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An experimental evaluation of the three types of corrosion, passivation, pitting, and uniform corrosion, by electrodeposited chromium-nano diamond composite coating on porous materials

The addition of nanoscale particles to metal coatings results in nano composite coatings, a brand-new class of materials with improved hardness, wear, and corrosion resistances. Pre-alloy metal powder metallurgy samples were electrolytically coated with pure chromium and Cr-ND in this work (Chromium-nano diamond). The effects of the co-deposited ND particles on the passivation, pitting, and uniform corrosion behavior of the chromium coatings were experimentally investigated and contrasted with pure chromium coating and non-coated specimens. Under 3.5%wt. NaCl solution, the corrosion behaviors of the samples were examined using the measuring techniques of Polarization Resistance, Cyclic Voltammetry, and Electrochemical Impedance Spectroscopy. Additionally, characterization tests were performed using an optical microscope, a SEM (Scanning Electron Microscope), EDS (Energy Dispersive X-Ray Spectroscopy), XRD (X-Ray Diffraction), and AFM (Atomic Force Microscope). As a result of the ND particles being incorporated into the chromium matrix, it was shown that when compared to pure chromium coatings and non-coated specimens, Cr-ND coatings demonstrated a clear improvement in corrosion behavior.

Keywords: Nano diamond composite coating, corrosion, cyclic polarization, Tafel extrapolation, electrochemical impedance spectroscopy

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INTRODUCTION

Powder metallurgy, the high precision forming method, is popularly used in aerospace, mining, automotive and weaponry industries for its net shape production capability and the decent final tolerance of the parts without the need for machining. However, there exist certain limitations and flaws regarding this method in the manufactured parts by PM such as the pre-existing porosity and voids which mostly occur because of the property degradation in the used powder particles [1]. As a result, the tensile behavior of materials with pre-existing porosity is characterized by intense decreases in both strength and ductility with increasing porosity levels [1, 2, 3]. Pores can expose substrates to corrosive agents, reduce mechanical properties, and deleteriously influence density, electrical properties and diffusion characteristics. With the increasing demands from industries for improved performance, development of better surface coatings has become imperative with higher wear and corrosion resistance [2, 3].

Electrolytic coating is a technique for producing nanocomposites using deposition of dispersed nano particles (metallic, non-metallic or polymeric) in the matrix solution to fulfill the uniformity of the external layer of a part [3, 4]. Among the particles used for reinforcement in the field of composite coating, diamond is frequently studied and applied [5, 6] due to its high hardness, good oxidation resistance, chemical stability and wear resistance [1]. The ultimate properties of the composite coatings are dependent on the type, shape, size and properties of particles. Most of the studies have been carried out on the micro sized particles. However, the application of nano particles has been a new research field due to these particles' mechanical, electrical, magnetic and optical properties.

Juneghani et. al [7] coated AISI 1020 with pure Cr and Cr-SiC nano composite. They reported that the hardness of the nanocomposite coating is higher than the pure chromuim coating and with the increasing amount of SiC added to the solution, the hardness and the corrosion resistance of the coating have improved. Yousefpour et al. [8] studied the wear and corrosion behavior of Ck 75 steel coated with TiO_2, Al_2O_3 and SiO_2 particles reinforced chromium matrix and reported an increase in wear, corrosion resistance and micro hardness values. Gidikova et al. [5] coated the carbon steel C45 with electrochemical nano diamond-reinforced chromium in acid solution of CrO_3 and they found evolution in the hardness values by increasing nano diamond particle concentration. Isakov et al. [6], studied the surface properties of nano diamond-reinforced chromium on stainless steel chromic.

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The main goal of this study was to investigate the influences of ND particles on the surface morphology, phase structure, grain and crystal sizes and corrosion resistance within a chromium matrix on a sintered pre-alloy powder substrate.

EXPERIMENTAL PROCEDURES

Press and sintering

Given in Table 1, the chemical properties of the pre-alloy metal powder provided by the Toz Metal A. Ş. were as the following. To gain the shape of the test specimen, the mentioned powder was pressed at 550 MPa in a biaxial die into 31.7×12.7×7.9 mm. Afterward, the pressed specimens were sintered at 1120 °C for 25 minutes in %0.6 carbon potential atmosphere (CH_4+C_3H_8). The total sintering process time was 150 minutes.

