Surface analysis of electrochemically stripped CrN coatings

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Abstract

CrN multilayer coatings are possible replacements for hard chromium because of their good mechanical and chemical properties. This paper focuses on X-ray photoelectron spectroscopy (XPS) to study the mechanism of electrochemical stripping of multilayered Cr–N based coatings. The samples were produced by electron beam (e-beam) physical vapour deposition (PVD), on mirror polished M2 steel. Multilayers constituted three separate layers of CrN with intermediate interlayers of Cr (0.1 μm). The total coating thickness was in the range 4.5–5.5 μm. Under galvanostatic conditions, anodic oxidation of CrN leads to replacement of nitrogen in the CrN coating by oxygen, forming oxy-nitrides on the samples surface. Contrary to findings described by some authors, we have not detected Cr6+ in this research.

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1. Introduction

In the past decade, transition metal nitride coatings, mainly based on titanium and chromium, have attracted considerable attention due to their promising potential applications in many fields such as magnetic, electronics, optical and/or decorative coatings. In particular, chromium nitride (CrN) is well suited to wear and corrosion protection, because of its good mechanical (wear resistance, low friction coefficient and high hardness) and chemical properties (oxidation and corrosion resistance).

Chromium nitride coatings are usually prepared by physical vapour deposition (PVD) techniques, mainly electron beam, arc or magnetron sputtering. The film properties strongly depend on the chemical composition and microstructure. For instance, changing the nitrogen pressure during deposition produces films ranging in composition from mixtures of Cr and Cr2N, or single phases from pure Cr2N through Cr2N–CrN to pure CrN [1]. For this reason, a lot of effort has been invested in establishing the relationship between deposition parameters and physical properties [2–8]. Further improvement to the properties of PVD coatings has been achieved through the deposition of multilayer. Multilayers possess improved corrosion and mechanical properties, including hardness and fracture toughness, as compared to homogeneous single layer coatings [9].

Ultimately, the coating will wear out, and since these coatings are frequently applied to tooling made from high cost tool steels, it may be economically viable to strip the remaining coating and recoat the repaired surfaces. The complexity of the stripping process increases with multilayered structures. In previous work [10] the authors have studied the effectiveness of stripping using an alkaline oxidising solution under galvanostatic conditions. The greater activity of the nitride in this medium leads to formation of more soluble species, allowing good control of the nitride removal rate and a high sensitivity to changes of coating thicknesses of the CrN layers.

This present paper focuses on X-ray photoelectron spectroscopy (XPS) to study the mechanism of electrochemical stripping of multilayered Cr–N based coatings. XPS analyses were performed on samples at different stages of the stripping process so that oxides and other compounds formed during the removal of the coating could be identified, leading to a sequence of CrN dissolution. In addition, quantitative results have been
obtained for the surface composition, for different chromium nitride coatings.

2. Experimental details

The base material is M2 tool steel. Glow Discharge Optical Emission Spectroscopy (GDOES) analysis showed the composition to be (wt.%): C 0.97%, Si 0.2%, Mn 0.2%, Cr 4.11%, W 6.3%, V 1.8%, Mo 4.9%, Fe balance.

Chromium nitride multilayer coatings were deposited by Tecvac Ltd. (Cambridge), using electron beam (e-beam) PVD. Coatings were deposited on mirror-polished M2 steel. Multilayers, formed of three separate layers of CrN with intermediate interlayers of Cr (0.1 μm) made up a total thickness in the range of 4.5–5.5 μm. The coatings were analysed by optical microscopy, scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), X-ray diffraction (XRD Cu Kα radiation) and X-ray photoelectron spectroscopy (XPS).

Specimens were analysed by XPS over a range of stripping times. Stripping was performed at room temperature under galvanostatic conditions in an alkaline oxidising solution, which chemical composition is commercially confidential. The current applied was 2 mA on an exposed surface area of 0.22–0.29 cm², which defined adequate current density values ranging between 7–9 mA/cm² [10]. This current value allows combining an adequate stripping rate with a good resolution of the end of the stripping process avoiding unwanted damage of the substrate.

