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INFLUENCE OF HEAT TREATMENT ON PROPERTIES OF Ni-B/B COMPOSITE COATINGS

The results of research on preparations of alloy Ni-B/B composite coatings produced by chemical reduction method on a carbon steel substrate are collected in this paper. The alloy Ni-B coatings were also investigated for comparative purposes. The produced coatings were subjected to a heat treatment process. The boron powder with the particles size below 1 µm was used as the dispersion phase. The structure of the coatings was examined by X-ray diffraction method. Boron powder particles as well as surface morphology and topography were characterized by scanning electron microscopy. The roughness test, microhardness and corrosion resistance by potentiodynamic method and surface wettability tests were carried out. Analysis of the chemical composition by the EDS method showed that the boron powder particles were evenly embedded in the entire volume of the coating. Ni-B/B composite coatings are characterized by higher hardness than alloy Ni-B coatings. As a result of heat treatment, the Ni_3B phase crystallized, which increased the hardness of the coating material. The incorporation of boron powder particles and heat treatment reduce the corrosion resistance of coatings. All produced coatings exhibited hydrophobic properties.

Keywords: Ni-B/B composite coating, Ni-B alloy coating, boron powder, heat treatment

1. Introduction

Coatings produced by chemical reduction method are increasingly used in technical applications. A great advantage of the coatings obtained with this method is the possibility to deposit them on elements with complicated shapes and made from various materials. Among the coatings obtained with the chemical reduction methods, the most common are nickel coatings, owing to their advantageous properties, like high hardness and resistance to friction-induced wear, as well as a resistance to corrosion. The properties of nickel coatings produced by chemical reduction method can be modified by adding during the plating process various chemical compounds as reducing agents. The reducing agent's type determines the chemical composition of the coating. An electroless nickel plating process in a bath containing sodium hypophosphite as reducing agent will produce a Ni-P alloy coating. The use of boranes will produce Ni-B alloy coatings. If hydrazine is used to reduce nickel ions, the obtained coating will be pure nickel [1]. A Ni-B alloy coating, when compared to a Ni-P coating, demonstrates a greater hardness [2,3] and a greater resistance to wear [4,5]. The advantageous properties of electroless plating-produced Ni-B coatings cause them to be increasingly used in technical applications [6,7]. Ni-B coatings' properties may be adjusted to a small degree by varying the proportion of boron in the coating [8]. The functionality of such coatings can be furthermore enhanced by heat treatment and embedding dispersed phase particles of other materials (metals, polymers, ceramics) in their matrix to obtain composite coatings [7,9-12]. Properties of composite coatings are affected by the matrix material, the type of the dispersed phase, the shape and size of the particles in the dispersed phase and its content in the composite material. In the current work, the subject of study were Ni-B alloy coatings and Ni-B/B composite coatings that were subjected to heat treatment. The analytical research that was carried out concerned the determination of the bath's composition and the parameters of the plating process, the production of the coatings and the characteristics of their structure and selected properties.

2. Research methodology

Ni-B alloy coatings and composite coatings with a Ni-B matrix and a dispersed phase in the form of boron powder particles (by Sigma Aldrich) were obtained with the method

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of chemical reduction in an alkaline bath with components provided in Table 1.

TABLE 1

Compositions of solutions used for the coating productions and process parameters

Coating	Chemical composition of baths	Process parameters
Ni-B	nickel chloride, sodium borohydride, ethylenediamine, sodium hydroxide, lead nitrate	pH 14 T = 90°C 100 rpm
Ni-B/B	nickel chloride, sodium borohydride, ethylenediamine, sodium hydroxide, lead nitrate boron powder	

The plating process was accomplished in a temperature of 90°C; mechanical mixing with a rotational speed of 100 rpm was used to obtain a good dispersion of the powder in the bath, to avoid a sedimentation of particles and to facilitate their transfer during the process. The coatings were deposited on a substrate of S235JR carbon steel previously grinded, degreased with acetone and activated with a 15% H_2SO_4 solution. The produced coatings were heat treated at 360°C for 20 minutes in an air atmosphere.

