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Effects of Diamond Nanoparticles on the Microstructure, Hardness and Corrosion Resistance of Chromium Coatings

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Abstract: Electrodeposited coatings of chromium and diamond nanoparticles on steel were obtained. The chromium is plated directly on the steel matrix without any intermediate layers. The influence of the electrodeposition current density, the electrodeposition time and the concentration of diamond nanoparticles in the chromium-plating electrolyte on the microstructure, the phase composition, the microhardness and the corrosion resistance of the chromium coatings were investigated. The phase and chemical compositions of the composite coating (chromium and diamond nanoparticles) were examined using X-ray Diffraction (XRD) and Scanning Electron Microscopy - Energy-Dispersive X-ray Spectroscopy (SEM-EDS) techniques. The microstructure and microhardness were examined with a metallographic microscope and a microhardness tester. The corrosion resistance was investigated in 3.5 wt % NaCl solution using the gravimetric method. The bond between the chromium coating and the steel matrix has diffusion character. A sublayer of separate irregular shape formations appears at concentration of diamond nanoparticles 25 g/l and more. The formation of these structures depends only on the concentration of diamond nanoparticles and is not influenced by the other electrodeposition parameters. With the increase of the concentration of diamond nanoparticles in the electrolyte the rate of chromium coating deposition increases and respectively the thickness of the coating increases also. This increase is more than twice the thickness of chromium coating without nanodiamonds. The microhardness of the composite coatings rises also compared to unmodified chromium coating. With the increase of the concentration of the diamond nanoparticles 2 times greater microhardness is achieved and up to 5 times greater corrosion resistance compared to monochromium coating. The values of the other electroplating parameters are constant.

Keywords: Diamond Nanoparticles, Chromium Coating, Electrodeposition, Hardness, Corrosion

1. Introduction

Alloying steels with Cr, Ni and other transition metals like Mo, Ti, W and V improves their chemical and mechanical properties such as hardness and corrosion resistance in aggressive environment. However, the production of alloyed steels is associated with a number of technological difficulties - high temperature (1600°C – 1700°C), special furnaces, etc. To find cheaper alternatives coatings are applied. Some coatings obtained by sol-gel technology provide enhanced corrosion resistance [1]. But they are very thin less than 1 μm, and cannot be applied on items exposed to abrasion and wear conditions. Surface treatment of plain, unalloyed steels with hard and corrosion resistant metals is economically advantageous and has a high technological effect. One technique used for this purpose is electrochemical metal plating, electrochemical chromium plating included. Still more important for the properties of the surface is the application of composite coating of chromium and diamond nanoparticles (ND) on unalloyed low and medium carbon steel. The properties and yield of diamond nanoparticles produced by detonation synthesis differ with the different methods – wet and dry [2]. The wet synthesis is much more effective. Chromium plating with diamond nanoparticles at different electrochemical conditions was studied [3]. The data published in the scientific literature on modified with nanodiamonds chromium-plated coatings and their properties are incomplete and controversial [4-9]. It has been found that

they have increased microhardness and increased resistance to corrosion in hostile environment compared to non-modified chromium coating. Surface morphology and chemical composition of coatings are studied by V. P. Isakov et al [4]. According to V. Y. Dolmatov et al the wear resistance of composite coatings is 13% higher [5]. On the other hand K. L. Tikhonov et al, using different diamond stock, achieve 1.4 to 1.8 times higher wear resistance [8]. There are numerous studies on the subject of various types of substrate materials coated with nanoparticles-modified coatings. Chromium coating with ND plated on sintered steel items improves considerably their hardness, wear and corrosion resistance [10]. The influence of ND on the structure and tribological properties of chromium composite coatings is investigated [11]. The mechanical and chemical properties of the coatings are improved. The deposition of nickel coatings with TiO_2 nanoparticles on aluminum alloys increases their hardness and corrosion resistance [12]. Modified with diamond nanoparticles chromium coating applied on aluminum alloys enhances the mechanical and chemical properties of their surface [13, 14].

The objective of the present research is to obtain composite coatings of chromium and ND with increased chemical and mechanical properties on unalloyed medium carbon steel and to investigate the impact of the electrochemical parameters and the concentration of diamond nanoparticles (C_{ND}) in the chromium plating electrolyte on the characteristics and the properties of the composite coating.

