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THE DEPOSITION OF Ni/Cr-Cr_3C_2 COMPOSITE COATINGS BY Arc-EB HYBRID TECHNOLOGY[1]

Jerzy Smolik[2]
Adam Mazurkiewicz[2]
Maria Richert[3]
Ilona Nejman[3]
Przemysław Jakieła[2]

Abstract

The new hybrid technology is a combination of electron beam evaporation and arc-evaporation processes, enabling the creation of the anti-erosion multilayer composite coating Ni/Cr-Cr_3C_2 with different volume of Cr_3C_2 filling in soft Ni/Cr matrix. The soft matrix made of Ni/Cr alloy and hard filling of Cr_3C_2 are created at the same time and directly during the electron beam and arc-evaporation process. Changes of the parameters of the hybrid process, i.e. pressure, current of arc discharge and substrate bias voltage U_{bias}, make it possible to control the volume of Cr_3C_2 and are a factor in filling the soft Cr/Ni matrix with carbides Cr_3C_2. With the use of the developed surface treatment hybrid technology, the multilayer composite coating Ni/Cr-Cr_3C_2 were obtained. For all composite layers created, the material properties, such as morphology, phase and chemical compositions, hardness, and Young modulus were investigated. The paper presents the original technological equipment, methodology, and technological parameters for the creation of the composite coating Ni/Cr-Cr_3C_2.

Key words: Electron beam evaporation; Hybrid surface treatment technology.

A DEPOSIÇÃO DE REVESTIMENTOS Ni/Cr-Cr_3C_2 COMPOSTO PELO Arco-EB TECHNOLOGIA HIBRIDA

Resumo

A nova tecnologia híbrida é uma combinação de evaporação de feixe de elétrons com processos evaporação-arco, permitindo a obtenção de um revestimento anti-erosão Cr/Ni-Cr_3C_2 compósitos com diferentes tamanhos de partículas Cr_3C_2 e intensidade diferentes de enchimento macio Ni/Cr matriz com partículas rígidas Cr_3C_2, incluindo nanopartículas. A matriz macia composta por Ni/Cr e ligas de partículas duras de Cr_3C_2 é criada ao mesmo tempo e directamente durante o feixe de eletrões e o processo de evaporação-arco. As alterações dos parâmetros deste processo híbrido, isto é, pressão, corrente de descarga do arco e o substrato tensão de polarização Ubias, tornam possível controlar o tamanho das partículas Cr_3C_2 e é um fator de enchimento da matriz macia de Ni/Cr com partículas Cr_3C_2. Com o uso da desenvolvida tecnologia híbrida de tratamento de superfície, o revestimento composto por Ni/Cr-Cr_3C_2 foram obtidos. Para todas as camadas criadas, as propriedades do material e a morfologia ou seja, composições de fases e o química, dureza e módulo de Young foram investigados. O trabalho apresenta o equipamento tecnológico original, a metodologia e os parâmetros tecnológicos para a criação do revestimento compósito Ni/Cr-Cr_3C_2.

Palavras-chave: Tecnologia Híbrida de tratamento de superfície; Revestimentos de barreira térmica.

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[2] *Institute for Sustainable Technologies – National Research Institute, 26-600 Radom. Pułaskiego 6/10, Poland.*

[3] *AGH – University of Science and Technology, 30-059 Krakow, Mickiewicza 30, Poland.*

1 INTRODUCTION

The modification of the surface layer is the most effective way to develop exploitation properties of tools and machine parts. Past several years saw the development of many industries which was determined by the possibilities offered by surface engineering and plasma-chemical deposition method of thin coatings, in particular.[1,2] Thanks to new material and technological developments it was possible to gradually expand the area of using surface engineering in the industry, e.g. for high performance machining[3] and plastic forming.[4,5]