Table 1. The chemical properties of the used metal powder

Composition	AHC	Cu	Graphite F10	Graphite KS44	MnS	Lube E
% wt.	96.8	1.5	0.2	0.2	0.5	0.8

Deposition of Chromium and Chromium-Nanodiamond coatings

The surface oxide layer of the specimens was demolished, through a reduction process in H_2 at 950 °C for 45 minutes. The next step, degreasing in 1.2 dichloroethane solution for 10 minutes was carried out before coating. The galvanic electrodeposition bath used for pure chromium and chromium-nanodiamond coating was based on the Hull-Cell bath. Lead was used as the anode. The distance between the anode and the cathode was 50-60 mm. The electrodeposition bath composition and parameters are given in Table 2.

Table 2. Electrodeposition bath composition and parameters

Electrodeposition bath composition and parameters	Values
CrO_3	220 g/l
H_2SO_4	2.2 g/l
ND concentration	0.25 g/l
Current density	45 A/dm^2
Temperature	50 °C
Stirring rate	100 rpm
pH	5.5-5.8
Average ND size	6 nm

CHARACTERIZATION OF THE MATERIALS

Microstructure and surface morphology tests

The densities of the sintered and coated specimens were calculated with Archimedes Principle. The porosity percent, coating thickness of the coated and non-coated specimens were calculated from the average value of the taken pictures of the cross section by optical microscope using ImageJ software. The surface morphologies of electrodeposited Cr and Cr-ND composite coatings were investigated using Scanning Electron Microscope (SEM). The chemical composition of coatings was analyzed by Energy Dispersive X-Ray Spectroscopy (EDS) and X-Ray Diffraction (XRD). The 3D surface topography of the surfaces was taken from a 1×1 μm2 area by Atomic Force Microscope (AFM). The grain and crystal size of the coating was calculated using the Intersection Method and Scherrer Formula as demonstrated in Equation 1.

$$\tau = \frac{K\lambda}{\beta cos\theta} \qquad (1)$$

where τ is the mean size of the ordered (crystalline) domains, K is a dimensionless shape factor, with a value close to unity, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians and θ is the Bragg angle.

Corrosion tests

Polarization resistance, Cyclic Voltammetry and electrochemical impedance spectroscopy measurements under %3.5 NaCl solution versus standard calomel electrode were taken advantage of to analyze the corrosion behavior of the samples. The experiments were carried out in a 3-electrode system corrosion cell. The cathodic pole was set to be Platinum. The polarization resistances tests were carried out at a scan rate of 0.125 mV/s in the range of ±0.02 V of open circuit potential (OCP) with 10 minutes of immersion. Tafel extrapolation theory was carried out in order to analyze the obtained graphs and results. The pitting and passivation properties of the samples were analyzed using Cyclic Voltammetry method at a range of -1.8 – 0.2 V and at a scan rate of 50 mV/s. The electrochemical impedance spectroscopy experiments were conducted at the ranges of 10^4 – 10^{-1} Hz of frequency at constant current using the IviumSoft corrosion analyzer.

RESULTS AND DISCUSSION

The density of the sintered specimens was measured at 6.90 g/cm^3. Figure 1a and b show the surface porosities of the sintered specimens before coating. The measurements of the non-coated samples showed the total porosity rate was %11.751 and the average surface porosity rate was %10.870. The big porosities on the sintered surface can be based upon to the copper`s low melting point which caused the increase in the porosity while sintering. The pure chromium surface has numerous cracks and crevices compared to Cr-ND coating [1].

Figure 2a and b demonstrate the microstructures of coated specimens. The average grain size of the Cr-ND coating was calculated 14.28 µm, however this value was 39.68 µm for pure Cr. The average thickness of the pure chromium and Cr-ND coated samples were 17.26 and 19.02 µm, respectively. It is worth noting that the chromium yield noticeably increased [5, 6] to %1.55 by enhancing the ND particles in the bath for the 25 g/l concentration while this value was %1.13 for the pure chromium. This phenomenon can be explained by the incorporation of the particles into the metal coating by the Gugliemli Model [4, 8]. The Guglielmi Model is mainly a two-step process [9, 10]. Initially, the particles approach the cathode and are weakly absorbed onto the cathode surface. The ion cloud surrounds the weakly bound particles. In the second stage, the particles leave the ion cloud surrounding them due to the chemical reaction and are absorbed more strongly on the cathodic surface. Additionally, the increase in particle on the cathode surface, according to the two-step model. As a result, there is an increase in the coating's particle content.

