Structure of sputtered nanocomposite $\text{CrC}_x/a\text{-C:H}$ thin films

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This work presents the structural evolution of nanocomposite $\text{CrC}_x/a\text{-C:H}$ coatings prepared by unbalanced magnetron sputtering of a metallic Cr target in $\text{Ar}+\text{CH}_4$ glow discharges using low negative dc bias voltages. Raman spectroscopy and x-ray photoelectron spectroscopy were used to characterize the phase composition and the chemical bonding in the films deposited at different experimental conditions. The results were correlated to the chemical composition obtained by elastic recoil detection analysis. The coating microstructure was investigated on selected samples by high-resolution transmission electron microscopy combined with electron energy-loss spectroscopy analysis. The nanocomposite coatings can be divided into hard CrC_x dominated films, when prepared at low CH_4 partial pressure to total pressure (p_t) ratios ($p_{\text{CH}_4}/p_t < 0.4$), and into low-friction $a\text{-C:H}$ dominated films, when prepared at $p_{\text{CH}_4}/p_t > 0.4$. The structure of the low-friction $a\text{-C:H}$ dominated coatings consists of 2–10 nm sized fcc CrC crystallites embedded in a Cr containing $a\text{-C:H}$ matrix. © 2006 American Vacuum Society. [DOI: 10.1116/1.2216713]

I. INTRODUCTION

Nanocomposite hard coatings consisting of an amorphous hydrogenated carbon [$a\text{-C:H}$ or diamondlike carbon (DLC)] phase and a hard crystalline carbide phase have been studied intensively within the last decade due to their beneficial mechanical and tribological properties such as high hardness, low coefficient of friction, and high resistance to wear at temperatures below 250 °C.^{1–5} Many reports deal with coatings where Ti, Ta, or Cr carbides are embedded in a DLC matrix due to their superior properties such as corrosion and oxidation resistance.^{6–11}

Although recent research activities on this class of coatings focus on major challenges such as reducing the generally high compressive stresses and avoiding the degradation of the highly cross-linked carbon-carbon bonding structure at

elevated temperatures, only few systems have been fully explored in terms of their structural evolution. In particular, for $\text{Cr/CrC}_x/a\text{-C:H}$ and Cr/DLC coatings produced via sputter deposition, the origin and constitution of the nanocomposite strongly depend on the deposition parameters due to the complex interaction between the chosen growth conditions and the competitive formation of the $a\text{-C:H}$ network and CrC_x phases.^{6,7,10} Therefore, this work is addressed to the structural evolution within the coating system $\text{CrC}_x/a\text{-C:H}$ produced via unbalanced magnetron sputtering, where basic mechanical and tribological data have already been reported in Ref. 12.

II. EXPERIMENTAL DETAILS

The coatings investigated in this work were deposited with an unbalanced dc magnetron sputtering system, described in detail in Ref. 13. $\text{CrC}_x/a\text{-C:H}$ coatings were de-

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posited onto silicon (100) and high-speed steel (DIN 1.3343, AISI M2) substrates via sputtering of a metallic chromium target in an $\text{Ar}+\text{CH}_4$ discharge at different CH_4 partial to total pressure ratios (p_{CH_4}/p_t). The target was positioned 9 cm away from the parallel-plate substrate assembly. The base pressure in the chamber was $\leq 1.5 \times 10^{-3}$ Pa, and the working pressure was kept constant at 0.4 Pa. Prior to deposition, the steel substrates were metallographically ground and polished to an average roughness R_a of 12 nm and all substrates used were ultrasonically cleaned in ethanol and acetone. After target precleaning (sputtering in 0.4 Pa Ar atmosphere at a power of 3.3 W/cm^2 for 15 min) and ion etching of the substrates (dc glow discharge in 3.5 Pa Ar atmosphere at -1250 V for 20 min) within the deposition chamber, coatings with an average thickness of $3 \mu\text{m}$ were deposited at a constant substrate temperature of 150°C . Langmuir wire probe and deposition rate measurements were used to acquire the plasma characteristics such as ion/atom flux ratio J_i/J_a and ion energy E_i adjusted via an external pair of Helmholtz coils and substrate bias potential according to the procedures described in Refs. 14–16. All coatings investigated were prepared with J_i/J_a and E_i below 0.45 and 50 eV, respectively, and by adjusting a deposition rate of $\sim 1.5 \mu\text{m/h}$ by varying the sputter power density between 2.5 and 3.4 W/cm^2 for p_{CH_4}/p_t variations between 0.24 and 0.50.

