

Full Length Article

Application of valence-to-core X-ray emission spectroscopy for identification and estimation of amount of carbon covalently bonded to chromium in amorphous Cr-C coatings prepared by magnetron sputtering



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ABSTRACT

Cr-C coatings containing different amount of carbon ranging from ~5 to 50 at.% were prepared by the direct current (DC) magnetron sputtering on a polished substrate of polycrystalline silicon. The thickness of the samples was about 400 nm. We characterized the composition and the structure of the as-received coatings and those annealed at 500 °C by X-ray diffraction (XRD), Energy dispersion X-ray spectroscopy (EDX) and valence-to-core X-ray emission spectroscopy (vtc-XES) methods. As follows from XRD measurements, the samples with the carbon content above 35 at.% do not demonstrate any sign of the long-range order and annealing at 500 °C does not change their crystallinity. The vtc-XES curves of the as-prepared and annealed samples can be fitted as a superposition of corresponding spectra of chromium metal and chromium carbide (Cr₃C₂) phases. After the annealing, the content of carbides in the samples (and, correspondingly, the content of covalently bonded carbon) somewhat increases. This suggests that the as-received coatings contain a certain amount of carbon that is not covalently bonded to chromium (most likely, elemental carbon) and their annealing at 500 °C transforms this carbon into the additional (of the order of 2–5 at.%) amount of chromium carbide compounds. It deserves mentioning that for Cr-C coatings prepared by the electrochemical deposition from Cr(III) electrolytes containing organic compounds we have not observed changes in the vtc-X-ray emission spectra after similar annealing. This suggests that electrochemical deposition method in contrast to magnetron sputtering technique even at low temperatures favors the formation of only covalently bonded carbon.

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1. Introduction

Chromium coatings formed by various methods are widely used in many technology fields. First of all, this is associated with special properties of these coatings such as their high hardness, wear resistance, corrosion resistance, unique decorative characteristics, etc. Beginning from the late 60s – early 70s of the last cen-

tury, the attention was focused on the coatings (including those of chromium) with the amorphous structure. Such coatings are usually formed by the physical methods that employ quick cooling (quenching) of metals from their melts. It is assumed that the quick heat removal (cooling at a rate of about 10³–10⁴/s) prevents the formation of equilibrium crystalline structure. The methods of quick quenching of metals from melts as well as the methods of high-energy treatment of the surface of crystalline samples (intense laser irradiation, plasma, electrospray, etc.) associated with the quick heat removal to the metal bulk form the well-known approach to synthesizing amorphous surface layers (e.g., see [1,2]). It is usually assumed that the metastable structure of amorphous metals (considered in certain cases as nano-crystalline) is stabi-

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lized in the presence of metalloids (P, C, B, Si, etc.). However, the mechanism of stabilization is still insufficiently clear.

The electrochemical deposition of metals from aqueous solutions containing as precursors certain chemical compounds that include in their composition one of the metalloids listed above is an alternative method of synthesizing sufficiently thick (from 0.1 to several tens of μm) amorphous coatings with the properties resembling those of coatings formed by the mentioned physical methods (see, e.g., [3–10] and references therein). Note that a considerable advantage of electrodeposition of amorphous coatings lies in the fact that this method requires no intricate and costly equipment and the film thickness can be easily regulated by the charge passed during the electrochemical process. Furthermore, the electrochemical method makes it possible to form coating on the intricately shaped parts, which cannot always be realized by physical methods.

Another method of formation of protective coatings (including those of amorphous chromium) is the magnetron sputtering. The peculiarities of the composition and structure of Cr-C coatings obtained by this method, their corrosion stability and some other characteristics were discussed in recent publications [11–17]. In this case, an obvious question arises whether the structure of coatings formed electrochemically is identical on the atomic level to the structure of amorphous metals formed by physical methods. It also deserves mention that up to recently the chemical state of metalloids incorporated into the structure of electrochemical coatings remained unclear. Thus, according to the general opinion it is believed that, (i) the films contain metalloids in their elemental form which can segregate along the boundaries of metal grains and (ii) the metal-metalloid compounds (the corresponding carbides, phosphides, etc.) can be formed only as a result of thermal treatment and crystallization of these films (e.g., see [18–24]). Alternative mechanisms took into account the formation of carbide compounds during the electrochemical process of coating deposition. These mechanisms were based on the data of XPS investigations which found the presence of carbide carbon in the deposits (see [3–10] and references therein). Recently, Danilov and co-authors [9] put forward a new original mechanism for electrodeposition of Cr-C coatings from Cr(III) electrolytes containing organic additives. This mechanism includes a step of reduction of adsorbed organic molecules to elemental carbon by Cr(II) species that are the intermediate product of the Cr(III) reduction process. As follows from the corresponding equations shown in [9], the reduction reactions of both Cr(III) to Cr(0) and organic compound to elemental carbon are independent processes. Under these conditions one can suggest that Cr-C coatings formed during electrodeposition could contain elemental carbon. However, it should be mentioned that no direct data confirming the formation of metal-metalloid compounds and the presence (or absence) of elemental metalloids in the electrochemically formed deposits were available up to recently.