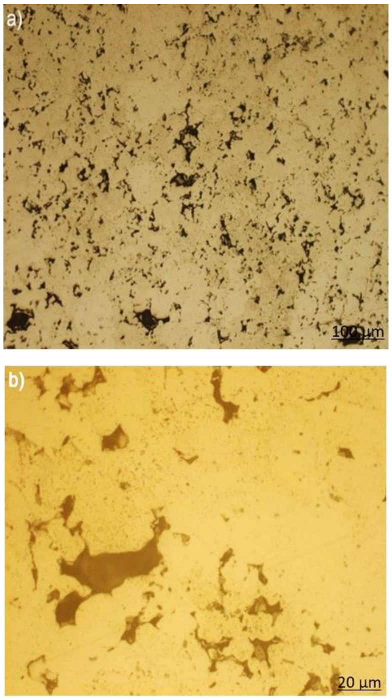

Figure 1. The surface porosities of the samples before coating; a)100X, b)500X

The XRD pattern is indicative of the fact that the electrodeposited Cr-ND coating is mainly of a solid solution in a mono-phase matrix as shown in Figure 3. Pure chromium deposit has exhibited (110), (200) and (211) diffraction peaks. The representative (111) peaks of nanodiamond in the coatings in the XRD graphs affirm the existence of the diffused nanodiamond particles in the chromium matrix. The intensity of the (200) diffraction peaks of the chromium in the nano composite coating is lower, the (211) diffraction peaks are higher, and the peak width is broader than that of the pure chromium coating [4, 11, 12].

The XRD pattern of the pure Cr and Cr-ND coating demonstrates that the crystal sizes of the chromium have decreased with the incorporation of ND particles in chromium with respect to pure chromium coating.

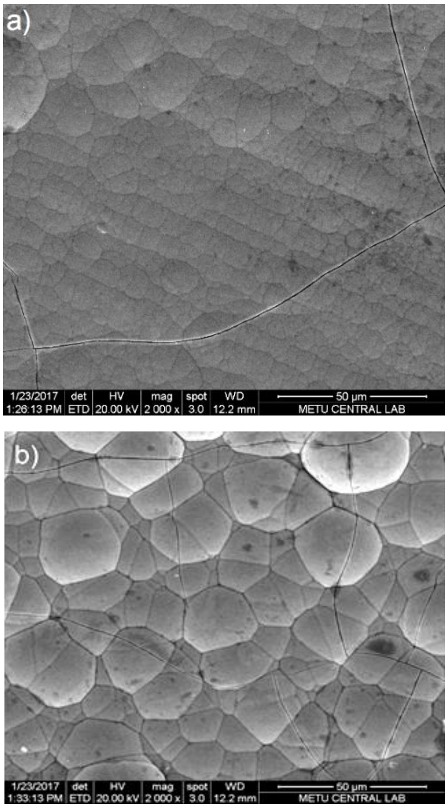

Figure 2. The SEM images of the surfaces of the coated samples; a) Cr-ND, b) Pure Cr

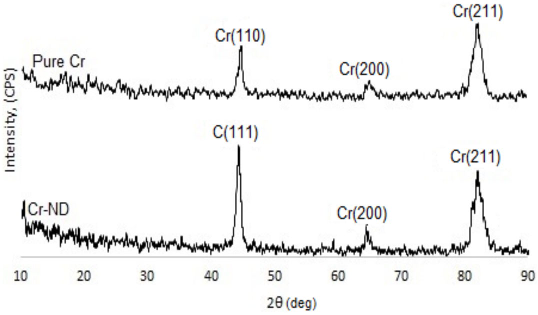

Figure 3. The XRD pattern of pure Cr and Cr-ND coatings

The EDS analyses expressed the composition of the electrodeposited Cr–ND coating in which the weight percent of Cr is %84.94 wt. and that of ND is %5.05 wt. form EDS which is given in Figure 4.

The cyclic voltammetry graphs for pure chromium and Cr-ND electrodeposited and non-coated sample in %3.5 wt. NaCl solution are illustrated in Figure 5 and Figure 6 respectively. The reverse anodic peaks correspond to the partial conversion of $Fe(OH)_2$ to $Fe(OH)_3$ which formed on the electrode surface and impaired the passive layer. The pore and the holes grew in the direct anodic scan because of the lower protection potential value rather than the pitting potential. SEM examination micrographs showed that the Cr-ND deposit is smoother and has fewer cracks and crevices than pure chromium. The difference between the direct and reverse curves of Cr-ND coating is smaller than for the pure Cr coated and uncoated sample. This is a hint of the lesser tendency of the Cr-ND for pitting in comparison with pure Cr and uncoated samples. The passivated platelet of the Cr-ND coating is wider than for the pure Cr and uncoated specimens. The electrodeposition of ND particles in Cr matrix hinders the growth of the corrosive pits and accelerates the passivation process of the film. The current density peak values and the anodic scan curves in Cr-ND are lower than for the pure Cr and uncoated samples. The current peak values decreased with increasing concentration of the nanoparticles.