A Horiba Dilor Raman spectrometer with a He–Ne laser (wavelength of $\lambda=532.2 \text{ nm}$, total power of 100 mW) has been used to identify the bonding structure within the formed $a\text{-C:H}$ phase fraction of the coatings.

A Phillips CM20 analytical microscope working at 200 kV was used for transmission electron microscope (TEM) studies of our $\text{CrC}_x/a\text{-C:H}$ coatings. Their average particle size was determined by recorded bright- and dark-field images, and the overall crystal structure was investigated by selected area electron diffraction (SAED) patterns. Additionally, structural statistics regarding the mean size of crystalline phases were derived from the dark-field pictures. On selected sample cross sections, high-resolution transmission electron microscopy (HRTEM) was conducted with a JEOL 3010 electron microscope operating at 300 kV (point-to-point resolution of 0.17 nm). Cross-sectional samples for TEM analysis have been prepared by cutting the samples and embedding the pieces face to face in a special Ti grid. The embedded samples were mechanically ground, polished, and subsequently thinned by ion milling at 10 keV by Ar^+ ions. In order to minimize the ion beam damage the bombarding ion energy was decreased to 3 keV in the final stage.

To determine the chemical composition and the bonding behavior, electron energy-loss spectroscopy (EELS) measurements were carried out with a VG HB501 UX dedicated scanning transmission electron microscope (STEM). This microscope is equipped with a cold field emission source and with a parallel EELS detector (Gatan UHV Enfina system). The C K and the Cr $L_{2,3}$ edges were acquired simultaneously using a dispersion of 0.3 eV/channel and with acquisition times ranging from 15 to 25 s. For the chosen dispersion, an

energy resolution of 0.9 eV was achieved as determined by the full width at half maximum of the zero loss peak. All data were corrected for dark current and detector channel-to-channel gain variation. The preedge background was extrapolated using a power law function and subtracted from the original data.¹⁷ The spectra were recorded either using a stationary electron beam or scanning an area of about $3 \times 4 \text{ nm}^2$, both with a beam diameter of $\sim 1 \text{ nm}$.

X-ray photoelectron spectroscopy (XPS) analysis was applied to evaluate the phase compositions using a Physical Electronics Quantum 2000 ESCA system with monochromatized Al $K\alpha$ radiation. After the removal of adventitious contamination corresponding to an $\sim 2 \text{ nm}$ thin carbon layer by ion sputter cleaning (3 keV Ar^+), the $\text{C}1s$ and $\text{Cr}2p$ core levels were recorded. The elemental composition was quantified using the sensitivity factors of the manufacturer's software (Phi MULTIPAK). The obtained quantitative composition results were corrected for the differences arising from the different mass densities and inelastic mean free paths of the investigated coatings and graphite which is used as the carbon reference in the software library. To compensate for electrostatic charging effects that may shift the energy scale from one sample to another, the energy referencing in this series of measurements was done by aligning the maxima of all $\text{Cr}2p_{3/2}$ spectra to the same energy. This procedure assumes the same chemical shift for all CrC_x species in the investigated coatings; this assumption is justified by the fact that after this energy referencing procedure the binding energy values for the unpolarized carbon (i.e., $a\text{-C:H}$) lie at the same binding energy value of $284.5 \pm 0.3 \text{ eV}$. An additional proof is the onset of the valence band density of states (VB-DOS) which lies (after charge correction) for all coatings at $0.3 \pm 0.1 \text{ eV}$.