Boron powder particles' characteristics and the analyses of the coatings' morphology and topography were carried out with a JOEL JSM-IT100 LA scanning electron microscope. The identification of the coatings' structure was realized with the X-ray diffraction method (Rigaku MiniFlex II), using a lamp featuring a copper anode with a wavelength λ = 0.154 nm. Roughness parameters of the substrate's surface and coatings were defined with a SJ-210 profilometer. The coatings were subjected to wetting tests to determine their hydrophobic properties. The measurements of the contact angle were performed with the sessile drop method; a 5 μl droplet was released from a height of ca 5 mm on the surface of the tested coating. The contact angle was determined with the ImageJ software with the Drop Analysis plugin. Hardness tests were achieved with the Knoop method with a T1202 Wilson hardness tester on cross sections perpendicular to the coatings' surfaces, under a 10 G load. Corrosion testing was performed with the potentiodynamic method, using a Bio-Logic SP-200 potentiostat in a three-electrode configuration. The reference saturated calomel electrode had a potential of +244 mV, the counter electrode was in platinum, and the working electrode was the analyzed sample. The analysis was carried out in a 0.5 M NaCl solution, at a temperature of ~20°C and in ambient atmosphere. The polarization of the tested coatings was carried out within the potential ranges of –250 to +250 mV with respect to the OCP potential and at a scan rate of 0.2 mV/s.

3. Research results

The image of the boron powder particles used to produce composite coatings and obtained with a scanning electron microscope (SEM) is shown in Fig. 1.

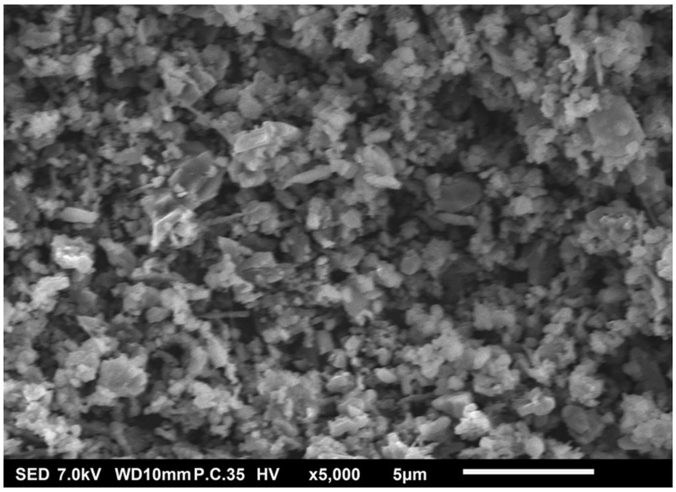

Fig. 1. SEM image of boron powder particles

Powder particles display an irregular shape, a size under 1 μm, and a propensity to form agglomerates.

In Fig. 2 are shown X-ray diffraction spectra of Ni-B and Ni-B/B coatings before and after heat treatment.

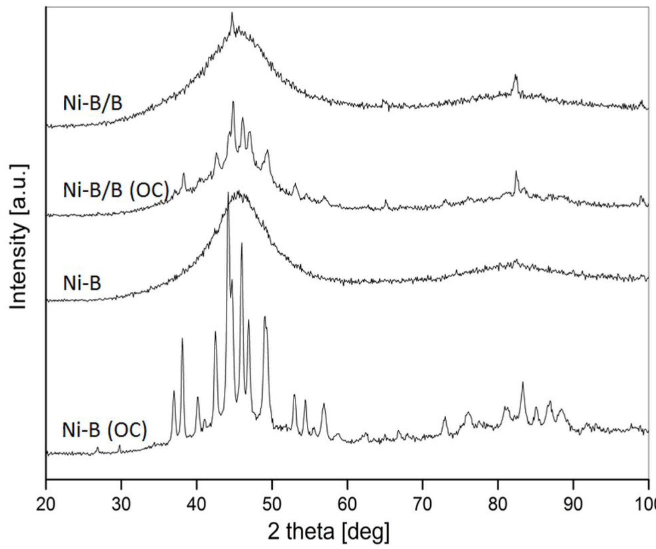

Fig. 2. The diffraction pattern of Ni-B and Ni-B/B coatings before and after heat treatment (OC)

