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Titanium carbide/carbon nanocomposite hard coatings: A comparative study between various chemical analysis tools

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ABSTRACT

Titanium carbide/carbon nanocomposite hard coatings, which consist of TiC nanoparticles buried in amorphous carbon matrix, are prepared by a hybrid plasma process combining magnetron sputtering of a titanium target and plasma enhanced chemical vapor deposition using methane as a source for the growth of amorphous carbon. A particular attention was paid to the comparison of the surface and the bulk chemical compositions of the films determined by different analysis techniques: X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), wavelength dispersive X-ray spectroscopy (WDS) and energy dispersive X-ray spectroscopy (EDS). XPS and EDS show an underestimation in carbon concentration compared to RBS and WDS which provide similar values. This underestimation is more important in case of XPS and it is mainly attributed to the presence of oxygen contamination on the surface of the films strongly bonded to titanium. In case of EDS, the underestimation is related to the poor sensitivity of the used probe in regard to light elements such as carbon. Moreover, the structure of the coatings has been extensively probed by transmission electron microscopy, which has shown that the size of the TiC nanoparticles shrinks when increasing the carbon content within the films. We further demonstrate that this structural evolution has a direct impact on the hardness of the coatings which gets reduced when the grain size decreases.

1. Introduction

Over the last few years, titanium carbide/carbon nanocomposite hard coatings, consisting of hard and highly conductive TiC nanoparticles embedded in a soft and insulating amorphous carbon matrix, have attracted a special attention and an increasing interest in the field of protective coatings [1–12], electrical contact applications [13,14], and electrochemical sensors [15]. A recent study has shown that such films can be also used as hard conductive coatings for atomic force microscopy probes [16]. A variety of synthesis processes were developed over the years to grow titanium/carbon nanostructured thin films including reactive magnetron sputtering of a titanium target in an argon/hydrocarbon plasma [1,2,4,6,8,11,12,16–18], magnetron sputtering assisted pulsed-laser deposition [3], plasma based ion implantation [7], co-sputtering of a titanium and graphite targets [9,10,13–15] and reactive high power impulse magnetron sputtering [19]. It is important to mention that in case of using a hydrocarbon gas as a source for carbon deposition, the obtained films are assigned as titanium carbide/amorphous hydrogenated carbon nanocomposites (nc-TiC/a-C:H) due to the presence of hydrogen in the carbon phase; in the other case, where the carbon phase is hydrogen free, the films are assigned as titanium carbide/amorphous carbon nanocomposites (nc-TiC/a-C). In general, the properties of such films can be adjusted by an accurate control of the TiC nanoparticles characteristics (e.g. size, shape, and density) as well as the structure of the carbon matrix (e.g. hydrogen content, hybridization of carbon atoms, etc.). In general, these parameters are found to be dependent on the chemical composition of the coatings [1–3,10,11,20,21]. Therefore, understanding the structure-to-composition relationship is one of the main issues which should be explored before studying the properties of such material.

The surface chemical state of nc-TiC/a-C:H coatings is usually investigated by X-ray photoelectron spectroscopy (XPS) [2–7,13–18,22], whereas the bulk composition is often evaluated by Rutherford backscattering spectrometry (RBS) [2], wavelength dispersive X-ray spectroscopy (WDS) [6] or energy dispersive X-ray spectroscopy (EDS) [17,18]. Due to the different characteristics of the employed analysis techniques, such as the analyzed depth and the sensitivity of the used

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probe, the information provided by each tool may not be similar. For example, XPS is a surface analysis technique and in most of the cases the measurements can be altered by the surface contamination due to the exposure of the samples to the air [17,18,23]. In case of EDS, which is a bulk analysis technique, the used probe has a low sensitivity in regard to light elements such as carbon. Among the analysis techniques listed previously, WDS is expected to provide a reliable results thanks to the used probe allowing an accurate detection of light elements. Since in most of literature, the analysis techniques employed to evaluate the chemical composition of nc-TiC/a-C:H films are not always the same, it would be difficult to compare the properties of the material as a function of their composition. One way to overcome this drawback is by presenting the data as a function of the fraction of the amorphous carbon phase instead of the total carbon concentration in the coatings [10]. The fraction of the amorphous carbon phase forming the matrix can be directly determined using XPS [2,4,14,17,22]. However, since XPS is a surface analysis tool, the obtained data may not be representative of the bulk of the films. In case of using a bulk analysis technique, the fraction of the carbon phase can be determined by assuming that the titanium atoms are bonded to a part of the carbon ones in a stoichiometric TiC phase, while the remaining carbon atoms form the amorphous carbon phase [10]; however, since the TiC phase in such coatings is not stoichiometric (e.g. the stoichiometry evolves as a function of the deposition conditions) [14,22] such an assumption may result in a non-negligible uncertainty on the obtained data.

In the present work, we aimed to use XPS, RBS, EDS, and WDS in order to evaluate the chemical composition of nc-TiC/a-C:H coatings. The obtained results are compared and the origins of differences are discussed in details. Moreover, an extensive structural study is performed by cross-sectional TEM imaging in order to explain the evolution of the hardness of the coatings.

