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Electrochemical stripping of hard ceramic chromium nitride coatings

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Abstract

Chromium nitride—CrN—coatings have emerged as an alternative in machining applications thanks to thermal stability, low deposition temperature, excellent wear resistance and good corrosion resistance. However, under some circumstances it is often necessary to remove these kinds of coatings without attack of the base metal surface. In this work a stripping method based on electrochemical techniques has been developed to strip chromium nitride coatings in an oxidising alkaline solution process. Under galvanostatic conditions, it has been applied to strip CrN coatings with different configurations—monolayer and multilayer. The greater activity of the nitride in this medium leads to the formation of more soluble species. The complete removal of the chromium nitride layer is indicated by a sudden rise in the potential in time, which allows simple control of the stripping process. The surface appearance of the samples at the end of the coating removal process is good, since pitting is not detected and surface homogeneity is preserved, which are necessary conditions for redeposition of this type of coating.

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1. Introduction

Physical vapour deposition (PVD) has aroused great interest in recent years since it allows deposition of denser and more compact coatings than are obtained by chemical vapour deposition (CVD), leading to improved chemical and mechanical properties [1]. The technique may be used for a wide range of coatings and hard nitrides or carbides are widely used in the manufacture of tools and forming moulds because of their high wear resistance and low chemical inertia [2]. Of these, TiN coatings are the best established at industrial level. However, CrN coatings have emerged as an alternative in machining applications thanks to thermal stability, low deposition temperature, excellent wear resistance–not only abrasive but also adhesive–and good corrosion resistance [3–10]. This combination of properties makes CrN coatings especially attractive in applications where tools are routinely subjected to high temperatures and aggressive atmospheres, e.g. in the plastic injection industry, where the use of these coatings can substantially prolong the service life of coated parts [11].

However, when high cost tools of this type need to be repaired, e.g. when cutting edges need to be sharpened, it is often necessary to remove any coatings and subsequently recoat the repaired surfaces. Similarly, when faults in these coatings are detected it is necessary to remove them in order to redeposit a new defect-free coating.

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In this context the search for a method to remove hard coatings–stripping or decoating–has aroused great interest in the cutting and forming industry, since a stripping and recoating process would represent an economically more advantageous alternative to the replacement of worn parts, given the high cost of replacements. In order to be industrially viable, any process for removing hard coatings must be simple, efficient, cheap, and must not damage the substrate.

In the case of TiN coatings, the stripping process is more or less established at an industrial level with the use of alkaline solutions containing hydrogen peroxide, despite the instability of these solutions, but no stripping procedure has yet been established for CrN coatings. There are recent reports of chemical and/or electrochemical methods, based fundamentally on the combination of oxidising agents and/or the application of current in passivating media: hydrogen peroxide and oxalate; potassium permanganate in concentrated sulphuric acid [12]; and NaOH [13]. However, these authors also report that galvanostatic tests in poorly oxidising media induce severe attack of the substrates, due to the high current densities that must be applied to remove the coating, and furthermore that the use of an exclusively chemical method does not allow control of the stripping process. All of this makes it necessary to develop more competitive methods.

In this work a stripping process employing alkaline oxidising solutions using galvanostatic conditions has been applied to CrN coatings with different configurations—monolayer and multilayer [14]. A complete characterisation of the surface after each step of the stripping process has been carried out by means of scanning electron microscopy (SEM) and electron dispersive spectroscopy (EDS) analysis. The sensitivity of the technique has been demonstrated to allow control of the nitride removal rate and to determine thickness changes in the layers.

2. Experimental details

2.1. Samples

The substrates are 20 mm diameter and 3 mm thick discs of M2 high speed steel, with composition: C 0.97%, Si 0.2%, Mn 0.2%, Cr 4.11%, W 6.3%, V 1.8%, Mo 4.9%, and Fe balance. Discs were coated with CrN using the electron-beam ion plating PVD technique by Tecvac.

Coatings were applied in two different configurations, as shown in Fig. 1. The first consists of a CrN single layer of a total thickness of between 1.4–1.7 μm and a Cr interlayer of approximately 0.1 μm between the nitride and the substrate. The second group of samples consists of multilayer coatings of a total thickness of between 5 ~ 6 μm, in which each of the three CrN layers is separated from the previous one by an intermediate Cr layer of approximately 0.1 μm.