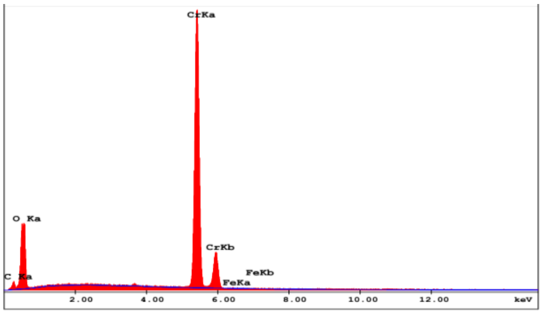

Figure 4. The EDS pattern of Cr-ND coating

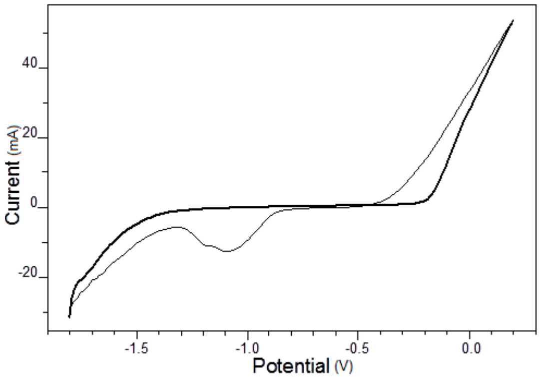

Figure 5. The cyclic polarization curves of the non-coated sample

Corrosion characteristics consisting of corrosion potential (Ecor), corrosion current density (Icor), corrosion rate (Cor. Rate) and polarization resistance (RP) and anodic/cathodic Tafel Slopes (βa and βc) were examined by the Tafel Extrapolation Method. The rightward shift in the diagrams in Figure 7 is indicative of the fact that there has been a reduction in absolute corrosion potential values due to the contribution of ND particles content in the plating bath. This potential change is attributed to the reduction in the active surface area of the cathode and decrease in the ionic transport by nano particles. Additionally, the corrosion current density decreased and also polarization resistance (RP) increased which illustrate a decline in the corrosion rate. In conclusion, the diffusive ND particles in the Cr matrix decrease the corrosion rate; and therefore, enhance the corrosion resistance in %3.5 wt. NaCl solution [4, 8]. The polarization resistance results of the Tafel extrapolation tests are given in Table 3.

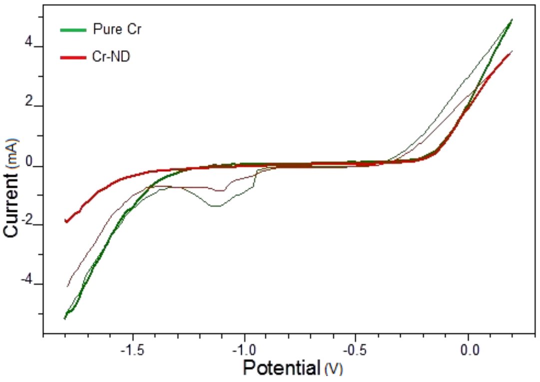

Figure 6. The Cyclic polarization curves of the coated samples

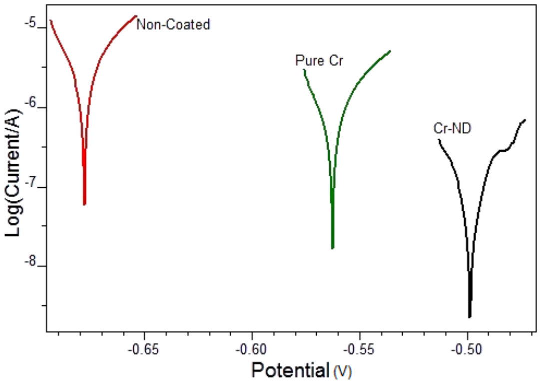

Figure 7. The Polarization Resistance curves of the Specimens

Table 3. The polarization resistance results of the samples

Sample	Non-coated	Pure Cr	Cr-ND
Ecor (V)	-0.6779	-0.5625	-0.4980
Icor (A/cm^2)	7.11E-06	1.25E-06	6.81E-07
Rp (ohm)	2636	1.08E+04	3.28E+04
Cor. Rate (mm/y)	1.02304	0.15191	0.08847