Before heat tretment, both the Ni-B alloy coating and the Ni-B/B composite coating are characterized by an amorphous structure, attested by a broad, fuzzy difraction reflex. In the case of the composite coating, the diffraction line profile shows traces of a cristalline phase stemming from the iron in the substrate. During heat treatment, depending on the percentage of boron in the Ni-B alloy, the material of the coatings crystallizes and the formation of crystalline phases: nickel and nickel borides (Fig. 4) takes place. Heat treatment of the produced coatings at 360°C for 20 minutes leads to crystallization of the amorphous phase and the appearance of the Ni_3B phase, as shown in Fig. 3. The obtained results are in line with literature reports [14-16].

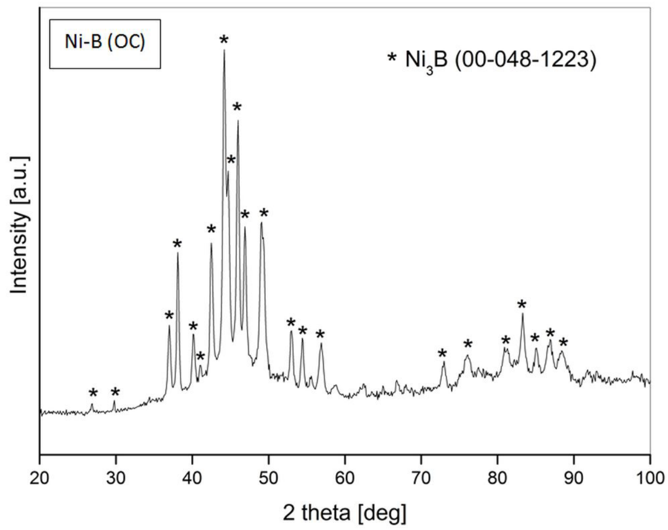

Fig. 3. The diffraction pattern of Ni-B (OC) with marked phase Ni_3B

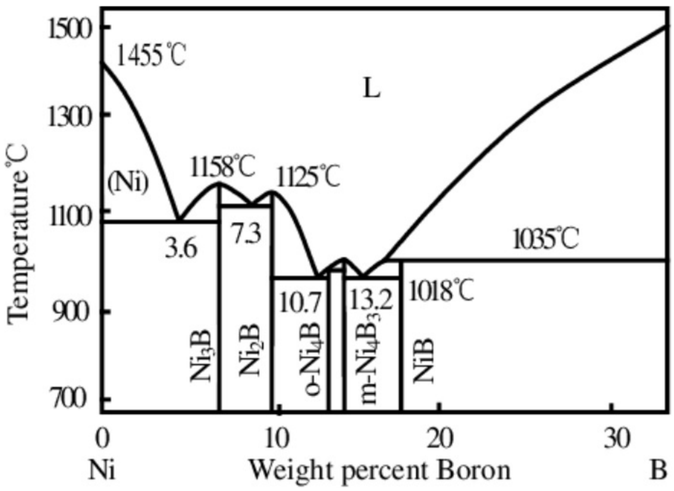

Fig. 4. Phase diagram of Ni-B coating [13]

The SEM images of the surface topography and morphology of the produced Ni-B and Ni-B/B coating before and after heat treatment (OC) are shown in Fig. 5.