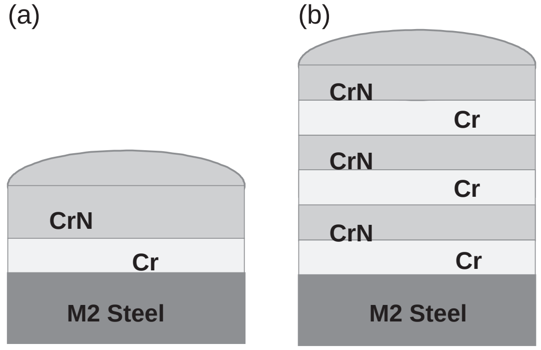

Fig. 1. General configuration of CrN samples: (a) monolayer (b) multilayer.

2.2. Microstructural characterisation

Changes in the morphology of the CrN coatings due to stripping process have been studied by field emission gun scanning electron microscopy (SEM-FEG) JEOL 6500F and the analyses were made with a Link-Inca Energy Dispersive Spectrometer. Secondary electron images have been recorded working at 7 kV in normal and 30° tilted geometry. Backscattered electron images were taken at 10 kV.

2.3. Electrochemical characterisation

Electrochemical tests were carried out using a conventional three-electrode cell consisting of a saturated calomel reference electrode (SCE), a platinum counter electrode, and the studied samples as the working electrode. The exposed area of the CrN samples was of the order of 0.25 cm^2.

The chemical composition of the alkaline oxidiser solution was provided by Tecvac. The composition of this electrolyte is commercially confidential.

Before testing, samples were cleaned with acetone in an ultrasonic bath for 5 min followed by 5 min further in isopropanol.

2.3.1. Polarisation

Polarisation curves were performed at a scanning rate of 0.16 mV s^{-1}. The potential scan was started after a potential stabilisation time of 900 s.

Using uncoated samples, potentiodynamic curves were performed applying a potential step in the cathodic direction until reaching a value of -0.2 V from the corrosion potential, obtaining a potential from which scanning was begun in the anodic direction until reaching a value of 0.6 V versus E_{corr}.

In addition to scanning in the anodic direction, using identical conditions to the bare M2 steel samples, coated samples were also subjected to the reverse cycle to evaluate the alterations produced in the CrN by anodic polarisation of the material.

3. Results and discussion

The results obtained in the electrochemical tests reveal differences between the activity of the M2 steel substrate and the chromium nitride samples in these solutions. The polarisation curves performed for each sample in this solution (Fig. 2a) show that the corrosion potential of the M2 base steel is of the order of 0.36 V/SCE and the corrosion current (~ 0.2 mA/cm^2) is lower than that of the samples coated with CrN. The anodic branch of the curve for M2 shows a pseudo-passive region of about 100 mV in width, followed by a region of greater activity where the current density grows continuously with increasing potential.

The shape of the polarisation curves obtained for chromium nitride samples is similar to that described above. However, the corrosion potential is located at slightly more cathodic values and the anodic branch is shifted towards higher current density values than for M2 steel. It also presents certain instabilities in a potential range between 0.5 and 0.65 V/SCE, which could indicate breakdown or dissolution of the CrN coating.