2. Experimental

Test samples of cylindrical shape with a height of 60 mm and a diameter of 6 mm, made of medium-carbon steel C45, were used. The samples were pre-degreased with dichloroethane and ethanol, dried and pickled in 20 vol. % aqueous solution of H_2SO_4 at temperature of 50°C for 5 to 10 minutes, then washed thoroughly with water and dried. The ready samples were weighed on an analytical balance with an accuracy of $\pm 1.10^{-4}$ g. Electrochemical chromatization was carried out using an electrolyte with a composition of 220 g/l CrO_3 and 2.2 g/l H_2SO_4. The value of the deposition current density varied from 40 to 80 A/dm^2 and that of the deposition time from 15 to 45 min. The temperature of the electrolyte was in the interval 50°C - 55°C. The anode was made of lead. ND with dimensions ranging from 4 nm to 20 nm were added to the electrolyte in the form of an aqueous suspension. The ND were obtained by detonation synthesis. They were derived from graphite and carbon-rich organic compounds in special chambers, without heating, under high pressure and then thoroughly cleaned [15]. The electrolyte with added ND was activated before galvanization in an ultrasonic bath. The value of the concentration of diamond nanoparticles (C_{ND}) in the electrolyte varied from 10 to 40 g/l. During galvanization, the electrolyte suspension was stirred with a magnetic stirrer at 150 rpm to disperse the ND and to prevent their sedimentation. The following characteristics of the chromium-plated samples were defined by gravimetric

(change of weight) and metallographic analyzes: chromium yield (the quantity of chromium deposited on the cathode) and the layer's thickness, microstructure and microhardness. The phase and chemical compositions of the composite coating (chromium with diamond nanoparticles) were examined by X-ray Diffraction (XRD) analysis with Siemens D500 diffractometer and Bragg-Brentano (B-B) technique and Scanning Electron Microscopy - Energy-Dispersive X-ray Spectroscopy (SEM-EDS) techniques. The microstructure and microhardness were examined on metallographic specimens with a Polywar-Met metallographic microscope and a Micro-Duromat 4000 microhardness tester at a load 50 g, loading time 10 s and holding time at the maximum load 10 s. The changes of the coating properties were investigated as a function of current density, duration of the process and C_{ND}. The distribution of chromium along the layer thickness and its phase composition were studied using Energy Dispersive Spectrometry (EDS) and X-ray diffraction analysis (XRD), respectively. The corrosion resistance was investigated in 3.5 wt % aqueous solution of NaCl using the gravimetric method.

3. Results and Discussion

Figure 1 shows the relation of chromium yield on current density and C_{ND} at constant value of time. As can be seen from the figure, the chromium yield increases with the rise of the current density and C_{ND}. The optimum value of the yield is reached for values of the current density in the range from 40 to 80 A/dm^2, which was the range for our study.
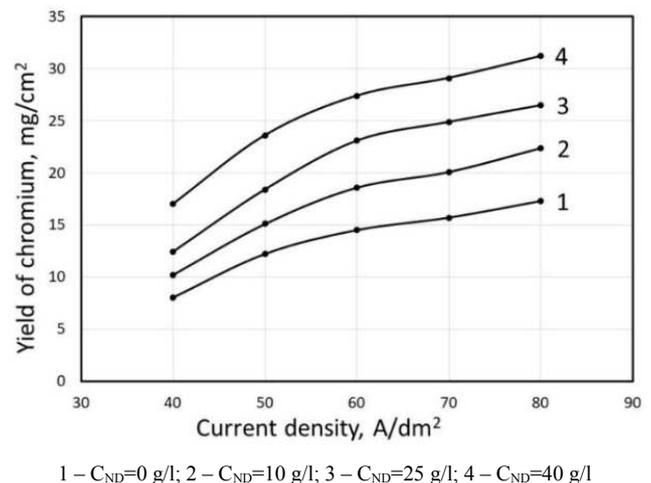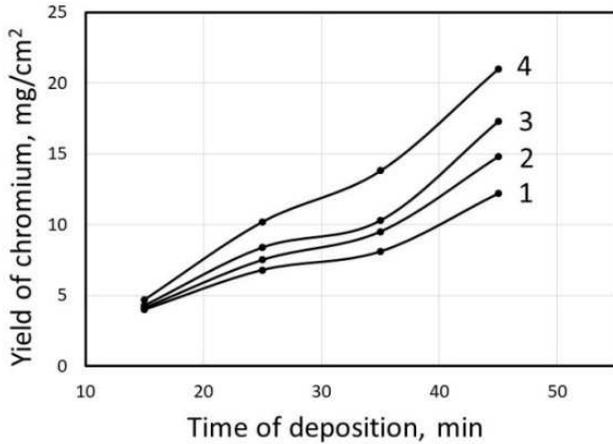

