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SURFACE CHEMISTRY OF PLASMA DEPOSITED ZrC HARD COATINGS

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X-ray Photoelectron Spectroscopy (XPS) was used to investigate the chemical state of ZrC coatings deposited by cathodic arc method. A chemistry model of the ZrC films has been proposed. It was pointed out that on the films surface a highly oxidized passive layer, containing also carbon and oxygen as contaminants, was formed. The film bulk was composed by a mixture of ZrC (the dominant phase), ZrO_2 and free carbon.

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1. Introduction

As it is well known, the main properties of the nitrides, carbides or carbonitrides hard coatings deposited by plasma assisted PVD methods strongly depend on the film composition [1] – [7]. Beside the current determination of the film stoichiometry in the case of binary or ternary compounds, some other compositional investigations are of special interest: the elemental depth profiles, the optimum content of alloying elements (Si, B, Y, Cr) for some quaternary or quinternary hard compound coatings [8], [9], the composition of the passive layer existing at the coating surface, the chemical binding state of the films [10] – [12]. From the analysis of the influence of the deposition conditions on coating composition, the optimum process parameters for the film preparation can be selected. A considerable attention has been given to the titanium based films, while less research work has been devoted to other transition metal nitride or carbide coatings. The objective of this work is to analyze the elemental composition and the chemical bindings of the ZrC hard coatings prepared by the cathodic arc technique [13].

2. Experimental

The experimental set-up has been described elsewhere [14]. The ZrC films, with a thickness of about 200 nm, were prepared on plain carbon steel substrates, in a reactive atmosphere consisting of a mixture of Ar and CH_4. The base pressure in the deposition chamber was of about 10^{-3} Pa. Specimens to be coated were ultrasonically cleaned with trichloroethylene and mounted on a rotating holder inside the chamber. Prior to deposition, the samples were sputtered by Zr ion bombardment (1000 V; 5 min.).The main deposition parameters were: cathode material – Zr; Ar flow rate – 40 cm^3/min; CH_4 flow rate – 30 cm^3/min; arc current – 135 A; substrate bias – 100 V.

Chemical composition of the films was determined by X-ray Photoelectron Spectroscopy (XPS). A VG ESCA 3 MK II spectrometer with monochromatized Al K_α radiation (1486.6 eV) was used. The analysis chamber was maintained at ultra high vacuum (~10^{-9} mbar) and the sample was positioned at 45° in respect to the analyzer. The XPS spectra were recorded with a 20 eV window, 20 eV resolution and 256 channels recordance. The spectra were processed using Spectral Data

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Processor v 2.3 software, which allows smoothing and deconvolution of the curves. The spectra were calibrated with respect to the C 1s peak (285 eV). The XPS analysis was performed both on the film surface and below the surface. For the in-depth information, the coatings were sputter etched with an argon ion beam of 5 keV for different periods (5 and 20 min.)

3. Results and discussion

The compositions of the films were determined from Zr 3d, C 1s and O 1s peaks. Fig.1 shows the XPS spectra of the as-deposited and sputter etched specimen (curves: 1-as-deposited film; 2- sputter etched (5 min.) film; 3- sputter etched (30 min.) film). The main existing phases, along with the corresponding binding energies, are marked. The differences between the acquired spectra are clearly observable. For example, in the case of the C 1s peak, the as-deposited sample exhibits only the C-C binding. For the sputtered samples (curves 2 and 3), the peaks corresponding to Zr-C bonds became apparent. It can also be seen that no major differences exist between the spectra of the sample sputtered for 5 and for 30 min, so that one may presume that the spectra acquired after 30 min sputtering reveal the approximate composition of the film bulk.