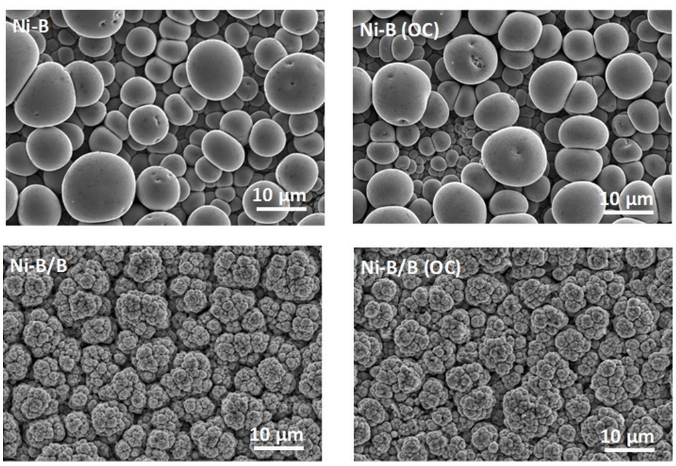

Fig. 5. Surface morphology and topography of Ni-B and Ni-B/B coatings before and after heat treatment (OC)

The surface of the Ni-B alloy coatings is characterized by a structure containing spherical elements, while the Ni-B/B composite coatings feature cauliflower-shaped ones. The surface of the composite coatings features visible incorporation boron particles (Fig. 6, Table 2).

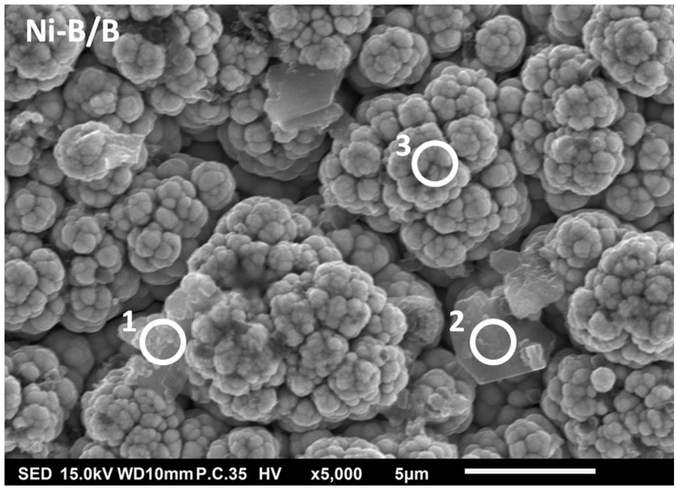

Fig. 6. Topography of the Ni-B/B coating with marked areas of chemical composition testing

TABLE 2

Chemical composition of Ni-B coating in marked areas

Area	The content of elements in composite coatings [% at.]			
	Ni	B	C	O
1	4.14	92.51	2.08	1.27
2	8.24	87.45	2.64	1.67
3	62.64	24.76	10.68	1.93

The embedding of dispersed phase particles in the Ni-B matrix material results in changes in the morphology and the degree of the development of its surface. The results of measurements of the roughness of the substrate's surface and the Ni-B alloy and Ni-B/B composite coatings are provided in Table 3.

TABLE 3

Parameters of the surface roughness of the substrate and the coatings produced

Material	Roughness [µm]	
	Ra	Rz
steel	0.04	0.29
Ni-B	1.68	9.98
Ni-B (OC)	1.25	8.01
Ni-B/B	0.89	6.06
Ni-B/B (OC)	0.67	5.18

Substrate surface's roughness parameters were substantially smaller than those of the produced coatings. The embedding of dispersed phase particles in the Ni-B matrix causes a reduction of the degree of development of the coatings' surface. Furthermore, the composite coating is characterized by a more than two times lower value of the Ra parameter when compared to the Ni-B coating without boron particles. As a result of heat treatment, the surface roughness of coatings is slightly reduced.

The structure of the alloy and composite coatings in a cross section perpendicular to the surface is shown in Fig. 7.