To answer the question on the chemical state of metalloids in the coatings electrodeposited from Cr(III) solutions with additions of certain organic compounds (oxalic and formic acids, etc.) or hypophosphite ions and also from Ni(II) and Fe(II) electrolytes with additions of hypophosphite ions or dimethylaminoborane, the relatively new technique valence-to-core X-ray emission spectroscopy (vtc-XES) was used for the first time in our studies [25–29]. On the qualitative level, the principle of vtc-XES is as follows: the irradiation of a metal (or alloy) sample with X-rays with an energy above the Fermi level of a given metal atom excites an electron from its 1s level to an unoccupied orbital or a continuum level. The observed vtc-X-ray emission spectrum (also known as the $K\beta$ satellite lines spectrum) corresponds to the transition of a valence electron of the metal atom to this unoccupied 1s level and contains $K\beta_{2,5}$ lines, which lie immediately below the Fermi level, and a $K\beta''$ weaker peak which appears at lower fluorescence (or lower

binding) energies. The $K\beta$ satellite lines are thus very sensitive to the local environment of the metal atoms since the character of the valence orbitals strongly depends on the nature of the ligand in the first coordination shell around the metal atom. Analysis of these spectra allows one to distinguish the bands corresponding to the transitions of valence electrons to the unoccupied 1s level from atoms of this metal in its metallic state and from metallic atoms bonded covalently with metalloid atoms. Moreover, the observed intensities of $K\beta$ satellite lines can be related to the corresponding concentrations of atoms of this metal in its metallic state and metallic atoms bonded covalently with metalloid atoms in a given sample.

In view of aforementioned possibility of acquiring information on the number of covalent bonds metal-metalloid (i.e., the chemical state of metalloids) in different samples, the comparison of vtc-X-ray emission spectra between as-received and annealed samples is of particular interest. If the as-received samples prepared by one of the methods mentioned above contain the metalloid atoms unconnected by covalent bonds with metal atoms, then we can expect the formation of the corresponding metal-metalloid compounds (carbides, phosphides, etc.) during the annealing. Evidently, this should induce a change (increase) in the intensity of the bands in the observed vtc-X-ray emission spectrum that corresponds to the formation of covalent metal-metalloid bonds. Based on these results, one can draw conclusions on the chemical state of metalloids in the as-received samples and on the processes that occur during their annealing.

In [25–27], we compared the diffraction patterns of the as-received crystallographically amorphous Cr-C and Cr-P samples prepared by electrodeposition with the diffraction patterns of the same samples after their annealing at 500 °C and higher temperatures. In this case, we observed a transition from the “halo” present in the spectra of as-received samples to the clearly pronounced peaks pointing to the presence of metal chromium and chromium carbides (phosphides) in the annealed samples. However, the comparison of vtc-X-ray emission spectra of as-received and annealed samples revealed quite a different picture. The spectra of the as-received samples presented a superposition of $K\beta$ satellite lines of metallic chromium and also of chromium atoms connected covalently with the corresponding metalloid atoms. It should be noted that annealing had virtually no effect on these spectra. These results allowed us to draw a qualitative conclusion that the corresponding carbide (phosphide) compounds of chromium are formed during the electrochemical deposition of coatings rather than during their subsequent annealing, in contrast to the assumptions made in the majority of studies cited above. We can also conclude that the as-prepared deposits did not contain elemental metalloids because the presence of the latter would result in the growth of the amount of carbide (phosphide) compounds of chromium after annealing. In other words, annealing does not change the Cr coordination but induces a partial crystallization that gives rise to the diffraction peaks.

In view of the results of studying the composition and chemical state of metalloids in chromium coatings electrodeposited from Cr(III) electrolytes, surveyed above, the following objectives are formulated:

1. by using the method of collecting spectra of $K\beta$ satellite lines, to analyze the composition of Cr-C coatings and estimate the amount of carbon atoms coordinated with chromium atoms in these coatings prepared by magnetron sputtering;
2. to compare the acquired data with the analogous data for chromium coatings prepared by electrodeposition from Cr(III) electrolyte.

2. Experimental

The samples of Cr-C coatings were obtained by DC magnetron sputtering on a polished substrate of polycrystalline silicon. Targets consisted of 99.9% pure chromium disc of 100 mm in diameter, on the erosion region of which graphite discs of 20 mm in diameter were placed symmetrically. After evacuating the chamber to less than 5×10^{-5} Pa, 99.999% pure argon gas was introduced and the deposition was performed at 0.3 Pa and 0.5 A for 10 min. 0.3 Pa was the optimal pressure because at the lower pressure it was impossible to obtain the stable discharge. At the same time, at the higher pressure the films were insufficiently dense or (at still higher Ar pressure) they had the morphology of cauliflower (according to SEM data). To get the deposited films of uniform composition and thickness, the substrate holders were rotated around the central axis of the chamber as well as their own axis. It should be noted that the substrate holder was water-cooled, i.e., the deposition was performed near room temperature. Under the conditions shown briefly in Table 1, five samples with different [Cr]: [C] ratios were formed. Their thickness was about 400 nm.