![Fig. 1. a) Potential evolution for galvanostatic stripping of CrN multilayer. SEM micrographs showing the surface finished for samples: b) after 800 s of stripping — position A in Fig. 1a, c) after 2000 s — position B, d) after 3600 s — position C, e) after, 4500 s — position D.](image-url)
A high vacuum VG-CLAM XPS system was used with a magnesium anode (Kα 1253.6 eV), working at 15 kV, 20 mA and using an argon ion acceleration of 5 KeV. The photoelectron detection was normal to the specimen surface. Broad scan spectra were obtained with pass energy of 150 eV, while narrow scans of Cr 2p, O 1s, N 1s and Fe 2p used a pass energy of 20 eV. All XPS spectra are referenced to the C 1s line of hydrocarbon-type carbon, which we have taken to be the most common literature value of 284.8 eV [11].

3. Results and discussion

XPS analyses have been performed on CrN-coated samples in pristine condition, with different times of stripping and after a complete removal of the coating. The stripping method used was developed and optimised by the authors [10]. By perturbing the system galvanostatically is possible to induce the dissolution of the CrN layer pointing out the coating removal by an increase in the potential recorded. Preliminary tests estimated that applying current densities of between 5–12 mA/cm² would allow the layers to be removed in a relatively short time period. This current density allows combining the effectiveness and rate of the stripping process without inducing any damage on the substrate.

Increasing the current, the stripping process would occur faster but also the potential jump which points out the end of the stripping is lower than 100 mV. This lower resolution of the end of the process together with the higher current flow would make the method less sensitive to detect the final of the process increasing the probability to induce corrosive attack on the substrate.

Fig. 1 shows the different times (A, B, C and D on the stripping curve) at which the samples were removed from the solution, rinsed in pure water and dried immediately before analysis. These points correspond to different stages of the stripping process of a CrN multilayer sample, leaving different surface compositions and surface finishes for the XPS analysis.

3.1. Pristine CrN specimens

The pristine CrN XRD pattern is a characteristic f.c.c. CrN with a trace of hexagonal Cr₂N signal (Fig. 2). Both presented a strong (200) preferred orientation and other minor reflections, including (111), (311) and (400), all of which are related to the CrN cubic phase and (110), (002) and (302) for the hexagonal Cr₂N. This indicates that the structure is denser than that usually seen for TiN coatings, and so we could expect to see a limited number of through coating defects (e.g. pinholes) making the CrN coatings less permeable to the corrosive attack, as observed by Liu et al. [12]. Han et al. [13] report that CrN coatings obtained by unbalanced magnetron sputtering exhibit a dense structure with preferential (200) orientation, which would confer strong coating adhesion but lower hardness. Because the X-rays penetrate right through the coating, we also observed peaks attributable to Cr (chromium interlayer) and Fe (base metal).

General XPS spectra for CrN revealed that after 30 min of sputtering all the surface impurities have been removed and the peaks corresponding to the main elements – Cr, N and O – are clearly identified.

The N 1s spectrum shows a single wide peak at 397 eV, which can be decomposed into two chemical species at B. E. 396.8 and 398.0 eV. The Cr 2p spectrum is fitted with two peaks at B. E. 574.0 and 576.4 eV, which correspond to Cr₂N and CrN, respectively. The O 1s spectrum is fitted with two peaks at B. E. 530.7 and 533.7 eV, which correspond to Cr₂O₃ and Cr₂O₅, respectively.

Fig. 2. X-ray diffraction pattern for CrN multilayer specimens.

Fig. 3. Peak fitting for pristine CrN multilayer specimens, a) N 1s, b) Cr 2p, c) O 1s.
398.0 eV (Fig. 3a). This can be assigned to the metallic nitride, CrN (theoretical peak 396.6–396.8 eV), with the lower intensity at 398.0 eV associated to Cr$_2$N. This assumes that the Cr$_2$N energy is slightly higher than the standard value of 397.6 eV.

