Characterization of nano-composite PVD coatings for wear-resistant applications

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Abstract

Various methodologies for the characterization of nano-composite coatings are discussed, which consist TiC nano-particles distributed in an amorphous hydrocarbon (a-C:H) matrix. Complications that arise from the influence of coating roughness and underlying substrate on the properties are evaluated and suitable solutions are proposed. Experimental techniques such as nano-indentation, EPMA, XPS, XRD and (cross-sectional) SEM and TEM are used for a detailed characterization of 1-2 µm thick nano-composite coatings. The nano-structure and columnar morphology of two coatings of different Ti content has been characterized. The deformation and failure behavior of the two coatings is characterized with the combined use of nano-indentations, TEM and FIB techniques. A lower Ti content results in smaller TiC particle size, restrained columnar growth and an improved elastic recovery.

Keywords: nano-composite coating; characterization, TEM, XRD, XPS.

1 Introduction

Nano-composite coatings based on an amorphous hydrocarbon (a-C:H) matrix are promising material systems for low friction and wear resistant applications. A detailed characterization of its structure permits to understand the deformation behavior and how this depends on the different microstructures that can be achieved. The interest in developing a structure-property relationship for this material system stems from the promising properties in the field of tribological coatings for automotive applications [1]. The characterization of nano-composite materials in the form of 1-2 µm thick films is complicated due to the influence of
the surface roughness and the underlying substrate. The characterization techniques should have an appropriate depth resolution to avoid the influence of the substrate. Techniques with a high lateral resolution permit the characterization of cross-sectional structures of the coatings. The mechanical properties can be measured through nano-indentations, and the use of the continuous stiffness measurement (CSM) technique is a convenient way of excluding contributions from the surface roughness and the underlying substrate. Although in general transmission electron microscopes (TEMs) have sufficient resolution for this task, only field emission gun (FEG) scanning electron microscopes (SEMs) can attain the resolution necessary to image cross-sections of the coatings or low-load nano-indentation impressions on their surface. Indeed, a combination of instrumented nano-indentation and SEM can give insight into the deformation and failure mechanisms of the coatings. The recent development of the focused ion beam (FIB) technique permits to study the cross-sectional structure of the coatings after deformation in the TEM without tedious sample preparation [2], by obtaining electron-transparent samples from nano-indentated locations of the coating surface. Energy filtered (EF) imaging using an analytical TEM fitted with a Gatan image filtering (GIF) system permits semi-quantitative elemental maps particularly sensitive to light elements, with a lateral resolution of about 1 nm. Wavelength-dispersive electron probe micro-analysis (EPMA) investigations with the use of standards are commonly employed to characterize the composition of thin films. Nevertheless the technique is not sensitive to the chemical status of the elements and the energy of the electron probe must be reduced to 5 keV if 1-2 µm thick coatings are analyzed. X-ray photoelectron spectroscopy (XPS) and grazing-angle X-ray diffraction (XRD) are important to monitor the formation of chemical compounds and crystalline phases as transition metals are introduced within the matrix material at various concentrations. XPS has the chemical sensitivity necessary to monitor the bonding environment of the elements in the coating. XRD techniques probe the formation of crystalline compounds, but a grazing-angle geometry must be employed during the investigation of thin films, as normal penetration depth of X-rays in materials exceeds the coating thickness.

In this paper a characterization study is performed on two TiC/a-C:H nano-composite materials of different Ti content. XPS and XRD are employed to verify the formation of carbide nano-crystallites. The grazing-angle XRD results with the Scherrer equation leads to estimates of the mean size of the nano-crystallites. HR-TEM, instead, is able to image the nano-particles directly, permitting a study of the particle size distributions in the different coatings. Cross-sectional TEM is employed to characterize compositional variations along the coating thickness through energy filtered (EF) TEM analysis and to characterize growth-induced columnar features in the coatings.