As will be shown in more detail below, according to X-ray diffraction data, the original Cr-C samples had the amorphous (nanocrystalline) structure. In order to follow the evolution of their structure in the course of crystallization, the deposits were annealed in vacuum (to avoid oxidation) at the residual pressure of 10^{-5} – 10^{-6} Torr at 500 °C. The elemental composition of deposits was determined by energy-dispersive X-ray spectroscopy (EDX) on electron microscope ISIS (Jeol, Japan) with the ISIS microprobe energy-dispersive analyzer (Oxford Instruments, Great Britain) with the accelerating voltage of 20 kV. Table 1 shows the total amount of carbon in the prepared samples. This amount includes carbon covalently bonded to chromium atoms (details see below) and elemental carbon, i.e., that is not covalently bonded to chromium.

High energy resolution X-ray emission experiments for as-formed and annealed chromium samples were performed at the high brilliance ID26 beamline of the ESRF synchrotron (Grenoble, France). The electron energy was 6.0 GeV and the ring current varied between 200 and 150 mA. The incident energy (6020 eV), which is above the Cr K-edge (5989 eV), was selected by means of a pair of Si(111) single crystals. A reference Cr metallic foil was used to calibrate the incident energy by setting the first inflection point of the Cr K-edge at 5989 eV. Higher harmonics were suppressed by three Si mirrors working under total reflection at 2.5 mrad. The beam size on the sample was about 0.5 mm in horizontal and 0.1 mm in vertical with a total flux of the order of 5×10^{13} photons/s. According to our estimates [25], the heating of samples due to the high beam intensity did not exceed 50 °C. The emission spectrometer employed five spherically bent Ge(333) analyzer crystals that were arranged with the sample and avalanche photodiode detector in a vertical Rowland geometry ($R = 1000$ mm). The total experimental broadening, determined as the average of the full width half maximum of the elastic profiles, was 1.3 eV. Both $K\beta$ main (from 5925 to 5960 eV) and $K\beta$ satellite (from 5950 to 6010 eV) lines spectra were measured. The samples were measured in a fluorescence geometry oriented at 45 ° to the incident beam and at 45 ° to the central analyzer crystal [30,31]. A Cr foil (Goodfellow, 0.005 mm), a magnetron sputtered Cr sample and Cr_3C_2 (Alfa Aesar, 99.5%) were measured as reference samples. It was found that vtc-X-ray emission spectra of Cr foil and magnetron sputtered Cr sample were identical. Thus, the latter spectrum that is characterized by only a $K\beta_{2,5}$ peak together with the spectrum of Cr_3C_2 that is characterized by two peaks $K\beta_{2,5}$ and $K\beta'$, were used in the quantitative analysis of the vtc-X-ray emission spectra of our samples (Cr-C films on the polycrystalline Si).

To perform a quantitative analysis of vtc-X-ray emission spectra, first of all, we subtracted the background arising from the tail of the main $K\beta$ line (polynomial fitting was used for calculating the background curves). The detailed description of this procedure can be found in our publications [27,28]. Then, in order to correctly (i.e., quantitatively) compare the vtc-X-ray emission spectra of different samples, we calculated normalized dependences. To do this, we divided the background-corrected spectra by the calculated integral intensity of the $K\beta$ main and satellite emission lines (5925–6010 eV). More information about the procedure of constructing normalized vtc-XES intensities vs. emission energy dependencies can be found in our papers [27–29].

It should be noted that a specific feature of vtc-XES method that distinguishes it from XPS and AES methods is the fact that it provides information on the bulk (rather than the surface) characteristics of the sample. It is well-known that the XPS and AES methods usually detect considerable amounts of carbon and oxygen on the surface of samples (especially if the latter were in contact with the atmosphere). This may give rise to certain complications in the interpretation of experimental data obtained by these methods. Due to the large penetration depth of X-rays the influence on the vtc-X-ray emission spectra of carbon and/or oxygen containing particles on the surface was absent in the present study.

To deduce the composition of Cr-C samples, we compared the normalized experimental spectra of these samples with those representing the linear combination (LC) fit of the vtc-X-ray emission spectra of the magnetron sputtered Cr sample and the reference sample $\text{CrC}_{2/3}$ (Cr_3C_2). The results of LC fitting allowed the direct quantification of the concentration of chemically bonded carbon in the Cr-C samples to be carried out. In our LC calculations, we did not use any vtc-X-ray emission spectra of other carbide compounds of Cr (Cr_7C_3 and Cr_{23}C_6) as the spectra of reference samples because, as it was demonstrated before [27], the results of such fitting (the amount of metallic Cr and chromium carbide compound) are insufficiently sensitive to the nature of chromium carbide compounds.

The phase composition of the magnetron-deposited samples before and after annealing was characterized by X-ray diffraction (XRD). The XRD patterns were obtained with the help of Bruker D-8 Advance diffractometer, using $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5406$ Å).