1 – C_{ND}=0 g/l; 2 – C_{ND}=10 g/l; 3 – C_{ND}=25 g/l; 4 – C_{ND}=40 g/l

Figure 1. *The relation of chromium yield (on the cathode) on C_{ND} and current density at constant value of time - 45 min.*

The chromium yield was determined by gravimetric method as the difference in the weights of the samples prior to and after galvanization per unit surface area. Its relation on time at different values of C_{ND} for constant current density 40 A/dm^2 is presented in Figure 2.

1 – C_{ND}=0 g/l; 2 – C_{ND}=10 g/l; 3 – C_{ND}=25 g/l; 4 – C_{ND}=40 g/l

Figure 2. *The relation of chromium yield (on the cathode) on C_{ND} and time of deposition at constant current density 40 A/dm².*

It can be seen from the figure that the chromium yield rises with the increase of deposition time at constant C_{ND} and also with the increase of C_{ND} at constant values of temperature and current density. The thickness, microstructure and microhardness of the plated layer were determined using metallographic analysis. Metallographic specimens were cut out from the plated test pieces, polished and pickled to reveal their structure. The microstructures were examined with a Polywar metallographic microscope. The thickness of the plated layer was measured using Olympus microimage quantitative analysis system. Figure 3 shows the microstructures of electrodeposited layers of nanodiamond-modified chromium coatings obtained from electrolytes with varying C_{ND} at constant values of current density and deposition time. Figure 3a shows the microstructure of a monochromium coated sample (C_{ND}=0 g/l). Figures 3b, 3c and 3d show the microstructures of composite coatings electrodeposited using electrolytes with C_{ND} values of 10, 25 and 40 g/l, respectively.
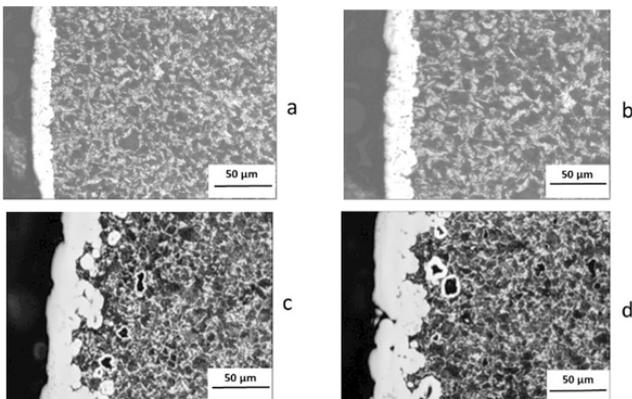
a) C_{ND}=0 g/l; b) C_{ND}=10 g/l; c) C_{ND}=25 g/l; d) C_{ND}=40 g/l;

