibit high hardness and low friction coefficient, making it an optimal coating for tribological applications in machining and moulding industries [1–3]. In addition, multilayered structured CrN/Cr [5] or CrN/TiN [6] exhibit further enhancements in adherence and toughness.

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The outstanding oxidation and corrosion resistance properties of CrN, arising from its almost total chemical inertness, can be a drawback to industrial applicability because PVD CrN is difficult to strip without damaging the surface of the supporting component. This may limit the use of CrN as a protection coating for expensive or added components, since manufacturers and end users are concerned by a loss of quality due to an inappropriate stripping treatment. Although several “recipes” have been developed and used for removing Ti-based coatings such as TiN or TiAlN, a standard formula for stripping CrN, with negligible substrate damage, has not yet been proposed or circulated.

This paper investigates wet stripping of PVD CrN coatings grown on various technical substrates and its collateral effects in terms of the surface damage to the substrates and the tribological performance of the coatings after stripping and recoating steps.

2. Experimental

Chemical stripping was performed in a solution composed of KOH and a strong oxidising agent such as H₂O₂.

The experimental procedure to investigate the efficiency of the chemical stripping, as well as the tribological performance of some selected samples was as follows: a first batch of standard test discs of technical materials (see below) were CrN coated (Pristine) and tested (chemical, mechanical). The same batch was chemically stripped and CrN recoated (Recoated) in order to compare the tribological performance of the recoated samples. Surface damage of the chemically stripped substrates (i.e. before recoating) was also evaluated.

Chromium nitride coatings (~0.5–2.0 μm thick) were grown by three different PVD techniques: electron beam (e-beam), arc discharge and DC unbalanced magnetron sputtering. Coatings were deposited on mirror polished and hardened AISI M2 steel (HSS-13343), AISI 316 (Inox) and Co-cemented WC test discs.

Following stripping, scanning electron microscopy (SEM: Cambridge Stereoscan 250 Mk2) and energy dispersive X-ray (EDX: Link Analytical QX200) analyses were used to examine superficial damage caused during the process. In some cases, macroscopic changes were observed and recorded using a JVC TK-1280E Colour Video Camera. An electron microprobe manufactured by the Cavendish Laboratory, University of Cambridge, was used to obtain wavelength dispersive X-rays (WDX) data from some of the specimens.

Chemical depth profile analysis of the coatings was obtained by glow discharge optical emission spectroscopy (GDOES) in a 1000 RF Jovin-Yvon spectrometer, equipped with a 35-channel hemispherical monochromator. RF sputtering power was set to achieve a depth resolution of 50 nm.

Ultra-microhardness data were obtained with a Fischer-scope ultra-microhardness indenter H100XY VP, set to a

Table 1

Summary of analytical techniques used in this investigation, CrN coatings and substrates tested

Analytical technique	Purpose	Coating/substrate system
SEM+EDX	Substrate damage evaluation	Arc CrN on AISI M2 and 316 steel substrates Magnetron sputtered CrN on WC-Co substrate
GDOES	Coating composition and compositional analysis of interfaces	E-beam CrN on AISI M2 steel and WC-Co substrates
Ultra-microhardness	Hardness and elastic modulus	E-beam CrN on WC-Co, AISI M2 and 316 steel substrates
Profilometry	Surface roughness	E-beam CrN on WC-Co, AISI M2 and 316 steel substrates
Profilometry	3D topographical images of wear tracks	E-beam CrN on AISI M2 steel substrates
Pin on disc	Friction coefficient measurements	E-beam CrN on AISI M2 steel substrate

final load of 10 mN, using a Vickers indenter. Friction coefficients were measured using a Falex Isc-320pc tribometer in a pin-on-disc configuration (Wear track 20 mm diameter) at ambient conditions, with a 3 mm diameter spherical WC-Co ball tester, linear speed of 10 cm s⁻¹ and a 5 N applied load. Pin on disc tests were performed over 5000 cycles (corresponding to a sliding distance of 314 m) and 20,000 cycles (corresponding to a sliding distance of 1257 m). A Wyco RST 500 optical profilometer, which performs vertical scanning and phase shift interferometry, was used to obtain 3D topographical images of the wear track and surface roughness measurements. The vertical resolution of the optical profilometer was better than 10 nm.