Analysis of the peak shapes using curve fitting on the $\text{C}1s$ and $\text{Cr}2p$ peaks allowed the separation of CrC_x and $a\text{-C:H}$ phases at different p_{CH_4}/p_t . In order to calculate the phase composition the results of the peak fitting (ratio between CrC_x and $a\text{-C:H}$) were combined with the elemental composition results, assuming the presence of Cr_2O_3 , CrC, metallic Cr, and $a\text{-C:H}$. Since the coatings were deposited in a reducing atmosphere, the lowest oxide (Cr_2O_3) was used to account for the measured oxygen content.

In order to determine the chemical composition including the absolute atomic concentration of hydrogen without the need of calibration samples, heavy ion elastic recoil detection analysis (HI-ERDA) measurements were carried out with a mass and energy dispersive time-of-flight setup using ^{126}Xe ions of 230 MeV. The uncertainty of these measurements is less than 10%.¹⁸

The coating hardness was investigated with a computer-controlled microhardness tester (Fischerscope H 100C) using a Vickers indenter and a continuously applied load of 25 mN. For all samples the indentation depth was below 10% of the film thickness.

Coating friction coefficients were studied during dry sliding experiments at room temperature (humidity of 35%–50%) using a CSM ball-on disc tribometer. Alumina balls

FIG. 1. Normalized Raman spectra of $\text{CrC}_x/\text{a-C:H}$ with increasing p_{CH_4}/p_i .

with 6 mm in diameter served as the frictional counterpart. A load of 2 N and a sliding speed of 0.1 m/s were used in all experiments. The radius of the wear track was 5 mm, and the number of test cycles was 63 695 to reach a sliding distance of 1000 m after which the friction coefficient was taken.

III. RESULTS AND DISCUSSIONS

An amorphous or nanometer-sized structure of our films, independent of p_{CH_4}/p_i , has been identified by broad, low-intensity peaks during x-ray diffraction, as already reported in Ref. 12. Raman spectroscopy measurements clearly show increasing intensities of the modes characteristic of a-C:H with increasing p_{CH_4}/p_i (see Fig. 1). The increasing signals can be correlated to the *G* and *D* modes for a-C:H at a Raman shift of 1570 and 1350 cm^{-1} , respectively. The coating deposited at $p_{\text{CH}_4}/p_i=0.24$ yields no Raman signal in the observed spectral range. This indicates that this coating contains no a-C:H phase. As also the crystalline CrC_x phases should yield Raman active modes due to their defect structure,¹⁹ which is common in materials prepared by sputtering, the spectra shown in Fig. 1 indicates that these CrC_x phases are either amorphous or crystalline with very small crystals and, hence, almost free of lattice defects due to their consequently short distances to the nearest sink (i.e., interface).²⁰ This, in turn, results in a low Raman intensity which can easily be superposed by fluorescence within the observed scattering regime.^{3,19–21} The absence of a significant C–C bonding contribution and, thus, the absence of

FIG. 3. (a) HRTEM micrograph of a cross-sectional specimen of a $\text{CrC}_x/\text{a-C:H}$ coating deposited at $p_{\text{CH}_4}/p_i=0.24$; (b) corresponding SAD pattern.

a-C:H in the coating for $p_{\text{CH}_4}/p_i=0.24$ was corroborated by XPS using the $\text{C}1s$ peak, as shown in Fig. 2(a). The coatings are CrC_x dominated for $p_{\text{CH}_4}/p_i \leq 0.42$ (see the peak at 283.2 eV) and show a pronounced a-C:H contribution for $p_{\text{CH}_4}/p_i \geq 0.42$ (cf. the peak at 284.6 eV). This can especially be seen from the phase mole fractions deduced from fitting the XPS $\text{C}1s$ peaks shown in Fig. 2(b).