Figure 3. *Microstructures of composite chromium coatings obtained by electrodeposition from electrolytes with varying values of C_{ND} at current density 40 A/dm² and time of deposition 45 min.*
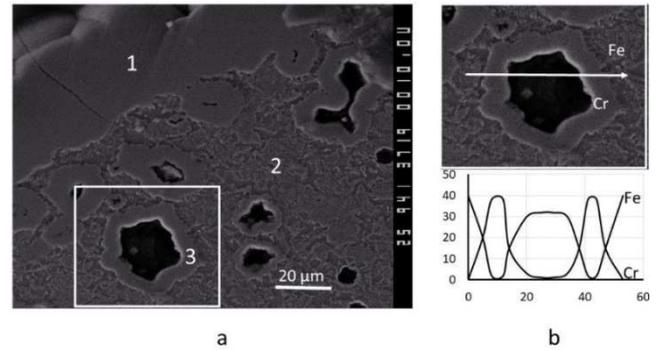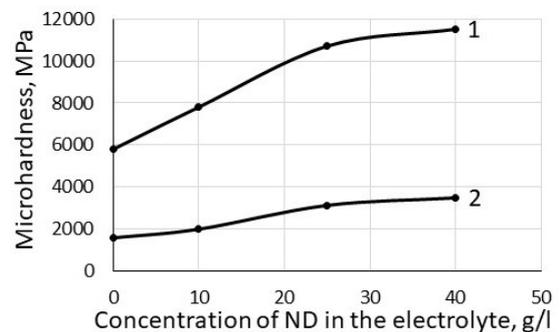

Figure 4. *Composite chromium coating, electrodeposited from an electrolyte with C_{ND}=25 g/l at current density 40 A/dm² and time of deposition 45 min.*

a) SEM image: 1 – chromium coating with ND; 2 – steel matrix; 3 - minisection
b) Intensity of Kα lines of Fe and Cr across the "minisection" structure.

The "minisections" are partially or fully covered with a bright shell of varying thickness and only the fully covered "minisections" are part of the main composite coating (Figure 4a). Figure 4b shows the change in the intensity of the Kα lines of Fe and Cr at various points in and around a "minisection" studied with X-ray microanalyser. As can be seen ~~that~~ in the matrix area (the steel) the intensity of the Kα line of Fe is high, while that of Cr is zero. At the point, positioned at the boundary of the matrix area with the bright shell, the intensity of the Kα line of Fe decreases, while that of Cr increases. At the shell the intensity of the Kα line of Cr is the highest, and that of Fe is zero. That is to show that the bright shell of the "minisections" consists of chromium only. Another evidence is that the microhardness of the "minisection" shell, which is 9125 MPa, is comparable with that of the main composite coating – 9613 MPa (Figure 4a).

Figure 5 shows the change of the microhardness of the composite coatings, electroplated at the same values of the electroplating parameters, as a function of C_{ND}. The microhardness of the steel matrix at the area just beneath the coating is also shown.

1 – chromium coating; 2 – steel matrix

Figure 5. *Change of the microhardness H of composite chromium coatings as a function of C_{ND} at current density 40 A/dm² and time of deposition 45 min.*

It can be seen that the microhardness of the composite coatings increases with the rise of C_{ND}. At C_{ND}=40 g/l, the microhardness is 11600 MPa, which is twice that of the

unmodified chromium coating. The microhardness of the steel matrix at the area just beneath the coating also increases approximately two times compared to chromium coating only. It is obvious that the formation of a sublayer containing the "minisections" at increased C_{ND} values is due to the presence of ND in the chromium-plating electrolyte. ND obtained by detonation synthesis (such as those used in this study) have surface electronic configuration with a predominance of sp^2 electrons [15]. After being obtained, they are cleaned thoroughly by subjecting them to a series of techniques including treatment with oxidizing acids, heating in air and in Ar atmosphere, hardening, washing and deagglomeration. In the course of these, on the surface of the particles ions and entire functional groups have been adsorbed, which move with them. Part of the sp^2 electrons form sp^3 hybridized electron configuration, which is the normal electron configuration of the carbon atom [16]. The authors assume that the diamond nanoparticles, present in the electrolyte, adsorb chromate and other ions - CrO_4^{2-}, $Cr_2O_7^{2-}$, Cr^{3+}, Cr^{2+}, H^+, SO_4^{2-}. Between ions with different chemical composition and electrode potential, which are adsorbed on the surface of the ND, occur processes of electron exchange and oxireduction. As result of these processes neutral atoms of chromium are obtained that form the "minisections". This line of reasoning allows for the presence of diamond nanoparticles in the coating structure. Studies of the phase and elemental composition of the layer were performed with X-ray Diffraction (XRD) and Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM-EDS) techniques. The results obtained are presented in Figures 6 and 7.
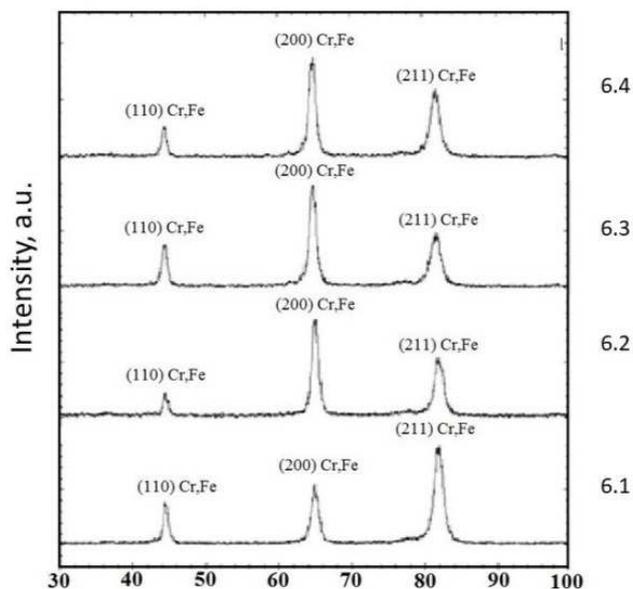