Note that at this initial stage of the present investigation, only e-beam CrN coatings were subjected to surface roughness, GDOES, ultra-microhardness measurements and tribological tests. The effect of the stripping solution on the different substrates was only evaluated on specimens that had been CrN-coated by magnetron sputtering and arc, as shown in Table 1.

3. Results

3.1. Chemical and microscopic analysis

Fig. 1a–c shows SEM micrographs of stripped (a) M2-steel, (b) AISI-316 and (c) Co-cemented WC. Secondary electron micrograph 1a) shows two well-defined zones, a flat region (1) and a second one (2) containing dark particles within bright patches or just bright patches. The difference in contrast is due to a topographical effect that is consistent with etching in the bright areas. EDX analysis of zone 1 in Fig. 1a reveals bulk compositions in terms of Cr, Mo, V and Fe, all arising from the M2-steel substrate. EDX analyses of dark

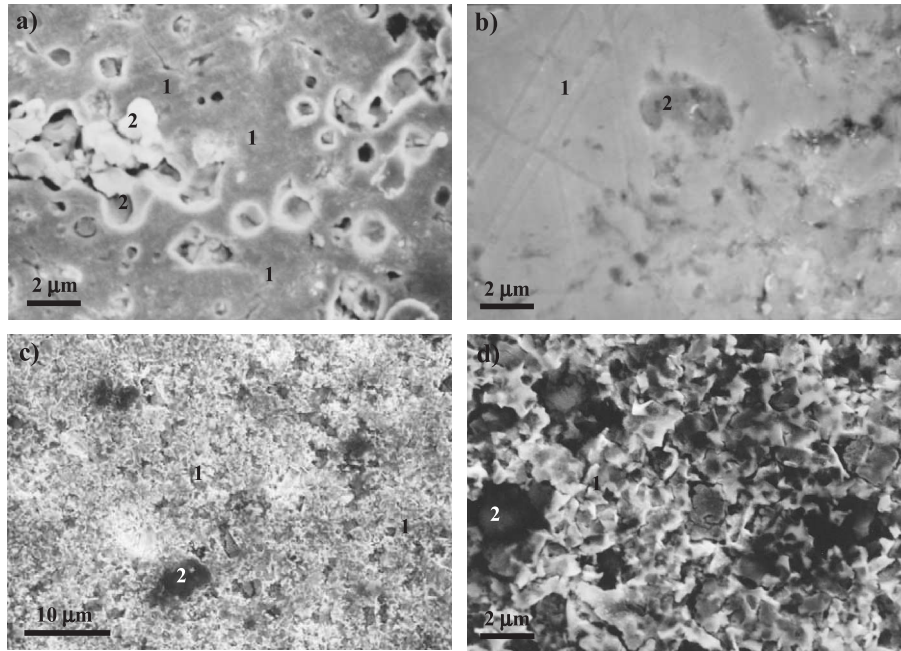


Fig. 1. SEM secondary electron photomicrographs of (a) stripped M2 steel substrate previously coated with arc CrN, (b) stripped 316 steel substrate previously coated with arc CrN, (c) and (d) stripped WC-Co substrate previously coated with sputtered CrN.

particles within bright patches in area 2 of Fig. 1a reveals Mo-, V- and Fe-signals similar to the bulk, whilst the Cr signal is slightly higher, indicating that these dark particles are probably chromium carbides. Unfortunately it was not possible to analyse for carbon, as this particular EDX system is not capable of detecting light elements accurately. This result suggests that the dark particles are the remains of larger chromium carbides which have been partially etched, creating the topographical features that are shown in the SEM secondary electron micrograph (Fig. 1a). This observed effect indicates that the chromium carbide particles on M2 steel substrates are being preferentially etched during the stripping process, which has been designed specifically to etch Cr and Cr-based compounds such as CrN.

The SEM micrograph of the 316 steel substrate (Cr content 18% by weight) is shown in Fig. 1b. EDX analyses performed in areas (1) and (2) revealed that the darker area (2) has a higher chromium and sulphur content than area 1. Some etched areas could also be identified in some AISI-316 discs. The total stripping time for this specimen was 55 min. The coating thickness was not uniform, and varied from 1.7 to 2.2 μm , and so there has been some etching of the substrate, some areas of which were exposed for longer than others. It should be noted that the typical size of pits resulting from chemical etching was not larger than 3.0 μm . These pits are probably the result of preferential etching of chromium present in the stainless steel.