Figure 3(a) is a HRTEM micrograph of the coating deposited with $p_{\text{CH}_4}/p_i=0.24$ where no distinct crystals can be observed. The corresponding SAD pattern [Fig. 3(b)], shows diffuse rings suggesting the presence of amorphous or nanometer-sized crystalline CrC_x phases. This is in perfect agreement with the Raman results (Fig. 1). The diffraction rings can be related to preferential nearest neighbor distances rather than to diffraction planes within a certain lattice. Both SAD rings can be assigned to the preferred close order of 0.122 and 0.219 nm within the Cr_7C_3 (JCPDF No. 36-1482) and Cr_3C_2 (JCPDF No. 35-0804) unit cells. These carbides have orthorhombic unit cells within the space group $Pnma$ 62. The metastable fcc CrC phase (JCPDF No. 47-1424) reported for hard coatings produced by physical vapor deposition^{22–24} (PVD) shows no correlation with the observed SAD pattern [Fig. 3(b)]. The obtained results of TEM and SAD investigations fit the chemical compositions of the coatings derived by ERDA of chromium, carbon, and hydrogen (Fig. 4), which yielded a Cr/C atomic ratio of ~ 1.23 for $p_{\text{CH}_4}/p_i=0.24$. For this coating, the hydrogen content is

FIG. 2. (a) $\text{C}1s$ and $\text{Cr}2p$ XPS spectra of $\text{CrC}_x/\text{a-C:H}$ coatings with increasing p_{CH_4}/p_i . (b) Evolution of CrC_x/Cr and a-C:H phase fractions with p_{CH_4}/p_i derived from $\text{C}1s$ XPS data by peak fitting.

FIG. 4. Coating constitution of $\text{CrC}_x/\text{a-C:H}$ coatings derived by ERDA vs p_{CH_4}/p_t .

~12 at. %, but XPS and Raman scatterings indicate no a-C:H phase. Consequently, hydrogen is not, to a significant extent, chemically bonded to carbon.

Figure 4 shows that increasing the p_{CH_4}/p_t pressure ratio from 0.24 to 0.35 causes an increase of the carbon and hydrogen content from ~37% to 47% and from ~12% to 16%, respectively. Simultaneously, the chromium content decreases from ~45% to 34%. Thus, the Cr/C ratio decreases from 1.23 to 0.72 with increasing p_{CH_4}/p_t from 0.24 to 0.35.

Our Raman and XPS results (Figs. 1 and 2, respectively) clearly indicate that increasing p_{CH_4}/p_t from 0.24 to 0.35 favors the formation of a significant volume fraction of a separate a-C:H phase. The D and G Raman peaks for a-C:H can clearly be distinguished for $p_{\text{CH}_4}/p_t=0.35$ although having low scattering intensities. Furthermore, the formation of an unpolarized carbon species, i.e., a-C:H , is explicitly evidenced by the increasing XPS C1s contribution at 284.6 eV, while the intensity of the CrC_x contribution at 283.2 eV is concomitantly decreasing with increasing p_{CH_4}/p_t [see Fig. 2(a)]. Although the phase content of a-C:H considerably increased from ~0% to 22%, the H/C ratio showed only a slight increase from 0.32 to 0.35, with p_{CH_4}/p_t increasing from 0.24 to 0.35. This can be interpreted to a changed hydrogen incorporation, where the major content of the hydrogen chemically bonded as a-C:H increases and the content of free, dissolved hydrogen decreases with p_{CH_4}/p_t .

