Nanostructural and mechanical properties of nanocomposite *nc*-TiC/*a*-C:H films deposited by reactive unbalanced magnetron sputtering

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Thin films of *nc*-TiC/*a*-C:H nanocomposite have been deposited by reactive magnetron sputtering at substrate bias values of -240 and -91 V. The grain size and grain separation, which together define the nanostructure, are correlated to the amount of the amorphous phase. From the size of the TiC grains measured by x-ray diffraction and the amorphous hydrogenated carbon (*a*-C:H) phase content determined by x-ray photoelectron spectroscopy, the mean grain separation is estimated using a simple model for the nanostructure. Films deposited at -240 V show a hardness enhancement for *a*-C:H phase contents in the range 10% to 30% with TiC grain sizes around 5 nm. The mean grain separation for such films was estimated to be 0.3 nm. Films with higher *a*-C:H phase contents still have 5 nm small grains, but their mean grain separation is larger than 0.5 nm; their hardness is thus determined by the properties of the amorphous matrix. A less pronounced hardness enhancement is observed for films deposited at -91 V. They have larger grains and larger mean grain separations and show smaller hardness values. The hardness of the films, among other mechanical properties, is controlled by the nanostructure. Raman measurements have shown that *a*-C:H is present in films with mean grain separation down to 0.2 nm. Coefficients of friction against steel lower than 0.3, independent of the substrate bias, are found for films with mean grain separations as low as 0.15 nm. Self-lubrication due to *a*-C:H can explain the observed friction behavior, although the presence of *a*-C:H cannot be proved by Raman spectroscopy for films with mean grain separations smaller than 0.2 nm. It is shown that the substrate bias is crucial in obtaining increased hardness of *nc*-TiC/*a*-C:H nanocomposite thin films. In contrast to the hardness of the coatings, their friction behavior is not affected by the substrate bias. © 2004 American Institute of Physics. [DOI: 10.1063/1.1650898]

I. INTRODUCTION

Nanocomposite hard coatings have attracted considerable attention in the last decade because of their increased hardness. They are of importance for potential industrial applications due to their improved properties in comparison to conventional protective coatings. An extensive review of nanocomposite coatings has been given by Vepřek.¹ Nanocomposite hard coatings consist of particles of the order of 5–10 nm which are surrounded by a matrix of amorphous material. Although their mechanical properties, such as hardness, are clearly connected to the microstructure of the materials, a complete understanding of the mechanism leading to the observed behavior is still lacking. Different nanocomposite systems consisting of nanocrystalline (*nc*) and amorphous (*a*) materials (referred to as *nc/a*) deposited by different ion-assisted techniques show a hardness enhancement

at certain compositions which are intimately linked to nanostructural characteristics. Examples are *nc*-TiN/*a*-Si₃N₄,^{2,3} Me-C:H,⁴ *nc*-TiC/*a*-C,^{5,6} and *nc*-TiC/*a*-C:H;^{7,8} the latter will be discussed in this article. Hardness maxima for nanocomposites can be correlated to the amorphous phase content and to the thickness of the amorphous phase.⁹ These maxima correspond to typically 20% of amorphous phase content.

A deposition parameter of prime importance for the mechanical properties of hard coatings is the substrate bias. For *a*-C and *a*-C:H hardness maxima between -300 and -500 V were reported.^{10,11} Higher bias values generally lowers the hardness.¹² Incorporating titanium in the coatings leads to the formation of TiC nanocrystallites which are embedded in a matrix of *a*-C or *a*-C:H. Coatings of *nc*-TiC/*a*-C deposited at substrate biases between 0 and -550 V showed an increasing hardness with increasing bias.¹³ In the case of *nc*-TiC/*a*-C:H with titanium concentrations up to 25 at. % only a weak influence on bias was found in the range -20 – -60 V.¹⁴ Other authors deposited films with titanium concentration from 10 to 20 at. % at bias values ranging from

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–50 to –200 V and observed an increase of the hardness with increasing bias, although at low values between 5 and 13 GPa.¹⁵

