

CHARACTERIZATION OF PVD Cr-C, Cr(C,N) AND Cr-N HARD COATINGS

KARAKTERIZACIJA Cr-C, Cr(C,N) IN Cr-N TRDIH PREVLEK, PRIPRAVLJENIH S PVD POSTOPKOM

Miha Ćekada¹, Marijan Maček^{1,2}, Peter Panjan¹, Boris Navinšek¹

¹ Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

² University of Ljubljana, Faculty of Electrotechnical Engineering, Trška 25, 1000 Ljubljana, Slovenia

Prejem rokopisa – received: 1999-11-17; sprejem za objavo – accepted for publication: 1999-11-22

Cr-N hard coatings have been widely investigated for over 10 years and successfully implemented in industry. Recently, work has been done on Cr-C hard coatings and some industrial applications were reported, in particular, the protection of tools for aluminium die-casting. However, information about the ternary Cr(C,N) hard coating is scarce.

We prepared several Cr(C,N) hard coatings with different C:N ratios by varying the N₂ and C₂H₂ flow. Stoichiometric, as well as nonstoichiometric Cr-N and Cr-C coatings were prepared for comparison. The coatings were deposited by evaporation in a thermionic arc ion plating BAI730M (Balzers) apparatus. Polished tool steel disks, silicon wafers and polished alumina ceramics were used as substrates.

Oxidation of the coatings was carried out by heating the samples at 750-900°C in an oxygen atmosphere while measuring the weight gain and the thickness increase. The depth profiles of the samples, oxidized at various temperatures, were measured by Auger electron spectrometer (AES). Microhardness, adhesion and surface roughness were also measured.

We investigated the influence of the N₂ and C₂H₂ partial pressures on the above mentioned physical and chemical properties. The results show that Cr-C coatings do have the potential for industrial application.

Key words: hard coatings, physical vapour deposition, microhardness, adhesion, oxidation resistance

Raziskave Cr-N trdih prevlek potekajo že več kot 10 let in so se uspešno uveljavile v industriji. Zanjih nekaj let se raziskuje tudi Cr-C trde prevleke in prišlo je že do prvih industrijskih aplikacij, konkretno za prekrivanje orodij za tlačenje aluminija. Toda informacij o ternarni Cr(C,N) trdi prevleki je malo.

Pripravili smo več Cr(C,N) trdih prevlek z različnim atomskim razmerjem C:N tako, da smo spreminjali pretok N₂ in C₂H₂. Za primerjavo smo pripravili tudi stehiometrične in nestehiometrične Cr-N in Cr-C prevleke. Prevleke smo pripravili z napajanjem v termionskem sistemu BAI730M (Balzers) za ionsko prekrivanje. Za podlage smo uporabili polirane plošče iz orodnega jekla, silicijeve rezine in polirano aluminij-oksido keramiko.

Vzorci smo oksidirali tako, da smo jih segrevali pri temperaturah 750-900°C v kisikovi atmosferi in merili prirastek mase in debeline. Globinski profil vzorcev, ki smo jih oksidirali pri različnih temperaturah, smo izmerili z Augerjevim elektronskim spektrometrom (AES). Izmerili smo tudi mikrotvrdoto, adhezijo in hrapavost površine.

Izmerili smo vpliv delnega tlaka N₂ in C₂H₂ na zgoraj omenjene fizikalne in kemijske lastnosti. Rezultati kažejo, da so Cr-C prevleke potencialno uporabne v industrijske namene.

Glavne besede: trde prevleke, vakuumski postopki nanašanja, mikrotvrdota, adhezija, oksidacijska obstojnost

1 INTRODUCTION

PVD Cr-N coatings have been widely investigated for over 10 years and successfully implemented in industry for the last decade. There are numerous references to their properties and applications¹⁻⁶. PVD Cr-C coatings, on the other hand, are relatively new in this field. Recently, some industrial applications were reported^{7,8}. However, information about the ternary PVD Cr(C,N) coating is scarce. These papers on Cr(C,N) concentrate on the deposition parameters and phase composition^{9,10}, as well as on more application-oriented measurements such as microhardness, adhesion, oxidation and wear resistance^{11,12}.