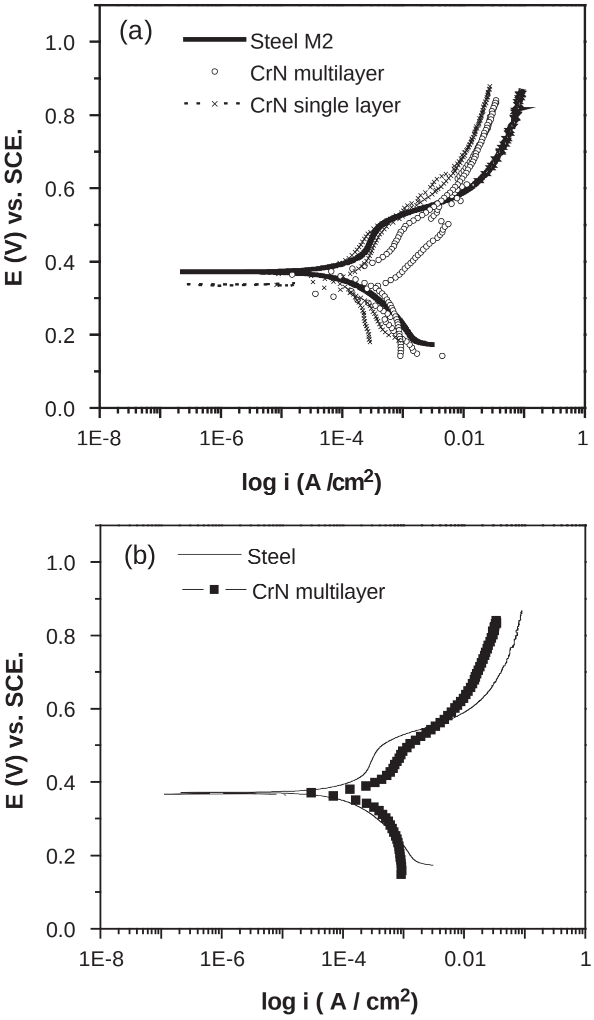

Fig. 2. (a) Polarisation curves for CrN and bare M2 steel. (b) Comparison between reverse scan of the nitride simple and the steel substrate.

On the other hand, the reverse scan passes through lower current density values, indicating that changes promoted during the anodic polarisation of the curve have taken place on the surface. In principle, the similarity between the anodic branch for M2 steel and the cathodic (reverse) scan of the coated sample suggests that partial removal of the CrN layer may have taken place during anodic scanning, which would explain the drop in current density recorded during the return cycle and the shift in corrosion potential in the anodic direction towards values closer to those of the M2 substrate (Fig. 2b).

These results indicate that polarising the CrN-coated specimens and maintaining these conditions for the necessary time would lead to oxidation of the nitride and thus dissolution of the coating. Therefore, by perturbing the system either potentiostatically or galvanostatically it would be possible to induce the dissolution of the PVD nitride layer. If the applied perturbation is of the potentiostatic type, e.g. polarising the samples at potential values of the order of 0.5 V, the dissolution of the coating would appear as an abrupt drop in the current density. On the other hand, if the perturbation is of the galvanostatic type, the removal of the coating would appear as an increase in the potential recorded.

Preliminary tests carried out in each condition led to the conclusion that better discrimination of the coating removal process is achieved in galvanostatic conditions. On the other hand, by applying Faraday's law for the specific testing conditions–area to be removed and current intensity employed–it is possible to estimate the time necessary for these changes in potential to occur.

From the polarisation curves it was estimated that applying current densities of between 5–12 mA cm^{-2} would allow the layers to be removed in a short time period.

The first stripping tests were carried out on the samples with a single CrN layer (and Cr interlayer), applying a current of 2 mA on an exposed surface area of 0.22–0.29 cm^2, which defined adequate current density values of the order of 7–9 mA cm^{-2}.

The variations in potential recorded during the removal of CrN from specimens with a monolayer type configuration are shown in Fig. 3a. Initially a first oxidation region appears at potential values of the order of 0.58 V/SCE, which may be associated with removal of the outer CrN layer, followed by a potential drop to values close to 0.52 V/SCE for a short time of about 85 s, probably associated with removal of the intermediate Cr layer. Finally, the potential rises to values of