In a previous article, we presented the hardness and tribological behavior for *nc*-TiC/*a*-C:H deposited by reactive closed field unbalanced magnetron sputtering at a substrate bias of –240 V.⁷ Some results were also shown for a substrate bias of –91 V. A pronounced hardness maximum was found for the samples with about 40 at. % titanium (corresponding to 80% TiC and 20% *a*-C:H) deposited at –240 V. Besides the high hardness at this composition, the coatings also exhibit low friction. This behavior was less distinct for the set of samples deposited at –91 V. Recently Feng *et al.* reported on TiC/*a*-C:H coatings deposited by a hybrid chemical/physical vapor deposition technique at substrate bias of –50 V.¹⁶ They could not observe a hardness maximum in the region around 40 at. % titanium. However, an increase of the coefficient of friction from 0.10 to 0.30 was found as the titanium concentration was increased from 0 to 45 at. %. To understand the disagreement between the observations from Feng *et al.* and ours, additional samples deposited at –91 V with a composition around 40 at. % were prepared and have been added to the previously published set of samples.⁷ In the present article, in addition to the mechanical and tribological characterization, results from Raman measurement are presented. A comparison of the results obtained for –240 and for –91 V illustrates the decisive influence of the bias on the mechanical and tribological behavior.

II. EXPERIMENT

A. Deposition

In this study, thin films of *nc*-TiC/*a*-C:H (Ti-C:H) with various titanium concentrations are deposited in a reactive closed field unbalanced four magnetron sputtering configuration combined with a plasma assisted chemical vapor deposition. Details of the deposition system is described elsewhere.⁷ Only one titanium target (99.98% purity) is used as the metal source; acetylene (C₂H₂) as the carbon source is fed in the reactor through a concentric gas ring. The substrates are biased with a 13.56 MHz rf generator with a matching network. The base pressure in the reactor is about $2 \cdot 10^{-4}$ Pa. During depositions, the total pressure is measured with a capacitance manometer. All the experiments were carried out with 26.6 sccm argon flow, which is injected around the magnetron, leading to a total pressure of 2 Pa by throttling the turbomolecular pump gas inlet. The dc power of the magnetron was kept constant during deposition (4 W/cm²) while the acetylene flux was varied between 0 and 10 sccm. This setup allows the deposition of coatings with any desired Ti:C ratio. For comparison two sets of samples have been deposited. The rf self-bias voltage applied during deposition was kept constant at –240 V in the first set, in the second set at –91 V. The growth rate at –240 V is about twice that at –91 V.

The films are grown to a thickness of 1.5–2.5 μm on single crystal Si(100) wafers for structural and chemical characterization and on hardened 1.2436 steel substrates for

mechanical tests. After the initial 2 min argon plasma cleaning the acetylene flux is adjusted to the desired value. The temperature in the center of the chamber during the deposition, as measured by an encapsulated thermocouple never exceeded 200 °C. An interlayer of metallic titanium of about 200 nm is used to improve the adhesion of the films on the steel substrates. For titanium concentration below 40 at. %, i.e., films with carbon excess, a graded Ti to TiC/*a*-C:H interlayer is necessary to prevent delamination.

B. Characterization

The chemical composition of the coatings was determined by x-ray photoelectron spectroscopy analysis using a Physical Electronics Quantum 2000 ESCA system with monochromatized Al K α radiation. After the removal of adventitious contamination corresponding to about 2 nm of carbon by ion sputter cleaning (4 keV Ar⁺), the elemental composition was measured from the peak areas of Ti2p, C1s, and O1s. Using the built-in sensitivity factors, the concentrations are determined from the respective areas. Analysis of the peak shapes using curve fitting on the Ti2p_{3/2} and C1s peaks with carefully chosen profiles allowed the separation of TiC and *a*-C:H phases at different acetylene fluxes (for details, cf. Ref. 7). At titanium concentrations below 50 atomic percent (at. %), only TiC and *a*-C:H are found. Metallic titanium is found in samples with titanium concentrations above 50 at. %. The noncarbide carbon species has been identified as being *a*-C:H by Raman scattering [cf. Figs. 3(a) and 3(b)].