The SEM secondary electron micrographs of the Cemented WC substrate (Fig. 1c–d) show a general etching of both carbides and cobalt matrix. EDX analyses were carried out in both areas ((1) for the cobalt matrix and (2) for carbides in Fig. 1c–d). Intense potassium peaks, associated

with the stripping solution, were detected in EDX analyses of both Co matrix and carbides, indicating that the solution reacts with the WC-Co substrate to form a compound over the specimen surface, which was not removed during the rinsing and drying process. This stripping by-product could be responsible for the observed change in colour of the WC-Co, to dark brown/grey, compared to shiny silver before stripping. It is interesting to note that these peaks associated with elements from the stripping solution could not be detected by EDX analyses of either stripped M2 or stripped 316 steel substrates.

Fig. 2a,b shows the chemical depth profile of e-beam CrN coatings deposited on M2 (Fig. 2a) and Hard Metal (Fig. 2b) as measured by GDOES. The profiles indicate that the stoichiometry of the coatings is in all cases close to Cr_2N . The film thickness was 1.5–1.75 μm , with oxygen concentrations below 7 at.%. The depth profiles of the pristine CrN (bottom part of Fig. 2a,b) show a well-defined interface between layer and substrate, with an estimated interface resolution better than 100 nm. Chemical analysis of Recoated e-beam CrN (i.e. after 1st stripping) by GDOES shows that the interface of the Recoated e-beam CrN/M2-steel becomes broader in terms of depth resolution, increasing up to 450 nm, suggesting a slight increase of the substrate roughness due probably to preferential chemical etching during stripping. In the case of the hard metal substrates, the effect of the stripping is even more dramatic (Fig. 2b). The interface CrN/WC-Co shows a significant depletion of tungsten and carbon and an accumulation of the binder elements, Ni and Co, of the carbide, in good agreement with the observations by SEM-EDX reported above. In addition, the film-substrate inter-

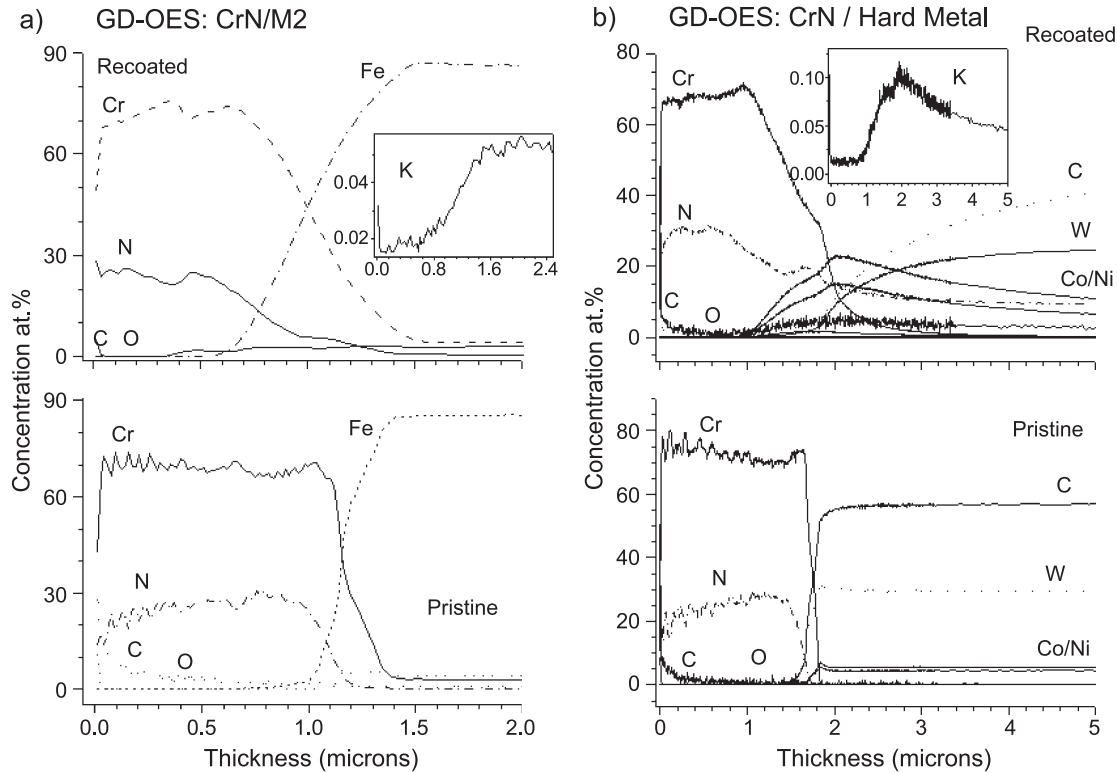


Fig. 2. GDOES in-depth profile of Pristine (bottom) and Recoated (top) e-beam CrN on (a) M2-steel and (b) WC-Co substrates.

