



Research Article

Structure and morphology of composite coating of chromium with diamond nanoparticles on sintered steels

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Abstract

Electrochemical chromium coatings modified with diamond nanoparticles (ND) were deposited on sintered steel materials obtained from iron powder and ultrafine graphite powder. The diamond nanoparticles were produced by detonation synthesis. Their average size is 6 nm. The sintered steel consisted of 0.2, 0.4, 0.6 and 0.8% C (added in the form of graphite) by weight. The produced composite coatings consisting of Cr + ND were compact, tightly adhering to the substrate, with thickness of about 25–35 μm . The surface morphology and microstructure of the coatings were investigated by SEM and EDS analyzes. The main objective of the study was to explore the presence of ND in the coating by the X-ray photoelectron spectroscopy and the impact of the ND concentration in the electrolyte on the presence of the diamond nanoparticles in the coating. The spectra of the C1s photoelectronic line were obtained, the sp^3/sp^2 ratio and the $sp^3 + sp^2$ sum were determined electronically on the surface of the coatings (depth 10 nm). The Cr2p photoelectronic line spectra were also obtained. The coatings were deposited from electrolytes with ND concentrations of 10, 25 and 40 g/l. A diamond-like phase has been found in coatings obtained at concentrations of diamond nanoparticles in the electrolyte of 25 and 40 g/l. The sp^3/sp^2 ratio with a value equal to or greater than 1.2 is an indication of the presence of a diamond-like phase in the coatings and the ratio depends on the concentration of ND in the electrolyte.

Keywords Diamond nanoparticles · Sintered steel · X-ray photoelectron spectroscopy (XPS) · Electrochemical chromium coating

1 Introduction

The electrochemical chromium coatings, modified with diamond nanoparticles, deposited on wrought steel, sintered steel and other metals and alloys increase several times their hardness, wear and corrosion resistance in comparison to the monochromium coatings. Our studies unambiguously showed the influence of the diamond nanoparticles in improvement of the chemical and mechanical properties of the composite Cr + ND coatings [1–3]. The role of the diamond nanoparticles in the built-up of the coatings and their presence in the layer are controversial. The ND added to the electrolyte were obtained

by detonation synthesis. According to [4] the obtained product may contain up to 80% of nanoparticles. They are cleaned from soot and other by-products by a series of oxidation–reduction and thermal processes. ND have a high adsorption capacity of different ions and functional groups due to their high specific surface area of about 300–450 m^2/g [5].

The goal of our research was to ascertain the presence of the diamond nanoparticles in the electrodeposited composite coating by the X-ray photoelectron spectroscopy.

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2 Experimental

The steel samples were prepared of pure iron powder NC 100-24 (Höganäs AB) and ultrafine graphite C-UF (Höganäs AB). The carbon content (in the form of graphite) in sintered steels was 0.2, 0.4, 0.6 and 0.8 wt% respectively. The samples were compacted at 660 MPa and sintered at 1250 °C in protective gas mixture consisting of 95% N₂–5% H₂. Following sintering, the electrolytic process was employed to obtain composite coatings. The chromium electrolyte had the following composition: CrO₃—220 g/l, H₂SO₄—2.20 g/l. The anode was lead. The diamond nanoparticles were produced by detonation synthesis in NDDS Production Unit at the Altai Research Institute, Russia. The diamond nanoparticles were added to the electrolyte as an aqueous suspension at concentrations of 10, 25 and 40 g/l. The electrochemical deposition for all samples was carried out at equal current density of 45 A/dm² and duration of 45 min.

Surface morphology was investigated using an image of secondary electrons (SEI) with scanning electron microscope JEOL 6390 and INCA Oxford solid-state detector for the characteristic X-ray radiation. The accelerating voltage was 20 kV.

X-ray photoelectron analysis was performed by an AXIS Supra electron spectrometer with monochromatic Al radiation of 1486.6 eV. Each analysis begins with a full spectrum in an energy range of 0–1200 eV with a transmitting energy of 160 eV and a step of 1 eV. After a detailed analysis of the spectrum, the characteristic lines of the surface components were selected for analysis. The narrow slits are scanned at transmitting energy of 20 eV with step 0.1 eV.