The results of the x-ray photoemission spectroscopy (XPS) compositional analyses and thickness were cross-checked by Rutherford backscattering spectroscopy (RBS) for three different sample angles using a 2.2 MeV He⁺ beam. Elastic recoil detection analysis (ERDA) was used for the quantitative detection of hydrogen.

Raman spectra were taken with a Renishaw Raman-Imaging Microscope using a HeNe laser with an excitation wavelength of 632.8 nm and 30 mW radiation power. The structure and grain size are determined by x-ray diffraction (XRD) with a Siemens D5000 diffractometer operated with Cu K α radiation in a glancing incident configuration ($\Theta = 1.5^\circ$). The hardness is measured by nanoindentation with a MTS Nanoindenter XP®. Maximal indentation depths between 100–150 nm (5–10% of film thickness) ruled out possible influences of the surface roughness and of the substrate. Measurements of the friction coefficient against 100 Cr6 balls with 6 mm in diameter are carried out using a pin-on-disk Tribometer from CSEM, Switzerland. All pin-on-disk measurements are done in 65% relative humidity, 5 N normal load and with a displacement velocity of 10 cm s^{-1} , the values are taken after 700 m of total displacement.

III. RESULTS

A. Chemical bonding

All samples consisted, with changing phase ratio according to the deposition conditions, of nanocrystalline TiC, *a*-C:H or metallic titanium, as evidenced by XRD, XPS, and Raman scattering (cf. Ref. 7).

FIG. 1. Titanium concentration (from XPS) as a function of the a -C:H phase content for $U_{\text{bias}} = -240$ and -91 V.

XPS allows the unambiguous distinction of these phases by the different XPS core level binding energies of $\text{C}1s$ and $\text{Ti}2p$ for the phases under investigation.⁷ Using this fact makes it possible to separate the contributions of TiC and of a -C:H to the total $\text{C}1s$ signal. A plot of the total Ti content (TiC + metallic Ti) versus the a -C:H content shows that the phase composition at any given a -C:H content is the same at both bias values of -240 and -91 V (Fig. 1).

The hydrogen concentration as determined by ERDA is plotted in Fig. 2(a). It shows that the hydrogen content of the films deposited at -91 V is higher, which is in agreement with the observations for pure a -C:H deposited by Zou et al.¹⁷ It also shows that the absolute hydrogen content decreases as the a -C:H phase content decrease (increasing TiC phase content). However, the ratio H/C is higher at low concentrations of a -C:H. If the nature of a -C:H was independent of the TiC content a straight decrease of the hydrogen content could be expected, as indicated by the dashed straight line. Assuming that hydrogen is only bonded to carbon atoms from the a -C:H phase, the hydrogen fraction $\text{H}/(\text{H} + \text{C}_{a\text{-C:H}})$ in a -C:H can be calculated by multiplying the carbon concentration from the RBS measurement with the percentage of the carbon atoms not bonded to Ti, which was obtained from fitting of the $\text{C}1s$ peak of the XPS measurement. This atomic ratio is plotted in Fig. 2(b). It shows an almost unchanged ratio H/C for the samples deposited at -240 V, while those prepared at -91 V have significantly

FIG. 2. (a) Hydrogen concentration (from ERDA) as a function of the a -C:H phase content for $U_{\text{bias}} = -240$ and -91 V. The dashed line indicates the expected hydrogen content following a rule of mixture. (b) Hydrogen fraction in a -C:H as a function of the a -C:H phase content for $U_{\text{bias}} = -240$ and -91 V. The dashed line indicates the expected hydrogen content for unchanged a -C:H for all TiC/ a -C:H compositions.

FIG. 3. Raman spectra of nc -TiC/ a -C:H nanocomposites deposited at $U_{\text{bias}} = -240$ V (a) and -91 V (b) as a function of the a -C:H phase content.

higher hydrogen contents at low a -C:H contents. This enhanced H:C ratio in a -C:H is indicative for a reduced cross-linking of the carbon network. Excess hydrogen is bonded to carbon and thus reduces the amount of C–C bonds forming the amorphous network and in this way reduces the strength of the amorphous phase.

