

	Experiment title: Comparison of the chemical state of carbon in Cr-C coatings prepared by physical and electrochemical method	Experiment number: CH-4188
Beamline: ID26	Date of experiment: from: November 12, 2014 to: November 18, 2014	Date of report: February 26, 2017
Shifts: 18	Local contact(s): Dr. P. Glatzel, Dr. S. Lafuerza	<i>Received at ESRF:</i>
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Report:

The goal of the proposal was to elucidate the differences in the chemical state of carbon in amorphous Cr-C coatings prepared by electrochemical and physical methods. To answer this question we used the method worked out Dr. P. Glatzel at ID26, i.e., valence-to-core X-ray emission spectroscopy (v-t-c XES). This method allows direct qualitative identification and quantitative estimation of the presence of carbon in the first coordination shell of Cr.

Cr-C samples were prepared by two different ways, i.e., by electrochemical deposition and by magnetron sputtering. Electrochemical deposition of Cr-C samples was carried out from the Cr(III) solution with the addition of oxalic acid. Conditions of formation of Cr-C samples by magnetron sputtering and the carbon content in them are shown in the table.

Table.

Conditions of formation of magnetron sputtered Cr-C samples and the carbon content in them.

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

It should be mentioned that the electrochemical deposition of samples was carried out at the Department of Electrochemistry of Moscow State University, Russia and magnetron sputtering of samples was carried out by our colleagues from Hokkaido University, Japan.

We divided every of the prepared samples into 3 parts and 2 of them were annealed at 200 and 500°C, respectively. All these samples together with the samples of metal Cr, chromium carbides and chromium oxides (as standards) were used in our v-t-c XES measurement at ID26. All in all, 25 samples were considered.

Comparison of v-t-c XES data of electrochemically deposited samples with those of magnetron sputtered samples allowed us to formulate the following qualitative conclusions:

1. The as-received magnetron sputtered coatings contain a certain amount of elemental (free) carbon and their annealing transforms this carbon into the additional (of the order of 2–5 at. %) amount of chromium carbide compounds (see Figure). It deserves mention that when analyzing the v-t-c XES data of Cr-C coatings obtained by the electrochemical deposition, we observed no changes in their 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 (free) carbon. On the other hand, here we have shown that at the formation of amorphous Cr-C layers by magnetron sputtering, not all carbon contained in these coatings is covalently bonded with chromium atoms. At the annealing, this elemental (free) carbon may interact with chromium atoms to yield a certain additional amount of chromium carbides.
2. It follows from the chemical formula of chromium carbide 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 the rough quantitative estimations from v-t-c XES data, the carbon content in Cr-6C and Cr-8C samples approaches just this value (35 and 37 at. % of carbon, respectively). Note that this and the previous conclusions are based on the data acquired by analyzing the v-t-c XES data, and it is the latter data that allowed us to identify the chemical state of metalloids and assess their quantitative content in the metal-metalloid coatings formed by different methods.
3. Preparation of publication of these results is now under the final stage.

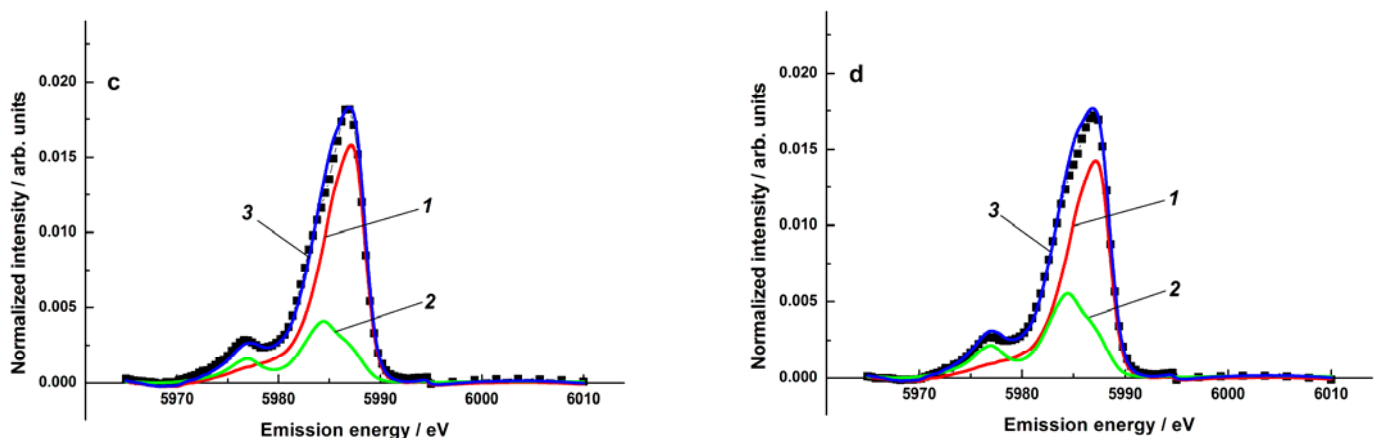


Figure. Comparison for the as-received (c) and after annealing at 500°C (d) Cr-6C samples of experimental v-t-c XES data (points) with the spectra (curve 3, blue) found by superposition of spectra for metal chromium (curve 1, red) and chromium carbide Cr_3C_2 (curve 2, green) multiplied by the corresponding coefficients.