3. Results and their discussion

3.1. XRD investigations of magnetron sputtered Cr-C samples

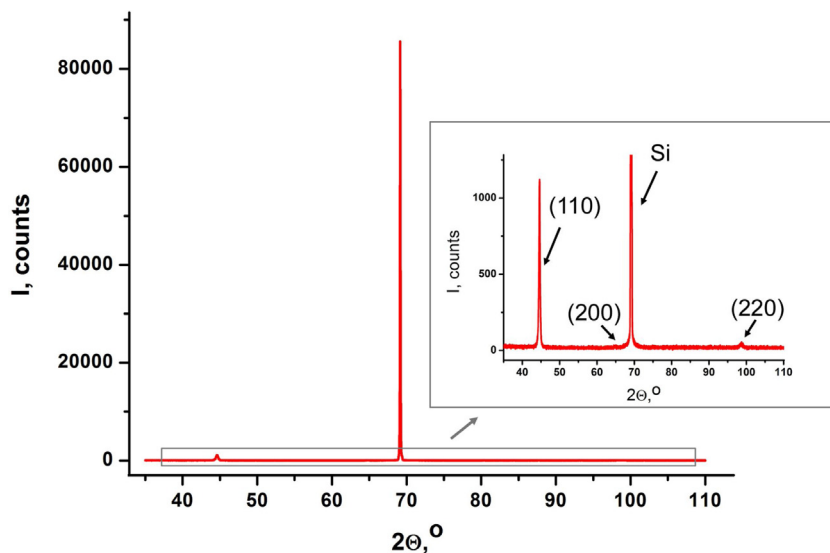
In thin magnetron-sputtered coatings, the XRD study revealed the presence of crystalline Cr in several samples designated below as “Cr”, “Cr-500”, “Cr-2C”, “Cr-2C-500” and “Cr-4C-500” (addition of “500” to the names of samples listed in Table 1 indicates that the samples were annealed at 500 °C). For “Cr-4C” and samples with the higher carbon content, no diffraction peaks (except the peak of Si substrate) were revealed even after annealing at 500 °C. Table 2 shows the ratio of intensities of the Cr(110) peak to the substrate (400) peak for samples studied.

As one can see, the relative intensity of Cr peaks becomes slightly higher after annealing at 500 °C, indicating that crystallinity of the samples also increases. Better crystallinity of the annealed samples is also confirmed by decreasing FWHM of the Cr(110) reflections. These data can be explained by the partial agglomeration during the annealing of small (may be, nanosized) Cr metal particles in the as-prepared Cr-2C and Cr-4C samples and the substantial decrease in the amount of such particles in the samples with the higher content of carbon. As to the chromium carbide phases that are present in all as-received and annealed samples (see below), one can see that corresponding peaks are absent in the observed XRD patterns. We believe that the following reasons can explain this fact. Firstly,

Table 1

Conditions of formation of Cr-C samples by magnetron sputtering and the carbon content in them measured by the EDX method.

No.	Designation of samples	[C]/at. %	U/V	I/A	t/min
1.	Cr	0	300	0.5	10
2.	Cr-2C	6.9	400	0.5	10
3.	Cr-4C	16.0	450	0.5	10
4.	Cr-6C	35.0	550	0.5	10
5.	Cr-8C	49.0	675	0.5	10

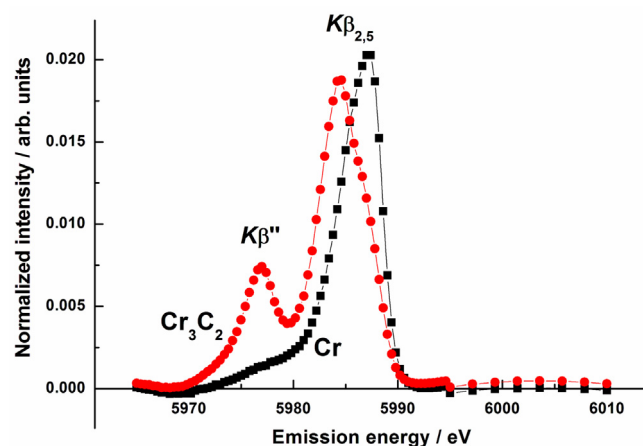
**Fig. 1.** XRD pattern for the “Cr-2C-500” sample. Cr reflections are indicated in the inset.**Table 2**

Relative intensities of Cr(110)/Si(400) XRD reflections and full width at half maximum (FWHM) of Cr(110) peaks for the magnetron sputtered samples before and after their annealing at 500 °C.

Sample	$[I(\text{Cr } (110))/I(\text{Si } (400))] \times 100/\%$	FWHM of Cr(110) peak/degree
Cr	0.45	0.40
Cr-500	0.48	0.35
Cr-2C	1.08	0.40
Cr-2C-500	1.28	0.37
Cr-4C	0	–
Cr-4C-500	0.13	0.29
Cr-6C	0	–
Cr-6C-500	0	–
Cr-8C	0	–
Cr-8C-500	0	–

from our viewpoint, the annealing temperature 500 °C was insufficiently high for the fast crystallization of amorphous chromium carbide phases. Indeed, our similar investigations [29] dealing with Cr-C coatings obtained by the electrodeposition demonstrated that the annealing at 500 °C (1 h) resulted in the appearance in the XRD patterns of chromium carbide peaks of rather weak intensities. The second factor that introduces additional difficulties into observation of chromium carbide peaks in XRD patterns is the small thickness (less than 0.5 μm) of Cr-C coatings obtained by magnetron sputtering. The comparison of intensities for the different pairs of samples cannot be correct because, most probably, they may have different thickness of the deposited layer.