Among the PVD coatings enhancing the durability of machine parts and tools in difficult or even extreme operating conditions such as high mechanical and thermal loads,[6] intensive friction[7] or corrosive influence of the environment,[8] greatest attention should be paid to coatings which increase erosion wear resistance. Different shape, weight, speed, incidence angle of bombardment particles and also cyclic nature and high dynamics of the process causes that not many coatings effectively prevent erosion wear. The coating most commonly used for this purpose is the Ni/Cr-Cr_3C_2 composite coating, which consists of Cr_3C_2 hard carbide phase dispersed in Ni/Cr soft matrix, and is produced by thermal spraying of powders.[9,10] The necessity to use adequately prepared powders and the high dynamic growth rate causes that the coatings obtained through the use of thermal spraying method are characterized by high roughness and relatively large and irregular thickness which in practice results in their inability to increase the erosion resistance of precision components. The application of plasma surface treatment methods (Arc-Evaporation or Magnetron Sputtering) commonly used to create Ni/Cr-Cr_3C_2 composite coatings in order to ensure their reduced surface roughness is, however, not possible in practice as it is difficult to compose composite coatings using these methods. In addition, the use of magnetic field to the location of discharge in Arc-Evaporation and Magnetron Sputtering methods practically makes it impossible to effectively sputter ferromagnetic materials, and that includes nickel as well. Another type of a coating enhancing erosion wear resistance which may be obtained from plasma methods is a Cr/CrN multilayer coating. The multilayer structure of hard component layers and layers with higher plasticity stacked alternately increases erosion resistance of the coating.[11]

The development of technological studies in surface engineering combining different methods of surface treatment into one continuous technological process, development of hybrid technologies[12,13] in particular, has created new opportunities for making complex coating materials. The authors of the article used their own experience in the field of creating coatings with the use of methods of Arc-Evaporation[14] and Electron Beam Evaporation[15] in order to develop hybrid surface treatment technology, the Arc-EB PVD method, enabling the creation of both nanostructure multilayer coatings and nanostructure composite coatings.

This paper presents the results of the research on the use of Arc-EB PVD hybrid method used in the process of the creation of Ni/Cr-Cr_3C_2 multilayer coating with the nanometre thickness of individual component layers. Because of its structure, Ni/Cr-Cr_3C_2 multilayer coating has an increased resistance to erosion wear.

2 TECHNICAL REALIZATION OF Arc-EB PVD HYBRID TECHNOLOGY

High-density discharge located in the micro area of cathode spots is the basic phenomenon that can be observed in Arc-Evaporation method. As a result of the high-density discharge, the cathode material evaporates rapidly and is then ionized. A stream of highly ionized plasma, directed toward the surface of polarized negative potential ($U_{bias} \approx -150 \div -200V$) is created, and thus the coating material is crystallized. The process of arc evaporation of the metallic cathode in the reactive atmosphere allows the deposition of metal nitrides or carbides on the surface. Electron Beam Evaporation method's main objective is to cause the material placed in the melting pot to evaporate through its bombardment with high energy electron beam. In order to create Ni/Cr-Cr_3C_2 multilayer coating the combination of two different surface treatment methods, i.e. Electron Beam Evaporation method and Arc Evaporation method, into one hybrid Arc-EB PVD was proposed (as shown in Figure 1).

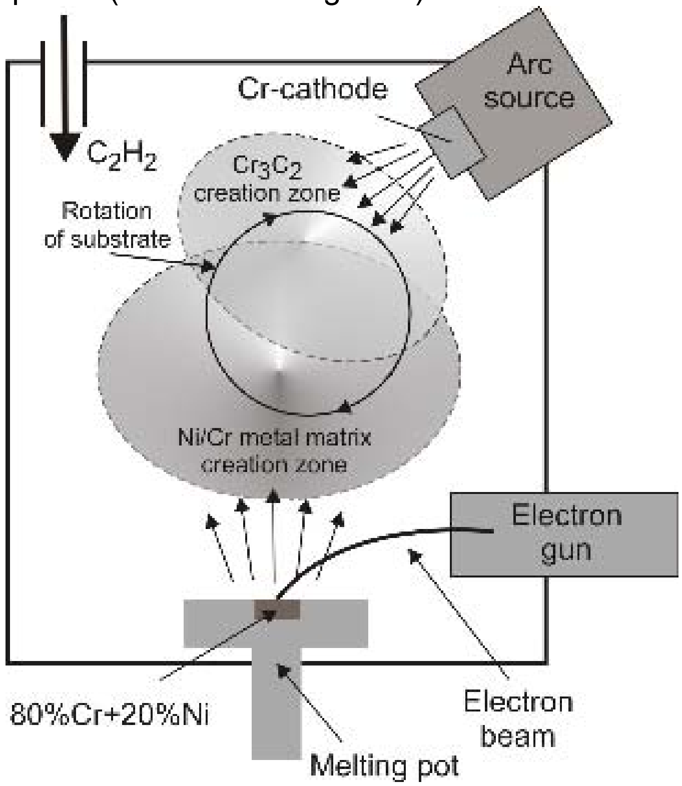

Figure 1. The scheme of Arc-EB PVD hybrid surface treatment technology.