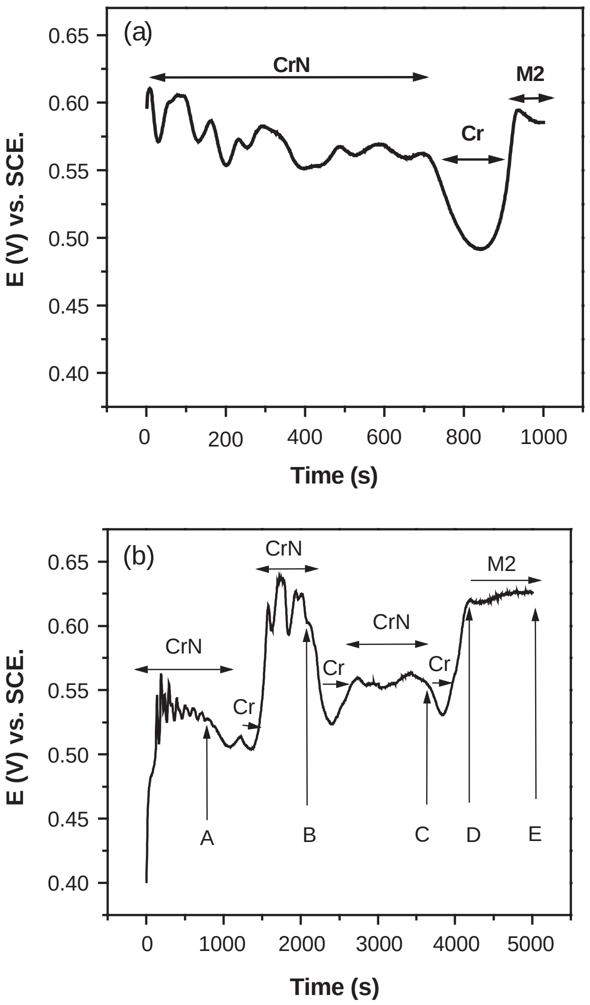

Fig. 3. (a) Galvanostatic test for CrN-monolayer sample. (b) Galvanostatic test for CrN-multilayer sample.

approximately 600 mV, corresponding to the M2 steel substrate.

The time necessary to remove the coating was estimated using Faraday's law, bearing in mind that the coating consists of two stages and it is therefore necessary to estimate the time necessary to remove the outer CrN layer (thickness 1.5 μm) and the inner Cr anchor layer (thickness 0.1 μm), whose oxidation kinetics will be different. The two contributions are determined from the expressions:

$$\mathrm{time}_{\mathrm{CrN}} = \frac{96500\mathrm{C}\cdot m(\mathrm{gr})}{I(\mathrm{A})\cdot\dfrac{\mathrm{AWCrN(gr/mol)}}{ne^{-}(6)}}$$

$$\mathrm{time}_{\mathrm{Cr}} = \frac{96500\mathrm{C}\cdot m(\mathrm{gr})}{I(\mathrm{A})\cdot\dfrac{\mathrm{AWCr(gr/mol)}}{ne^{-}(6)}}$$

where the mass, m, is obtained from the theoretical volume data for the exposed area and the density of the layer to be removed. Though PVD coatings present substantial variations in their density, depending on the method used [15–17], the values considered in this study are 5.9 g cm^{-3} for CrN and 7.2 g cm^{-3} for pure chrome [18], which have been reported in the literature for layers deposited in a similar way to those described here. Table 1 shows the coating removal times estimated from Faraday's law and obtained experimentally for the specimens coated with a monolayer configuration.

Multilayer samples were also evaluated. In principle, if the potential drop recorded prior to the final increase in potential is taken to represent the dissolution of the Cr interlayer, this drop should be trebled in the case of the multilayer samples. Fig. 3b displays the variation in potential versus time for this type of samples. There is a delay in reaching the potential of the nitride, which in principle would indicate the different surface state of each sample. After this the curve shape recorded for the monolayer samples is repeated in triplicate. A first potential drop appears at values of 1250 s, followed by a second at approximately 2300 s, and finally a third at around 3800 s. The potentials corresponding to the dissolution of each of the layers are not the same, which in principle may denote a different composition in each one; perhaps related to the existence of nitrides of different stoichiometries or the presence of chromium oxynitride and chromates [19,20] on the surface originated during the coating removal process.

The duration of the potential variation corresponding to the removal of each layer is different in each case,

Table 1
Calculated time obtained from Faraday's equation on CrN samples

Sample			Theoretical time for CrN (s)	Theoretical time for Cr (s)	Total theoretical time (s)	Total experimental time (s)
CrN-monolayer	1	0.226 cm^2	800	73	871	816
	2	0.255 cm^2	924	84	1008	930
	3	0.221 cm2	799	72	871	812
	4	0.229 cm^2	829	75	905	843
CrN-multilayer	5	0.255 cm^2	3090	251	3342	3328
	6	0.287 cm^2	3481	283	3765	4058
	7	0.264 cm^2	3200	260	3460	3151
	8	0.292 cm^2	3539	287	3827	3975

Current applied I=2 mA.

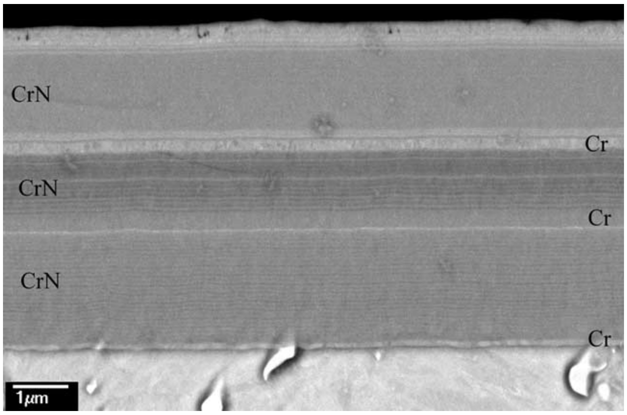

Fig. 4. Cross-section of a CrN-multilayer sample.

suggesting that the layers do not possess a homogenous thickness. This was corroborated with a cross-section of the multilayer coating (Fig. 4), which revealed the different thickness of each of the deposited layers.