The simultaneous formation of a-C:H and CrC_x phases during growth with $p_{\text{CH}_4}/p_t > 0.24$ leads to a nanocomposite coating structure which is proven by HRTEM, where crystallites of 3.43 ± 1.38 nm in diameter, as derived from dark-field TEM images, are embedded in an a-C:H matrix [see Fig. 5(a)]. The HRTEM micrograph shows somewhat larger crystallites (~4–5 nm) than the overall statistics derived from dark-field TEM. The crystalline phase can be identified by SAD as metastable fcc CrC where all major reflections can be observed [Fig. 5(b)]. The presence of bcc Cr cannot be excluded by SAD. The nanocomposite coating shows an essentially constant grain size of 2–5 nm across the whole thickness.

FIG. 5. (a) HRTEM micrograph of a cross-sectional specimen of a $\text{CrC}_x/\text{a-C:H}$ coating deposited at $p_{\text{CH}_4}/p_t=0.42$; (b) corresponding SAD pattern.

Figures 6(a) and 6(b) are images of the same region close to the metallic chromium interlayer of the sample deposited at $p_{\text{CH}_4}/p_t=0.42$ obtained in the STEM bright-field and the high-angle annular dark-field (HAADF) modes, respectively. The CrC_x particles appear dark in the STEM and bright in the HAADF image due to their higher average atomic number compared to the a-C:H matrix. EELS data were acquired for the differently appearing regions, and the results are shown in Fig. 6(c) together with the spectrum obtained from the sample deposited at $p_{\text{CH}_4}/p_t=0.24$. In all three spectra, a strong peak occurs at the C K edge at 284 eV, which lies at the same energy-loss level as the π^* peak in graphite and amorphous carbon.¹⁷ The major difference of the C K energy-loss near-edge structure (ELNES) is the maximum intensity of this pronounced peak. The highest intensity of this peak is found for the sample containing no a-C:H ($p_{\text{CH}_4}/p_t=0.24$), and within the nanocomposite coatings ($p_{\text{CH}_4}/p_t=0.42$) the intensity is higher for the EELS spectra

FIG. 6. (a) TEM bright-field, (b) HAADF micrograph, and (c) EELS spectra of a $\text{CrC}_x/\text{a-C:H}$ coating deposited at $p_{\text{CH}_4}/p_t=0.42$ and 0.24.

FIG. 7. (a) HRTEM micrograph of a cross-sectional specimen of a $\text{CrC}_x/a\text{-C:H}$ coating deposited at $p_{\text{CH}_4}/p_t = 0.50$; (b) corresponding SAED pattern.

obtained from the CrC_x particles compared to the matrix. The broad peak at around 295 eV, which is similar to the energy-loss value of the σ^* peak in amorphous carbon,¹⁷ shows only minor changes in width for the spectra obtained from CrC_x particles and the matrix in the nanocomposite coating, but a more pronounced difference in both peak width and shape for the sample prepared at $p_{\text{CH}_4}/p_t = 0.24$ compared to the spectra taken for the nanocomposite. The Cr $L_{2,3}$ edge shows only minor modifications concerning the L_3 to L_2 ratio between the investigated samples.

The quantification of the EELS data revealed a Cr/C atomic ratio of about 1 for the CrC_x particles in the sample prepared with $p_{\text{CH}_4}/p_t = 0.42$, which corresponds very well to the results of the SAD investigation [Fig. 5(b)] indicating the presence of fcc CrC. The Cr/C ratio of the matrix is around 0.7, indicating that a high amount of chromium is present. However, as the electron beam diameter with around 1 nm is similar to the separation distance between the nanocrystalline CrC_x particles, their contribution to the recorded “matrix” spectra cannot be excluded. This is fostered by the result that the overall average Cr/C ratio of this coating is ~ 0.51 , as obtained from ERDA (Fig. 4). The corresponding XPS C1s peak fitting results [Fig. 2(b)] reveal a composition of 40% $a\text{-C:H}$ and 60% CrC_x . Consequently, as for this coating $x = 1$, the amorphous matrix should contain about 8 at. % dissolved Cr.