The Cr 2p$_{3/2}$ peaks have been systematically decomposed into three components of similar intensities at energies of 574.0 eV, 575.0 eV and 576.4 eV (Fig. 3b). These correspond to metallic Cr (574.0 eV), CrN (575.0 eV, compared to the reference value 575.8 eV), and Cr$_2$N (576.4 eV). Note that the Cr$_2$N peak amplitude, and its location at higher energies than those described in literature [13], could be masking the existence of oxides type Cr$_2$O$_3$ (usually between 576 and 576.6 eV). This would suggest an overlap of Cr$_2$N and Cr$_2$O$_3$ peaks.

Finally, Fig. 3c shows the O 1s spectrum after 30 min of sputtering, which can be fitted with two peaks at 530.7 and 533.7 eV. The first component at 530.7 eV represents lattice oxygen (O$^-$), while 533.7 eV could correspond to oxygen in a water bond (O–OH): this has been reported elsewhere [14] at 533.3 eV for specimens with water absorption.

It can be concluded that the reference pristine CrN are mainly composed of CrN and Cr$_2$N, with a little Cr$_2$O$_3$: these conclusions are in accordance with X-ray diffraction patterns.

Fig. 4 shows how the exposed surfaces, and the spectra of the main elements, change as a consequence of dissolution due to the oxidising solution and the test conditions, as a function of stripping time. Spectra have been shifted vertically by arbitrary amounts for better visibility. Compared to the pristine reference, Cr 2p spectrum shows increasing intensity with stripping time up to 3600 s, after which intensities decrease indicating that the substrate has been reached. On the other hand, the N 1s peak exhibits a continuous decrease of intensity with stripping time. In addition, O 1s and Fe 2p peaks are better resolved with time since the oxidation of the CrN controls the removal of the layer, and after 3600 s, the iron substrate becomes visible.

We shall now analyse the data as a function of stripping time, to investigate how the process evolves.

3.2. A.—Stripping time: 800 s

Fig. 1 point A, and micrograph (a) correspond to specimens stripped for 800 s. It is observed that surface morphology becomes porous losing the initial homogeneity distinctive of the pristine specimens. Using a symmetrical peak model (Fig. 5) for the detailed analysis of the Cr2p$_{3/2}$ energy levels a good fitting is obtained with three contributions corresponding to Cr−N (574.4 eV), Cr−N−O (574.8 eV) and Cr−O (576.2 eV).

There is much discussion in the literature of these peaks. According to Milosev et al. [15] the peak corresponding to a clean CrN surface (e.g. after sputtering) should be at 574.5 eV with a Full Width at Half-maximum Intensity (FWHM) of 2.9 eV. If this is the case, we would attribute the chemical shift of this binding energy compared with our Cr−N peak (574.4 eV), Cr−N−O (574.8 eV) and Cr−O (576.2 eV).

Fig. 4. XPS spectra recorded after 800, 2000, 3600 and 4500 s of stripping for O 1s (a), Cr 2p (b), N 1s (c) and Fe 2p (d).
intensity of the Cr peak observed in Fig. 4 which Milosev et al. [15] relate with the presence of oxidized components.

Other authors [11,16] however, are of the opinion that the CrN peak should be centred at 575.8 eV instead of 574.5 eV. If this is the case, the component observed at 574.4 eV would relate to metallic Cr, indicating that the outer CrN layer has been removed. Its smaller size would be explained as a result of the oxidation promoted by the electrochemical stripping. The second peak, at intermediate B. E. 574.8 eV, whose intensity has increased relative to the reference, could be related with the presence of chromium oxy-nitrides, Cr(N,O) formed by substitution of nitrogen by oxygen. Similarly, the third peak at 576.3 eV could also be related to Cr2O3 with some contribution from Cr2N, whose B.E. is very close to the oxide. This would be supported by the broad FWHM (4.5), observed for this peak.

In general, observation of Cr 2p shifted to higher binding energy (575 eV), together with higher intensity envelope of the Cr 2p3/2 peak, indicates formation of some Cr(N,O) and oxide Cr2O3 species.