This result highlights the sensitivity of the test, since the potential fluctuations and the values obtained are intimately dependent on the volume of CrN removed. On the other hand, this difference in thickness explains the discrepancies that are obtained between the theoretical calculations and experimental results (Table 1), since in every case the same thickness was considered for each of the 3 layers that comprise the multilayer system.

Table 1 indicates the different stripping times obtained for the multilayer samples, both experimentally and theoretically from Faraday's expression. It is noted that small variations in the exposed area are reflected in the stripping times. Although small changes in the surface area mean a change in the volume of CrN removed, the approximations are very good.

In this respect, one of the main advantages of the method is that the differences in potential between the different layers of the coating offer a simple control of the removal process. In other words, from the experimental data it is possible to calculate the thickness of the complete coating of each of the CrN and Cr nanolayers. These experimental results show that the thickness of the different layers is not homogeneous, with the intermediate CrN layer being much thinner, as can be verified by the respective SEM/back-scattering analysis.

Finally, SEM inspection of the specimen surface at different points on the stripping curve makes it possible to study the layer dissolution process and to observe the state of the substrate surface once the coating has been completely removed. Fig. 5a and b shows the surface appearance of the samples before treatment and after 800 s. While the appearance of the specimens is initially homogenous, observation of the specimens at point A on the stripping curve reveals generalised attack of the surface, in the form of an increase in coating porosity.

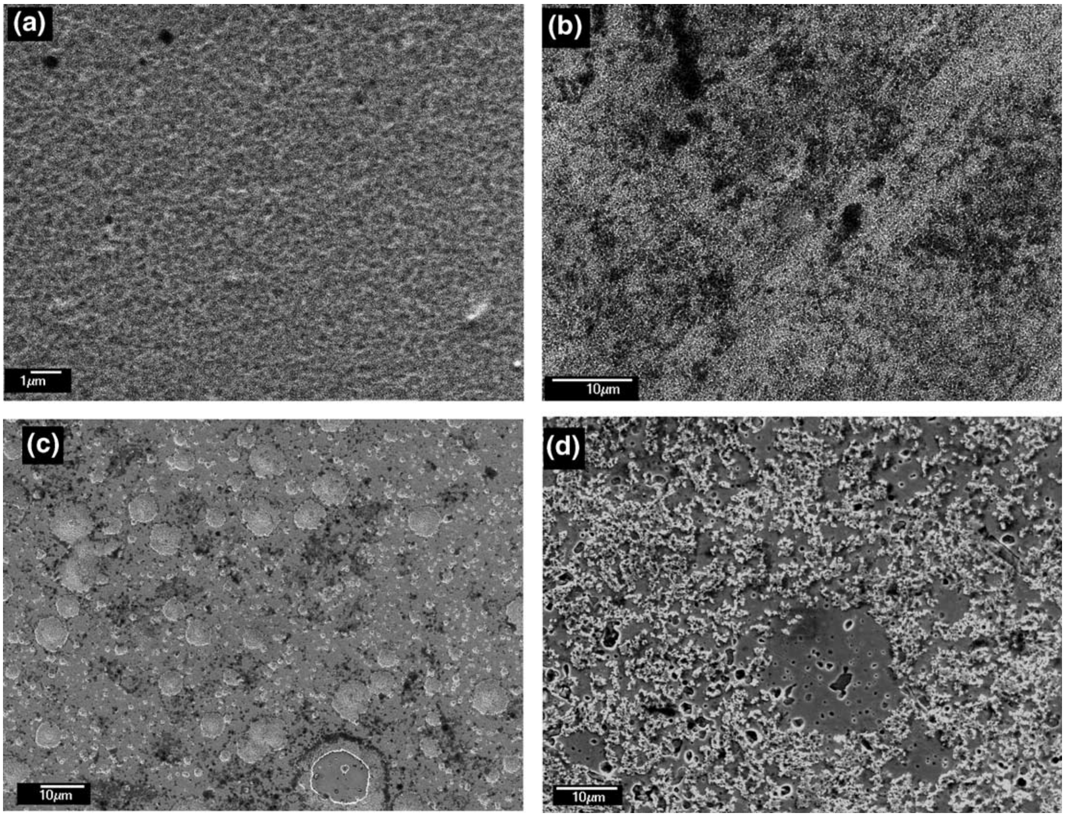

Fig. 5. SEM images of the surface of (a) as-received CrN-multilayer specimen; (b) after 800 s of stripping (position A on Fig. 3b); (c) after 2000 s (position B); and (d) after 3650 s (position C).

