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COMPOSITE COATINGS OF CHROMIUM AND NANODIAMOND PARTICLES ON STEEL

Chrome plating is used to improve the properties of metal surfaces like hardness, corrosion resistance and wear resistance in machine building. To further improve these properties, an electrodeposited chromium coating on steel, modified with nanodiamond particles is proposed. The nanodiamond particles (average size 4 nm measured by TEM) are produced by detonation synthesis (NDDS). The composite coating (Cr+NDDS) has an increased thickness, about two times greater microhardness and finer microstructure compared to that of unmodified chromium coating obtained under the same galvanization conditions. In the microstructure of specimen obtained from chrome electrolyte with concentration of NDDS 25 g/l or more, "minisections" with chromium shell were found. They were identified by metallographic microscope and X-ray analyser on etched section of chromium plated sample. The object of further research is the dependence of the presence of NDDS in the composite coating from the nanodiamond particles concentration in the chroming electrolyte.

Keywords: composite chromium coating, nanodiamond particles, SEM-EDS analysis

1. Introduction

It is known that nanodiamond particles added in chromium electrolyte influence the chemical and mechanical properties of the electrodeposited on iron alloys chromium coatings. Published literature essentially reflects the morphological changes of the surface and the increased values of microhardness and wear resistance of chromium coatings modified with nanodiamond particles [1-8]. The maximum increase of the composite coatings microhardness is about 2.5 times compared to the unmodified coatings [1-6]. Data on increased wear resistance at dry friction are quite diverse: 15% [2], 1.4-1.8 times [4] and up to 10 times according to the authors of the paper [8]. Nanodiamond particles added to chromium electrolyte have different origin [2-5]. The most commonly used nanodiamond particles are derived from graphite and carbon-rich organic compounds in special chambers, without heating at high pressure through the so-called "detonation synthesis" (NDDS). It is characteristic for the detonation synthesis that the basic part of the obtained diamond particles are with dimensions 4-5 nm [9,10]. Detonation nanodiamonds from different producers may differ significantly in their properties. This concerns also their crystal structure and outer shell [11-13].

Furthermore N. Mandlich and J. Dennis [3] use nanodiamond particles produced by chemical way of the companies – Du Pont Co and Straus Chemical Corp. G. Burkat and others [6] use superdispersed particles of the Japanese company Nano Amondo with dimensions of 4.5 ± 0.7 nm. By examining the surface morphology of the composite coatings of chromium modified with nanodiamonds with a scanning electron microscope (SEM) and an atomic force microscope (AFM) their grain refining has been proven [1,4,6] without clarifying the influence of the nanodiamond particles on the mechanism of the layer formation. By X-ray microanalysis the chemical composition of coating is determined and only presence of Cr in the layer is registered [1]. According to P.A. Vityas and others [4] the content of the nanodiamonds in the coating varies from 0.05 to 0.15 wt. %. The determination of the nanodiamonds was done by Coulomb method of AN-7529 Express analysis of the total carbon content in the coating. We cannot accept this result as reliable one, being in such wide limits, providing that the substrate material, the steel, also contains carbon. The role of nanodiamond particles in the creation of composite coating, their participation in the phase and structure formation of the modified chromium layer is not clarified as well as the influence of the nanodiamond particles participation in the layer on the characteristics and properties of the composite chromium coating.

The objective of present research was to establish the influence of the nanodiamond particles and their concentration in the electrolyte on the properties of the electrodeposited chromium coating at predefined other parameters of the galvanization and to investigate and determine the phase and microstructure formation of the electrodeposited chromium layer, modified with nanodiamond particles.

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2. Experimental procedure

Experiments were carried out with cylindrical carbon C45 steel samples with height 60 mm and diameter 6 mm. The electrochemical plating was performed with standard composition of the electrolyte – acid solution of CrO_3. The current density was 45 and 60 A/dm^2 and the duration of the plating was 45 minutes. The temperature of the electrolyte was 50-55°C. The anode was lead. The aggregates of nanoparticles with dimensions of 20 to 100 nm (the average size of single nanoparticle was 4 nm) were added to the electrolyte in the form of aqueous suspension after activation treatment. The concentrations of the nanodiamond particles (C_{NDDS}) in the electrolyte were: 0, 0.6, 10, 25 and 42 g/l. The coating obtained after the galvanization process was smooth and shiny. The layer thickness, its phase composition, microstructure, surface morphology and microhardness of the chromium plated samples was determined. Studies of the coatings were carried out by metallographic and scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD).