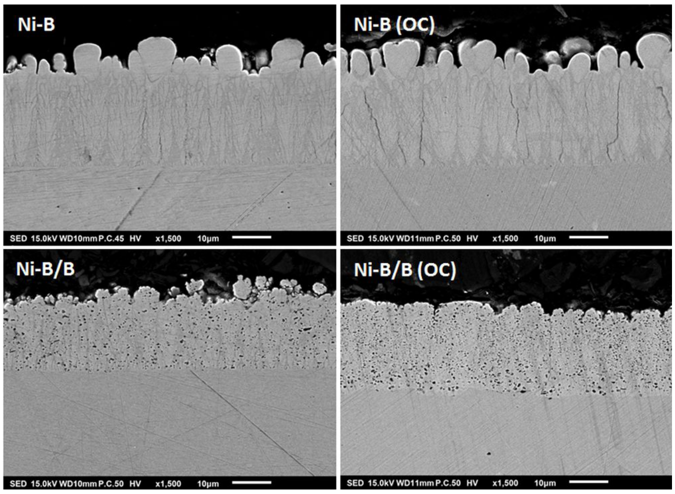

Fig. 7. Cross sections of the produced coatings before and after heat treatment (OC)

The produced coatings have a compact structure, a uniform thickness and a good adhesion to the substrate. The coating's material has a columnar-like structure [15]. Boron powder particles uniformly embedded in the matrix are visible in the entire volume of the composite coatings. The composite coating has a lesser thickness than the alloy one produced in a process with same parameters, due to a concurrent embedding of boron particles preventing the development of the nickel coating.

Figures 8 and 9 show select areas of chemical analysis in a cross section of the produced coatings. The results of a chemical analysis within select areas of produced coatings are provided in Tables 4 and 5.

The featured chemical analytical results confirm the embedding of boron powder particles in the volume of the composite coatings.

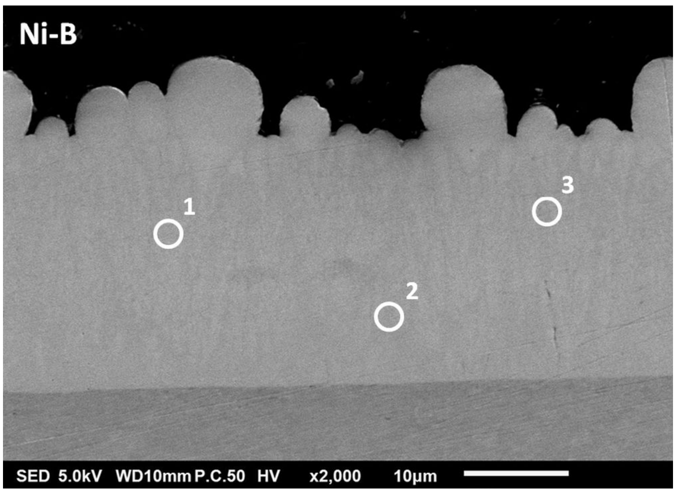

Fig. 8. Cross section of Ni-B coating with marked areas of chemical composition testing

TABLE 4

Chemical composition of Ni-B coating in marked areas

Area	The content of elements in composite coatings [% at.]			
	Ni	B	C	O
1	81.2	12.4	0.8	1.0
2	80.0	10.3	4.1	5.6
3	81.8	13.2	3.2	1.9

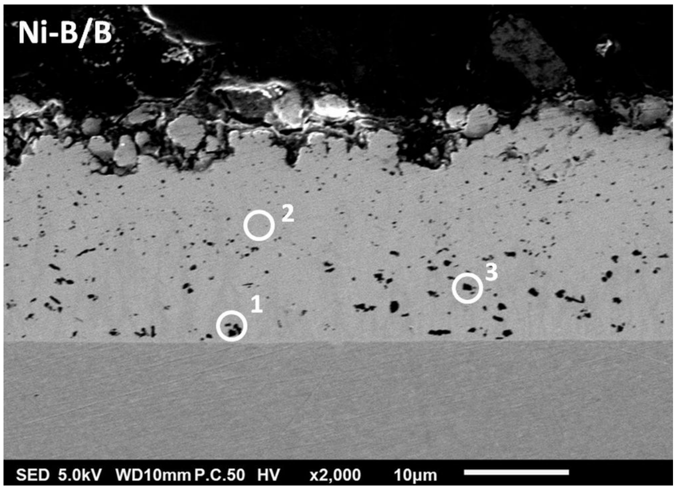

Fig. 9. Cross section of Ni-B/B coating with marked areas of chemical composition testing

TABLE 5

Chemical composition of Ni-B/B coating in marked areas

Area	The content of elements in composite coatings [% at.]			
	Ni	B	C	O
1	16.6	82.1	—	1.3
2	24.4	70.8	2.6	2.2
3	16.6	77.9	2.7	2.8

A microhardness testing of the produced coatings with the Knoop method is shown in Fig. 10.