We deposited several Cr(C,N) coatings by varying the partial pressures of the reactive gases nitrogen and acetylene. Keeping the working gas (argon) pressure constant the total pressure was varied as well. We investigated the influence of these process parameters on the physical and chemical properties of the coatings. These properties were: atomic composition,

microhardness, adhesion and resistance to oxidation. Rather than being linear, these relationships could exhibit a peak or valley, which would have a great influence on possible applications. Besides the ternary carbonitrides Cr(C,N), the binary coatings Cr-N and Cr-C were also deposited, stoichiometric, as well as substoichiometric.

The next step in our work would be the determination of the optimum deposition parameters for possible application of these coatings in industry.

2 EXPERIMENTAL PROCEDURE

The coatings were deposited by evaporation in a Balzers BAI730M thermionic arc ion plating apparatus at a relatively high temperature (450±50°C). The deposition rate was about 4 μm/h and the bias on the substrates was -125V. Details of the deposition procedure are described elsewhere¹³.

Chromium was used as the target material, argon served as the working gas and the source (reactive) gases

for nitrogen (in nitrides) and carbon (in carbides) were N_2 and C_2H_2 , respectively. The working gas (argon) pressure was kept constant at 1.5×10^{-3} mbar. Four series of coatings were deposited with total pressures of 2, 2.5, 3 and 3.5×10^{-3} mbar. Subtracting the constant argon pressure, the combined pressures of both reactive gases were 0.5, 1, 1.5 and 2×10^{-3} mbar. For convenience, from now on the term "total pressure" is used for this quantity. In each series, several coatings were deposited by varying the nitrogen-to-acetylene ratio. Putting the nitrogen partial pressure to zero and introducing only acetylene as the reactive gas, a chromium carbide (Cr-C) coating formed. Introducing only nitrogen gas into the chamber, on the other hand, caused the deposition of a chromium nitride (Cr-N) coating. If both reactive gases were present, a chromium carbonitride (Cr(C,N)) coating formed.

The coatings were deposited on polished high-speed steel disks (DIN PMS6-5-3-8) for microhardness and adhesion measurements, and on polished alumina ceramics ($R_a=25nm$) for oxidation tests.

Oxidation was studied by annealing the samples in a tube furnace with an oxygen flow. Periodically, the specimens were taken out of the furnace and weighed using a precise microbalance (Mettler Toledo UMT2). For the microhardness measurements a Mitutoyo MVK-H2 microhardness tester was used. Adhesion was evaluated by the scratch test method using a Revetest Scratch Tester (loading rate 100N/min, scratching rate 10mm/min, loading range 0-100N). Thickness and roughness were measured with a Taylor-Hobson Talysurf 2 profilometer. The atomic ratios of the coatings were determined by Auger electron spectrometer (AES).

3 RESULTS AND DISCUSSION

Atomic composition

Fig. 1 shows the partial pressures of both reactive gases (N_2 and C_2H_2) during the deposition of the coatings. The coatings situated on the x-axis are chromium carbides since there was no nitrogen in the chamber. The coatings situated on the y-axis were deposited without acetylene and are chromium nitrides. The coatings in between are chromium carbonitrides. The coatings on the same inclined lines were deposited at the same total pressures. Most of our analysis is based on the dependence of a particular property on the nitrogen-to-acetylene ratio at a certain total pressure.

The dependence of the atomic ratios of the coatings on the pressures is presented in more detail in **Fig. 2**. The upper plot (**Fig. 2a**) shows the atomic percentage of chromium in the coatings as a function of the reactive gases ratio. At higher total pressures (1.5 and 2×10^{-3} mbar) the percentage of chromium is constant at 50%, regardless of the reactive gases composition. This means

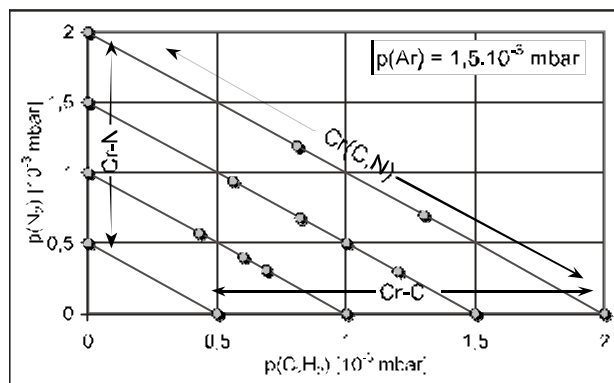


Figure 1: Partial pressure of acetylene (x-axis) and partial pressure of nitrogen (y-axis) for different deposition runs. Atomic composition was determined by AES. Each dot represents one deposition run.