face becomes rather broad, also indicating substrate damage due to stripping. Chemical analysis reveals the presence of potassium, an element associated with the stripping solution (up to 0.12 at.%, see inset of Fig. 2b), at the interface between the Recoated CrN on WC-Co, but significantly less in the Recoated CrN/M2-steel interface (cf. inset of Fig. 2a). This last result could also be confirmed with the EDX analysis performed in the stripped M2-steel and AISI-316.

3.2. Tribological response

Table 2 summarises the universal hardness (HU), Young's Modulus, and surface topography (roughness, Ra and Rq), obtained from the e-beam CrN coatings as a function of the

coating/substrate system (i.e. M2-steel, WC-Co and AISI 316) and stripping process. The pristine e-beam CrN coatings exhibit a HU of 13 GPa regardless of the substrate used. This value is consistent with the hardness of the Cr₂N phase, which is reported to be around 13 GPa [7]. This comparison, and the stoichiometry referred to above, indicate that these growth conditions lead to hexagonal hcp Cr₂N (and not to cubic CrN phase, which is denser and softer). Recoated CrN films show lower hardness than the pristine e-beam CrN, although the difference is within experimental error values. The hardness measured on the re-coated WC-Co cermets drops significantly upon recoating with e-beam CrN, down to 500 N/mm² with a dispersion of up to 50%. Since the low load used (10 mN) caused an overall penetration ~5–7% of the coating thickness, any contribution to the hardness value from the substrate is negligible. The only exception was the Recoated CrN coating on the WC-Co substrate, as the penetration was ~50% of the film thickness. This low recorded hardness can be related to several effects, such as influence of the substrate, changes in coating growth or increased roughness affecting the accuracy of ultra-microhardness measurements. Changes in the coating properties probably resulted from nucleation and growth on the damaged substrate surface.

Further insight into the effects of chemical stripping can be obtained from the surface roughness for both cases, Pristine and Recoated e-beam CrN, is shown in Table 1 for the three substrates. All the Pristine CrN coatings show very low roughness, comparable to those obtained by magnetron

Table 2

Universal hardness (HU), reduced Young's modulus (E') and surface roughness (Ra and Rq) measured for the pristine and recoated e-beam CrN films deposited on AISI M2 steel, AISI 316 and WC-Co test discs

Coating system	HU and E' (GPa)		Roughness	
	HU (10 mN)	$E'/(1-\nu^2)$	Ra (nm)	Rq (nm)
Pristine on AISI M2-steel	13±1	337±6	12±4	25±6
Recoated on AISI M2-steel	11±1	279±6	18±3	29±6
Pristine on WC-Co	14.3±0.9	526±10	13±1	21±1
Recoated on WC-Co	0.53±0.25	150±10	270±14	330±17
Pristine on AISI 316	12.6±0.7	330±7	11±1	20±2
Recoated on AISI 316	11.3±0.8	280±6	16±2	22±10

sputtering [8], characteristic of the hexagonal lattice structure of Cr_2N . The balance between R_a and R_q indicates that the surface topography is homogeneous. The overall roughness of the Recoated e-beam CrN increases by approximately 50% for steels, and by an order of magnitude in the case of the WC-Co substrates. The loss of resolution at the recoated layer/substrate interface, as revealed by the GDOES measurements, is probably related to such changes in surface roughness. Another factor contributing to the increased surface roughness measured for the Recoated samples is, undoubtedly, the second sputter cleaning to which the substrates were submitted immediately prior to recoating (a second 5 min sputter cycle), as opposed to Pristine specimens, which were only subjected to a single 5 min sputter cleaning cycle. It is well known that extended sputter cleaning times can cause visual matting of polished surfaces. Therefore, the second short sputter cleaning episode (5 min) will cause a further increase in surface roughness.