Figure 6. *Diffraction patterns of chromium coatings electrodeposited at deposition time 45 min.*

6.1 and 6.2 are obtained from chromium-plating electrolyte with $C_{ND}=0$ at current density 40 A/dm² and 60 A/dm² respectively;
6.3 and 6.4 are obtained from chromium-plating electrolyte with $C_{ND}=10$g/l at current density 40 A/dm² and 60 A/dm² respectively

Figure 6 shows the diffraction patterns of chromium coatings on steel obtained from chromium-plating electrolyte free of diamond nanoparticles (6.1 and 6.2) and with $C_{ND}=10$ g/l (6.3 and 6.4). The values of the current density and deposition time are the same for both types of coatings: 40 and 60 A/dm² and 45 min respectively. The X-ray diffraction patterns in Figure 6 were taken with Bragg-Brentano (B-B) technique. They identify the presence of chromium in the layer. No diffraction effect of ND in the layer was found. The X-ray diffraction analysis established that the well-defined peaks at $2\theta=44°$, $2\theta=64°$ and $2\theta=82°$ corresponding to diffraction planes (110), (200) and (211) are the same for the unmodified chromium coatings (6.1 and 6.2) and the composite coatings (6.3 and 6.4). The surface morphology and the distribution of elements Cr, Fe and C along the layer thickness were investigated with SEM-EDS techniques. The results obtained are presented in Figure 7.
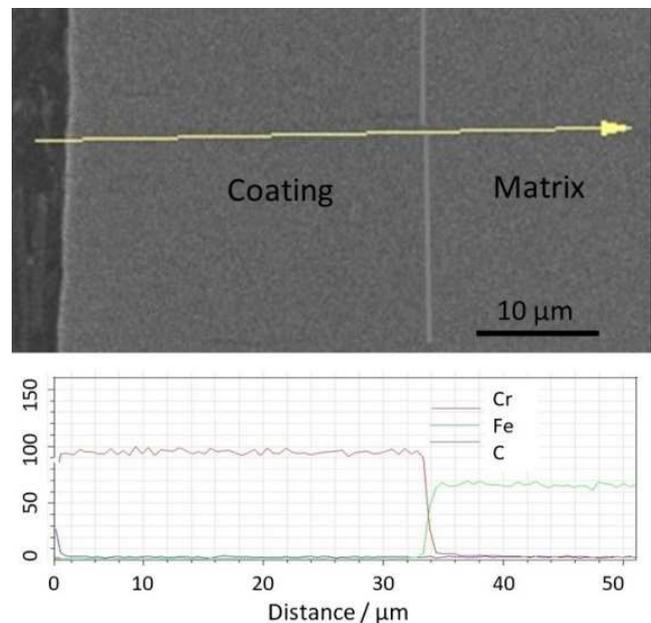

Figure 7. *Distribution of elements of a chromium coating electrodeposited from electrolyte with $C_{ND}=40$ g/l*

Figure 7 presents the microstructure of metallographic sample cut from the coating. The electrolytic process is performed from electrolyte with $C_{ND}=40$ g/l at current density 60 A/dm² and deposition time 45 min. The concentrations of Cr, Fe and C, expressed in mass %, are along the line in the coating. It can be seen that the chromium content is high and constant along the entire coating. The chromium content decreases in the area adjacent to the matrix and that of Fe increases. The two curves - of the decreasing Cr content and of the increasing Fe content - intersect. In the area outlining the boundary between the coating and the matrix, the change of the chromium and the iron content is not sharp which shows the diffusion character of the bond between the two metals. The carbon content in the coating is zero, rising in the transition zone and in the steel. There is no evidence of ND participation in the chromium coating.