Slika 1: Delni tlak acetilena (os x) in parcialni tlak dušika (os y) pri različnih depozicijah. Atomska sestava je bila določena z AES. Vsaka točka predstavlja eno depozicijo.

that we always get a stoichiometric coating. At lower total pressures however, the flux of reactive gases is too low to build a stoichiometric nitride or carbide coating. Instead, a substoichiometric coating is formed. This effect is more pronounced in the carbides. At the lowest acetylene pressure (0.5×10^{-3} mbar), no carbon is incorporated into the coating at all – in this case a pure chromium coating is formed.

In **Fig. 2b** the atomic percentage of nitrogen in the coating is presented as a function of the reactive gases

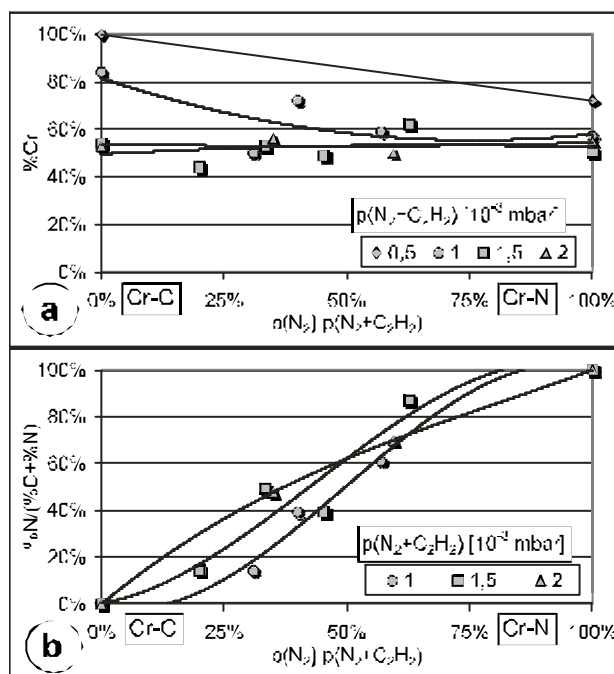


Figure 2: a) Atomic percentage of chromium as a function of reactive gases ratio; b) Atomic percentage of nitrogen as a function of reactive gases ratio.

Slika 2: a) Atomski delež kroma kot funkcija razmerja reaktivnih plinov; b) Atomski delež dušika kot funkcija razmerja reaktivnih plinov.

ratio. A linear relationship would be expected – the higher the percentage of acetylene in the chamber, the higher the percentage of carbon in the coating. From the figure it is clear (especially for 1.5 and 2×10^{-3} mbar total pressures) that this relationship is not linear; it has a rather S-like dependence. Small quantities of acetylene in a predominantly nitrogen atmosphere do not alter the nitride significantly. Conversely, small quantities of nitrogen in a predominantly acetylene atmosphere have little influence on the carbide.

Mechanical properties

The microhardness was measured for all samples. In order to avoid substrate influence the indentation load should be as low as possible, however such indentations are very small and difficult to evaluate. The lowest load applied was 25g force, which still involves some substrate influence. We determined that the Cr-C coatings have a smaller microhardness than the Cr-N coatings. The results for a $4\mu\text{m}$ thick coating deposited on HSS steel ($900 \text{ HV}_{0.025}$) are as follows: Cr-N $2500\text{--}2700 \text{ HV}_{0.025}$, Cr-C $1600\text{--}2000 \text{ HV}_{0.025}$. The intermediate Cr(C,N) phases have similar values to the Cr-N, but there is a significant drop at the carbon-rich side. Differences between the coatings prepared at different total pressures (but with the same reactive gases ratio) are not observable.

The adhesion of the coatings was also evaluated on an HSS substrate. There are many criteria for the evaluation of the adhesion but the most reproducible quantity is the critical force for total delamination of the coating, which correlates with the scratching force jump. Due to high scattering of the results, only basic assumptions can be made. The critical force for the Cr-N and the Cr-C coatings is around 50N. The adhesion of intermediate Cr(C,N) coatings is 10-20 N lower, which could present an obstacle to possible applications.

Oxidation

The oxidation was studied in the range $750\text{--}900^\circ\text{C}$. In all cases, the oxidation proceeded parabolically as described by the diffusion theory for at least one hour of the oxidation, so the coefficient of parabolic oxidation could be determined. The higher the coefficient, the faster the oxidation. **Fig. 3** presents this coefficient as a function of the reactive gases ratio for the total pressure of 1.5×10^{-3} mbar. The behavior at other total pressures does not differ significantly.