It is worth noting the significant decrease in the Young's modulus recorded for the Recoated WC-Co specimen. This reduction is consistent with the decrease in hardness, which suggests that the coating is less dense and its growth structure was influenced by the roughened substrate surface. One possible explanation for this could be a higher energy requirement for increased mobility of adatoms arriving at the very much rougher substrate surface in order to produce a coating as dense as one growing on a polished surface. The resulting deficiency in adatom mobility would result in a more columnar; less dense; less hard; lower Young's modulus coating. Another feasible explanation for reduced hardness and elastic modulus is the increased roughness itself (a few hundreds of nanometres), which probably had a detrimental effect on the accuracy of ultra-microhardness measurements in this particular specimen.

Fig. 3 shows the evolution of the friction coefficient during pin on disc testing to 5000 cycles of the Pristine (bottom) and Recoated (top) e-beam CrN coatings grown on M2 steel. The friction coefficient of the Pristine e-beam CrN increases smoothly from 0.1 up to 0.3 within the first 500 cycles, and then remains constant around 0.35 for the rest of the test. Measured friction coefficients are in agreement to those measured by Carrera et al. in CrN/MoS₂ multilayers or CrN/Cr multilayers [8]. In both cases the coatings showed small wear scars even for the large values of the applied Hertzian contact. Interestingly, the friction coefficient of the Recoated e-beam CrN on M2-steel exhibits the same evolution as that shown by the pristine e-beam CrN grown on the same substrate. In addition, the wear coefficient of the Recoated e-beam CrN, as tested using optical profilometry, could not be measured under these conditions because the smooth wear track produced during the pin-on-disc tests was smaller than can be measured using the equipment which has a resolution of 10 nm in depth.

To obtain a more qualitative insight of the wear resistance, another wear test was performed in the Recoated e-beam CrN using the same load of 5 N but increasing the number of

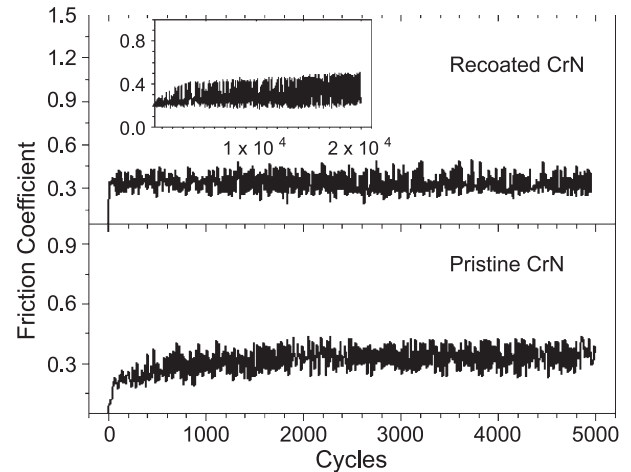


Fig. 3. Evolution of the friction coefficient during 5000 cycles against a WC-Co pin 3 mm in diameter and a 5 N applied load for: pristine e-beam CrN (bottom) and recoated e-beam CrN (top) on M2-steel. The inset shows the evolution of the friction coefficient for a Recoated e-beam CrN during 20,000 cycles.

cycles to 20,000. The friction coefficient obtained from this test is shown on the inset of Fig. 3. The friction coefficient remains constant at 0.35–0.40 up to 20,000 cycles, indicating that the Recoated CrN has a good tribological performance, comparable to that exhibited by WC:H films [9].

The profile of the wear track produced during the pin-on-discs experiments on Pristine and Recoated e-beam CrN on M2-steel, respectively, after 20,000 wear cycles, is shown in Fig. 4. Both films display a very narrow wear track. After 20,000 cycles pin-on-disc Wear tests, the wear track was still too small to be measured, even though the profilometer resolution was better than 10 nm. The wear behaviour reported in this work for the pristine e-beam CrN coating is comparable to that of arc-discharge CrN films, and can be explained in terms of the good combination of high hardness and also low roughness that the e-beam CrN exhibits. The good tribological performance of Recoated e-beam CrN on steels is to be expected since the stripping process has been demonstrated not to affect significantly the layer/substrate interface. Although a ~50% increase in surface roughness of the Recoated steel specimens appears to be a large increase, it does, in fact, result in a surface that still remains relatively highly polished (see roughness values listed in Table 2). This increase in surface roughness was not detrimental to the wear response when the supporting material is steel-based, since similar wear performances were observed for both Pristine and e-beam CrN-recoated steel substrates. Moreover, the chemical analysis clearly indicated that the interface did not accumulate significant amounts of residuals from the stripping solution, within the GDOES detection limit (some ppm). This lack of significant amounts of reagents suggests that there is no chemical interaction between the vast majority of the constituents of the steels, which are chromium-free, and also explains the low level of damage produced on both M2 and 316 steels. However, the