The configuration of Arc-EB PVD hybrid method shown in Figure 1 enabled the separation of deposition zones of Cr_3C_2 carbide by Arc-Evaporation method and the separation of Ni/Cr matrix using EB Evaporation method. The introduction of the rotation of the substrate provides a selective deposition of individual materials as well as the composition of the multilayer structure.

3 TECHNICAL REALIZATION OF Arc-EB PVD HYBRID TECHNOLOGY

In order to present the technical realization of hybrid technology shown in Figure 1 the authors designed an original technological process implemented in the hybrid multisource device (Figure 2), produced at the Institute for Sustainable Technologies – National Research Institute in Radom (Poland).

Figure 2. The hybrid multisource device produced at the Institute for Sustainable Technologies – National Research Institute in Radom.

The device has been equipped with two arc sources with the cathode diameter of ø=80 mm and with the 60kW electron gun with the dynamic electron beam deflection circuit and steering system. The device is equipped with modern, reliable power systems, substrate polarization system, multichannel process gases dosing system as well as the systems of monitoring and measuring substrate temperature and atmospheric gas pressure.

The optimization of technological parameters of Cr_3C_2 carbide production through Arc-Evaporation method and Ni-Cr matrix through Electron Beam Evaporation method was carried out in order to develop technological parameters of creating Ni/Cr-Cr_3C_2 composite coating with the use of Arc-EB PVD hybrid method. Both methods have been used in one hybrid technological process, whose parameters are shown in Table 1.

Table 1. Technological parameters of Ni/Cr-Cr_3C_2 composite coating deposition through Arc-EB PVD hybrid method

Atmosphere	Pressure p [mbar]	Arc current I_{ARC} [A]	U_{bias} [V]	Substrate temperature T [^oC]	Electron beam current I_{BEAM} [mA]	Time of deposition t [min]
100% Ar	2.0×10^{-4}	70	–900	up to 430	-	-
100% C_2H_2	1.2×10^{-2}	70	–150	reduce to 290	150	120

Technological processes of creating Ni/Cr-Cr_3C_2 multilayer coating through Arc-EB PVD hybrid method have been realized for Armco iron samples ø=30 mm in diameter and 10 mm thick. The coatings obtained were then tested in the metallographic examination process (optical microscope Neophot 32), chemical composition analysis using EDS method (SEM Hitachi 2670 and microanalyzer Noran Instruments), hardness testing (Nano Hardness Tester CSEM; type of intender: Berkowich) and phase composition analysis using X-ray method (diffractometer Philips with X-Pert goniometer). To determine the morphology of the coating obtained, HRSEM (High Resolution Scanning Electron Microscope) research was conducted. In order to determine erosion wear resistance Armco iron samples, both uncoated and coated with Ni/Cr-Cr_3C_2 multilayer coating, were tested. The erosion test was carried out using shot glass with diameter of ø = 40-60 µm. Erosion intensity was measured with PGI 830 profilometer produced by Taylor Hobson Precision Company.

4 RESULTS AND DISCUSSION

4.1 Material Investigations

The material research conducted, shows that although Ni/Cr-Cr_3C_2 coating obtained using the hybrid method has even thickness of around 4µm over the entire surface of the sample, at the same time it has different hardness (Figure 3a) and different chemical composition (Figure 3b) within the distance function from its surface. Chemical composition research included the analysis of the changes in the content of Cr, Ni and C within the distance function from the surface of the Ni/Cr-Cr_3C_2 and Fe coating in order to identify the phase boundary with the substrate. The analysis of the changes in the chemical composition (Figure 3b) indicates the tripled structure of Ni/Cr-Cr_3C_2 coating.

The coating is characterized by a clearly increased content of chromium in relation to the middle zone especially in the zone with thickness of about 1,5 µm from the substrate and in the zone with thickness of about 1 µm from the surface.

