Characterisation of Pristine and Recoated electron beam evaporation plasma-assisted physical vapour deposition Cr–N coatings on AISI M2 steel and WC–Co substrates

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Abstract

This paper is focussed on the characterisation of electron beam evaporation plasma-assisted physical vapour deposition Cr–N coatings deposited on AISI M2 steel and hardmetal (K10) substrates in two different conditions: Pristine (i.e., coated) and Recoated (i.e., stripped and recoated). Analytical methods, including X-ray diffraction (XRD), scanning electron microscopy, scratch adhesion and pin-on-disc tests were used to evaluate several coating properties. XRD analyses indicated that both Pristine and Recoated coatings consisted of a mixture of hexagonal Cr₂N and cubic CrN, regardless of substrate type. For the M2 steel substrate, only small differences were found in terms of coating phases, microstructure, adhesion, friction and wear coefficients between Pristine and Recoated. Recoated on WC–Co (K10) exhibited a less dense microstructure and significant inferior adhesion compared to Pristine on WC–Co (K10). The wear coefficient of Recoated on WC–Co was 100 times higher than those exhibited by all other specimens. The results obtained confirm that the stripping process did not adversely affect the Cr–N properties when this coating was deposited onto M2 steel substrates, but it is clear from the unsatisfactory tribological performance of Recoated on WC–Co that the stripping process is unsuitable for hardmetal substrates.

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1. Introduction

Plasma-Assisted Physical Vapour Deposition (PAPVD) processes have been commercially used to deposit chromium nitride (Cr–N) coatings on steel substrates. Among these processes, electron beam evaporation PAPVD (EB PAPVD) has been successfully used to produce Cr–N coatings, mainly due to its high deposition rates and excellent surface finish obtained in polished components.

Industrial applications of Cr–N coatings include cutting and forming tools, as well as injection-moulding dies for plastics [1–4]. Cr–N has favourable tribological properties (i.e., low friction coefficient and high wear resistance) [5–11], allied to good oxidation and corrosion resistance [10–17], and is a possible replacement for hard chromium. Nevertheless, the industrial demand for Cr–N on tungsten carbide tools is still small.

Cr–N coatings usually have fine-grained and low stress structure, so that thicker (up to 10–25 μm) can be deposited, compared to conventional PAPVD coatings of a few microns [2]. As Cr–N usually has lower hardness and higher toughness than TiN, they are often deposited on soft substrates such as stainless steel, copper and aluminium.
alloys, which cannot provide enough support for more brittle and harder coatings [2,18].

Chromium nitride has two different crystalline phases: CrN (face centred cubic structure) and β-Cr2N (hexagonal structure). Cr–N coatings can be prepared with a wide range of phase structures, having only a single phase (CrN or Cr2N) or a mixed phase structure containing Cr and Cr2N or Cr2N and CrN, mainly depending on the nitrogen partial pressure [12,19–23]. Coatings having a single Cr2N phase [5,12,19–25] have been found to be hardest, whereas coatings possessing Cr2N and CrN phases with additional nitrogen [22] have highest internal stresses.

Cr–N coatings often provide good oxidation resistance up to 973–1073 K [12,15–17,26], which is accomplished by the formation of a protective top Cr2O3 layer [17]. The CrN phase appears to provide a superior oxidation resistance than Cr or Cr2N phases [12]. Cr–N coatings can also enhance the corrosion resistance of steel substrates [5,10,13,14]. Their corrosion resistance can be further enhanced by using interlayers such as metallic chromium [14], electroless nickel [27] and electroless nickel–phosphorous [28].

Paradoxically, the industrial use of Cr–N coatings on expensive or added value components is often limited by the good oxidation and corrosion resistance, making it difficult to strip without causing any damage to the substrate. As a new wet stripping process that causes little or negligible damage to steel substrates has been developed [29], it is relevant to compare some coating properties (crystalline phases, microstructure, adhesion and wear) for Pristine (i.e., coated) and Recoated (i.e., stripped and Recoated). In this paper, EB PAPVD Cr–N coatings deposited on AISI M2 steel and hardmetal (K10) substrates were characterised before, and after, stripping and recoating. Coating properties were evaluated using X-ray diffraction (XRD), scanning electron microscopy (SEM), scratch adhesion and pin-on-disc tests.