Two basic assumptions can be made. First, the oxidation resistance of the ternary phases is much weaker than that of the binary coatings Cr-N and Cr-C. At all temperatures there is a peak, i.e. the weakest oxidation resistance, at an approximately equal concentration of carbon and nitrogen. The second conclusion is that the oxidation resistance of the binary

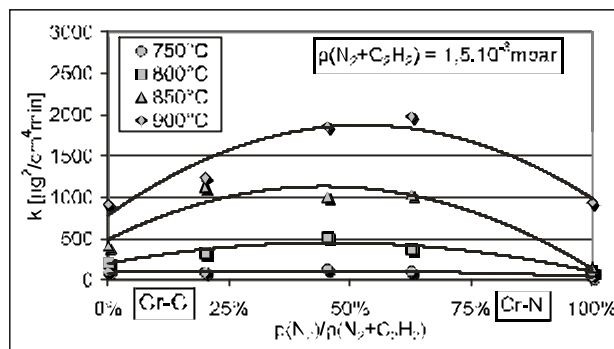


Figure 3: Coefficient of parabolic oxidation as a function of reactive gases ratio for different oxidation temperatures

Slika 3: Koeficient paraboli-ne oksidacije kot funkcija razmerja reaktivnih plinov za različne temperature oksidacije

coatings is comparable, with the Cr-N being slightly more resistant than the Cr-C.

4 CONCLUSIONS

Several Cr-N, Cr(C,N) and Cr-C coatings were prepared by evaporation at different partial pressures of the reactive gases (N_2 and C_2H_2).

The main results are as follows:

- Coatings deposited at total pressures of 1.5 and 2×10^{-3} mbar (excluding argon with a partial pressure of 1.5×10^{-3} mbar) were stoichiometric. This was not the case for lower total pressures, with a higher tendency towards substoichiometry for the carbon-rich coatings.
- The microhardness of $4\mu\text{m}$ thick coatings are: $2500\text{--}2700 \text{ HV}_{0.025}$ for Cr-N, $1600\text{--}2000 \text{ HV}_{0.025}$ for Cr-C, the values for Cr(C,N) are in-between
- The adhesions of Cr-C and Cr-N are comparable, while for Cr(C,N) it is 20-40% lower
- The oxidation resistance of Cr-C and Cr-N are also comparable, Cr-N resisting a little better. The ternary Cr(C,N) coatings exhibit up to 8 times lower resistance to oxidation than the binary coatings.

5 REFERENCES

- 1 B. Navinšek, P. Panjan, I. Milošev, *Surf. Coat. Technol.*, 97 (1997) 182-191
- 2 E. Broszeit, C. Friedrich, G. Berg, *Surf. Coat. Technol.*, 115 (1999) 9-16
- 3 Y.L. Su, S.H. Yao, *Wear*, 205 (1997) 112-119
- 4 P. Hones, R. Sanjines, F. Levy, *Thin Solid Films*, 332 (1998) 240-246
- 5 T. Hurkmans, D.B. Lewis, J.S. Brooks, W.D. Münz, *Surf. Coat. Technol.*, 86-87 (1996) 192-199
- 6 G. Bertrand, C. Savall, C. Meunier, *Surf. Coat. Technol.*, 96 (1997) 323-329
- 7 V. Agarwal, V.D. Vankar, K.L. Chopra, *Thin Solid Films*, 169 (1989) 281-288
- 8 O. Wanstrand, R. Fella, N. Axen, *Surf. Coat. Technol.*, 94-95 (1997) 469-475
- 9 G. Cholvy, J.L. Derep, M. Gantois, *Thin Solid Films*, 126 (1985) 51-60

¹⁰ E. Lugscheider, O .Knotek, C. Barimani, S. Guerreiro, H.K. Zimmermann, *Surf. Coat. Technol.*, 94-95 **(1997)** 416-421

¹¹ E. Schulz, E. Bergamnn, *Surf. Coat. Technol.*, 50 **(1991)** 53-56

¹² S.H. Yao, Y.L. Su, *Wear*, 212 **(1997)** 85-94

¹³ H. K. Pulker, *J. Vac. Sci. Technol.*, A 10 **(1992)** 4-Jul/Aug, 1669-1674