3. Results and discussion

The microstructure of electrodeposited chromium coating modified with NDDS, examined by light (LM) microscope Axio Vision-Zeiss, is shown in Figure 1a. The examination was made on non-etched cross-section of the samples. The coating is well-formed, integral, with visibly good connection to the base material.

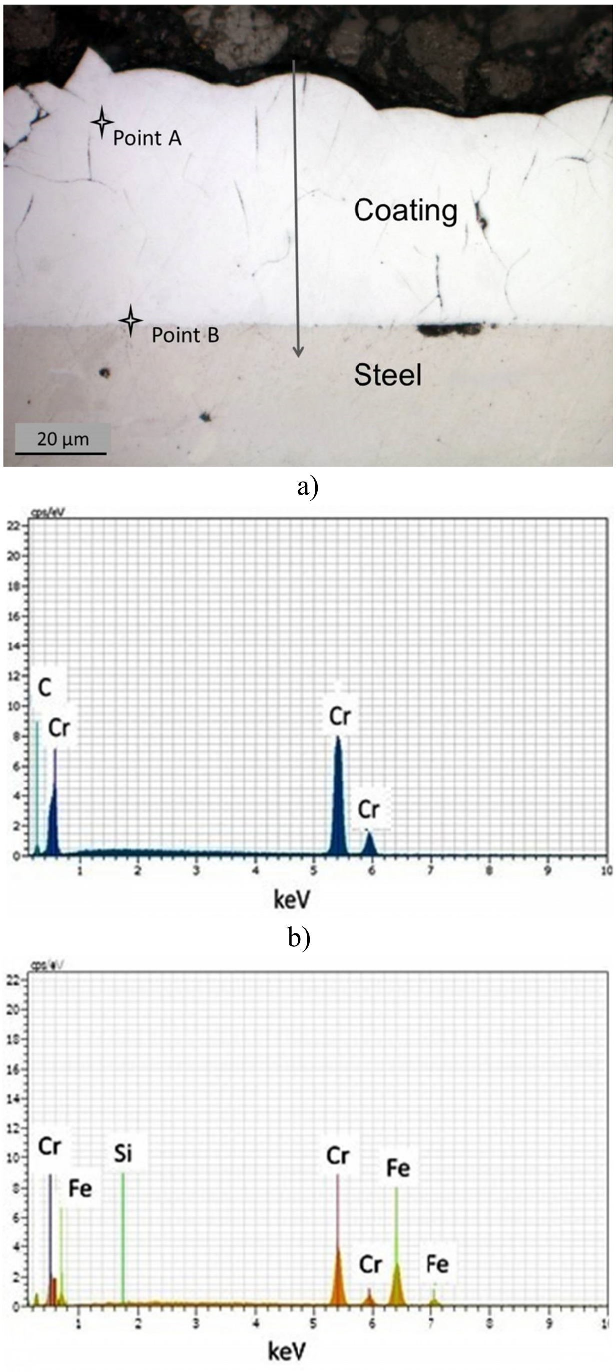
The identification of the chemical composition of the coatings was carried out using the EDS spectra at various points of the cross section of the layer with SEM-EDS. Figure 1b shows the EDS-spectrum of point A of the microstructure of the layer (Fig. 1a). Only the presence of Cr is registered, as it can be also seen in Table 1. In a zone of the coating, adjacent to the steel matrix – point B in the microstructure of the layer (Fig. 1a), the chromium content is decreased and the iron content is increased as it can be seen in Figure 1c and Table 2.

TABLE 1

Contents of Cr and C in point A of the microstructure
of the composite coating

Element	**Atomic number**	**Series**	**unn. C [wt. %]**	**norm. C [wt. %]**	**Atom. C [at. %]**	**Error (1 Sigma) [wt. %]**
Cr	24	L-series	100	100	100	11.79
		Total	100	100	100	

A proof of this statement is the distribution of Cr, Fe and C across the line, intersecting the layer in depth (Fig. 2a). Concentration changes in mass % are shown in Figure 2b. It can be seen that the concentration of Cr has a constant value through out the coating and rapidly decreases at the boundary with the steel matrix, while the content of Fe increases. According to the



a)

b)