Fig. 1 shows the typical X-ray diffraction pattern (for the Cr-2C-500 sample). As one can see from this figure, the intensities of (110) and (220) reflections of Cr are much higher as compared with that of (200) reflection. This may indicate that the chromium coating prepared by this method is strongly oriented with respect to the [001] axis.

**Fig. 2.** Normalized vtc-X-ray emission spectra of metal chromium and Cr₃C₂ carbide, which were used in modeling experimental vtc-X-ray emission spectra of Cr-C samples prepared by magnetron sputtering.

It should be noted that XRD data (**Table 2**) correlate well with the crucial reduce in the metallic Cr content which is observed with a growth of carbon content from 16 to 35 and to 49 at.% in the samples (see EDX data in **Table 1** that demonstrate the transition from Cr-4C to Cr-6C and to Cr-8C sample, respectively).

3.2. Analysis of vtc-X-ray emission spectra of magnetron sputtered Cr-C samples

Fig. 2 shows the normalized vtc-X-ray emission spectra of chromium metal and its carbide compound Cr₃C₂, which were used in modeling the experimental vtc spectra. Note that the appearance of covalently bonded carbon in the carbide compound induces

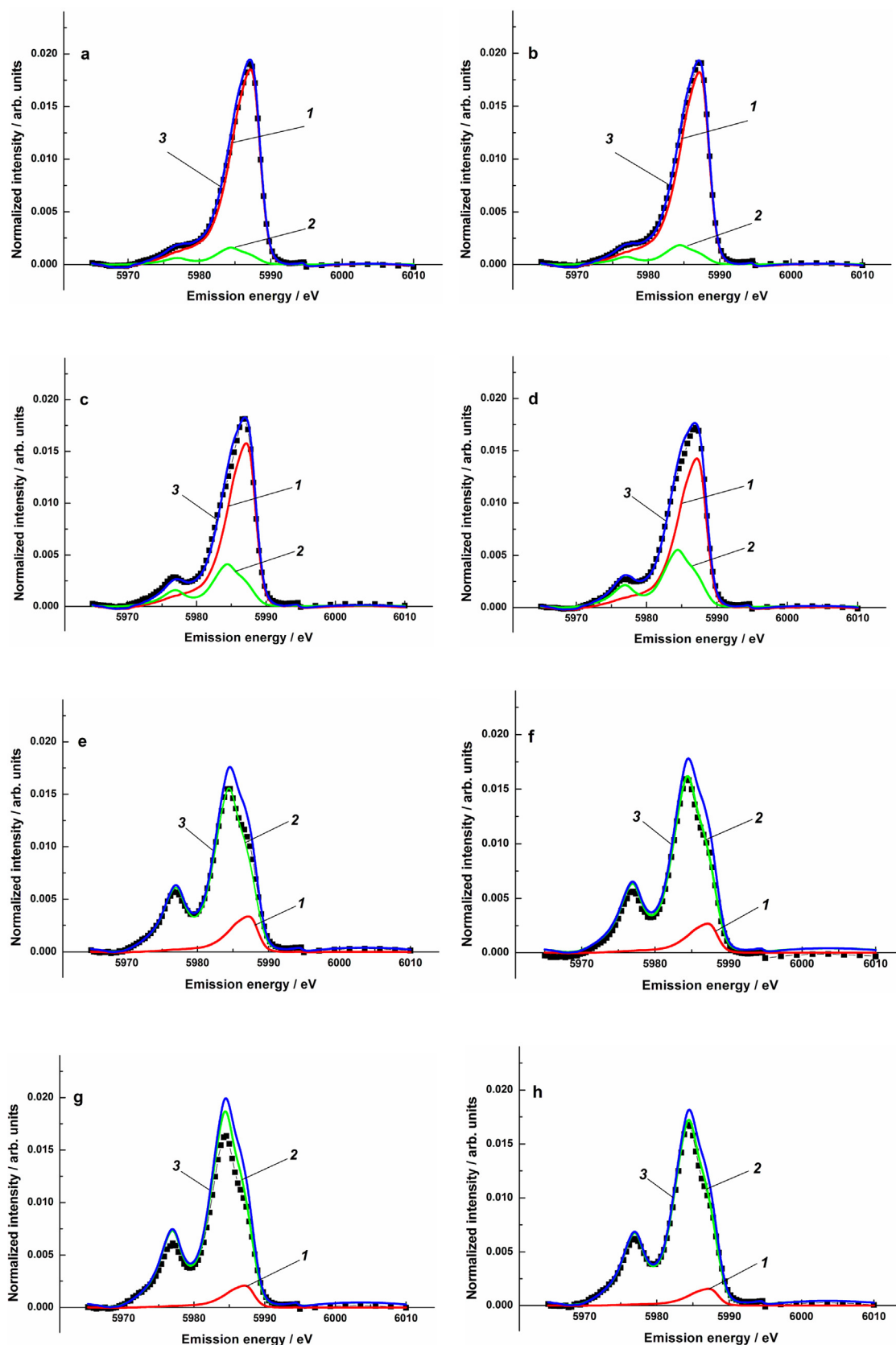


Fig. 3. Comparison of experimental vtc-X-ray emission spectra (points in a–h) with the spectra found by superposition (curves 3) of spectra for metal chromium (curves 1) and chromium carbide Cr_3C_2 (curves 2) multiplied by the corresponding coefficients (see Table 3). Dependences in figures a, c, e, and g characterize the as-received samples Cr-2C, Cr-4C, Cr-6C and Cr-8C, whereas dependences shown in figures b, d, f, and h characterize the same samples after annealing at 500 °C, respectively.