Structural information about the a -C:H phase can be obtained by Raman scattering spectroscopy from the region between 900 and 1800 cm^{-1} .^{10,18,19} Raman spectra of samples with different compositions deposited at -240 and -91 V are displayed in Figs. 3(a) and 3(b). These spectra can be decomposed into four Gaussian peaks following established procedures.^{20,21} The high frequency peak around 1585 cm^{-1} , labeled G1, corresponds to the undisturbed graphite E_{2g} mode. The second peak, around 1490 cm^{-1} , originates from amorphous sp^2 and is therefore labeled G2. The peak around 1350 cm^{-1} , labeled D1, corresponds to the disorder mode of graphite. The fourth peak around 1130 cm^{-1} attributed to disordered sp^3 , is labeled D2. This peak is also assigned to conjugated carbon–carbon chains.²¹ For the -91 V set the G1, G2, and D1 peaks are shifted by 5 cm^{-1} to lower wave numbers indicating that the sp^3 fraction in the a -C:H slightly increases.²² This finding, combined with the observation of the increased hydrogen concentration, is another indication of a more flexible, less rigid carbon network for samples at lower ion energy.

While all but the D2 peak vanish between 12 and 28% a -C:H for the -240 V series, a continuous decrease of all four peaks is observed for the -91 V series. Even at only four percent a -C:H all bands are still recognizable. This indicates that a -C:H remains, with minor changes, the same material for the -91 V series independent of the TiC content. In contrast to this, only the D2 band remains at 12% a -C:H, illustrating that the chemical bonding at low a -C:H contents, i.e., high TiC contents, is clearly altered. The assignment of this D2 band being indicative of conjugated C–C bonds suggests that there is a chemical link between the TiC crystal-

FIG. 4. (a) Total Raman intensity (log scale) and (b) $I(D1+D2)/I(G1+G2)$ as a function of the a -C:H phase content for $U_{\text{bias}} = -240$ and -91 V. The dashed lines in (a) represent the total intensity expected for a simple dilution model.

lites with the high elasticity typical for this type of compounds. The $D2$ peak is almost absent in the spectra of the -91 V samples, illustrating the inferior linking of the TiC crystallites to each other.

Figure 4(a) displays the total intensity of the Raman signals from Figs. 3(a) and 3(b) as a function of the a -C:H phase content. It can be seen that the intensity is higher for films deposited at -91 than at -240 V. Adding titanium to the films lowers the total intensity of the scattered light. As titanium is added to the films and nc -TiC grains are formed, the volume of the a -C:H phase probed by the Raman signal is expected to decrease. The attenuation to be expected from simple dilution is shown by the dashed lines. However, the intensity losses are stronger than expected from a simple dilution model without interactions. The phonon oscillations are perturbed due to the incorporation of TiC crystallites. The smaller the separation, the more the Raman intensity is diminished. This attenuation is more pronounced for the series deposited at $U_{\text{bias}} = -240$ V, since the TiC grains formed under -240 V bias are smaller than those under -91 V (cf. XRD results). Therefore their mean separation is smaller for -240 than for -91 V at the same composition, and as a consequence the attenuation of the total Raman signal is more distinct.

A decomposition of the broad absorption band between 1100 and 1550 cm^{-1} allows a more careful investigation into the nature of the amorphous phase. Comparing the disorder bands $D1$ and $D2$ (which are due to finite size effects of amorphous carbon phases) and the $G1$ and $G2$ bands arising from graphite (in-plane vibrations and conjugated systems) allows a description of amorphous carbon phases in terms of ordering. The ratio between these two components reflects thus the ratio between the disturbed surface (D) and undisturbed graphite islands (G). The data points in Fig. 4(b) were calculated for films where four Gaussians (as described above) could be fitted to the Raman spectra. This is the case for all films deposited at -91 V, but not for the spectra of samples prepared at -240 V and a -C:H phase contents below about 20%. In fact, the ratio $I(D)/I(G) \equiv I(D1+D2)/I(G1+G2)$, presented in Fig. 4(b) as a function of the a -C:H phase content, indicates a higher fraction of disturbed carbon for the -240 V series, as it occurs in highly cross-linked amorphous networks. This agrees with observations made for a -C:H films that $I(D)/I(G)$ increase with