The oxidation of the chromium nitride observed in Cr 2p spectra also agrees with changes observed in N 1s spectra (Fig. 5b). The nitrogen peak may be fitted by two peaks with different intensities corresponding to CrN (397.8 eV) and Cr2N (398.8 eV). The first high energy component is related to metallic nitrides — CrN, although its binding energy is rather close to Cr2N, (reference value 397.6 eV). These B.E. values are shifted towards higher energies with respect to the published data for Cr3N and CrN. This effect can be attributed to nitrogen atoms existing both at interstitial sites within the Cr (N) phase, and as nitrides [17], but another possible explanation for such a high B. E. close to 399 eV nitrides with a non-defined stoichiometry, could be the presence of oxy-nitrides compounds [18].

Finally, the O 1s peak is very asymmetrical, as may be seen from Fig. 5c, compared with the pristine sample. The peak can be decomposed into two components, at 530.6 eV and 532.2 eV. Both would be indicative of an oxide layer composed mainly of oxide and hydroxides on the surface.

3.3. B.—Stripping time: 2000 s

Specimens stripped for 2000 s had irregular surfaces, Fig. 1c: point B on Fig. 1a. This is attributed to the fact that coating dissolution nucleates in some areas in drop form, and grows...
According to our calculations derived from Faraday’s Law, after 2000 s, the external layers (outer CrN, Cr interlayer and a second CrN) have been removed [10] leaving the second Cr buffer layer exposed for XPS analysis. Therefore, in principle the XPS analysis could show similar results to those previously described.

The broad Cr 2p peak around 574 eV (Fig. 4b), is composed of two components corresponding to Cr (574.1 eV) and chromium oxy-nitrides (574.7 eV), together with a third peak at 576.7 eV related to the Cr$_2$O$_3$ and Cr$_2$N with very close binding energies [9]. The slight energy increase seen for metallic chromium in the previous sample could suggest the existence of a graded region at the coating–chromium interface.

As in A specimens, nitrogen and oxygen peaks are made of two peaks of different intensities corresponding to chromium nitrides and oxy-nitrides.

After stripping for 2000 s, specimens begin to reveal a low intensity peak associated with metallic Fe, Fig. 4. Milosev et al. found similar results when they oxidised CrN at high temperature [19].

### 3.4. C.—Stripping time: 3600 s

After 3600 s most of the coating has been stripped leaving just the last chromium buffer layer and the substrate. Nevertheless, as the coating removal does not occur homogeneously all over the surface, in some areas the base metal could be exposed earlier. This explains the presence of Fe spectra after 2000 s of stripping and the fact that it becomes better resolved with longer stripping time.

Fig. 6a shows a better defined Fe 2p spectrum which can be fitted with three components 706.7, 708.2, 712.8 eV. These can be attributed to metallic Fe (706.7, reference value 707 eV for the component 2p$_{3/2}$), oxide type Fe$_3$O$_4$ (708.2 reference at 708.2 eV), and Fe$_2$O$_3$ and hydroxides type FeOOH with reference energies of 710.8 eV and 711.3 eV.

The presence of these iron oxides result in a wider O 1s peak with a higher contribution of the oxide component than in the nitrogen peaks (Fig. 7). Peak fitting for Fe 2p and O 1s, corresponding to position D (samples submitted to 4500 s of stripping).

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samples submitted to shorter stripping times. Its fitting shows the presence of oxides and hydroxides at binding energies of 530 and 531.5 eV respectively, Fig. 6b. Chromium and nitrogen spectra are similar to those made for the specimens stripped for 2000 s, for this reason they are not included.

3.5. D.—Stripping time: 4500 s

The potential vs. time curve — Fig. 1 — shows that the coating has been completely removed after 4500 s, since the potential corresponds to that of the metal substrate. Therefore the analysis of XPS is made on the M2 steel base. Fig. 4 shows a large drop in the intensity of Cr 2p and N 1s spectra compared to the partially-stripped samples and this change, is even greater when compared to the pristine sample. At the same time O 1s and Fe increased drastically as seen in Fig. 4.