Table 3

Data on the content of chromium metal and chromium covalently bonded in carbide Cr_3C_2 in the as-received Cr-C samples and the same samples annealed at 500 °C, acquired based on the analysis of vtc-X-ray emission spectra; the concentration of covalently bonded carbon in samples was calculated from $[\text{Cr}_3\text{C}_2]$ values.

Samples	As-received			After annealing at 500 °C		
	[Cr] in Cr, at.%	[Cr] in Cr_3C_2 , at.%	[C] in Cr_3C_2 , at.%	[Cr] in Cr, at.%	[Cr] in Cr_3C_2 , at.%	[C] in Cr_3C_2 , at.%
Cr	100	0	0	100	0	0
Cr-2C	86.6	8.0	5.4	84.3	9.4	6.3
Cr-4C	68.0	19.2	12.8	58.8	24.7	16.5
Cr-6C	10.7	53.7	35.6	8.4	54.9	36.6
Cr-8C	6.4	56.1	37.4	4.8	57.1	38.1

spectral variations in the vtc lines compared to chromium metal: the position and form of $K\beta_{2,5}$ peak change and an additional $K\beta''$ peak appears. Note that the vtc-X-ray emission spectra of other carbides (Cr_7C_3 , Cr_{23}C_6) containing smaller amounts of covalently bonded carbon show an intermediate behavior between the spectra of Cr and Cr_3C_2 . Moreover, it is essential that the position of the $K\beta''$ peak on the binding energy axis is independent of the carbide nature (the corresponding dependences are shown in [27]).

Fig. 3 shows the experimental vtc-X-ray emission spectra of samples (points) prepared by magnetron sputtering before and after annealing in vacuum at 500 °C. The absence in these spectra of a peak at the emission energy equal to 5970 eV points to the absence of oxygen atoms (or their presence in concentrations not more than 2–3 at.%) covalently bonded to Cr atoms in the bulk of samples [27]. This figure shows also the calculated spectra (solid lines 3) of these samples found by superposition of the vtc spectra of metal chromium (curves 1) and carbide Cr_3C_2 (curves 2) multiplied by corresponding coefficients. The latter coefficients represent the atomic fractions (in at.%) of these components in the samples. They were calculated by the least square technique and their numerical values can be found in Table 3.

According to Fig. 3(a–h) and also to coefficients obtained based on the analysis of these figures, the procedure used makes it possible to describe the experimental data with sufficient accuracy. It follows from the data shown in Fig. 3 and Table 3 that the annealing of Cr-C samples results in the noticeable decrease in the amount of elemental chromium and the increase in the amount of chromium carbides in them, respectively. It should be noted, as well, that (due to the specific features of information derivable by the vtc-XES method) the data shown in Table 3 on the content of carbon in samples correspond to the carbon covalently bonded to Cr atoms (i.e., present in the closest surroundings of Cr atoms). These data can be compared with the data obtained by, e.g., EDX method (see Table 1). The latter characterize the total amount of carbon in the samples. Thus, such comparison allows one to separate the total amount of carbon in the samples into the amount of elemental carbon and carbon covalently bonded to chromium atoms.

4. Concluding remarks

The analysis of the data obtained makes it possible to draw interesting conclusions on the composition of Cr-C coatings prepared by magnetron sputtering.

1. It follows from Table 3 that after the annealing, the content of carbides in samples (and, correspondingly, the content of covalently bonded carbon) somewhat increases. Obviously, this suggests that the as-received coatings contain a certain amount of elemental carbon and their annealing transforms this carbon into the additional (of the order of 2–5 at.%) amount of chromium carbide compounds. It deserves mention that when analyzing the vtc-X-ray emission spectra of Cr-C coatings obtained by the electrochemical deposition from Cr(III) electrolytes containing certain organic compounds [26,27], we observed no changes in

these spectra after the annealing. This allowed us to conclude that the electrochemical process yields amorphous (nanocrystalline) coatings which consist of elemental chromium and its carbide compounds, i.e., this process produces no elemental carbon, in contrast to assumptions made in certain publications cited above. This allowed us to suggest, as well, that the reduction reactions of both Cr(III) and the organic component of solution are not independent during the electrochemical deposition (cf. with [9]). In other words, we believe that the electrochemical formation of Cr-C coatings is realized through the simultaneous reduction of Cr(III) and the organic ligand of the complex particle [Cr(III)-organic molecule]. At the same time, here we have shown that when amorphous Cr-C layers are formed by magnetron sputtering, not all carbon contained in these coatings is covalently bound with chromium atoms, i.e., not all carbon atoms participate in the reaction with Cr atoms. At the annealing, this elemental carbon may interact with chromium atoms to yield a certain additional amount of chromium carbides. From our point of view, in future these results may help us (or other specialists) to formulate in more detail the mechanism of formation of amorphous Cr-C coatings by the magnetron sputtering method. We can add, as well, that the results obtained here are relevant for the evaluation of some physico-chemical, mechanical or other properties of Cr coatings prepared by different methods.