FIG. 5. HRTEM of a nanocomposite nc -TiC/ a -C:H coating deposited at -240 V and a phase composition of 84% TiC and 16% a -C:H (micrograph by courtesy of C. Beeli, ETH Zurich).

increasing bias.^{10,23,24} Combining these results with the lower amount of hydrogen [see Fig. 2(b)] allows the conclusion that this disturbed carbon is not saturated by hydrogen but instead forms C-C bonds and thus contributes to enhanced cross-linking.

B. TiC grain size

The grain size of the nanocrystalline component is essential for the understanding of the nanostructure and hence of the properties of nanocomposite hard coatings.^{1,9} It was routinely evaluated from the XRD peak broadening taking the full width at half maximum (FWHM) of the TiC (111) peak in the Scherrer formula.²⁵ The data were corrected for instrumental broadening. The contribution of internal stress to the line broadening, assuming a compressive stress of 1 GPa (determined from the shift of the diffraction peaks), is about ten times smaller than the influence of the crystallite size on the peak width. The resulting grain size, taking only the grain size broadening into account, is therefore underestimated by about 10%. A comparison of these values with data obtained from high resolution transmission electron microscopy (HRTEM) showed that the values obtained from XRD agreed reasonably well. This is illustrated in Fig. 5 showing a HRTEM micrograph of a sample that had a grain size of 4.9 nm as determined from XRD peak broadening. The grain size as seen in the micrograph varies between 4 and 11 nm.

Films deposited at -240 V have grain sizes in the range 3–5 nm for a -C:H phase contents above 4%. Below 4% a clear increase of the crystallite size to values of more than 20 nm is observed. Also samples from the series at -91 V consist of small TiC grains (5–8 nm), although the samples between 4 and 14 at. % a -C:H have larger grain sizes due to enhanced deposition temperatures (280°C instead of 200°C). The evolution of the grain size with the a -C:H phase content, obtained from the full width at half maximum of the TiC(111) peak using the Scherrer formula, is displayed in Fig. 6.

C. Mechanical and tribological properties

The film hardness as a function of the a -C:H phase content is presented in Fig. 7. Films deposited at -240 V shows

FIG. 6. Grain size of the TiC nanocrystallites, calculated from the full width at half maximum of the TiC(111) peak, as a function of the *a*-C:H phase content for $U_{bias} = -240$ and -91 V.

a pronounced hardness enhancement in the range 4% to 30% of *a*-C:H phase contents. The maximum with a value of 35 GPa is reached at around 10% of *a*-C:H phase content. Below 4% the hardness is around 11 GPa and above 30% the hardness slowly decrease from 18 to 14 GPa. The hardness of the pure, TiC-free *a*-C:H phase is 18 GPa. A similar behavior is found for films deposited at -91 V, although less pronounced. The hardness maximum of 12 GPa is found around 4% of *a*-C:H phase content. From 4% to 30% of *a*-C:H phase content the hardness values are around 9 GPa. Above 30% the hardness slowly decrease from 7 to 5 GPa. The hardness of the pure *a*-C:H film is 16.5 GPa, thus harder than any of the Ti-containing films deposited at -91 V.