At longer treatment times (B) the surface inhomogeneity is even greater. The attack seems to nucleate in certain areas of the surface in drop form and grows concentrically, so that when several adjacent zones join up they leave a larger area of the Cr interlayer uncovered (Fig. 5c). Finally, observation of the samples treated for longer times (C) shows the base steel partially coated with the remains of the Cr layer (Fig. 5d).

At the end of the process (D), samples present a shiny appearance, whereas intermediate stages look grey–brown in colour. On the other hand, SEM analysis (Fig. 6) indicates that the substrate is not pitted. The black dots that appear on the micrograph are carbides that constitute the alloy, as can be seen in the EDS analysis, which reveals C and W enrichment in these zones. On the other hand, the cross-section of the specimens corroborates the great homogeneity of the substrate surface after the stripping process.

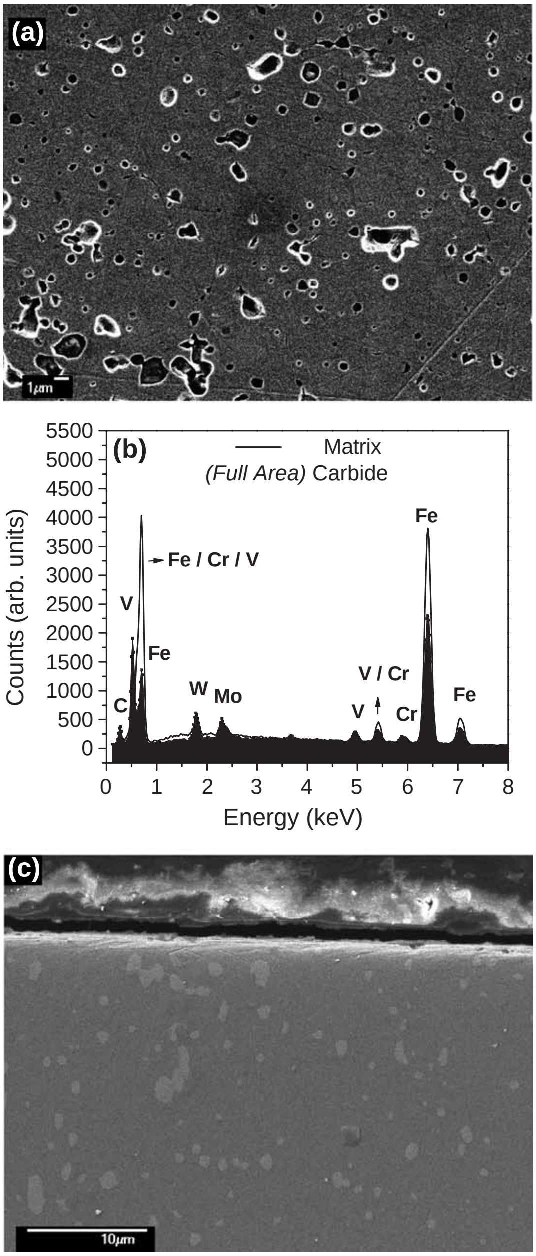

Fig. 6. (a) SEM micrograph after complete total stripping (position D). (b) EDS analysis of matrix and carbides of bare substrate. (c) Cross-section of the de-coated area.