2. We think that the following result derived from the aforementioned data is very interesting, as well. It follows from the chemical formula Cr_3C_2 (this chromium compound is the most saturated with respect to carbon) that the maximum carbon content in chromium carbides (i.e., the number of carbon atoms capable of forming covalent bonds with chromium atom) is 40 at.%. In other words, in samples with the carbon content above this value, the excessive carbon is uninvolved in carbide compounds. According to Table 3, the carbon content in Cr-6C and Cr-8C samples approaches just this value. Note that this and the previous conclusions are based on the data acquired by analyzing the vtc-X-ray emission spectra, and it is the latter data that allowed us to identify the presence of metalloid atoms covalently bonded to metal atoms and assess their quantitative content in the metal-metalloid coatings formed by different methods. Comparison of these data with the data on the total amount of carbon in the samples obtained by, e.g., EDX method (see Table 1) allows one to separate the total amount of carbon in the samples into the amount of elemental carbon and carbon covalently bonded to chromium atoms.

3. It also deserves mention that for as-received coatings with the carbon content much below 40 at.% (samples Cr-2C and Cr-4C), the XRD method makes it possible to observe that the intensity of peaks corresponding to crystalline chromium somewhat increases after the annealing at 500 °C indicating the crystallite growth. The coatings with the high carbon content (samples Cr-6C and Cr-8C) synthesized by magnetron sputtering do not demonstrate any sign of long-range order in their crystal structure. Annealing at 500 °C does not result in crystallization. These results correlate well with the literature data suggesting sta-

bilization of poorly crystalline structure by formation of Cr-C bonds.