2. Experimental details

2.1. Materials and treatments

Cr–N was deposited on hardened and polished AISI M2 steel discs (60 HRC, 29.5 ± 0.5 mm) and polished tungsten carbide (K10, nominal composition (wt. %): 92.7 WC; 1.0 TaC; 0.3 Cr2C3; 6.0 Co) discs (29.5 ± 4.8 mm) by EB PAPVD using a Tecxav IP70L coater. All specimens were subjected to a 5 min sputter cleaning step before initiating coating deposition (Pristine specimens). Some Cr–N coatings on both M2 steel and tungsten carbide substrates were chemically stripped as described elsewhere [29]. The stripping solution consisted of KOH and a strong oxidising agent. After stripping, substrates were recoated in the same way as the Pristine specimens and, therefore, subjected to another 5 min sputter cleaning cycle (Recoated specimens). The coating temperature was kept at 673–723 K for all coating cycles.

2.2. Coating characterisation

A Fischerscope X-ray XDL system was used to assess the coating thickness in all specimens. This system is an energy dispersive, high-performance X-ray fluorescence spectrometer and can detect elements from aluminium to uranium, even at very low concentrations (0.1–0.2 wt.%). Coating thickness or alloy composition is determined from the energy and intensity of the respective X-ray emission. The X-ray energy was set to 50 kV in all thickness measurements.

The scratch test method was used to assess coating adhesion. A CSEM Revetest scratch tester was used to perform the tests. The radius of the diamond indenter in the scratch test was 0.2 mm and the measurements were carried out at an increasing load rate of 10 N mm−1. Three critical loads (LC1, LC2 and LC3) were determined from a set of three scratches on each specimen. LC1 was taken as the load at which cohesive failures occurred; LC2 was the load corresponding to first occurrence of adhesive failure (i.e., the load at which the substrate was first exposed); and LC3 was the load at which the coating was completely removed from the scratch channel. The specimen surface and diamond tip were cleaned with isopropanol before each scratch. Although acoustic emission and frictional force were recorded during the tests, the critical loads were determined by optical microscopy.

Coating phase composition was investigated by means of XRD using Cu-Ka radiation (λ=0.154056 nm). The diffractograms were recorded with a 20 step of 0.02°/s from 20° to 90°. Scanning electron microscopy (Cambridge Stereoscan 250 Mk2 scanning electron microscope) was used to investigate the surface and fracture cross-section morphology of the coatings at an accelerating voltage of 20 kV.

Pin-on-disc wear tests were performed using a Falex Isc-320pcc tribometer, at ambient conditions. A 3 mm diameter WC–Co ball was used for the tests, which were set at a linear speed of 10 cm s−1 and a load of 5 N. The wear coefficients were determined after a sliding distance of 1257 m (20,000 cycles). A Wyco RST 500 optical profilometer, using vertical scanning and phase shift interferometry to a vertical resolution better than 10 nm, was used to obtain 2D topographical images of the wear tracks. The images were obtained over a scanned area of 0.9 × 1.2 mm.

3. Results and discussion

3.1. Coating thickness

Coating thickness obtained from X-ray fluorescence measurements for both Pristine and Recoated on M2 steel
and WC–Co substrates, are shown in Table 1. All coatings on WC–Co have similar (within 10%) thicknesses, whereas on M2 steel, Pristine is 1.0 μm (66%) thicker than Recoated.

3.2. X-ray diffraction analyses

XRD patterns of Pristine and Recoated on M2 steel are illustrated in Fig. 1a, whereas those of Pristine and Recoated on WC–Co (K10) are shown in Fig. 1b. Both Pristine and Recoated crystallised into hexagonal Cr₂N and cubic CrN phases, regardless of substrate type. Diffraction peaks corresponding to the M2 steel or WC–Co substrate were also present. For Recoated on either M2 steel or WC–Co, the higher intensity of substrate peaks in comparison to those of the coating suggests that these films are thinner than the Pristine (see Table 1).

By comparing the line intensities to those of a random sample, it can be concluded that the cubic CrN phase in Pristine (either M2 steel or WC–Co substrates) has a major (200) preferred orientation (I CrN (111)/I CrN (200) is 0.03 for M2 steel and 0.02 for WC–Co), whilst the hexagonal Cr₂N has a major (111) preferred orientation (I Cr₂N (002)/I Cr₂N (111) is 0.04 for M2 steel and 0.02 for WC–Co). Other crystalline orientations become more significant in Recoated on both substrates, indicating that these coatings have a more random texture (I CrN (111)/I CrN (200) is 0.23 for M2 steel and 0.39 for WC–Co and I Cr₂N (002)/I Cr₂N (111) is 0.31 for M2 steel and 0.44 for WC–Co).

The randomisation of texture for both cubic and hexagonal chromium nitride phases might be related to the higher surface roughness that resulted from stripping in Recoated samples [29]. For a certain adatom energy, a high substrate roughness will influence coating growth by effectively reducing their mobility and the appearance of other crystalline orientations will be promoted.