The Cr/C atomic ratio quantified from EELS data of the sample deposited at $p_{\text{CH}_4}/p_t = 0.24$ is around 1.26, in excellent agreement with the ERDA result of 1.23 (Fig. 4) as this film contains essentially no $a\text{-C:H}$ [Fig. 2(b)]. Thus, the Cr/C ratio is much higher than that of the crystalline particles in the nanocomposite ($p_{\text{CH}_4}/p_t = 0.42$). These results suggest that the coating is composed of Cr_3C_2 (Cr/C ratio of 1.5) rather than Cr_7C_3 (Cr/C ratio of 2.3), whereas SAD investigations [Fig. 3(b)] indicated that both phases could be possible. In addition, the C K ELNES features of this sample correspond to Cr_3C_2 ,^{25,26} indicating a similar bonding and carbon-chromium coordination as in Cr_3C_2 . Thus, it can be speculated that the short-range order in the sample deposited at $p_{\text{CH}_4}/p_t = 0.24$ fits the Cr_3C_2 , whereas the long-range order of Cr_3C_2 is not yet developed.

It is worth mentioning that the matrix composition and the ELNES features (especially the peak occurring at the C K edge at 284 eV) presented in this work are different from those observed by Fan *et al.*²⁷ This is related to the different preparation of the films. Compared to the nanocomposite coating structure for $\text{CrC}_x/a\text{-C:H}$ reported by Singh *et al.*,¹⁰ our coatings fully develop their characteristic nanocomposite structure at significantly higher chromium and lower hydrogen contents.

A further increase in p_{CH_4}/p_t from 0.42 to 0.50 favors additional $a\text{-C:H}$ phase formation at the expense of the carbide fraction, as both the *D* and *G* Raman peak intensities and the XPS C1s carbon-carbon bonding contribution show a pronounced increase in intensity (cf. Figs. 1 and 2). The overall carbon and hydrogen contents of the coating rise to 56% and 27%, respectively, whereas the chromium content decreases to 12%. The significantly higher fraction of non-crystalline material, which was identified as $a\text{-C:H}$, can clearly be identified in a HRTEM micrograph [see Fig. 7(a)]. For this coating, the size of the CrC crystallites is 3.03 ± 0.75 nm slightly smaller than the 3.43 ± 1.38 nm for the coating prepared with $p_{\text{CH}_4}/p_t = 0.42$. The reduced grain size and CrC phase fraction lead to slightly broader and more diffuse SAD rings compared to the coating prepared at $p_{\text{CH}_4}/p_t = 0.42$ [Fig. 7(b)]. Whereas the Cr/C ratio decreases from 0.51 to 0.23 by a factor of ~ 2 , the H/C ratio shows only a minor increase from 0.45 to 0.49 for p_{CH_4}/p_t increasing from 0.42 to 0.50. This implies changes regarding the Cr incorporation in the $a\text{-C:H}$ matrix as its phase content increases only by a factor of ~ 1.5 with the corresponding increase in p_{CH_4}/p_t from 0.42 to 0.50 [see Fig. 2(b)].

The differences in overall microstructure and CrC_x and $a\text{-C:H}$ phase fractions of our nanocomposite coatings result in corresponding changes of their mechanical and tribological properties. Exemplarily, Fig. 8 shows the evolution of coating hardness and coefficient of friction as a function of the $a\text{-C:H}$ phase fraction (obtained from XPS); the top axis in Fig. 8 shows the corresponding p_{CH_4}/p_t ratios used during deposition. In agreement to previous findings about nanocomposites,⁵ the hardness of our films shows a maxi-

FIG. 8. Evolution of coating hardness, taken from Ref. 12, and coefficient of friction of CrC_x/a-C:H coatings with a-C:H phase content.