2. Experimental section

2.1. Coating deposition

The nc-TiC/a-C:H hard coatings were deposited by a hybrid plasma process which was described elsewhere [24]. In such a process, a radio frequency (rf) generator was connected, via a matching box, to an unbalanced magnetron source operating at 13.56 MHz. A titanium disk (99.995% in purity and 50 mm in diameter), placed at 80 mm from the substrate, was used as a sputtering target. Another rf generator was connected through a matching box to a one turn stainless steel coil (80 mm in diameter), located at half distance between the target and the substrate, to generate additional plasma. In pure argon atmosphere, the reactor operated in the PVD mode and, therefore, only titanium was deposited. When injecting methane in the chamber, the additional plasma ignited using the coil led to the fragmentation of the CH_4 molecules to CH_x radicals. Thus, simultaneously to the deposition of titanium by sputtering, these CH_x radicals were deposited by PECVD onto the substrate. By adjusting the methane fraction (designed as $F_{CH_4} = \frac{\phi_{CH_4}}{\phi_{CH_4}+\phi_{Ar}} \times 100$ where ϕ_{CH_4} and ϕ_{Ar} stand for methane and argon flow respectively) injected in the deposition chamber, the carbon content within the films was controlled. In addition to the dissociation of methane, the additional plasma generated by the coil ensures a good stability for the plasma discharge especially at high methane fractions which allow extending the experimental window for the growth of the coatings [25]. The total gas flow of the injected argon and methane into the deposition chamber was fixed to 12 sccm. The base pressure before deposition was about 1.10^{-4} Pa, whereas the deposition pressure was 0.67 Pa. The rf powers applied to the magnetron and to the coil were both fixed at 150 W. Neither heating nor bias was applied to the substrate during the growth of the films. The nc-TiC/a-C:H coatings were grown to a thickness of 1 μm on single crystal silicon (100) p type wafers.

2.2. Material characterization

The surface composition was evaluated by *ex situ* XPS using a Leybold-Heraeus LHS 560 spectrometer and Mg Kα radiation. All the measurements were performed after cleaning up the surface using an argon ion gun operating at 5 keV with a current density of about 1 μA cm^{-2}. A sputter-cleaning time of 20 min was selected as an optimal condition based on our previous work reported elsewhere [17,18]. The C 1s, Ti 2p and O 1s were used for the quantification of carbon, titanium and oxygen, respectively. RBS was performed under irradiation with He^+ (energy: 2.2 MeV) using an electrostatic accelerator (NT-1700HS: Nisshin-High Voltage Co.). The WDS analyses were performed on a Zeiss Merlin SEM equipped with a WDS probe (Oxford Instruments). EDS measurements were performed on a JEOL 5800 microscope. For EDS and WDS, the K_α peaks of the different elements (e.g. C, Ti, and O) were used for the quantification. A Hitachi H9000-NAR microscope (LaB_6 filament, 300 kV, Scherzer resolution: 0.18 nm) was used for transmission electron microscopy imaging and selected area electron diffraction (SAED). The Oliver and Pharr method was employed to determine the hardness of the coatings. The measurements were performed using a Fischerscope H100 Depth Sensing Indentation (DSI) tester equipped with Berkovich indenter. The indentation depth was 200 nm.

3. Results and discussions

3.1. Surface composition

Carbon, titanium, and oxygen were detected by XPS. The oxygen was present due to the exposure of the samples to the air, and it was not possible to completely remove it even after a long (~100 min) cleaning up of the surface using an argon ion gun [18]. The atomic concentrations of these three elements were determined from the peak intensities of C 1s, Ti 2p and O 1s (not presented in here). Typical XPS spectra of these three elements were reported in our previous work [17,18,25]. When increasing the methane fraction, the carbon concentration increases, whereas the ones of titanium and oxygen decrease (Fig. 1). The trends in the obtained data are consistent with the results that we have reported in a previous work [17].

3.2. Bulk composition

In Fig. 2 are displayed the evolutions of the elements present in the coatings as found by RBS, EDS, and WDS. In case of RBS and EDS, only carbon and titanium were detected. In addition to these elements a low amount of oxygen, not exceeding 1 at.%, was detected by WDS. This low oxygen contamination is probably resulting from the highly

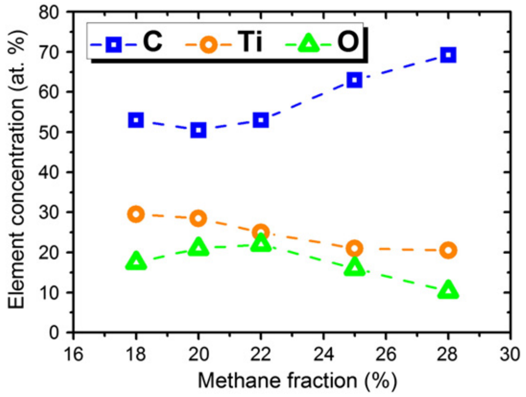

Fig. 1. Evolution of the element concentrations determined by XPS as a function of the methane fraction. All the analyses were performed after an *in situ* cleaning of the surface using an argon ion gun operating at 5 keV.

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