3.3. SEM examination

SEM images of surface morphology and fracture cross-section of Pristine and Recoated are shown in Fig. 2a–h. The surface morphology indicates an increase in surface roughness for Recoated on M2 steel and WC–Co substrates (Fig. 2c and g respectively), as previously detected by surface roughness measurements [29]. Nevertheless, larger defects/pores can be identified on the Recoated on WC–Co (Fig. 2g).

Fracture cross-sections of Pristine and Recoated on M2 steel (Fig. 2b and d respectively) reveal that both coatings have similar dense structures. Although their structure is columnar in nature, the high density results in unclear column boundaries, resembling the coating structure described as ‘Zone 2’ in Ref. [30].

The Pristine on WC–Co (Fig. 2f) also exhibits a dense film structure, similar to those found in Pristine and Recoated on M2 steel. However, the structure of Recoated on WC–Co is very distinctive, being less dense and having a granular appearance (Fig. 2h). Such a microstructure probably developed from coating growth on the damaged substrate, which had a high surface roughness (one order of magnitude higher than the other samples [29]).

3.4. Scratch tests

The critical loads for Pristine and Recoated are illustrated in Table 2. For Pristine on both substrates, cohesive failures (i.e., failures occurring within the coating)
occurred in two different modes: cracking and chipping. Small cracks at the edge of the scratch channel start to develop at very low loads in these coatings. As the load increased, a pattern of semicircular cracks (tensile cracks) could be observed at the scratches [31]. The tensile cracking mode is characteristic of well-adherent coatings [31]. The cracks form as a result of tensile stresses behind, balancing the compressive frictional stresses in front of, the trailing edge of the stylus [31]. Except for Recoated on WC–Co, chipping of the coating was a cohesive failure that could also be detected at higher loads.

For the M2 steel substrate, the difference in the critical loads of Pristine and Recoated is small. Pristine and Recoated displayed similar $L_{C2}$ values, whilst higher $L_{C1}$ chipping and $L_{C3}$ values were recorded for Recoated, having a thickness of 1.5 mm. As an increase of critical loads with thickness is observed [32], the previous results suggest that the stripping process was not detrimental to the coating adhesion, as Recoated exhibited higher critical loads than Pristine.

![Fig. 2. Surface (a,c,e,g) and fracture cross-section (b,d,f,h) SEM images of Cr–N coatings on (a,b) Pristine M2 steel; (c,d) Recoated M2 steel; (e,f) Pristine WC–Co (K10) and (g,h) Recoated WC–Co (K10).](image)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Critical loads (N)</th>
<th>$L_{C1}$ cracking</th>
<th>$L_{C1}$ chipping</th>
<th>$L_{C2}$</th>
<th>$L_{C3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine M2 steel</td>
<td>12 ± 1</td>
<td>31 ± 3</td>
<td>60 ± 3</td>
<td>92 ± 5</td>
<td></td>
</tr>
<tr>
<td>Recoated on M2 steel</td>
<td>–</td>
<td>37 ± 2</td>
<td>55 ± 3</td>
<td>109 ± 1</td>
<td></td>
</tr>
<tr>
<td>Pristine on WC–Co (K10)</td>
<td>22 ± 2</td>
<td>33 ± 4</td>
<td>109 ± 14</td>
<td>115 ± 15</td>
<td></td>
</tr>
<tr>
<td>Recoated on WC–Co (K10)</td>
<td>–</td>
<td>–</td>
<td>7 ± 2</td>
<td>14 ± 1</td>
<td></td>
</tr>
</tbody>
</table>

Table 2
Critical loads obtained from scratch adhesion tests
For the WC–Co substrate, very low critical loads were recorded for Recoated in comparison with Pristine. Recoated displayed only adhesive failures, indicating that the stripping process caused significant damage to the hardmetal substrate, as reported elsewhere [29].

It is interesting to note that Pristine on WC–Co showed higher critical loads than Pristine on M2 steel. This is probably due to the higher hardness of the hardmetal substrate in comparison to that of the M2 steel, which improves the load support for the Cr–N coating [33,34].

3.5. Pin-on-disc tests

Results from pin-on-disc tests are shown in Table 3. The friction coefficients exhibited the same order of magnitude as those reported for Cr–N films in the literature [35]. Regardless of substrate type, the decrease in the friction coefficient from Pristine to Recoated was very small.