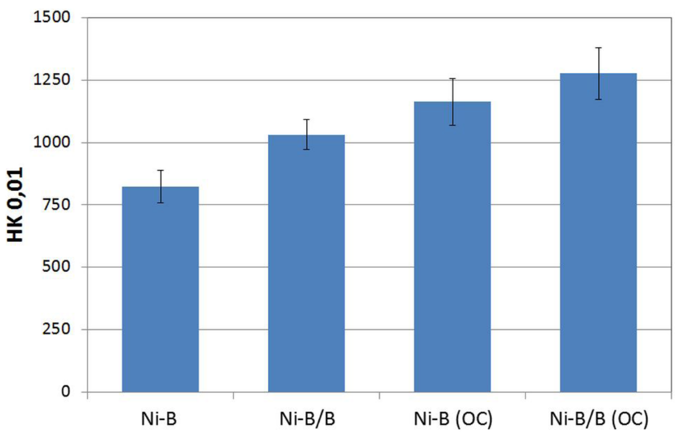

Fig. 10. Microhardness of the produced coatings before and after heat treatment (OC)

Incorporation of boron particles into the Ni-B alloy matrix increases the hardness of the coating material, which is associated with the dispersion strengthening mechanism [17,18]. Heat treatment of coatings causes in both cases an increase in the hardness of both Ni-B and Ni-B/B composite materials. This is due to changes in the material, the Ni-B material crystallizes, and the hard Ni_3B phase separates [14,16]. The heat treatment Ni-B/B composite coating has the highest hardness of 1278 HK0.01. Literature reports show that it is most advantageous to conduct heat treatment at a temperature of about 300-400°C. Higher temperatures cause a decrease in the hardness of the heated coatings [19,20].

The results of corrosive properties' tests of the produced coatings are shown in the form of polarization potentiodynamic $I = f(E)$ curves in Fig. 11. The polarization curves were used to determine the corrosion current density (I_{cor}) and the corrosion potential (E_{cor}) of the tested coatings' material (Tab. 6).

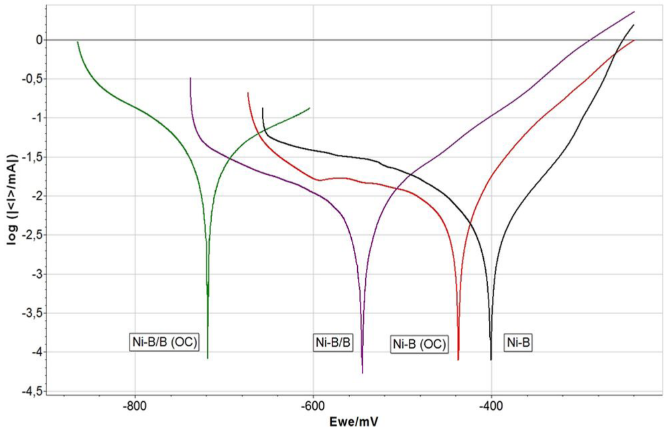

Fig. 11. Potentiodynamic curves of the produced coatings before and after heat treatment (OC)

TABLE 6

Corrosion parameters of the produced coatings in the 0.5 M NaCl environment

Coating	E_{cor} [mV]	I_{cor} [μA/cm²]
Ni-B	–400	2.4
Ni-B (OC)	–436	4.1
Ni-B/B	–545	6.3
Ni-B/B (OC)	–718	5.5

The highest corrosion resistance is exhibited by the Ni-B alloy coating before heat treatment. The embedding of dispersive phase particles in the form of boron powder particles leads to a decrease in corrosion resistance of the coating material. Heat treatment reduced the corrosion resistance of the coating material of both Ni-B and Ni-B/B coatings. This is probably related to the occurrence of local cracks in the volume of the coating material (Fig. 12).