mum of ~ 23 GPa for $p_{CH_4}/p_t = 0.29$, where CrC_x nanocrystallites are separated by a thin (~ 0.2 nm) a-C:H phase. Further increase in p_{CH_4}/p_t which consequently leads to an increase of the a-C:H phase content up to 57% causes a reduction of the film hardness to ~ 9 GPa, as our a-C:H is a relatively soft DLC phase at the chosen deposition conditions.³ The coefficient of friction continuously decreases from 0.45 at $p_{CH_4}/p_t = 0.24$ to 0.12 at $p_{CH_4}/p_t = 0.5$. Especially at p_{CH_4}/p_t ratios above 0.42 [and hence an a-C:H fraction above 40%, Fig. 2(b)] the coefficient of friction rapidly decreases below 0.3. The development of the friction behavior and mechanical properties with the microstructure of our coatings and their content of a-C:H phase agree well with the findings about the analogous nanocomposite system TiC/a-C:H.^{28,29}

IV. CONCLUSIONS

Within this work, the structural evolution and the mechanical and frictional properties of coatings in the system CrC_x/a-C:H, produced via unbalanced magnetron sputtering at low ion energies and for CH₄ to total pressure ratios p_{CH_4}/p_t between 0.24 and 0.50, were investigated employing XPS, TEM, EELS, ERDA, Raman spectroscopy, and micro-indentation and ball-on disc tests. At $p_{CH_4}/p_t = 0.24$, an amorphous or subnanocrystalline Cr/Cr₃C₂ structure is obtained, with a significant amount, ~ 12 at. %, of incorporated hydrogen. Increasing p_{CH_4}/p_t above 0.24 results in the formation of a CrC_x/a-C:H nanocomposite structure, with increasing phase content of a-C:H, verified by XPS, TEM, and Raman spectroscopy. The nanocrystalline phase embedded in a-C:H is indicated by EELS and SAD to be amorphous or subnanometer-sized Cr₃C₂ for $p_{CH_4}/p_t = 0.35$ and nanocrystalline fcc CrC for $0.35 \leq p_{CH_4}/p_t \leq 0.50$. The comparison of the overall chemical composition with the individual phase fractions of our coatings indicates that Cr is incorporated in the a-C:H matrix, which is corroborated by EELS measurements of the coating deposited at $p_{CH_4}/p_t = 0.42$. The size of the CrC crystallites embedded in a-C:H is found to decrease from 3.43 at $p_{CH_4}/p_t = 0.42$ to 3.03 at $p_{CH_4}/p_t = 0.50$.

The microstructural changes, in terms of different crystallite phases, grain size, and CrC_x/a-C:H phase fractions, of

our coatings for varying the CH₄ gas content, $p_{CH_4}/p_t = 0.24$ – 0.50 , during deposition lead to different mechanical and frictional properties. The hardness maximum of ~ 23 GPa of our films is obtained for $p_{CH_4}/p_t = 0.29$, corresponding to an estimated a-C:H content of $\sim 17\%$. Further increase of the a-C:H phase content results in a decrease of the film hardness to ~ 9 GPa at the highest a-C:H content of 57%. Corresponding to the increasing a-C:H phase content, the coefficient of friction of our coatings decreases from 0.44 (essentially no a-C:H phase) to 0.12 (57% a-C:H). Especially for a-C:H contents above 40%, the coefficient of friction rapidly decreases to values below 0.3. Based on our results it can be concluded that the mechanical and tribological properties of nanocomposite CrC/a-C:H coatings can be tailored for advanced and individual applications by unbalanced magnetron sputtering.