2 Experimental

Nano-composite nc-TiC/a-C:H coatings were deposited via closed-field unbalanced reactive magnetron sputtering in an Argon/acetylene (Ar/C₂H₂)
atmosphere with a Hauzer HTC-1000 coating system, which was equipped with two Cr targets and two Ti targets opposing each other and Ar and acetylene gas sources. The detailed set-up of the coating system has been documented elsewhere [3]. Polished stainless steel (SS) substrates and Si wafers were sputter-cleaned in an Ar plasma and subsequently a graded interlayer was deposited, consisting of a Cr adhesion layer, a Cr/Ti graded layer and a Ti/TiC intermediate layer, with a gradual carbon enrichment towards the coating. The deposition was performed by controlling the sputtering power applied to the metallic targets. After the deposition of the Cr adhesion layer the power applied to the Cr targets was gradually ramped down to zero, while the power applied to the Ti targets was simultaneously ramped up to the value chosen for coating deposition. Subsequently, an increasing flow of acetylene gas was introduced in the chamber, up to the value chosen for coating deposition (26 and 36 % of the total gas flow for coatings A and B, respectively). Finally, the nano-composite coating deposition was carried out to a final coating thickness of 1.4 µm. During the interlayer deposition the negative substrate bias was increased gradually, and the coating was deposited at -100 V bias. A Philips XL30S SEM was employed to study the cross-sectional structure of the samples. Low acceleration voltage (3 kV) and small a working distance (3 mm) were employed to improve the obtained resolution, and the special through lens detector (TLD) of the microscope was used in high resolution (HR) mode. Electron probe microanalysis (EPMA) with a Cameca SX-50 equipment was used to determine the chemical composition of the coatings. An acceleration voltage of 5 keV was employed to avoid excitation of X-rays from the interlayer area of the coating. XPS investigated the bonding environment of C and Ti atoms in coatings A and B and on a pure carbon sample obtained from a carbon sputtering target of 99.999 at. % purity for reference. A fully calibrated MTS Nano Indenter XP was employed to measure the hardness and Young’s modulus of the coatings with a Berkovich indenter using the continuous stiffness measurement (CSM) technique. The microscopy investigation of the nanostructures was carried out with a high-resolution TEM (HR-TEM) (JEOL 4000 EX/II, operated at 400 kV) and an analytical TEM (JEOL 2010F-FEG, operated at 200 kV). Bright Field (BF), High-Resolution (HR), Selected Area Electron Diffraction (SAED) and Energy Filtering (EF) imaging techniques were employed to characterize planar and cross-sectional samples of the coatings. EF images were acquired using a GIF system with a two-window technique. The energy window width was set at 20 eV and the frame acquisition time at 30 s. Intensity maps were acquired of the C K, Ti L$_{32}$ and Cr L$_{32}$ electron energy loss edges with a pixel size of 0.8×0.8 nm. The samples for electron microscopy were prepared by cutting, grinding, dimpling and ion milling to electron transparency coated stainless-steel substrates. A dual beam FIB was employed to cut samples corresponding to the apex of nano-indentations performed on the coatings deposited over SS substrates with a cube corner indenter at a maximum indentation depth of 1000 nm. XRD 28 scans were acquired in a Philips PW1877 diffractometer operated with a Cu K$_{α}$ radiation source placed at 1.5 ° incident angle to the coating surface. A sketch of the experimental setup is shown in Fig. 1.
3 Results and discussion

The fractured cross-sections of the two coatings are shown in Fig. 2, as observed with HR-SEM. The decrease in Ti content from coating A to B results in a considerable reduction of the columnar features leading to a “glassy” microstructure.

The hardness and Young’s modulus of the coatings are depicted in Fig. 3a as averaged over 20 indentations as a function of the normalized indentation depth. The onset of the indentation does not give reliable results because of the influence of the surface roughness, and the values measured beyond 1/10 of the coating thickness are influenced by the underlying Si substrate, which is especially evident in the case of coating A in Fig. 3a. It is possible to identify “plateaus” in the hardness and effective Young’s modulus curves, within which the values were averaged to give final values of 20.0 and 15.6 GPa for the hardness and 241.1 and 143.5 GPa for the reduced Young’s modulus ($E^*=E/(1-\nu^2)$), for coatings A and B, respectively. Clearly the CSM technique provides a suitable method to avoid the influence of external parameters such as roughness and substrate material on an accurate determination of the thin films mechanical properties through nano-indentation. EPMA experiments showed that the concentration of Ti in the two coatings is 31.7 and 17.8 % at., therefore the increase in hardness and Young’s modulus is connected with the concentration...
of Ti. The C 1s and Ti 2p shells XPS spectra of the coatings and of a C standard are reported in Fig. 3b. The core level binding energies of the Ti 2p shell are centered at 454.8 eV for both samples A and B, which confirms the formation of TiC in the coatings [4]. There is a clear increase in the intensity of the carbide C-Ti peak as the Ti concentration increases, indicating the progressive increase in the volumetric fraction of TiC phase.