The analyses were conducted at the 90° take-off angle, allowing maximum X-ray penetration into the sample, respectively the depth from which the elemental composition information was obtained was not greater than 10 nm. In this way the spectra of C1s, O1s, Cr2p, N1s, Na1s were recorded. The resulting spectra were subjected to further processing, such as surface concentration calculations and deconvolution. The deconvolution of C1s and Cr2p spectra was performed using specialized software XPS PEAK 4.1.

3 Results and discussion

The morphology of the composite chromium coating on sintered steel containing 0.2 wt% C is shown in Fig. 1. The slightly folded and fine-grained structure of the coating

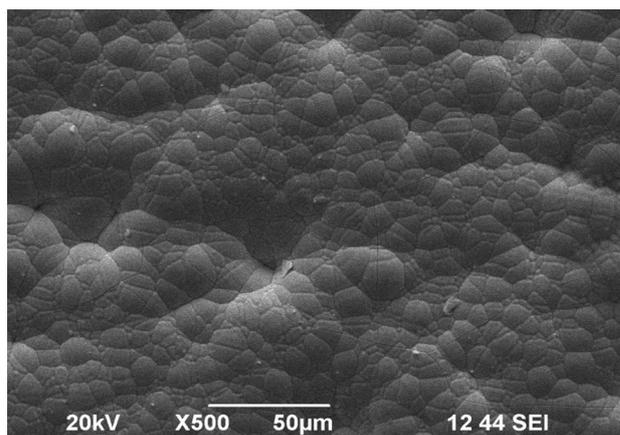


Fig. 1 Surface morphology of chromium composite coating with diamond nanoparticles on sintered Fe–0.2%C steel, obtained from electrolyte with 25 g/l diamond nanoparticles concentration

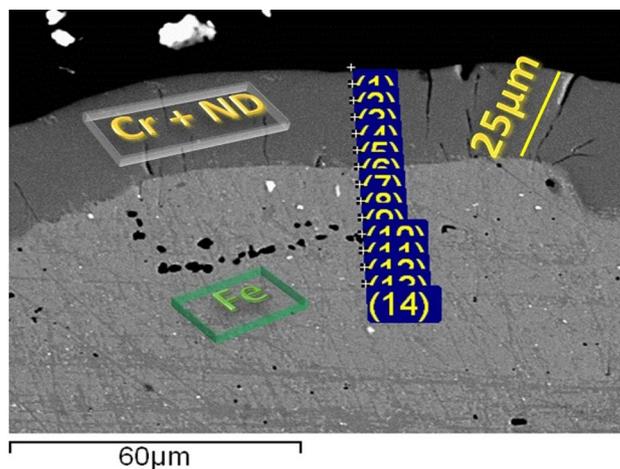


Fig. 2 Microstructure of composite Cr+ND coating on sintered Fe–0.2%C steel showing the points of the SEM–EDS analysis

surface is clearly observed. The coating follows the surface of the sintered sample.

Scanning Electron Microscopy—Energy Dispersive Spectroscopy (SEM–EDS) analysis of the cross section of chromium composite coating with diamond nanoparticles on sintered steel was performed. The coating was obtained from electrolyte with 25 g/l concentration of diamond nanoparticles. It was deposited on sintered Fe–0.2% C steel. The analysis was made along a line at 14 points with 5 µm between them in the coating and the matrix (Fig. 2). The obtained coating was compact, well adhering to the matrix, with thickness of about 30 µm.

Changes in the amount of Cr and Fe in atomic % along the investigated line are shown in Fig. 3. The coating is monolithic and has a constant 100% chromium content.