Figure 8 shows the evolution of the coefficient of friction against steel from pin-on-disk measurements as a function of the *a*-C:H phase content. For films deposited at -240 V, the coefficient of friction starts from 0.18 for the *a*-C:H film, then decreases to about 0.14 (around 75% of *a*-C:H phase content) and reaches 0.27 at *a*-C:H phase contents between 4 and 50 at. %. A steep rise to 0.57 is observed for *a*-C:H phase contents below 4 at. %, independent of the sample bias voltage. Films deposited at -91 V show a continuous rise of the coefficient of friction from 0.04 at 100%

FIG. 8. Coefficient of friction from pin-on-disk measurements as a function of the *a*-C:H phase content for $U_{bias} = -240$ and -91 V.

a-C:H phase content to 0.25 at 2%. Films with very minor amounts of *a*-C:H (0% to 1%) have a coefficient of friction of 0.70.

IV. DISCUSSION

A. Grain size

It is known that the grain size of films exposed to ion bombardment during deposition decreases as the energy of the ion is increased.^{26,27} The ion energy is, in collisionless

FIG. 9. (a) Sketch of a simple model to estimate the mean grain separation in a nanocomposite material. (b) Calculated mean grain separation using the grain size values from Fig. 5 and the *a*-C:H phase content as a function of the *a*-C:H phase content for $U_{bias} = -240$ and -91 V.

FIG. 7. Hardness as a function of the *a*-C:H phase content for $U_{bias} = -240$ and -91 V.

plasmas, proportional to the applied substrate bias. Increasing the substrate bias will therefore result in films with smaller grain sizes. This is also observed in the present case, where smaller grains are found in the samples deposited at $U_{\text{bias}} = -240$ V as compared to those deposited at -91 V.

However, the ion energy effect explains only qualitatively the lower crystallite size at higher bias values. There seems to be another mechanism that influences the grain size in a decisive way with a pronounced dependence from the phase composition. The immiscibility of the phases in nanocomposite hard coatings causes quenching of the crystalline phase growth (in this case TiC) and forces it to renucleate wherever the growing crystallite is covered by the amorphous phase. Obviously this must be a function of the amorphous phase content in the material. This is in fact observed at high fractions of the amorphous phase, i.e., from 100 at. % to about 5 at. % for the -240 V series. Only at very small amounts of $a\text{-C:H}$ (below 5 at. %) the coverage of the TiC grains is insufficient and therefore renucleation is no longer dominant which, in turn, leads to the growth of larger grains. A rough estimate of the grain coverage thickness at the transition from small grain sizes to higher ones actually yields a coverage thickness of about one monolayer [see also next section and Fig. 9(b)].

B. Nanostructural considerations

Besides the grain size, the grain separation seems to play a central role on the observed hardness. The mean grain separation in this class of nanocomposite materials is so small that no analytical technique is known to determine the actual thickness of the phase which separates the nanocrystallites from each other. Nevertheless, this value can be estimated from measured values, i.e., the phase composition and the mean size of the TiC nanocrystals. To obtain an estimation of the mean grain separation a simple schematic nanocomposite model was developed. Such a model should provide descriptions for all compositions. A model using spheres of uniform size (representing nanocrystallites) could only describe nanocomposites with amorphous phase contents between 26% and >100%, since a closed packed array of spheres has a space filling of only 74%. It is therefore meaningful to use cubic nanocrystallites placed on the nodes of a three-dimensional cubic mesh which are separated by the amorphous phase. This model, as sketched out in Fig. 9(a), allows the description of any phase ratios. The volume between the cubes is filled with the matrix material, in our case $a\text{-C:H}$. Using the TiC nanocrystallite size c obtained from the XRD measurement (Fig. 6) and $[a\text{-C:H}]$, the $a\text{-C:H}$ phase content obtained from XPS, an estimation of the mean grain separation a can be calculated with formula (1).

$$a = c \left(\sqrt[3]{1 + \frac{M_{a\text{-C:H}}}{(M_{\text{TiC}} + M_{a\text{-C:H}})} \cdot \frac{\rho_{\text{TiC}}}{\rho_{a\text{-C:H}}} \cdot \frac{\frac{[a\text{-C:H}]}{100}}{\left(1 - \frac{[1\text{-C:H}]}{100}\right)} - 1} \right). \quad (1)$$

In this expression, $M_{a\text{-C:H}}$ stands for the atomic weight of $a\text{-C:H}$ taken equal to that of carbon (12.0 amu), M_{TiC} for the atomic weight of TiC (59.9 amu), ρ_{TiC} the density of TiC (4.91 g cm^{-3}), and $\rho_{a\text{-C:H}}$ the mean density of $a\text{-C:H}$. $\rho_{a\text{-C:H}}$ was taken to be 2.2 g cm^{-3} .¹⁷ The mean grain separation is proportional to the grain size and is a nonlinear function of the $a\text{-C:H}$ phase content. The calculated values for the mean grain separation, based on this model, are presented as function of the $a\text{-C:H}$ phase content in Fig. 9(b).