The incorporation of boron particles in the Ni-B matrix material had a positive impact on the hydrophobic properties of the coatings. The assumed wettability criterion is the contact angle between the surface of the sample and the droplet interface tangent. A surface's wettability depends primarily upon

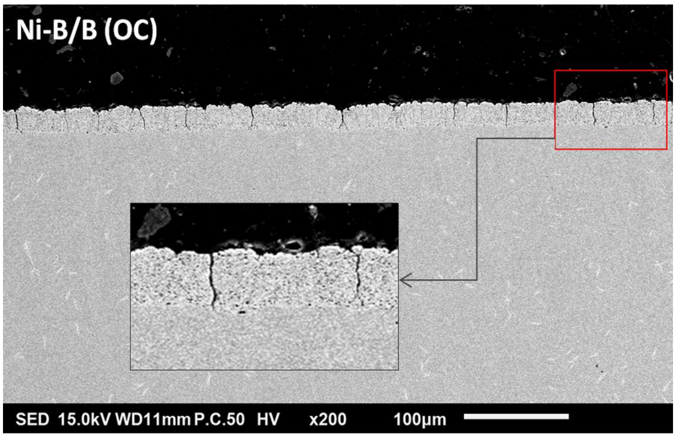

Fig. 12. Example of cracks in the composite coating Ni-B/B after heat treatment (OC)

its chemical properties and structure [21]. The results of the coatings' wettability tests are provided in Table 7, and Fig. 13 shows sample photos of water droplets on the surfaces of the tested coatings.

TABLE 7

The contact angle of the coatings produced

Coating	Contact angle [deg]	Standard deviation
Ni-B	102	13.3
Ni-B (OC)	121	2.0
Ni-B/B	113	8.5
Ni-B/B (OC)	97	2.5

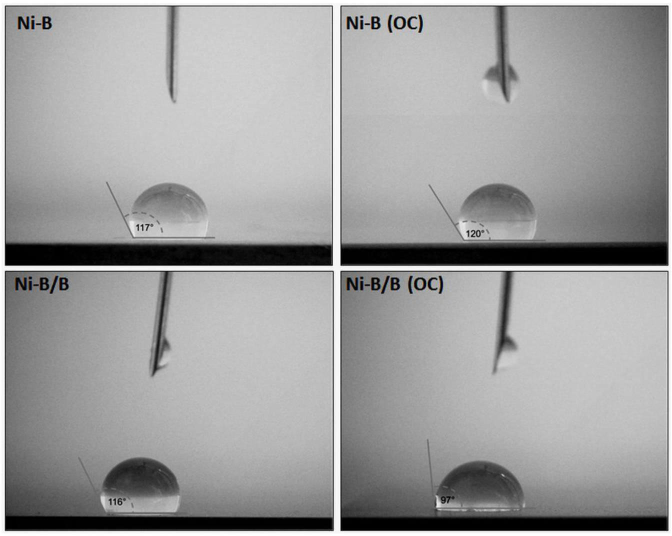

Fig 13. Example images of water drops on the surface of the tested coatings before and after heat treatment (OC)

On the basis of analytical results it can be asserted that all coatings display hydrophobic qualities, as their contact angle exceeds 90° [22]. The Ni-B alloy coating after heat treatment demonstrates superior hydrophobic properties, as its mean contact angle is 121°.

4. Conclusions

The material of Ni-B and Ni-B/B coatings produced by chemical reduction method is amorphous. The produced coatings are characterized by a compact structure and a good adhesion to the substrate. Boron powder particles are uniformly embedded in the entire volume of the composite coating. The incorporation of the dispersive phase particles in the Ni-B matrix material and heat treatment causes increased hardness and reduced corrosion resistance of coatings compared to Ni-B alloy coatings. The produced coatings demonstrate hydrophobic qualities.

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