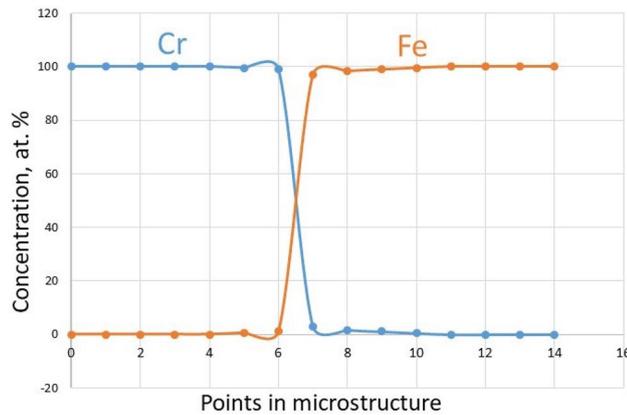


Fig. 3 SEM-EDS analysis of the chromium and iron content in the cross section of composite chromium coating with diamond nanoparticles, electrolyte containing 25 g/l ND, sintered Fe-0.2%C steel

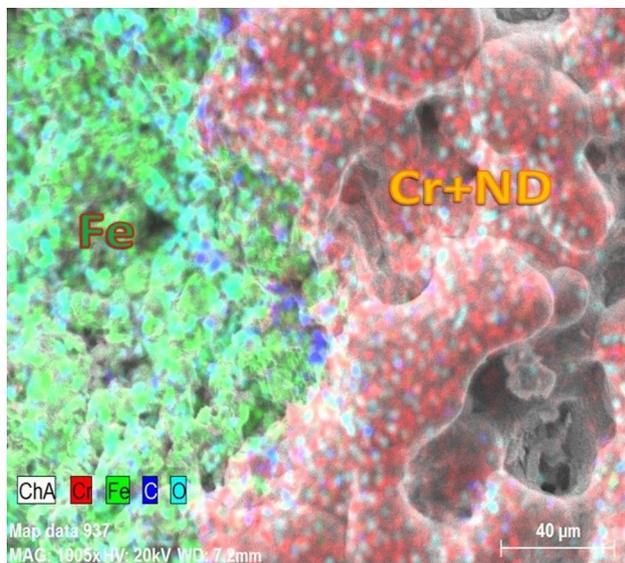


Fig. 4 Microanalysis of the fracture of Fe-0.2%C steel along the boundary of the coating and the steel matrix, Cr—red, Fe—green, C—blue

The coating is from point 0 to point 6 which corresponds to 30 μm thickness. From point 7 to point 14 in the matrix is 100% iron. The smooth change of the Cr and Fe concentration at the matrix—coating boundary (point 6–point 7) shows the diffusion character of the interaction between the two metals.

The microanalysis of the fracture of the matrix and the chromium layer is shown in Fig. 4. The coating was obtained from electrolyte with 25 g/l concentration of ND. It was deposited on sintered Fe-0.2%C steel. The chromium coating deposited on the sintered steel follows its surface. The electrodeposited chromium fills part of the pores in depth and width of the matrix. This process is in

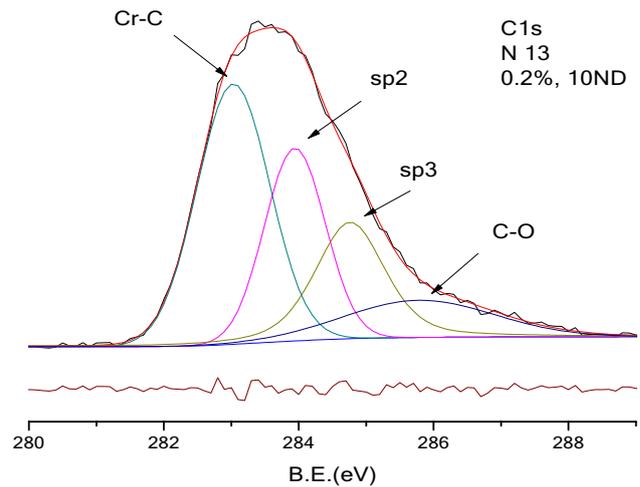


Fig. 5 Spectrum of C1s photoelectron line of composite Cr+ND coating (after deconvolution). Diamond nanoparticles concentration in the electrolyte 10 g/l