The changes in nickel content in Ni/Cr-Cr_3C_2 coating are reverse to the changes in chromium content. Nickel content is significantly reduced, both closer to the substrate and closer to the surface. Carbon content in Ni/Cr-Cr_3C_2 coating is correlated with the changes in chromium content in the zone closer to substrate and with changes in nickel content in the zone closer to the surface.

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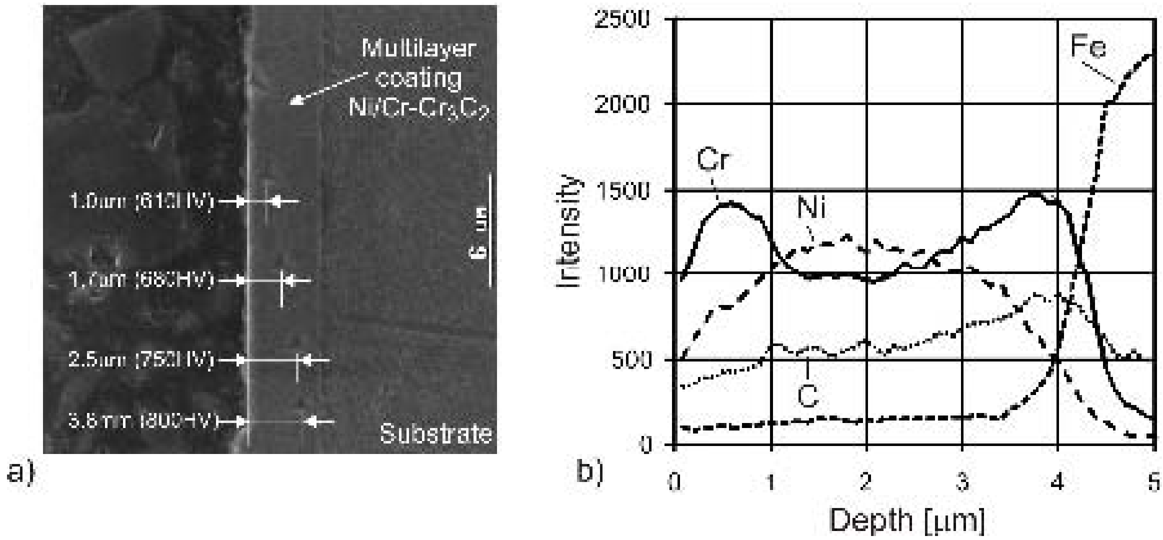

Figure 3. Changes of hardness (a) and chemical compositions (b) of Ni/Cr-Cr3C2 multilayer coating obtained through the use Arc-EB PVD hybrid surface treatment method.

The phase structure research using X-ray method was carried out with the use of CuK_{α} (λ = 0.1541837 nm) in 2 theta = $20^{o} \div 110^{o}$ angel range and its results are shown in Figure 4.