The mean grain separation at the hardness maximum for films deposited at -240 V is around 0.3 nm. This corresponds to about two to three C-C bond lengths in amorphous carbons (0.143–0.152 nm [Ref. 22]). At the same $a\text{-C:H}$ phase contents films deposited at -91 V have a mean grain separation of 0.7 nm which is more than twice the value for -240 V.

C. Hardness

The hardness measurements showed that incorporating small amounts of titanium (<15 at. %) into $a\text{-C:H}$ results in a softening of the films compared to the hardness of the pure $a\text{-C:H}$ phase. This effect is very clear on the -91 V series but only minor for the -240 V series. A similar behavior was

already observed by Knotek,⁶ Klages and Memming²⁸ and Meng *et al.*²⁹ for films deposited at low bias voltages; they related this finding to the change in bonding configurations of the $a\text{-C:H}$ random network as titanium is incorporated. For the -240 V series a distinct hardness increase is observed between 5 at. % and 30% $a\text{-C:H}$, reaching a maximum at around 10% of $a\text{-C:H}$ phase content. This is the case for both ion energy levels (bias values) investigated, however, to a much greater extent for high bias values (cf. Fig. 7).

Molecular dynamics simulations of nanocrystalline metals have shown that the grains are free of dislocations as long as their size is below about 10 nm.^{30,31} Similar experimentally determined values have been reported for CrN (15 nm) (Ref. 32) and for TiC (13 nm) (Ref. 33). This means that a crystallite of this dimension does not deform. Only at larger grain sizes the interior of grains start to emit dislocations and they thus become deformable. This transition can be observed in the hardness curve for the -240 V series, where reduced resistance to deformation (i.e., lower hardness) is obtained when the grain size increases (below 5 at. % $a\text{-C:H}$). For the -91 V samples the grain size is larger due to the incomplete coverage of the growing grains by the

FIG. 10. Combined presentation of the grain size (from Fig. 6), hardness (from Fig. 7) and grain separation [from Fig. 9(b)] for the two experimental series at bias voltages of (a) -240 and (b) -91 V.

amorphous carbon. Already from the different size one would expect lower hardness for the -91 V series. Figures 10(a) and 10(b) combine the data of grain size (from Fig. 6), hardness (from Fig. 7) and grain separation [from Fig. 9(b)] for the two experimental series at bias voltages of -240 and -91 V, respectively. The comparison shows that hardness enhancement for the series at -240 V [Fig. 10(a)] occurs only for small grain size (5 – 7 nm) and grain separation below 0.5 nm. Figure 10(b) evidences that, although small grain sizes (around 5 nm) are observed at a -C:H contents above 20 at. %, no hardness enhancement is observed. This evidences that the grain size alone is not responsible for the hardness enhancement. On the other hand, if only the grain separation would lead to enhanced hardness, this should be found for all coatings having mean separation values between 0.2 and 0.5 nm, i.e., in the range where increased hardness is observed for the -240 V series (from about 7 at. % to 40 at. % a -C:H). Again, Fig. 9(b) shows that there is only a very minor hardness enhancement (from 7 GPa at 42 % a -C:H to 12 GPa at 7 at. % a -C:H) observable for these conditions (i.e., from about 3 at. % to 15 at. % a -C:H).