All samples show high wear resistance (1/k), except Recoated on WC–Co. (Table 3). The wear coefficient of the latter was ~100 times higher than those recorded for the other specimens, including both uncoated substrates. These results were corroborated by 2-D surface profilometry of the wear tracks (Fig. 3a–f). It is interesting to note that Pristine on WC–Co exhibited a higher wear resistance than Pristine on M2 steel. As the hardness and surface roughness of Pristine on both substrates were similar [29], the superior performance of the Pristine on WC–Co must be related to an improved load support from this substrate to the Cr–N coating, as evidenced by scratch test results.

The small increase in surface roughness for Recoated on M2 [29] was not detrimental to the tribological performance, as similar wear coefficients were obtained for Pristine.

Table 3
Friction (μ) and wear coefficients (k) obtained for uncoated substrates, Pristine and Recoated coatings after pin-on-disc tests. Tests were performed using a 3 mm diameter WC–Co ball and 5 N applied load.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>μ</th>
<th>k (m² N⁻¹ m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated AISI M2 steel</td>
<td>0.6</td>
<td>7.0 × 10⁻¹⁶</td>
</tr>
<tr>
<td>Pristine on M2 steel</td>
<td>0.5</td>
<td>2.4 × 10⁻¹⁶</td>
</tr>
<tr>
<td>Recoated on M2 steel</td>
<td>0.3</td>
<td>3.2 × 10⁻¹⁶</td>
</tr>
<tr>
<td>Uncoated WC–Co (K10)</td>
<td>0.4</td>
<td>&lt;1.0 × 10⁻¹⁶</td>
</tr>
<tr>
<td>Pristine on WC–Co (K10)</td>
<td>0.3</td>
<td>&lt;1.0 × 10⁻¹⁶</td>
</tr>
<tr>
<td>Recoated on WC–Co (K10)</td>
<td>0.3</td>
<td>2.9 × 10⁻¹⁴</td>
</tr>
</tbody>
</table>

Fig. 3. 2-D topographical images of the wear tracks produced after pin-on-disc tests on: a) Uncoated M2 steel; (b) Pristine on M2 steel; (c) Recoated on M2 steel; (d) Uncoated WC–Co (K10); (e) Pristine on WC–Co and (f) Recoated on WC–Co. Tests were carried out using a 3 mm diameter WC–Co ball and 5 N applied load over a sliding distance of 1257 m.
and Recoated on M2 steel. Therefore, pin-on-disc results indicate that the tribological response of Cr–N coatings on M2 steel substrates was not adversely affected by the stripping process.

The unsatisfactory tribological response of Recoated on WC–Co probably results from its high surface roughness [29], low hardness [29] and poor adhesion (Table 2), showing that the stripping process caused significant damage to the WC–Co substrate.

3.6. Summary

Previous results obtained from glow discharge optical spectroscopy, surface roughness and ultra-microhardness measurements showed that the stripping process caused significant damage to the WC–Co substrate but not to the M2 steel substrate [29]. SEM results also indicated that the stripping process was detrimental to the WC–Co substrate, as evidenced by the less dense coating structure that resulted from recoating (Recoated sample). The similar performances achieved by Pristine and Recoated Cr–N on M2 steel in scratch adhesion and pin-on-disc wear tests further validate the stripping process for this substrate. Conversely, the unsatisfactory performance of Recoated Cr–N on WC–Co indicates that this stripping process cannot be used on carbide substrates.

4. Conclusions

Pristine and Recoated (i.e., stripped and then recoated) Cr–N coatings on M2 steel and WC–Co (K10) substrates were characterised using XRD, SEM, scratch adhesion and pin-on-disc wear tests. XRD analyses revealed that all Pristine and Recoated Cr–N coatings, regardless of substrate type, consisted of a mixture of hexagonal Cr2N and cubic CrN phases. However, a more random texture resulted in the Recoated specimens. SEM examination of fracture cross-sections indicated that Pristine and Recoated Cr–N on M2 steel and Pristine on WC–Co had similar dense columnar structures. However, the coating structure in Recoated on WC–Co was less dense and had a granular morphology. Scratch test results revealed that the adhesion of Recoated on WC–Co was poor, as very low critical loads were recorded. The high critical loads obtained for the other coating/substrate systems indicated a satisfactory film/substrate adhesion. Although only small variations in the friction coefficient were detected from pin-on-disc wear tests among all Cr–N coatings and uncoated substrates (M2 steel and WC–Co), the wear rate of Recoated on WC–Co was ~100 times higher than all other coatings and uncoated substrates. The poor performance achieved by Recoated on WC–Co substrates in scratch adhesion tests and pin-on-disc tests invalidates the use of this stripping process on WC–Co substrates. Nevertheless, the similar tribological performances achieved by Pristine and Recoated on M2 steel reinforces the suitability of the stripping process for steel substrates.

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