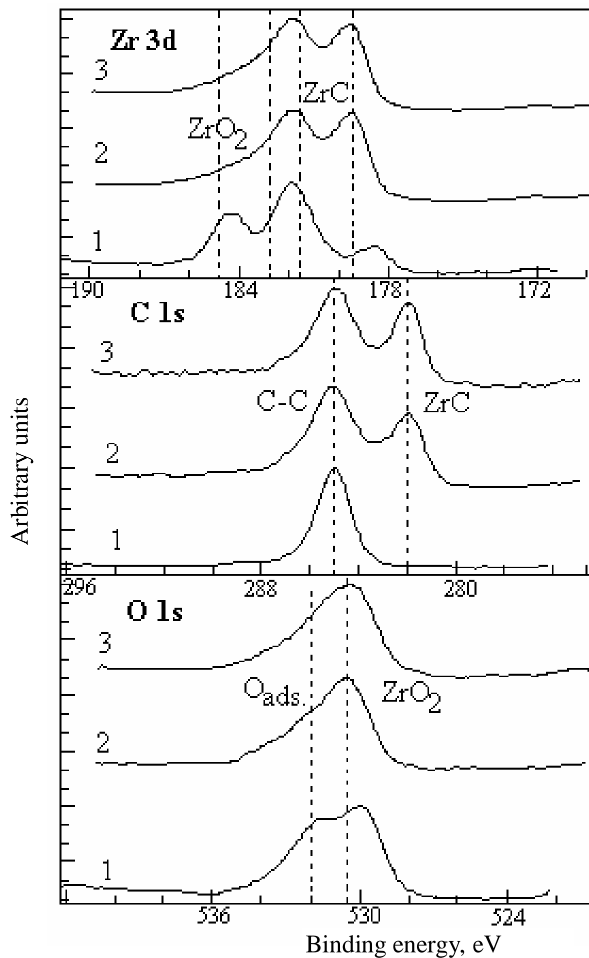

Fig. 1. XPS spectra from a ZrC film.

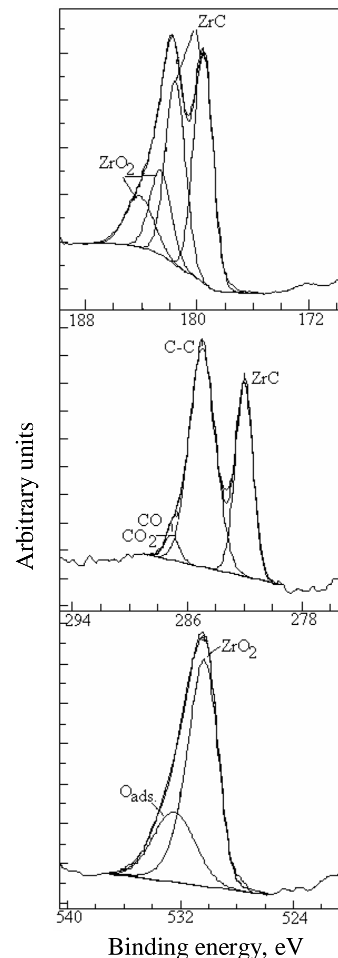

Fig. 2. Typical Zr 3d, C 1s and O 1s XPS spectra from a sputter etched (30 min) ZrC coating.

Tipical deconvolution of the Zr 3d, C 1s and O 1s peaks is illustrated in Fig. 2 (for the sample that was sputtered for 30 min). According to the literature data [15], [16], the Zr 3d peaks

were associated with ZrC and ZrO_2 (Zr $3d_{5/2}$ (178.6 – 179.6 eV) and Zr $3d_{3/2}$ (180.6 – 181.6 eV) to ZrC; Zr $3d_{5/2}$ (181.9 – 182.6 eV) and Zr $3d_{3/2}$ (184.3 – 184.9 eV) to ZrO_2). Considering the C 1s spectra, four carbon peaks were identified at the energies of 281.8 – 282.3 eV (attributed to ZrC), 285 eV (C-C bond), 286.7 – 287 eV (Co, CO_2) and 288.6 – 289 eV (COOH). As for the O 1s spectra, the detected peaks could be assigned to ZrO_2 (530.6 eV) and adsorbed oxygen (531.9 – 532 eV).

The phases detected by peak deconvolution and the corresponding binding energies are summarized in Table 1. The atomic percentage of elements in various phases is also given. Changes in the concentrations of the elements (Zr, C, O) after sputter etching of the sample (changes with depth) can be examined in Fig. 3.

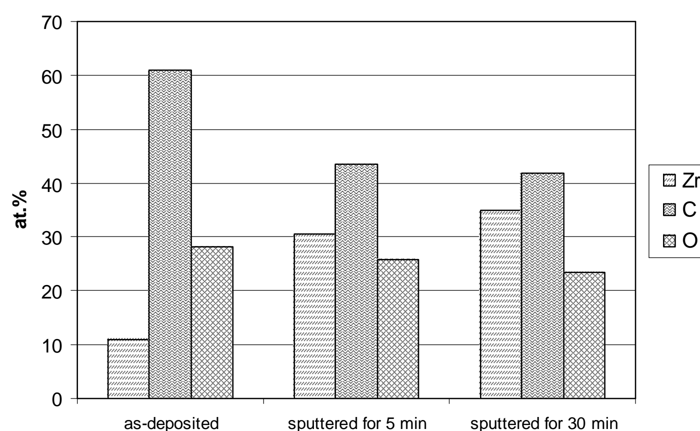

Fig. 3. Concentrations of elements from a ZrC coating (1 – as-deposited; 2 - sputter etched for 5 min; 3 – sputter etched for 30 min).