Figure 2: SEM micrographs of coatings A and B.

Figure 3: (a) variation of hardness and effective Young’s modulus as a function of normalized indentation depth for coating A (bottom) and B (top), the final values were averaged within the hashed area. (b) C 1s and Ti 2p shells XPS spectra of coatings A and B and a pure C standard.

The columnar structure of coating A was further studied in the TEM. A bright field (BF) image of the coating is shown in Fig. 4a. At the bottom of the figure the SS substrate is visible. On top of the substrate a Cr interlayer is present, next a mixed Ti-Cr layer, followed by a 150 nm thick TiC layer, and finally the coating, as indicated within the black box (b). SAED investigations indicate that within the coating area (1) no texture of the TiC phase is present, as rings form in the diffraction pattern corresponding to TiC lattice spacing (see top inset (1) in Fig. 4a), pointing at a random orientation of TiC nano-crystals. The bottom inset (2) in Fig. 4a shows an SAED pattern from the area (2) circled in Fig. 4a,
Figure 4: (a) BF-TEM micrograph of coating A. The circles indicate the areas from which SAED patterns were recorded. Inset (1) shows that the coating contains randomly oriented TiC nano-crystals, inset (2) shows that the TiC in the interlayer is textured. (b) composition profile of the graded interlayer area in (a), reported on top rotated clockwise 90°; the deposition parameters are reported in the bottom graph and the composition in the middle graph.

i.e. the TiC interlayer. This portion of the interlayer is clearly textured, as the TiC (111) planes preferentially orient parallel to the substrate surface, and textured diffraction spots are indicated by arrows. The coating nucleates and grows over the TiC interlayer up to a thickness of about 1.4 μm. Within the nano-composite layer columns develop of a width of around 150 nm. They run through the whole coating thickness and are separated by brighter areas, the columnar boundaries. The columnar boundaries were further studied by EF-TEM, they are enriched in carbon with respect to the column bodies. The interlayer area was further characterized through EF-TEM. The area (b) in Fig. 4 is reported on the right of the figure, rotated 90° clockwise. It is interesting to notice a contrast variation within the mixed Cr-Ti zone; clearly phase transitions occurred and were investigated with HR-TEM in [5]. An attempt was made to determine the compositional gradient within the interlayer quantitatively, relating the integrated EELS signals to the coating composition. Furthermore, the resulting compositional profile is compared to the variation of deposition parameters. Jump ratio images of the Cr, Ti and C EELS signals were integrated within the area depicted on top of Fig. 4b. The Cr content was set equal to 100 at. % within the Cr interlayer and 0 at. % within the nano-composite coating, respectively, whereas the Ti and C contents were set equal to 0 at. % within the
Cr interlayer and equal to the coating composition, as measured through EPMA, within the nano-composite coating. The integrated signals were scaled to the compositions indicated above, so as to indicate a compositional variation within the graded part of the interlayer, see Fig. 4b. The interlayer composition depends sensitively on the deposition parameters, as is shown in Fig. 4b. This is strictly true for the Cr-Ti graded zone, whereas the C concentration evolves in a non-linear manner, with the C content rapidly increasing towards the end of the intermediate layer deposition. Nevertheless there is a good correspondence between the variation of deposition parameters and the induced compositional gradient.

HR-TEM micrographs are depicted in Fig. 5 for coatings A and B. The average size of the TiC nano-crystals decreases together with the Ti content from 4.5 nm for coating A to 2.2 nm for coating B. The TiC particle size distributions of the coatings were determined by analyzing HR-TEM micrographs; the results of the analyses are shown in Fig. 6a. The particle size distribution is Gaussian for coating B, whereas the size distribution in coating A presents a tail towards larger particle size, indicating that particle coalescence has occurred [6]. Indeed, due to the higher concentration of Ti, the TiC particles lie very close to each other and may come into contact during growth, as is also seen in Fig. 5.