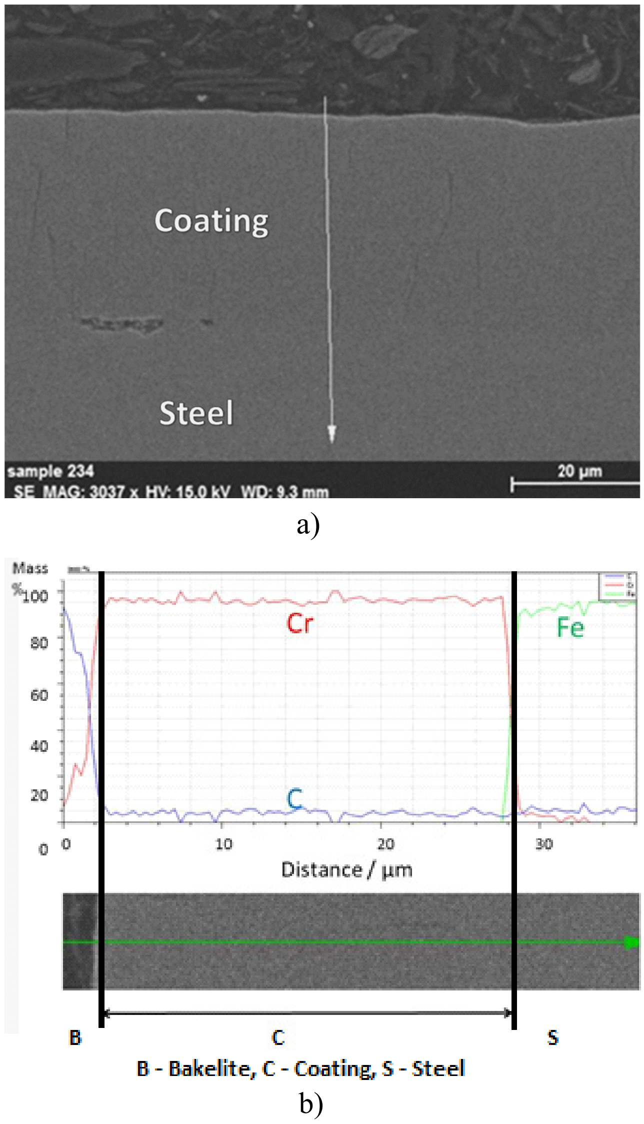
c)

Fig. 1. The microstructure and EDS-spectrum of composite chromium coating (I = 60 A/dm^2, t = 45 min, C_{NDDS} = 42 g/l); 1a) microstructure of non-etched section; 1b) SEM-EDS spectrum at point A of the microstructure; 1c) SEM-EDS spectrum at point B of the microstructure

TABLE 2

Contents of Cr and Fe in point B of the microstructure
of the composite coating

Element	**Atomic number**	**Series**	**unn. C [wt. %]**	**norm. C [wt. %]**	**Atom. C [at. %]**	**Error (1 Sigma) [wt. %]**
Fe	26	K-series	70	85	86	1.90
Cr	24	K-series	13	15	14	0.37
		Total	83	100.00	100.00	



a)

b)

Fig. 2. The microstructure and distribution of Cr, Fe, C in depth of the layer (I = 60 A/dm^2, t = 45 min, C_{NDDS} = 42 g/l); a) microstructure of non-etched section; b) distribution of the Cr, Fe, C in depth of the layer (along the line in Fig. 2A)

phase diagram of Fe-Cr system [9] solid solutions of Fe and Cr are created.

Figure 3 presents microstructures of samples electrodeposited by electrolyte with different nanodiamonds concentration at one and the same parameters of galvanization – I = 45 A/dm^2, t = 45 min. The metallographic investigations were done on cross-section of the 3% nital etched specimens. The microstructures were investigated using Polywar-Met metallographic microscope. It can be seen that the thickness of the electrodeposited layer of Cr increases with increasing the concentration of the nanodiamond particles in the electrolyte (Fig. 3). It can also be seen that “minisections” appear in the area adjoining to the matrix material when the nanodiamonds content is 25 g/l and more (Fig. 3c-d). It was found that their formation is not dependent on the other galvanization parameters (current density, duration) except for the concentration of the nanodiamond particles in the electrolyte.