Nano diamond particles expose better corrosion performance according to the mechanisms mentioned below. Firstly, the ND particles serve as an inert physical barrier against the diffusion of the corrosive media to the surface of electrode which leads to filling in the porosities as well as the relative reduction of the cracks on the mentioned surface and hence amending the microstructure of the chromium matrix. Secondly, due to the dispersion of ND particles in the chromium layer several corrosion micro cells are formed, consisting of the ND particles acting as cathode and chromium as anode, caused by the above standard potential of ND compared to chromium. Such corrosion micro cells assist the anodic polarization. The attendance of ND throughout the corrosion process prevents the formation of the localized corrosion, and the major corrosion can therefore be attributed to the homogeneous uniform one [1, 7, 11, 12]. Thirdly, by reducing the surface grain size, forming a less porous, less defective and smoother surface against corrosive circumstances.

The electrochemical impedance spectroscopy results demonstrate that corrosion rate is affected by the charge transfer resistance (Rct). Cr-ND coating has greater Nequest plot radius and Rct values compared to both pure Cr and non-coated specimens which indicates the Cr-ND represents better corrosion resistance behavior than pure Cr and non-coated samples as shown in Figure 8 [13].

The 3-D surface topography of the Cr-ND coating is shown Figure 9. The Ra surface roughness, and RMS surface roughness distribution values were calculated (Table 4). The surface roughness and its distribution values of Cr-ND are less than for both pure Cr and non-coated surfaces. This can be attributed to the contribution of ND particles, which created a more compact and smoother surface.

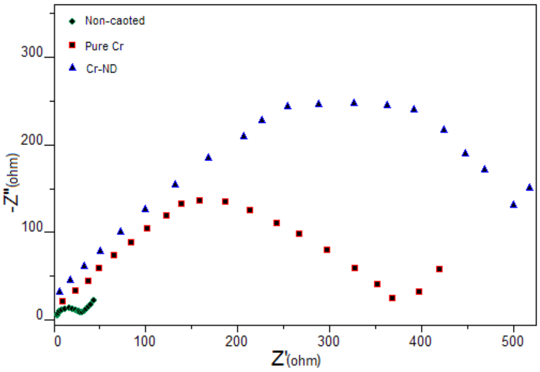

Figure 8. The Impedance Spectroscopy curves of the Specimens

CONCLUSION

X-ray diffraction analyzes performed a successful mono phase nanocomposite coating process on pre-alloy metal powder substrates by the electrolytic coating process.

The incorporation of ND particles during electrochemical deposition of chromium enhances the chromium yield and the thickness of the coating.

AFM and SEM clarified the embedding of ND particles in the chromium matrix and resulted in a layer with smaller crystallite and grain sizes and more compact and smoother surfaces with fewer cracks and roughness than those of pure Cr deposits.

The embedding of ND particles in the chromium matrix did not affect the chromium's inert coating performance; in addition, it enhanced the uniform and pitting corrosion behaviors of powder metallurgy substrates.

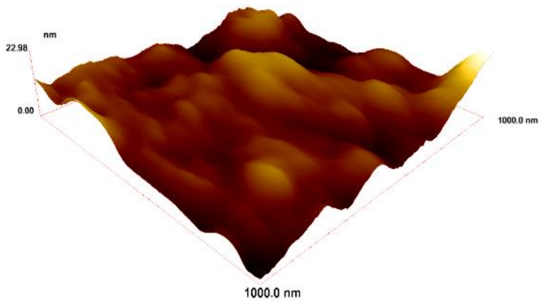

Figure 9. The AFM image of the Cr-ND coated sample

Table 4. The 3D surface topography Results of the Specimens

Sample	Ra (nm)	RMS (nm)
Non-coated	5.04	6.62
Cr	2.86	3.81
Cr-ND	2.12	2.65

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GÖZENEKLİ MALZEMELER ÜZERİNDE ELEKTROBİRİKİMLİ KROM-NANO ELMAS KOMPOZİT KAPLAMANIN ÜÇ FARKLI KOROZYON DAVRANIŞININ, PASİVASYONUN, ÇUKURLAŞMANIN VE HOMOJENLİĞİN DENEYSEL ANALİZİ