![Figure 5: HR-TEM micrographs of coatings A and B. TiC nano-particles are circled.](image)

Background-subtracted grazing angle XRD scans for the coatings are reported in Fig. 6b together with the fitted curve obtained from the sum of Lorentzian peaks for the TiC (111), TiC (200) and Cr (110) reflections. The Cr peak is evident for coating B and hardly visible for coating A; it is due to X-ray diffraction occurring within the Cr adhesion layer underneath the coating. The difference in its intensity is due to a different penetration depth of the X-rays in the two coatings: the higher concentration of Ti in coating B results in the formation of more TiC particles that absorb and diffract X-rays more than the a-C:H phase that is formed by light elements such as C and H and is amorphous. The presence of this peak indicates that the TiC intermediate layer between the Cr adhesion layer and the coating is also probed during the experiment,
nevertheless this phase is textured with the TiC (111) planes parallel to the coating surface as determined in the cross-sectional TEM study above, and these will not fulfill the diffraction conditions during the described grazing-angle XRD experiment. Therefore, it can be safely assumed that the TiC peaks are only due to the randomly oriented nano-particles, and their position and full width at half maximum (FWHM) are connected with the average particle size through the Scherrer equation. In fact, a contribution to peak broadening due to lattice distortion as a consequence of the compressive stresses was not observed, and, due to the nanometer particle size, the presence of small-angle grain boundaries within the grains can be excluded, therefore the only contribution to peak broadening in the present case is due to the reduced particle size. The calculation of the average particle size with this approach yields values of 3.7 and 2.2 nm for coatings A and B, respectively. The estimates of the particle sizes based on HR-TEM and grazing angle XRD are in good agreement, as shown in Fig. 6a. There exists a better correspondence between the XRD and HR-TEM average particle size values for coating B than for coating A. This is due to the fact that the Scherrer equation assumes a monodisperse distribution of particles of a specific diameter to calculate the average particle size, which will be a more accurate assumption for symmetric distribution, as in coating B, than for a wider asymmetric one, as in coating A.

Indentations were performed on both coatings A and B with a cube corner indenter up to a fixed indentation depth of 1000 nm. The SEM micrographs of the indented locations are reported in Figs. 7a&b. Since coating A is harder than coating B the final indentation load necessary to reach the preset indentation depth is higher for coating A than for coating B (41.5 mN load and 20.0 GPa hardness vs. 31.4 mN load and 15.6 GPa hardness). The permanent indentation depths differ for the two coatings but it is not possible to compute the elastic recovery values of the coating materials themselves since the underlying substrates are also plastically deformed. The TEM inspection of the FIB sliced samples is reported in Figs. 7c&d. For sample A the substrate and interlayer below the coating clearly failed. For coating B only a modest plastic deformation
of the substrate is observed. Multiple cracks develop within sample A, instead only one crack is observed within sample B, directly below the apex of the indenter. The cracks always develop at the substrate-coating interface. Although the actual value of the elastic recovery cannot be computed for the reason explained above, by observing both the indentation marks in Figs. 7a&b and the TEM indentation cross-section in Fig. 7c-d it is clear that the curved indentation walls in coating B point at an improved elastic recovery with respect to coating A. This behavior can be connected with the two different values of the resistance to plastic deformation parameter $H^3/E^2$ the two coating have, 0.14 vs. 0.19 GPa, respectively.

![Image of indentation marks and TEM micrographs](image)

Figure 7: a-b: Indentation marks for coatings A and B, white boxes indicate the locations where FIB samples were obtained. c-d: TEM micrographs of the FIB samples for coatings A and B.

4 Conclusions

The use of a FEG-SEM permits to image clearly the columnar structure of nano-composite coatings and low-load nano-indentations impressions on their surface. Nano-indentation experiments can determine the mechanical properties of the
coatings, and by using the CSM technique influences from the roughness and substrate material can be easily excluded from the measurement. EPMA can estimate the coating composition quantitatively if a low acceleration voltage is employed (5 keV), and XPS is able to monitor the formation of compounds within the material. Grazing-angle XRD and HR-TEM are able to measure the average particle size and size distribution of crystalline particles in nano-composite coatings, respectively, and the results of the two techniques agree very well with each other. Cross-sectional TEM investigations are able to unravel textures formation within crystalline areas of the coating (the interlayer) and EF-TEM is shown to be a very powerful technique that measures semi-quantitative compositional profiles with a lateral resolution of about 1 nm. The combination of nano-indentations experiments with FIB sample preparation and TEM observations permitted to characterize the differences of deformation behavior of coatings of different Ti content. It indicates that failure initiates at the substrate-coating interface. A lower Ti content in the coatings is related to smaller TiC particle size, restrained columnar growth and a higher $H^3/E^{*2}$ parameter. It was not possible to evaluate directly the elastic recovery of the coatings. Nevertheless, the analysis of the nano-indentated samples showed that the higher $H^3/E^{*2}$ parameter is indeed connected to a better elastic recovery and the generation of less cracks after indentations.

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