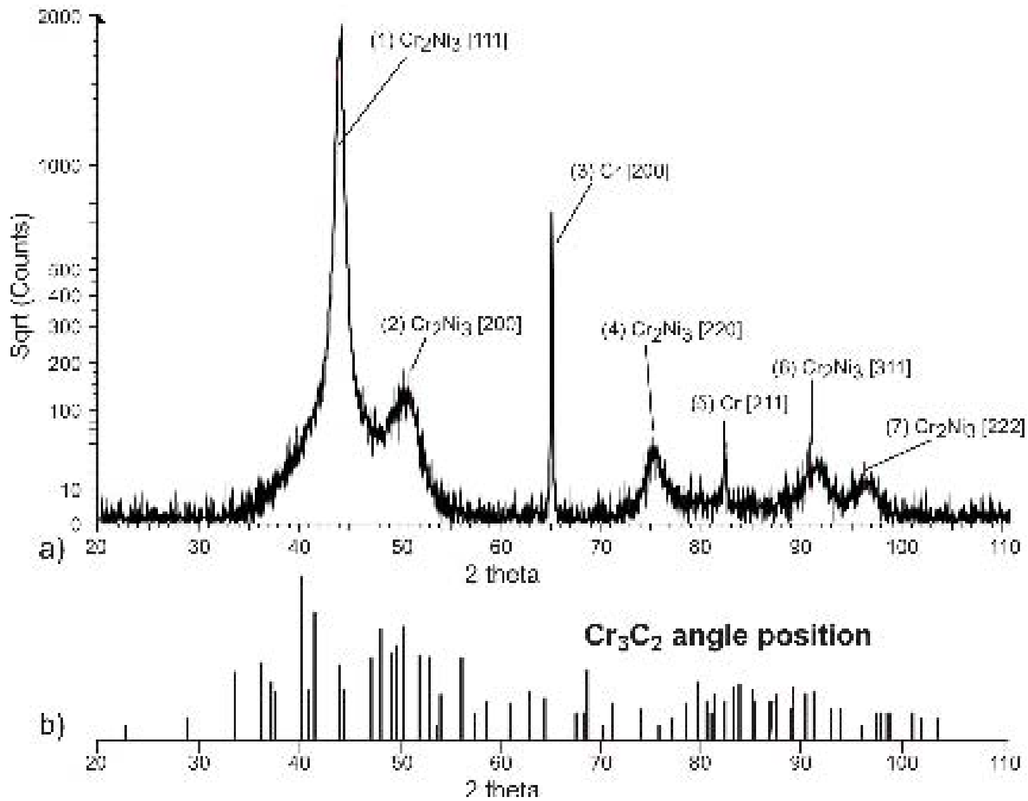

Figure 4. The results of X-ray phase analysis of Ni/Cr-Cr_3C_2 multilayer coating obtained through Arc-EB PVD hybrid surface treatment method (a) and angle positions for Cr_3C_2 phase (b).

The research revealed the presence of peaks for the metallic phase of chromium and peaks for Cr_2Ni_3 phase. Peaks for Cr phase, i.e. (3) Cr [200], (5) Cr [211], are acute and correspond precisely to 2 theta angle position as shown in the ASTM charter. Peaks for Cr_2Ni_3 phase, i.e. (1) Cr_2Ni_3 [111], (2) Cr_2Ni_3 [200], (4) Cr_2Ni_3 [220], (6) Cr_2Ni_3 [311], (7) Cr_2Ni_3 [222] are significantly blurred in the range of low intensity, which indicates the presence of another phase dispersed in Ni-Cr matrix. The marking of the location of 2 theta angle positions (Figure 4b), corresponds to the occurrence of peaks for chromium carbide (Cr_3C_2), and coincides with the position of peaks for Cr_2Ni_3 phase. According to the authors of the paper the angle blurring of the Cr_2Ni_3 peaks may be caused by the presence of Cr_3C_2 fine-crystalline chromium carbide phase dispersed in Ni-Cr matrix. Both the results of chemical composition research (Figure 3) as well as the results of the phase structure research (Figure 4) indicate that the Ni/Cr-Cr_3C_2 coating obtained has a different structure in its distance function from the surface. High Resolution Scanning Electron Microscope (HRSEM) has been used in the research in order to investigate the differences in morphology and phase structure of Ni/Cr-Cr_3C_2 coating. The results are shown in Figure 5.

Four zones with different morphology can be marked out in the investigated Ni/Cr-Cr_3C_2 coating. The deposition process starts at 430^oC, which in the presence of plasma provides sufficient surface diffusion rate to create both high density structure of the chromium carbide (Cr_3C_2) as well as Cr_2Ni_3 phase. As a result, Ni/Cr-Cr_3C_2 coating has, directly to the substrate (zone I; g≈0.7 μm), a clear multilayer structure with high density of each layer (Figure 5b). As the point analysis of the chemical composition revealed (Figure 5c), brighter layers, in comparison to dark layers, are characterized by increased carbon and chromium content and reduced nickel content. Zone II, with the same thickness of about ≈0.7μm, has multilayer structure as well, but is characterized by much greater thickness of the dark layer with lower carbon content. Changes of the thickness of each component layer are the result of the changes in Ni and Cr evaporation rate. During the deposition process 80% Cr + 20% Ni alloy was evaporated. The evaporation temperature decreases with decreasing pressure chromium,[16] while nickel evaporation temperature remains constant. In the first phase of coating deposition (zone I) the evaporation rate of chromium was greater, which resulted in multilayer structure with high density of component layers rich in chromium and less dense component layers rich in nickel. The evaporation rate of nickel increased with the loss of chromium in the melting pot. As a result the density of component layers rich in nickel increased and the density of component layers rich in chromium decreased (zone II – Figure 5d). As a result of substrate temperature decrease, the rate of surface diffusion in deposition process decreased as well, same as the ability to create new nucleation. This led to the lower density of the structure of each component layer and the appearance of numerous pores between formed columnar grains (zone III; g≈1.5 μm – Figure 5e). However, within the individual grains, the coating still has a multilayer structure. Further decrease in the substrate temperature caused significant reduction in the nucleation speed and the coating deposited adopted the needle-shaped structure (zone IV; g ≈ 1 μm – Figure 5f).