Nano ölçekli parçacıkların metal kaplamalarına dahil edilmesi, nano kompozit kaplamalar olarak bilinir ve artan sertlik, aşınma ve korozyon direncine sahip yeni bir malzeme şeklidir. Bu çalışmada, ön alaşımlı metal toz metalurji numuneleri, saf krom ve Cr-ND'nin (Krom-nano elmas) elektrolitik kaplamasına tabi tutulmuştur. Birlikte biriktirilen ND parçacıklarının krom kaplamaların pasivasyon, çukurlaşma ve üniform korozyon davranışı üzerindeki etkileri deneysel olarak incelenmiş ve saf krom kaplama ve kaplanmamış numunelerle karşılaştırılmıştır. Numunelerin korozyon davranışları, Polarizasyon Direnci, Dönüşümlü Voltametri ve Elektrokimyasal Empedans Spektroskopi ölçüm yöntemleri ile ağırlıkça %3,5 NaCl çözeltisinin altında analiz edilmiştir.. Ayrıca optik mikroskop, SEM (Taramalı Elektron Mikroskobu), EDS (Energy Dispersive X-Ray Spektroskopi), XRD (X-Ray Difraction) ve AFM (Atomic Force Microscope) kullanılarak karakterizasyon testleri gerçekleştirilmiştir. Elde edilen sonuçlara göre, saf krom kaplamalar ve kaplanmamış numunelerle karşılaştırıldığında, ND partiküllerinin krom matrisine dahil edilmesi nedeniyle Cr-ND kaplamaların korozyon davranışında ikna edici bir iyileşme elde edildiği gözlenmiştir.

Anahtar Kelimeler: Nano elmas kompozit kaplama, korozyon, dönüşümlü polarizasyon, Tafel ekstrapolasyonu, elektrokimyasal empedans spektroskopi

REFERENCES

1. M. Etaat, M. Emamy, M. Ghambari, E. Fadaei: Surface treatment and nickel plating of iron powder metallurgy parts for corrosion protection, Materials and Design, 30 (2009) 3560–3565.
2. Leisner P, Leu RC, Moller P.: Electroplating of porous PM compacts, Powder Metal, (1997) 40:207–10
3. Gabe DR.: Corrosion protection of sintered metal parts, Powder Metal, (1977) 20:227–31.
4. Abdel Aal A.: Hard and corrosion resistant nanocomposite coating for Al alloy, Material Science and Engineering A, (2008) 474:181-187.
5. Gidikova N., Cias A., Petkov V., Madej M., Sułowski M., and Valov R.: Wear resistant chromium coatings modified with diamond nanoparticles, Archives of Metallurgy and Materials, 59 (4), (2014) 1513-1516.
6. V. P. Isakov, A. I. Lyamkin, D. N. Nikitin, A. S. Shalimova, and A. V. Solntsev: Structure and Properties of Chromium–Nanodiamond Composite Electrochemical Coatings, ISSN 2070.2051, Protection of Metals and Physical Chemistry of Surfaces, (2010) Vol. 46, No. 5, pp. 578–581

7. Juneghani M. A., Farzam M., and Zohdirad, H.: Wear and corrosion resistance and electroplating characteristics of electrodeposited Cr–SiC nanocomposite coatings, Transactions of Nonferrous Metals Society of China, 23 (7), 1993-2001, (2013).
8. Yousefpour M. , Rahimi A.: Characterization and selection of optimal parameters to achieve the best tribological performance of the electrodeposited cr nanocomposite coating, Materials & Design, 54, 382- 389, (2014).
9. Z. Zeng, L. Wang, A. Liang, J. Zhang: Tribological and electrochemical behavior of thick Cr–C alloy coatings electrodeposited in trivalent chromium bath as an alternative to conventional Cr coatings, Electrochim Acta 52 (2006) 1366–1373.
10. Mandich, N. and Dennis, J.: Codeposition of nanodiamonds with chromium, Metal Finishing, 99 (6),117-119, (2001).
11. P. Gyftou, E.A. Pavlatou, N. Spyrellis: Effect of pulse electrodeposition parameters on the properties of Ni/nano-SiC composites, Applied Surface Science, 254 (2008) 5910–5916.
12. Hui Xu, Zhi Yanga, Meng-Ke Lia, Yan-Li Shia, Yi Huanga, Hu-Lin Li: Synthesis and properties of electroless Ni–P–Nanometer Diamond composite coatings, Surface & Coatings Technology, 191 (2005) 161–165.
13. Macdonald J. R., Johnson W. B.: Theory in impedance spectroscopy [J]. New York: John Wiley & Sons, (1987).