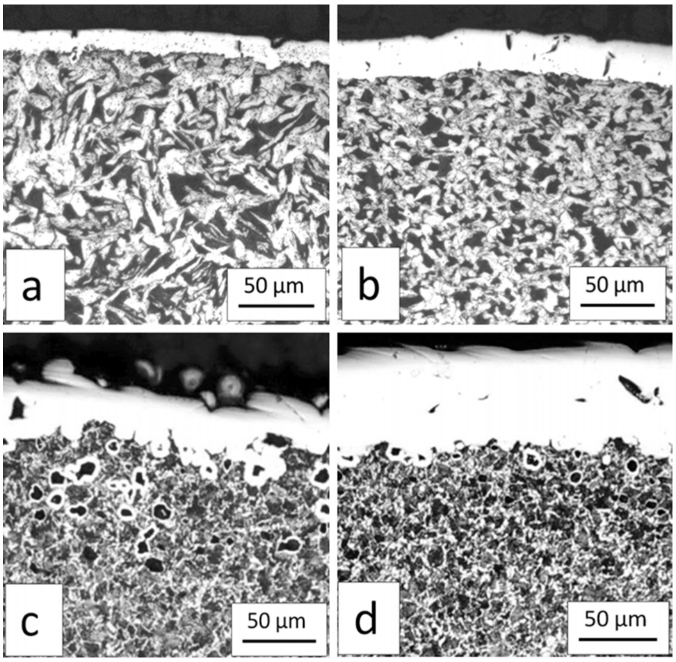


Fig. 3. Microstructures of composite chromium coatings, electrodeposited from the electrolytes with different content of nanodiamond particles (I = 45 A/dm^2, t = 45 min, etched sections); a) C_{NDDS} = 0; b) C_{NDDS} = 10 g/l; c) C_{NDDS} = 25 g/l; d) C_{NDDS} = 42 g/l

The values of the microhardness of the layer while the concentration of the nanodiamonds in the electrolyte is increasing at parameters of galvanization – current density 45 A/dm^2 and duration of the electroplating 45 minutes, are given in Figure 4. The microhardness was defined by microhardness tester MICRO DUROMAT under load of 50 G, duration 10 s and loading rate of 10 g/s.

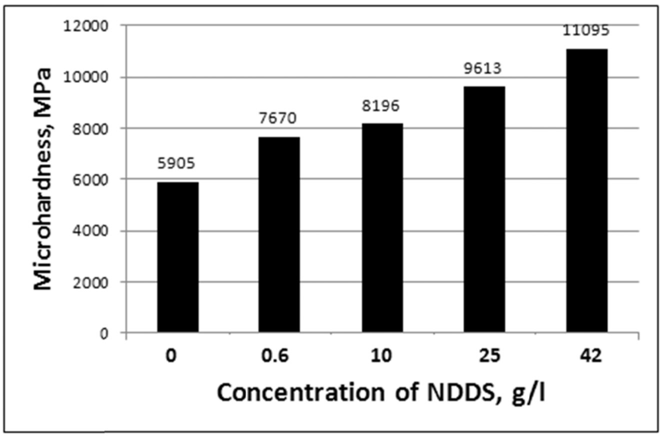


Fig. 4. The composite chromium coating microhardness vs. the concentration of the nanodiamond particles in the electrolite (I = 45 A/dm^2, t = 45 min)

As it is shown in Fig. 4, the microhardness of the electrodeposited chromium coating increases with increasing the nanodiamonds concentration (at C_{NDDS} = 42 g/l microhardness was 11095 MPa, or it was near 2 times greater than that of the unmodified coating).

The microstructure of modified layer is presented in Fig. 5. The "minisection" was formed around perlite or ferrite grains and has a Cr shell. It was found that the microhardness of the "minisection" shell is comparable with that of the main coating.

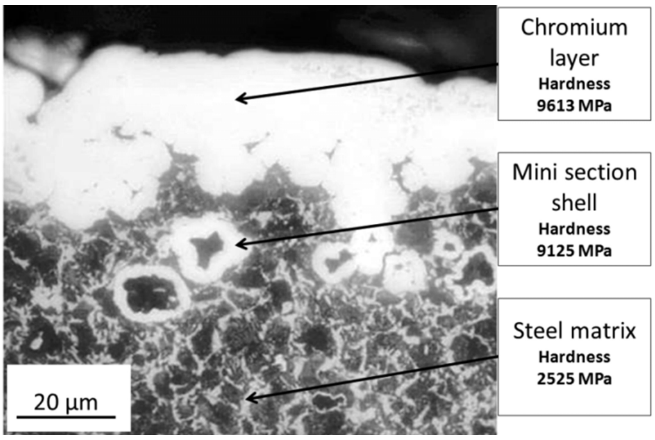


Fig. 5. The microstructure of composite chromium coatings with measured microhardness (I = 45 A/dm^2, t = 45 min, C_{NDDS} = 25 g/l)