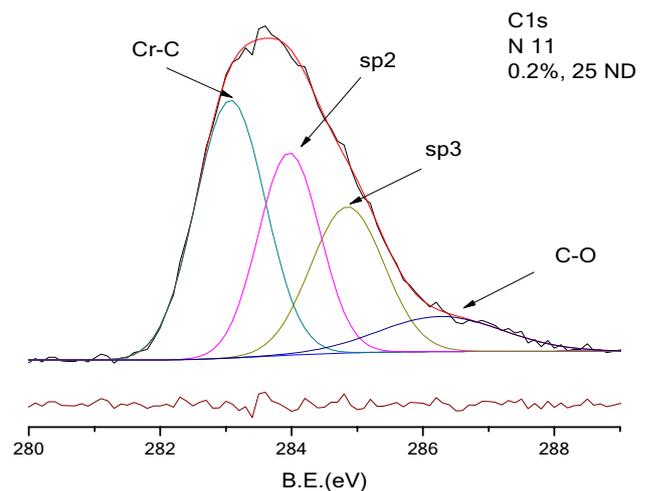


Fig. 6 Spectrum of C1s photoelectron line of composite Cr+ND coating (after deconvolution). Diamond nanoparticles concentration in the electrolyte 25 g/l

direct relation to the concentration of the diamond nanoparticles in the electrolyte and the duration of the process according to our previous investigations [3]. The fracture microanalysis definitely shows that there is only chromium on the surface; In the matrix mainly iron and very small amount of carbon was observed. Most probably this carbon comes from the sintered steel.

The electron structure of the diamond nanoparticles consists of sp^2 and hybridized sp^3 groups [5]. The spectra of the C1s photoelectron line of the coatings on sintered steels with 0.2 wt% C electrodeposited from electrolytes with ND concentration of 10, 25 and 40 g/l, respectively,

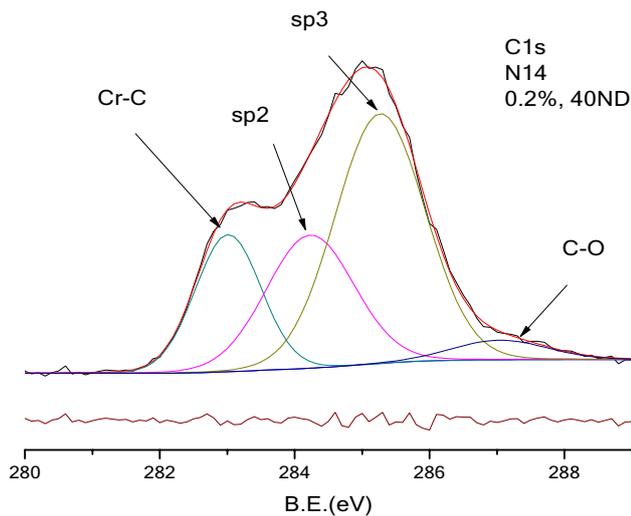


Fig. 7 Spectrum of C1s photoelectron line of composite Cr+ND coating (after deconvolution). Diamond nanoparticles concentration in the electrolyte 40 g/l

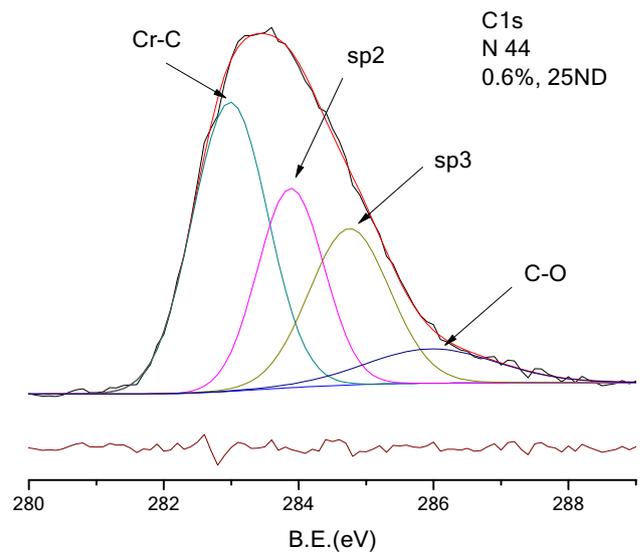


Fig. 9 Spectrum of C1s photoelectron line of composite Cr+ND coating (after deconvolution) electrodeposited on Fe-0.6%C sintered steel