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- ¹A. A. Voevodin and J. S. Zabinski, *Compos. Sci. Technol.* **65**, 741 (2005).
- ²C. Donnet and A. Erdemir, *Surf. Coat. Technol.* **180/181**, 76 (2004).
- ³J. Robertson, *Mater. Sci. Eng., R.* **37**, 129 (2002).
- ⁴A. A. Voevodin and J. S. Zabinski, *Thin Solid Films* **370**, 223 (2000).
- ⁵T. Zehnder and J. Patscheider, *Surf. Coat. Technol.* **133/134**, 138 (2000).
- ⁶D. G. Teer, *Wear* **251**, 1068 (2001).
- ⁷P. Eh. Hovsepian, Y. N. Kok, A. P. Eghasarian, A. Erdemir, J.-G. Wen, and I. Petrov, *Thin Solid Films* **447–448**, 7 (2004).
- ⁸P. Panjan, M. Cekada, D. Kek Merl, M. Macek, B. Navinsek, A. Jesih, A. Zalar, and M. Jenko, *Vacuum* **71**, 261 (2003).
- ⁹Y. L. Su and W. H. Kao, *Surf. Coat. Technol.* **137**, 293 (2001).
- ¹⁰V. Singh, J. C. Jiang, and E. I. Meletis, *Thin Solid Films* **489**, 150 (2005).
- ¹¹C. Corbella, M. Vives, A. Pinyol, E. Bertran, C. Canal, M. C. Polo, and J. L. Andújar, *Surf. Coat. Technol.* **177/178**, 409 (2004).
- ¹²G. Gassner, P. H. Mayrhofer, C. Mitterer, and J. Kiefer, *Surf. Coat. Technol.* **200**, 1147 (2005).
- ¹³P. Losbichler, C. Mitterer, P. N. Gibson, W. Gissler, F. Hofer, and P. Warbichler, *Surf. Coat. Technol.* **94/95**, 297 (1997).
- ¹⁴J. A. Thornton, *J. Vac. Sci. Technol.* **15**, 188 (1978).
- ¹⁵I. Petrov, V. Orlov, I. Ivanov, and J. Kourtev, *Contrib. Plasma Phys.* **28**, 157 (1998).
- ¹⁶J. Musil and S. Kadlec, *Vacuum* **40**, 435 (1990).
- ¹⁷R. F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope*, 2nd ed. (Plenum, New York, 1996).
- ¹⁸W. Böhne, J. Röhrich, and G. Röschert, *Nucl. Instrum. Methods Phys. Res. B* **139**, 219 (1998).
- ¹⁹C. P. Constable, J. Yarwood, and W.-D. Münz, *Surf. Coat. Technol.* **116–119**, 155 (1999).
- ²⁰P. H. Mayrhofer, C. Mitterer, J. G. Wen, I. Petrov, and J. E. Greene, *Acta Mater.* (submitted).
- ²¹R. L. McCreery, *Raman Spectroscopy for Chemical Analysis*, Wiley Chemical Analysis Series Vol. 157 (Wiley-Interscience, New York, 2000).
- ²²E. Pippel, J. Woltersdorf, and R. Schneider, *Mater. Corros.* **49**, 309

- (1998).
- ²³K. Bewilogua, H. J. Heinitz, B. Rau, and S. Schultze, *Thin Solid Films* **167**, 233 (1988).
- ²⁴M. Cekada, M. Macek, D. K. Merl, and P. Panjan, *Thin Solid Films* **433**, 174 (2003).
- ²⁵Data from G. Hug, R. Leapman, and M. Jaouen. *Microbeam Analysis-1992*, edited by E. S. Etzs (VCH, Breckenridge, 1995), p. 303 (<http://www.cemes.fr/~eelsdb/>).
- ²⁶T. Fujihana, Y. Okabe, and M. Iwaki, *Nucl. Instrum. Methods Phys. Res. B* **127/128**, 660 (1997).
- ²⁷X. Fan, E. C. Dickey, S. J. Pennycook, and C. K. Sunkara, *Appl. Phys. Lett.* **75**, 2740 (1999).
- ²⁸J. Patscheider, T. Zehnder, and M. Diserens, *Surf. Coat. Technol.* **146/147**, 201 (2001).
- ²⁹T. Zehnder, P. Schwaller, F. Munnik, S. Mikhailov, and J. Patscheider, *J. Appl. Phys.* **95**, 8 (2004).