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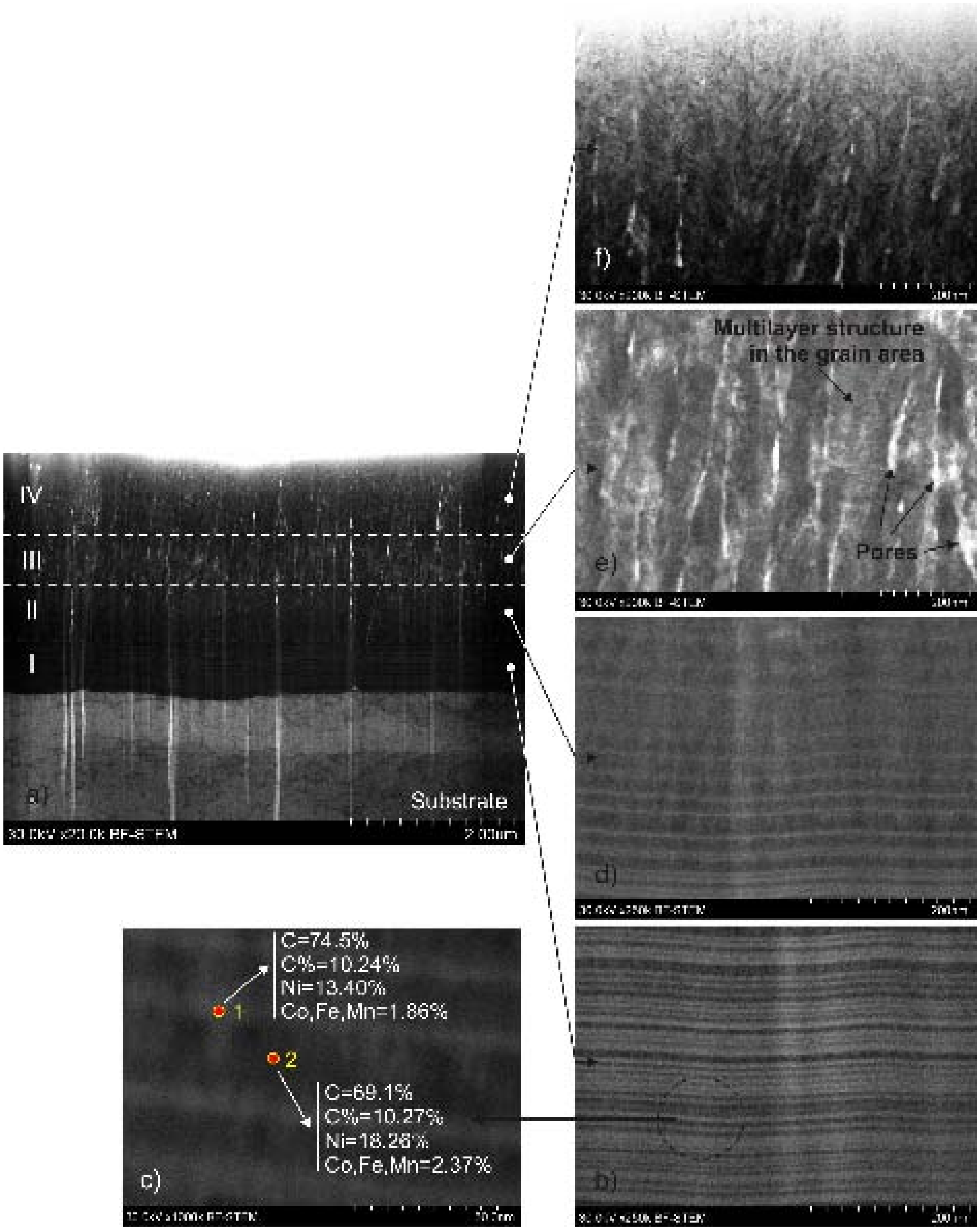

Figure 5. The results of the research of morphology of Ni/Cr-Cr_3C_2 multilayer coating obtained using Arc-EB PVD hybrid surface treatment method, carried out with the use of HRSEM (High Resolution Scanning Electron Microscope).