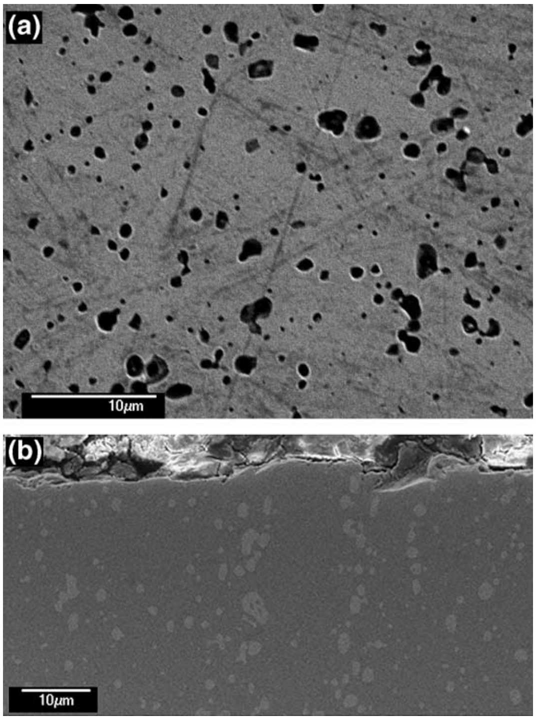

Fig. 7. SEM (a) plan view and (b) cross-section images of a sample held in stripping solution for 30% more time than requested for complete coating removal.

In contrast, an excess of around 30% in the treatment time would lead to a more severe attack of the substrate (Fig. 7), caused by dissolution of the carbides, and would generate an increase in surface inhomogeneity that would negatively affect the quality of the coating subsequently deposited on the sample and make it necessary to perform superficial machining in order to achieve an appropriate surface finish.

4. Conclusions

A method has been developed to strip chromium nitride coatings by the application of a current in an oxidising alkaline solution. The greater activity of the nitride in this medium means that in galvanostatic conditions the oxidation of the CrN takes place, leading to the formation of more soluble species. The complete removal of the chromium nitride layer is indicated by a sudden rise in the potential in time, which allows simple control of the stripping process.

The sensitivity of the technique makes it possible to determine the thickness of the deposited layers from the dissolution times obtained in the record of potential versus time in galvanostatic conditions. The surface appearance of the samples at the end of the coating removal process is good since pitting is not detected and surface homogeneity is preserved, which are necessary conditions for redeposition of this type of coating.

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References

[1] H.A. Jehn, Surf. Coat. Technol. 125 (2000) 212.
[2] J. Esteve, E. Martinez, A. Lousa, F. Montala, L.L. Carreras, Surf. Coat. Technol. 133/134 (2000) 314.
[3] E. Martinez, J. Romero, A. Lousa, J. Esteve, Surf. Coat. Technol. 163/164 (2003) 571.
[4] S. Ortmann, A. Savan, Y. Gervig, H. Haefke, Wear 254 (2003) 1099.
[5] L. Cunha, M. Andristschky, Surf. Coat. Technol. 111 (1999) 158.
[6] C. Liu, A. Leyland, Q. Bi, A. Matthews, Corros. Sci. 45 (2003) 1243.
[7] C. Liu, A. Leyland, A. Matthews, Corros. Sci. 45 (2003) 1257.
[8] S.H. Ahn, Y.S. Choi, J.G. Kim, J.G. Han, Surf. Coat. Technol. 150 (2002) 319.
[9] C. Liu, A. Leyland, Q. Bi, A. Matthews, Surf. Coat. Technol. 141 (2001) 164.
[10] J.W. Seok, N.M. Jadeed, R.Y. Lin, Surf. Coat. Technol. 138 (2001) 14.
[11] M. Urgën, A.F. Cakir, Surf. Coat. Technol. 96 (1997) 236.
[12] D. Bonacchi, G. Rizzi, U. Bardi, A. Scrivani, Surf. Coat. Technol. 165 (2003) 35.
[13] Y. Sen, M. Ürgen, K. Kazmanli, A.F. Cakir, Surf. Coat. Technol. 113 (1999) 31.
[14] C. Liu, Q. Bi, A. Matthews, Corros. Sci. 43 (2001) 1953.
[15] G. Bertrand, H. Mahdjoub, C. Meunier, Surf. Coat. Technol. 126 (2000) 199.
[16] L. Cunha, M. Andritschky, K. Pischow, Z. Wang, Thin Solid Films 355/356 (1999) 465.
[17] J. Xu, H. Umehara, I. Kojima, Appl. Surf. Sci. 201 (2002) 208.
[18] Handbook of Chemistry and Physics, 66th Edition 1985–1986, CRC Press.
[19] I. Milosev, H.H. Strehblow, B. Navinsek, Thin Solid Films 303 (1997) 246.
[20] L. Cunha, M. Andritschky, L. Rebouta, K. Pischow, Surf. Coat. Technol. 116/119 (1999) 1152.