The process of the electrochemical chromium deposition was carried out with the active participation of nanodiamond particles. NDDS have a large specific surface area – 350-450 m^2/g – and specific features of their structure [10], what determine their high adsorption properties. Nanodiamond particles produced by detonation synthesis have an electronic configuration on the surface predominantly of sp^2 electrons. After the detonation in the chamber they were cleaned in consecutive processes including: oxidizing acids, hydrochloric acid, heating in air and in argon, quenching, washing and de-agglomeration. During that, ions or whole functional groups are adsorbed on the particle surface and they move together with the nanoparticles [10]. Some of sp^2 nanoparticles form sp^3 hybridized electron's configuration. The nanodiamond particles, added to the electrolyte, adsorb also ions: $Cr_2O_7^{2-}$, CrO_4^{2-}, Cr^{3+}, Cr^{2+}, H^+. The ions and groups, adsorbed on the NDDS, are different in chemical composition and electrode potential and oxi-reduction processes take place between them. This leads to obtaining of electro-neutral chromium, deposited on the steel grains in the sublayer (Fig. 5). Increasing the nanodiamond particles concentration in the electrolyte increases the number of generated "minisections". Parallelly it increases the thickness of the main chromium layer on the steel sample due to increasing the flow of ions to the cathode with the fast moving nanodiamond particles. This leads to the conclusion that the nanodiamond particles are not directly involved in electroplating of Cr on steel and act only as carriers.

Conclusions

From the results obtained, the following conclusions can be drawn:

- The thickness of the electrodeposited coating of Cr on the steel and the microhardness of the layer increases with increasing of the concentration of the nanodiamond particles in the electrolyte compared to the unmodified chrome plating under the same galvanization parameters.
- When the concentration of the nanodiamond particles in the electrolyte are 25 g/l or more, independent of the other parameters of galvanization, "minisections" with chromium shell are formed in the sublayer which afterword join the main chromium coating.
- To show nanodiamonds in the layer, the other methods, like HRTEM on FIB prepared specimens, should be employed.

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REFERENCES

[1] V.P. Isakov, A.I. Lyamkin, D.N. Nikitin, A.S. Salimova, A.V. Solntzev, Fisikohimiya Poverhnosti I Zaschita Materialov **46** (5), 506-509 (2010).

[2] V.Y. Dolmatov, T. Fujimura, G.K. Barkat, E.A. Delova, M.V. Veretennikova, Powder Metallurgy and Metal Ceramics **42** (11-12), 587-591 (2003).

[3] N.V. Mandlich, J.K. Dennis, Metal Finishing **99**, 117-119 (2001).

[4] P.A. Vityas, V.I. Zhornik, R.G.Shtemplynk, S.A. Kovaleva, Trenie i Iznos **30** (2), 132-139 (2009).

[5] K.L. Tikhonov, G.K. Burkat, V.Y. Dolmatov, E.A. Orlova, Russian Journal of Applied Chemistry **80** (7), 1082-1086 (2007).

[6] G.K. Burkat, V.Y. Dolmatov, E. Osawa, E.A. Orlova, Sverkhtverdye Materialy **32** (2), 43-59 (2010).

[7] V.H. Nguyen, T.-N. Hoang, N-P. Nguyen, S.-C. Kwon, M. Kim, J.-Y. Lee, Trans. Nonferrous Met. Soc. China, **19**, 975-978 (2009).

[8] N. Gidikova, A. Cias, V. Petkov, M. Madej, M. Sulowski, R. Valov, Archives of Metallurgy and Materials **59** (4), 1513-1516 (2014).

[9] V.L. Kuznetsov, M.N. Aleksandrov, I.V. Zagoruiko et. al., Carbon **29** (4-5), 665 (1991).

[10] M. Yoshikawa, Y. Mori, H. Obata et.al., Appl. Phys. Lett. **67** (5), 694-696 (1995).

[11] V.Y. Dolmatov, G.S. Yuriev, M.V. Veretennikova, SR Structure Analysis of New Detonation Nanodiamonds and Method of Their Production, in Abstract Book of Int. Conf. of Carbon, World Conference on Carbon, July 13-18, 2008, Nagano, Japan, p. 188.

[12] A.I. Shames, A.M. Panich, M. Osawa, et al., J. Phys. Chem. Sol. **63** (11), 1993-2001 (2002).

[13] V.Y. Dolmatov, V.G. Sushchev, T. Fujimura, M.V. Veretennikova, J. Superhard Mater. (1), 23-29 (2004).

[14] C.I. Smithels, Metals Reference Book, 5th ed, Butterworths, London, 1976.

[15] A. Krueger, Journal of Materials Chemistry (18), 1485-1492 (2008).