The corrosion resistance of chromium coatings was studied in 3.5 wt. % aqueous solution of NaCl and temperature of 35°C using the gravimetric method. The duration of stay in the salt solution was 88 h and 200 h. The corrosion resistance was determined by the mass loss (the difference in weight before and after the corrosion test). It is calculated per unit area of the sample (mg/cm^2). Figure 8 shows the results obtained according to the mass loss method. The chromium coatings were prepared at the same values of the electroplating parameters: current density 40 A/dm^2, duration of the electrolytic process 45 min and the temperature of the electrolyte was 55°C. The values of C_{ND} were 0, 10, 25 and 40 g/l.
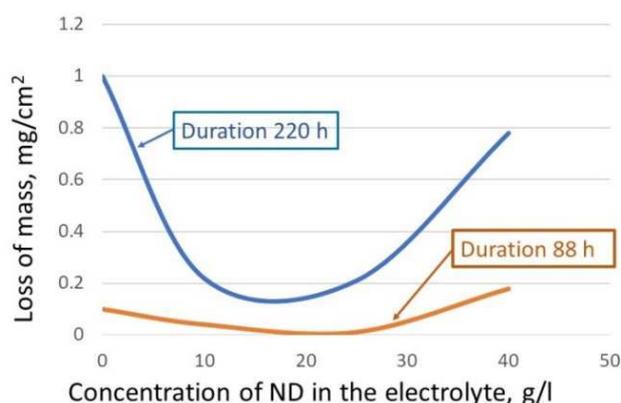

Figure 8. *Corrosion resistance as a function of C_{ND} of the chromium coatings in 3.5 w t % aqueous solution of NaCl.*

Corrosion resistance decreases with the rise of the duration time in the corrosion solution. The corrosion of the chromium coatings obtained from electrolytes with C_{ND} above 10 g/l at duration time in the corroding solution of 88 h is practically zero with little increase at C_{ND} 40 g/l. The corrosion resistance of the coatings obtained from electrolytes with C_{ND} varying from 10 to 25 g/l at duration in the corrosion solution of 200 h is 4-5 times greater than that of the unmodified chromium coating.

4. Conclusions

1) Electrochemically plated chromium coatings modified with diamond nanoparticles, deposited on unalloyed medium-carbon steel 45, were obtained.
2) The chromium coating is deposited directly on the steel matrix without any intermediate layers.
3) The chromium yield (the amount of metal deposited on the cathode) and respectively the thickness of the chromium coating with ND increases with the rise of the electroplating current density, the galvanizing time and the concentration of diamond nanoparticles in the electrolyte at constant composition and temperature of the electrochemical bath.
4) The mechanical and chemical properties of chromium coating with ND increase with the rise of the concentration of diamond nanoparticles in the electrolyte

C_{ND}, the values of the other galvanizing parameters remaining constant. For C_{ND}=40 g/l, the microhardness of the composite coating is 2 times higher than that of unmodified chromium coating. The corrosion resistance in a 3.5 wt. % NaCl solution for duration in the corrosion solution for 200 hours is 4 to 5 times greater for chromium coating obtained from electrolyte with C_{ND} in the interval from 10 to 25 g/l as compared to unmodified chromium coating.

5) Above a certain concentration threshold the diamond nanoparticles influence the mechanism of composite coatings building. With a concentration of ND in the electrolyte above 25 g/l a sublayer is formed which participates in the structure formation of the coating in a way not known by now.
6) The effect of modifying the chromium coatings on steel with diamond nanoparticles is significant and reveals new possibilities for surface processing technology of metals and alloys.

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