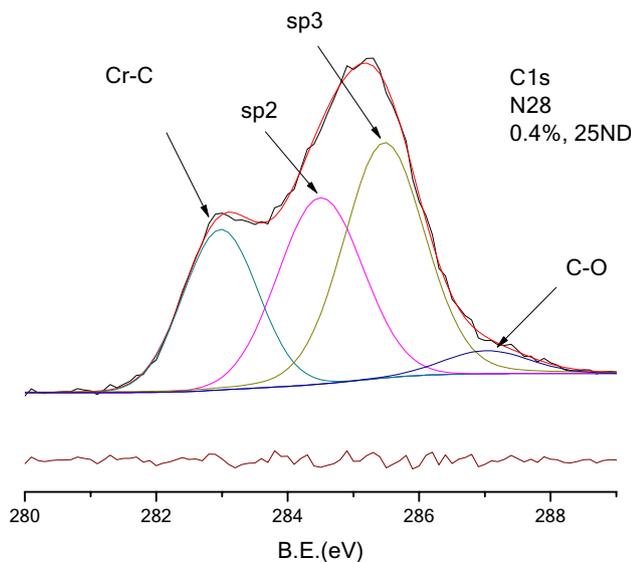


Fig. 8 Spectrum of C1s photoelectron line of composite Cr+ND coating (after deconvolution) electrodeposited on Fe-0.4%C sintered steel

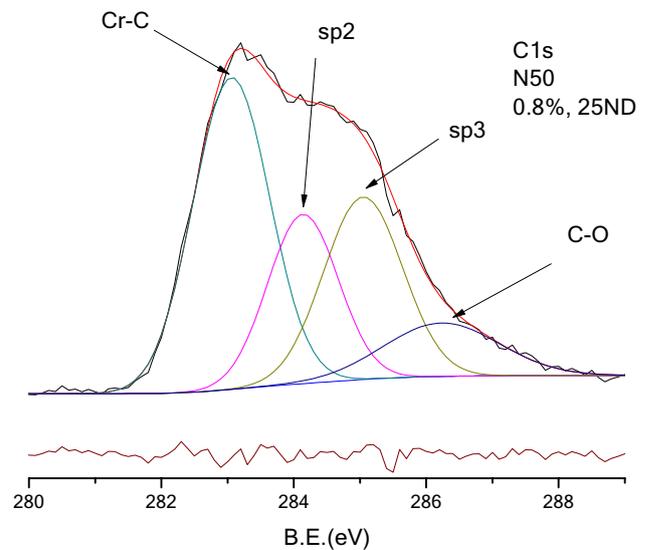


Fig. 10 Spectrum of C1s photoelectron line of composite Cr+ND coating (after deconvolution) electrodeposited on Fe-0.8%C sintered steel

after deconvolution, are presented in Figs. 5, 6 and 7. The spectra of the carbon line (C1s) consists of 4 peaks, associated with Cr-C, sp^2 , sp^3 , C-O bonds with binding energies 283 eV, 284.4 eV, 285.3 eV and 286.5 eV, respectively [6].

The spectra of the C1s photoelectron line of the composite Cr+ND coatings electrodeposited from electrolytes with diamond nanoparticles concentration of 25 g/l on sintered steels containing 0.4, 0.6 and 0.8 wt% C, respectively, after deconvolution, are presented in Figs. 8, 9 and 10.