These comparisons, together with the results from the Raman scattering, lead us to state that three conditions have to be fulfilled in order to obtain increased hardness in nc -TiC/ a -C:H nanocomposite coatings: (a) the grain size should not exceed 10 nm to prevent grain deformation, (b) the mean grain separation should not exceed 0.5 to limit crack initiation in the amorphous phase, and (c) the network of the amorphous phase has to be sufficiently dense and rigid. All three conditions are fulfilled for films deposited at -240 V and with a -C:H phase content between 10 % and

30 %. Films with 30 % to 80 % a -C:H phase content also have grain sizes around 5 nm, but the mean separation is larger than 0.5 nm due to the larger amount of amorphous phase. For these films the mean grain separation is already too large and the hardness of the films is mainly governed by the properties of the amorphous phase. Films deposited at -91 V having larger grains and larger mean grain separations, thus do not fulfill the conditions to show an enhancement of the hardness.

A comparison of our results with those published by Feng *et al.*¹⁶ shows, at first sight, a major disagreement in the hardness behavior. They did not observe a hardness enhancement, although the friction and wear behavior are almost similar to the values reported here. The main difference between the films described by Feng *et al.* and those described here, is that they used a bias voltage of -50 V, whereas our coatings were deposited at -91 and -240 V. Our experiments show hardness enhancement only for bias voltages of -240 V, but almost no such effect for samples deposited at -91 V. It is therefore no surprise that samples deposited at even lower bias voltages do not show a hardness enhancement.

D. Friction

It is known that the surface zones of a -C:H films and also of hydrogen-free a -C films transform under mechanical load into a highly disordered graphite-like transfer film which acts as a solid lubricant.^{34,35} The friction coefficient therefore decreases steadily, as the a -C:H fraction in the coatings is reduced at the expense of TiC. This is the case for both examined bias values. A surprising finding is that films with coefficients of friction below 0.3 are found at a -C:H phase contents as low as 4 at. % at -240 V and 2 at. % at -91 V. The mean grain separation of these films is of the order of 0.15 nm or one monolayer. This means that self-lubrication can occur with statistically only a single monolayer of carbon. Although this simplistic model gives only a mean grain separation, it shows that very little amounts of a -C:H are needed to obtain self-lubrication. The coefficient of friction and the wear increase immediately below 4 %, respectively, 2 % of the a -C:H phase content for films deposited at -240 and -91 V, respectively, to values which are typical for TiC. In this region no more noncarbide carbon can be found between the TiC grains and therefore the observed tribological behavior is determined by TiC alone.

V. CONCLUSION

We have shown in this article that the choice of the substrate bias has a decisive influence on the nanostructure of nc -TiC/ a -C:H nanocomposites. It is shown that the nanostructure of coatings with enhanced hardness has to meet certain criteria. The hardness of such coatings is controlled by the nanostructure which is crucially affected by the substrate bias. Increasing the bias from -91 to -240 V results in an increase of the hardness to values of about 35 GPa. Higher ion energy by means of the substrate bias leads to a reduction of both the grain size and of the grain separation. For films deposited at -240 V this enhancement of the hard-

ness is observed in a region with a -C:H phase contents around 15 at. % of a -C:H, which correspond to TiC concentrations of around 80 at. %. In this regime three conditions are fulfilled: the nanocrystallites are approximately 5 nm in size, the mean grain separation is about 0.3 nm, and the amorphous carbon network is sufficiently rigid. Films deposited at -91 V show only a slightly increased hardness, although the hardness value at the maximum is below that of the pure a -C:H film deposited at the same bias.

In contrast to the hardness, the tribological behavior of the films is not correlated to the nanostructure as long as a -C:H is present in the coatings. This is the case even when a single monolayer covers the TiC nanocrystallites. The coefficient of friction is then determined by the tribological properties of the amorphous hydrogenated carbon matrix. The amorphous carbon phase transforms into a self-lubricating solid, which results in low coefficients of friction. This low friction behavior is independent of the substrate bias value. It is shown that nanocomposite nc -TiC/ a -C:H coatings can be deposited under appropriate conditions that have an enhanced hardness of 35 GPa and a friction coefficient in air against steel of less than 0.3.

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