4.2 Erosion Test

The erosion wear resistance research was carried out in accordance to methodology shown in Figure 6a. Plane of the sample used in the test, was covered by a mask with the hole with the diameter of ø = 5mm centrally cut, and it was placed perpendicularly to the axis of the nozzle throwing grinding compound. The effect of the abrasive wear was the crater that was formed in the sample. Erosion wear resistance tests were carried out in accordance to the parameters shown in Table 2.

Table 2. Technological parameters erosion wear resistance tests of composite coating Ni/Cr-Cr_3C_2

Material	Granulation [μm]	Pressure p [bar]	Angle [°]	Distance from substrate L [mm]	Time [min]
Glas	40 – 80	4	90	85	4

In order to determine erosion resistance of Ni/Cr-Cr_3C_2 coating, comparative studies on Armco iron coated and uncoated samples were conducted. In order to determine the intensity of the erosion process, the depth measurements of formed craters were taken with PGI 830 profilometer by Taylor Hobson Precision Company. Results of those tests are shown in Figure 6.

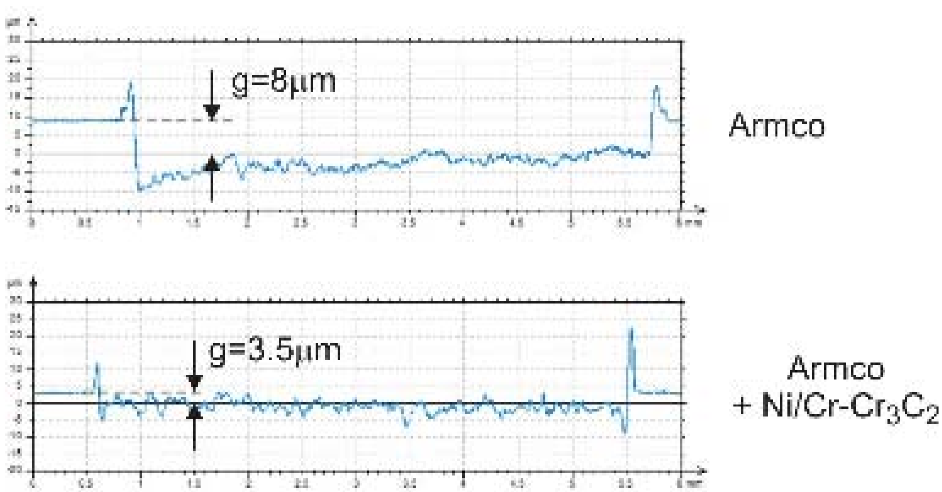

Figure 6. The results of laboratory erosion tests for Armco with no coating and Armco covered by Ni/Cr-Cr_3C_2 multilayer coating obtained using Arc-EB PVD hybrid surface treatment method.

5 CONCLUSIONS

The configuration of Arc-EB PVD hybrid surface treatment technology developed through the combination of Arc-Evaporation and Electron Beam Evaporation surface treatment methods, allows the creation of nanostructure coatings (nano-multilayer coatings and nano-composite coatings), i.e. Ni/Cr-Cr_3C_2 nano-multilayer coating with increased erosion wear resistance. Changing the hybrid process parameters such as arc discharge plasma ionization rate, Ni-Cr alloy evaporation rate and the precise control of the substrate temperature enables changing the morphology of deposited coating, including participation of hard chromium carbide phase in soft Ni-Cr matrix. The erosive wear tests demonstrate that in relation to the elements without coating, the erosion resistance of Armco iron elements coated with the 4 μm thick Ni/Cr-Cr_3C_2 nano-multilayer has doubled.

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