Table 1. The atomic percentage of elements in various phases detected from a ZrC coating (BE – binding energy; O_{ads} – adsorbed oxygen).

Coating	Zr (3d)			C (1s)			O (1s)		
	Phase	at.%	BE (eV)	Phase	at.%	BE (eV)	Phase	at.%	BE (eV)
ZrC As-deposited	ZrC ZrO_2	23.5 76.5	178.6($3d_{5/2}$) 180.6($3d_{3/2}$) 181.9($3d_{5/2}$) 184.3($3d_{3/2}$)	ZrC C CO, CO_2 COOH	2.9 87.6 6.3 3.2	282.3 285 286.7 288.6	ZrO_2 O_{ads}	5.6 44	530.2 532
ZrC Sputter etched for 5 min	ZrC ZrO_2	66.6 33.4	179.5($3d_{5/2}$) 181.5($3d_{3/2}$) 182.4($3d_{5/2}$) 184.4($3d_{3/2}$)	ZrC C CO, CO_2 COOH	32.7 56.4 9.4 1.5	281.9 285 287 289	ZrO_2 O_{ads}	79 21	530.5 532
ZrC Sputter etched for 30 min	ZrC ZrO_2	71.5 28.5	179.6($3d_{5/2}$) 181.6($3d_{3/2}$) 182.6($3d_{5/2}$) 184.6($3d_{3/2}$)	ZrC C CO, CO_2	35.9 60.3 3.8	282 285 287	ZrO_2 O_{ads}	92.6 7.4	530.6 532

Based on the data in Table 1 and Fig. 3, the following chemistry model of the ZrC film can be infered. From the XPS analysis of the as-deposited sample, it resulted that on the coating surface, a mixture of ZrC and ZrO_2 is formed (the dominant component is ZrO_2). The major surface contaminants are oxygen and carbon, what is currently reported for various nitride or carbide coatings. Relatively small amounts of other compounds (CO_2, CO, H_2O, COOH) were also detected. The presence of free oxygen and carbon is partially the result of deposition conditions (residual gas incorporated in the chamber walls; relatively high value of the base pressure) and partially the result of the contamination during sample handling in open atmosphere. In the case of carbon, as suggested

in ref. [11], the C-C signal is due not only to the carbon contamination, but also to an incomplete decomposition of the reactive gas (CH_4) or to the formation of Zr-C:H compound. Besides, one may presume that some species containing carbon did not react with Zr to form ZrC. These assumptions are sustained by the fact than the free carbon content remained still significant after sputter etching of the (see below).

After sputter removal of the near-surface layers (etching for 5 min), an increase in the Zr content (from 11 to 31%) with a simultaneous reduction in O and C concentrations (from 28 to 23 at.% and from 61 to 46 at.%, respectively) were observed. As for the chemical bindings, it is important to note that the atomic percentages of elements in different phases significantly differ from those existing on the films surface: a marked decrease was found for the atom contents of Zr, C and O in ZrO_2, free carbon and adsorbed oxygen, respectively.

The XPS spectra acquired after subsequent sputter etching for 30 min revealed a further decrease of the oxygen concentration, still kept at a relatively high value (~20 at.%). The presence of free oxygen can be accounted for by the diffusion of oxygen through the voids and pores existing in the film structure (as reported in ref.[17] for ZrN coatings), while the Zr-O bonds are due mainly to the deposition process itself. It was also observed a slightly decrease of the carbon concentration, along with an increase of the Zr content.

4. Summary and conclusions

To sum up, the XPS analysis of ZrC coatings deposited by cathodic arc technique revealed the formation of a thin passive layer on the film surface in which the predominant phase is ZrO_2. This layer contains also high amounts of free oxygen and carbon, along with a low percentage of ZrC compound (less than 10%). Bellow the surface, a graded layer, with increasing ZrC percentage and decreasing O_2 and C concentrations was found. The film bulk contains mainly ZrC phase, but significant amounts of ZrO_2 and free carbon, arising during the deposition process, are still present.

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