The calculations of sp^3/sp^2 ratio, the sum of sp^3 and sp^2 and the value of Cr-C bond of samples obtained from electrolyte with different ND concentration and samples with different graphite content in the steel matrix are presented in Table 1.

The sp^3/sp^2 ratio of 1.2 and above is typical for the diamond-like phase. It can be seen from the data presented in the Table 1 that in the coatings electroplated from electrolyte with ND concentration 25 and 40 g/l

Table 1 The values of the bonds in the spectra of the composite Cr+ND coating in relation with the graphite content in the steel matrix and the concentration of the ND in the electrolyte

Graphite content in steel matrix (wt%)	Concentration of ND in the electrolyte (g/l)	sp^3/sp^2 (ratio)	$sp^3 + sp^2$ (sum)	Cr–C bond (%)
0.2	10	0.81	46.32	41.43
0.2	25	0.86	50.96	39.57
0.2	40	1.89	75.99	19.98
0.4	25	1.27	72.04	24.13
0.6	25	0.97	49.67	41.57
0.8	25	1.2	46.7	42.43

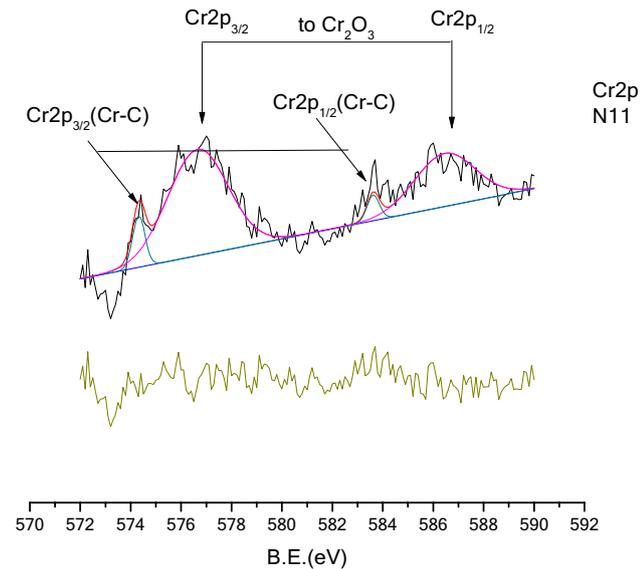


Fig. 11 Spectrum of Cr2p photoelectron line of composite Cr+ND coating (after deconvolution) electrodeposited on Fe–0.2%C sintered steel. Diamond nanoparticles concentration in the electrolyte 25 g/l

the ratio sp^3/sp^2 has a value equal or over 1.2. For this reason the authors assumed that it was possible nanodiamonds to be present in the surface layer of the these coatings.

The Cr2p spectrum (after deconvolution) of a sample prepared from electrolyte with diamond nanoparticles concentration 25 g/l is shown in Fig. 11. Cr2p binding energy is 574.2 eV and 576.6 eV, whereby it is possible to attract nanodiamond particle to the chromium ions (atoms). The presence of Cr_2O_3 lines is probably due to the air oxidation of the Cr coating after its production. The photoelectron line $Cr2p_{3/2}$ corresponds to the carbide bond Cr–C (574.2 eV) and respectively to the chemical compound Cr_3C_7 [7]. The question whether it is possible to obtain chromium carbide at nano level remains open for further research.

4 Conclusions

- It has been found that the composite chromium coating with diamond nanoparticles was characterised by fine-grained microcrystalline structure. The coating on the surface of the sintered Fe–? %C steel, was dense and well adhering to the matrix.
- It has been found by XPS that it is possible diamond nanoparticles to be incorporated into the surface structure of the electrochemically deposited composite coating on sintered steel.
- It has been found that ratio sp^3/sp^2 with value equal or over 1.2, which is an indication of the presence of a diamond-like phase in the coatings, depends on the concentration of ND in the electrolyte.
- The photoelectron line $Cr2p_{3/2}$ with binding energy 574.2 eV corresponds to the carbide bond Cr–C, respectively to the chemical compound Cr_3C_7 .

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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