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References

- [1] K. Suzuki, H. Fujimori, K. Hashimoto, Amorphous metals (Russian translation), Metallurgiya Moscow (1987).
- [2] A. Inoue, K. Hashimoto, Amorphous and Nanocrystalline Materials (Preparation, Properties, and Applications), Springer-Verlag, Berlin, Heidelberg, New York, 2001.
- [3] Y.M. Polukarov, V.A. Safonov, A.A. Edigaryan, L.N. Vykhodtseva, Chrome plating from sulfate-oxalate Cr(III) baths. Structure, composition, and corrosion behavior, Prot. Met. 37 (2001) 447–451.
- [4] A.A. Edigaryan, V.A. Safonov, E.N. Lubnin, L.N. Vykhodtseva, G.E. Chusova, Y.M. Polukarov, Properties and preparation of amorphous chromium carbide electroplates, Electrochim. Acta 47 (2006) 2775–2786.
- [5] F.I. Danilov, V.S. Protsenko, T.E. Butyrina, Chromium electrodeposition kinetics in solutions of Cr(III) complex ions, Russ. J. Electrochem. 37 (2001) 704–709.
- [6] V. Protsenko, F. Danilov, Kinetics and mechanism of chromium electrodeposition from formate and oxalate solutions of Cr(III) compounds, Electrochim. Acta 54 (2009) 5666–5672.
- [7] F.I. Danilov, V.S. Protsenko, V.O. Gordienko, S.C. Kwon, J.Y. Lee, M. Kim, Nanocrystalline hard chromium electrodeposition from trivalent chromium bath containing carbamide and formic acid: structure, composition, electrochemical corrosion behavior, hardness and wear characteristics of deposits, Appl. Surf. Sci. 257 (2011) 8048–8053.
- [8] S. Surviliene, O. Nivinskiene, A. Cesuniene, A. Selskis, Effect of Cr(III) solution chemistry on electrodeposition of chromium, J. Appl. Electrochem. 36 (2006) 649–654.
- [9] V.S. Protsenko, V.O. Gordienko, F.I. Danilov, Unusual chemical mechanism of carbon co-deposition in Cr-C alloy electrodeposition process from trivalent chromium bath, Electrochem. Commun. 17 (2012) 85–87.
- [10] Chen-En Lu, Nen-Wen Pu, Kung-Hsu Hou, Chun-Chieh Tseng, Ming-Der Ger, The effect of formic acid concentration on the conductivity and corrosion resistance of chromium carbide coatings electroplated with trivalent chromium, Appl. Surf. Sci. 282 (2013) 544–551.
- [11] P.Eh. Hovsepian, Y.N. Kok, A.P. Ehasarian, R. Haasch, J.-G. Wen, I. Petrov, Phase separation and formation of the self-organised layered nanostructure in C/Cr coatings in conditions of high ion irradiation, Surf. Coat. Technol. 200 (2005) 1572–1579.
- [12] M. Andersson, J. Höglström, S. Urbonaitė, A. Furlan, L. Nyholm, U. Jansson, Deposition and characterization of magnetron sputtered amorphous Cr-C films, Vacuum 86 (2012) 1408–1416.
- [13] M. Magnuson, M. Andersson, J. Lu, L. Hultman, U. Jansson, Electronic structure and chemical bonding of amorphous chromium carbide thin films, J. Phys.: Condens. Matter. 24 (2012) 225004 (7pp).
- [14] J. Hogstrom, M. Andersson, U. Jansson, F. Bjorefors, L. Nyholm, On the evaluation of corrosion resistances of amorphous chromium-carbon thin-films, Electrochim. Acta 122 (2014) 224–233.
- [15] K. Nygren, M. Samuelsson, A. Flink, H. Ljungcrantz, K. Å. Rudolphi, U. Jansson, Growth and characterization of chromium carbide films deposited by high rate reactive magnetron sputtering for electrical contact applications, Surf. Coat. Technol. 260 (2014) 326–334.
- [16] K. Nygren, M. Andersson, J. Höglström, W. Fredriksson, K. Edström, L. Nyholm, U. Jansson, Influence of deposition temperature and amorphous carbon on microstructure and oxidation resistance of magnetron sputtered nanocomposite Cr-C films, Appl. Surf. Sci. 305 (2014) 143–153.
- [17] M. Folkenant, K. Nygren, P. Malinovsky, J. Palisaitis, P.O.Å. Persson, E. Lewin, U. Jansson, Structure and properties of Cr-C/Ag films deposited by magnetron sputtering, Surf. Coat. Technol. 281 (2015) 184–192.
- [18] S.C. Kwon, M. Kim, S.U. Park, D.Y. Kim, D. Kim, K.S. Nam, Y. Choi, Characterization of intermediate Cr-C layer fabricated by electrodeposition in hexavalent and trivalent chromium baths, Surf. Coat. Technol. 183 (2004) 151–156.
- [19] B. Li, A. Lin, F. Gan, Preparation and characterization of Cr-P coatings by electrodeposition from trivalent chromium electrolytes using malonic acid as complex, Surf. Coat. Technol. 201 (2006) 2578–2586.
- [20] Z. Zeng, L. Wang, A. Liang, L. Chen, J. Zhang, Fabrication of a nanocrystalline Cr-C layer with excellent anti-wear performance, Mater. Lett. 61 (2007) 4107–4109.
- [21] D.B. Lee, Oxidation of Cr-C electroplating between 400 and 900 °C in air, Mater. Corros. 59 (2008) 598–601.
- [22] B. Li, A. Lin, X. Wu, Y. Zhang, F. Gan, Electrodeposition and characterization of Fe-Cr-P amorphous alloys from trivalent chromium sulfate electrolyte, J. Alloys Compd. 453 (2008) 93–101.
- [23] S. Ghaziof, K. Raeissi, M.A. Golozar, Improving the corrosion performance of Cr-C amorphous coatings on steel substrate by modifying the steel surface preparation, Surf. Coat. Technol. 205 (2010) 2174–2183.
- [24] H.A. Ramezani-Varzaneh, S.R. Allahkaram, M. Isakhani-Zakaria, Effects of phosphorus content on corrosion behavior of trivalent chromium coatings in 3.5 wt.% NaCl solution, Surf. Coat. Technol. 244 (2014) 158–165.
- [25] V.A. Safonov, L.N. Vykhodtseva, Y.M. Polukarov, O.V. Safonova, M. Sikora, S.G. Eeckhout, P. Glatzel, Valence-to-core X-ray emission spectroscopy identification of carbide compounds in nanocrystalline Cr coatings deposited from Cr(III) electrolytes containing organic substances, J. Phys. Chem. B 110 (2006) 23192–23196.
- [26] S.G. Eeckhout, O.V. Safonova, G. Smolentsev, M. Biasioli, V.A. Safonov, L.N. Vykhodtseva, M. Sikora, P. Glatzel, Cr local environment by valence-to-core X-ray emission spectroscopy, J. Anal. At. Spectrom. 24 (2009) 215–223.
- [27] O.V. Safonova, L.N. Vykhodtseva, N.A. Polyakov, J.C. Swarbrick, M. Sikora, P. Glatzel, V.A. Safonov, Chemical composition and structural transformations of amorphous chromium coatings electrodeposited from Cr(III) electrolytes, Electrochim. Acta 56 (2010) 145–153.
- [28] O.V. Safonova, L.N. Vykhodtseva, L.A. Fishgoit, N.N. Kononkova, P. Glatzel, V.A. Safonov, Elucidation of the chemical state of phosphorus and boron in crystallographically amorphous nickel electroplates, Russ. J. Electrochem. 46 (2010) 1223–1229.
- [29] V.A. Safonov, O.V. Safonova, L.A. Fishgoit, K. Kvashnina, P. Glatzel, Chemical state of phosphorus in amorphous Ni-Fe-P electroplates, Surf. Coat. Technol. 275 (2015) 239–244.
- [30] U. Bergmann, C.R. Horne, T.J. Collins, J.M. Workman, S.P. Cramer, Chemical dependence of interatomic X-ray transition energies and intensities—a study of Mn $K\beta''$ and $K\beta_{2,5}$ spectra, Chem. Phys. Lett. 302 (1999) 119–124.
- [31] P. Glatzel, U. Bergmann, High resolution 1 s core hole X-ray spectroscopy in 3d transition metal complexes—electronic and structural information, Coord. Chem. Rev. 249 (2005) 65–95.