The Fe 2p peak shows a high intensity and develops a marked asymmetry, as a consequence of the different contributions from the broad Fe 2p3/2 peak, Fig. 7a. Peaks correspond to metallic iron (706.9 eV), to the oxidized component Fe3O4 (708.4 eV), and at a peak at 712.1 eV could be due to the presence of FeOOH and Fe2O3. These results are in agreement with the literature for anodic oxidation of steels [20,21].

The findings are supported by the evolution of the O 1s peaks. Fig. 7b shows an increase in O = (530.4 eV), associated with oxide species Cr2O3 and also in OH− (532.2 eV) which corresponds to iron oxides as Fe2O3 (reference value 532.9 eV).

Finally, it has to be noted that although the CrN multilayer has been completely removed after 4500 s of stripping, nitrogen and chromium spectra still show some small peaks, (see Fig. 8). The N 1s peak shows the component corresponding to metallic nitrides, perhaps indicating traces of chromium nitrides or oxy-nitrides or even iron nitride [22]. These nitrides could be formed during the PVD process by nitrogen diffusion into the base steel. A similar gas nitriding effect, producing an outward growth of the nitride layer [23], has been observed in the case of titanium alloys and steels.

The Cr 2p Fig. 9 is completely in accordance with this model. Despite the low intensity we can distinguish three 2p3/2 components within the peak. The contribution of the smallest binding energy (574.2 eV), which corresponds to iron oxides as Fe2O3 (reference value 575.3 eV) is associated to that described at 577.2 eV, corresponding to metallic chromium. The very low intensity indicates that it may actually be due to Cr in the base steel. In addition, the second component is has extremely low binding energies compared to normal metallic nitrides (575.8 eV for CrN and 575.3 eV for oxy-nitride). The third component (577.2 eV) presents classical features for oxidised species, and is indicative of Cr(OH)3.

In principle, these results might suggest that longer stripping time would completely remove all traces of N and Cr. However, it should be taken into account that longer times also induce the substrate attack. As was demonstrated in a previous paper [10] that “overstripping” by 30% of the time needed for complete coating removal induces severe attack by the dissolution of carbides, increasing surface inhomogeneity, and negatively affect the quality of any subsequent coatings.

4. Conclusions

Multi-layer coatings of CrN—Cr—CrN—Cr—CrN—Cr— on M2 steel were stripped, using an electrochemical technique. The CrN layers were approximately 1.5 μm, and the Cr interlayers, 0.1 μm thick in these samples. The process was interrupted after the removal of each individual layer and XPS analysis was used to study the stripping mechanism. The composition of pristine (unstripped) CrN reference specimens was CrN and Cr2N, with a small amount of Cr2O3. As the stripping time increases, the Cr 2p3/2 peak indicates the formation of Cr(N,O) and oxide Cr2O3 species. After 800 s of stripping the first (outer) CrN layer should have been removed, but spectra still indicated the presence of CrN and Cr2N. This may be attributed to nitrogen atoms, trapped at interstitial sites within the Cr (N) phase, or even the presence of oxy-nitrides compounds. Increasing the stripping time to 2000 s, the coating/chromium interface starts to appear graded, and a low intensity metallic Fe peak starts to appear. After a total of 3600 s, iron oxides become more evident (the O 1s peak broadens) with little change in the chromium and nitrogen spectra. Finally, when the stripping has been completed, (4500 s), only N and Cr traces appeared in the spectra.

Lastly, it is interesting to note that Cr6+ has not been detected in this work, since no components at binding energies associated with Cr6+ (between 578.1 and 579.9 eV) were observed. Most probably this is due to fast diffusion in the bulk solution as a consequence of its high solubility in alkaline solutions. The same argument is applied to N2, (which would be seen at a binding energy of 402 eV), which is one of the reaction products of CrN to form Cr2O3. This was not seen, and so we conclude that it diffuses away fast and does not become trapped in the external oxide layers.

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References