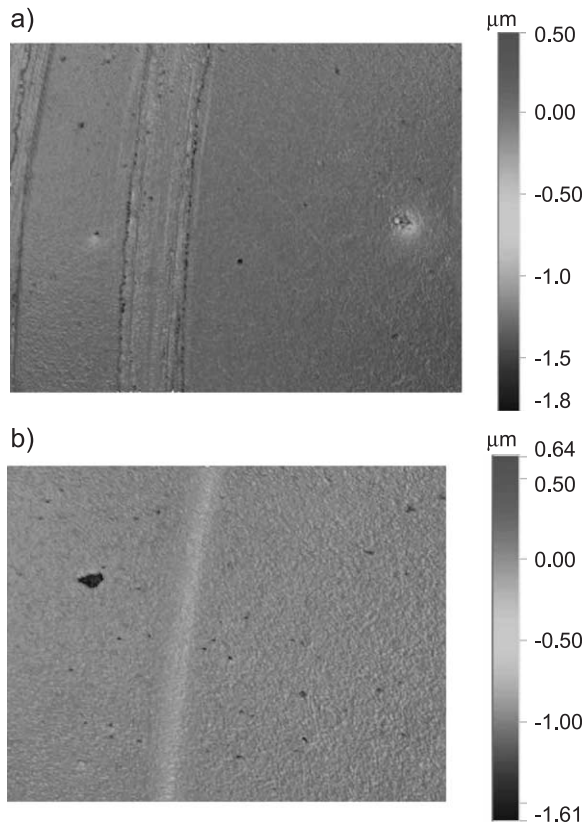


Fig. 4. Surface topography (1.0×1.0 mm) of the wear tracks produced after 20,000 cycles-pin on disc tests on (a) Pristine e-beam CrN/M2 steel and (b) Recoated e-beam CrN/M2 steel. Tests were performed using a 3 mm diameter WC-Co ball and 5 N applied load.

interaction of the stripping solution with the WC-Co cermet led to severe depletion of the tungsten and carbon, and left behind high surface concentrations of Co and stripping reagents at the WC-Co surface.

This makes the use of this particular stripping recipe unsuitable for use on hard metal tools.

3.3. Final remarks

Another possible contributing factor for some of the differences observed in GDOES analyses, hardness and Young's modulus between Pristine and Recoated specimens, especially on steel substrates, could be slight differences in the CrN coatings themselves as all Pristine were coated in one deposition cycle and the Recoated in another. Therefore, to test the hypotheses given above, i.e. that the observed differences are only due to changes in substrate surface roughness during stripping (and additionally, in the case of WC-Co, surface composition), it would be necessary to coat Pristine and Recoated samples in the same deposition cycle.

4. Conclusions

An aqueous alkaline oxidising solution was found to be suitable for stripping CrN coatings deposited on M2-steel and AISI 316 steel substrates. Substrate damage due to stripping was found to be small for both steels, although for the M2 high speed steel, preferential chemical etching of chromium carbides could not be avoided. In the case of the 316 stainless steel substrate, chemical etching of the substrate also occurred and pits of up to $3.0 \mu\text{m}$ diameter could be identified. Mechanical tests on steel based substrates reinforce the statement that the chemical etching applied during stripping did not affect the tribological performance of the Recoated CrN layer.

The same solution was not suitable for stripping CrN coatings deposited on tungsten carbide substrates. GDOES analysis indicated the presence of constituents of the etching solution, and a strong depletion of tungsten, on the specimen surface, suggesting that the chemical solution reacts with the cobalt matrix to form a compound over the specimen surface. The formation of a strongly etched interface is responsible for the abrupt increase in recoated CrN surface roughness, and for the low and variable hardness values obtained after recoating the WC-Co specimens.

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