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Effect of Heat Treatment on the Corrosion and Mechanical Properties of Electrolytical Composite Ni-B Coatings

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Electrodeposition of composite coatings with nickel matrix and boron micro-particles was investigated. Nickel - boron layers were deposited potentiodynamically at 12.5 mV/s on cylindrical samples prepared from iron powder in a stirred heterogeneous system formed by a Watts type nickel plating bath and dispersed boron micro-particles. The effect of boron powder amount in plating bath and heat treatment on the corrosion resistance and hardness of the composite Ni-B coatings was evaluated. Corrosion properties of coated cylindrical iron samples were investigated in 1 mol dm^{-3} NaCl solution using potentiodynamic polarization method. The structure of coating layers was established using scanning electron microscopy (SEM) and light optical microscopy (LOM). The content of incorporated boron particles increased with the boron amount in plating bath. Homogeneous distribution of boron particles in deposited coating layer was observed for both as-deposited samples and samples heat treated at 400 °C. Boron particles were not observed on the surface of the deposits heated at higher temperatures. Generally, addition of boron micro-particles to the nickel matrix as well as the heat treatment deteriorated the corrosion resistance of iron samples coated with composite Ni-B films. The dependence of the corrosion properties of composite layers on boron particle loading was not proved. The decrease of microhardness on the surface but increase of microhardness on the cross-section of composite Ni-B coating layer due to the heat treatment was observed.

Keywords: electrolytic deposition, composite Ni-B coating, corrosion, anodic polarization, microhardness

1. INTRODUCTION

Electrochemical methods of coating metallic layers are attractive due to the high degree of control obtainable by varying the experimental conditions. It is one of the most frequently used surface treatments. Electrodeposited nickel has been subjected to extensive scientific investigations in the areas of grain growth kinetics, mechanical properties and creep behavior [1-6]. Unfortunately, the electroplated nickel coatings are not hard enough and hence cannot be used in application where resistance to wear is the primary requirement [7]. Alloying of boron along with nickel improved the hardness, microhardness and wear resistance [8]. The high corrosion resistance is also required for practical application of Ni-B coatings. The modifications of boron content in a coating and the variations in the deposition conditions make possible to obtain a wide range of functional properties in the final coatings [9]. Nickel - boron is frequently used in the production of non-ferrous base metal materials and nickel base magnetic materials in engineering applications.

Among a variety of techniques applied for the fabrication of the Ni-B coatings, electroless and electrochemical plating processes have gained a considerable attention due to their cost-effectiveness and less complex processing sequence [8, 10, 11].

The baths containing strong reducing agents such as potassium or sodium borohydride and different amine boranes can be used for production of electroless Ni-B coatings; generally at high pH values (13-14) and high temperature (70-90 °C) [10-19]. Reducing agents release electrons which are received by metal cations, forming a metal thin film on substrates. Beside this, precipitation of metallic nickel in the bulk of the solution takes place. The stabilizing agent should be introduced into the solution to eliminate this bulk deposition [11].

Few reports are available on formation and characterization of electroless Ni-B coatings [20-22]. Properties of Ni–B films are mainly controlled by their boron content [11, 20]. To improve the mechanical properties of electroless Ni-B deposits, various heat treatments are applied [23]. Upon heat treatment above 380 °C, the film crystallizes completely and the tribological properties of the film are enhanced significantly as very well reported elsewhere [20, 21, 24]. The effect of heat treatment on the film structure was also observed to show variation depending on the boron content of the film [11].

Hard, wear and abrasion resistant electroless Ni-B deposits with good adhesion to the aluminium substrate were produced by Delaunois and Lienard [23]. The Ni-B deposits, with or without heat treatments, have good tribological properties. Anik et al. [20] determined the boron content dependency of the microhardness and the corrosion resistance of the electroless deposited Ni-B films. The effect of heat treatment on the properties of Ni-B film obtained in the reference coating bath was analyzed as well. With an increasing boron content of Ni-B film both the corrosion resistance and the microhardness of Ni–B film increased. Heat treatment resulted in a significant improvement in the microhardness but the reduced corrosion resistance of Ni-B film was observed as well. Electroless Ni-B deposits were synthesized on aluminium alloys by Vitry and co-workers [22]. Heat treatments of those coatings under a neutral atmosphere allowed an increase of the hardness caused by the crystallization of Ni, Ni_2B and Ni_3B phases but no diffusion at the interface was observed.

The baths containing the afforecited reducing agents may be used also for electrochemical deposition of Ni-B alloys [8, 10, 11, 25-27]. Compared to the electroless method, electrodeposition offers several benefits, such as low process temperature and high rate of deposition, uniform distribution of boron in the coating layer, simple regulation of the deposition procedure and maintenance of the electrolyte solution [10, 11]. Furthermore, content of boron in the coating, which determines the chemical, mechanical, and physical properties of deposited layers, can be effectively regulated [11]. Nevertheless, the electrochemical deposition of Ni-B coatings has been fewer investigated than electroless deposition.

Formation of Ni-B alloy coatings was studied by Krishnaveni et al. [8] with the aim to evaluate its structural characteristics, hardness and wear resistance. Ni-B alloy coatings were prepared by electrodeposition using a Watts nickel bath, which use a combination of nickel sulphate and nickel chloride, along with boric acid modified with the addition of dimethylamine borane, which also served as the source of boron. The Ni-B coatings heat-treated at 400 °C exhibited higher hardness than the as-plated Ni-B coatings. The effect of heat treatment on the composition and structural features of the nanocrystalline Ni-B coatings obtained by electrochemical deposition was investigated by Lee et al. [11]. The decrease in wear resistance while increase in internal stress and hardness of Ni-B films was observed with increasing content of boron.

Electrodeposition is also well-known as a typical coating method of composite thin films. The technique is low cost, simple, and easy to control growth rate [7, 26, 27]. Electrodeposition makes it easy to obtain composites which often have previously unattainable properties. However, studies on electrodeposition of composite Ni–B coatings are rather limited.

There have been few attempts to obtain composite Ni-B coatings by electroplating nickel from a bath containing dispersed boron particles [7, 28, 29]. Both electrochemical and electroless deposition of Ni-B composite coatings from a borohydride bath were reported by Rajagopal [7]. The Ni-Ni_3B composite was formed after heating of nickel deposits containing dispersed boron particles to 300 °C. The Ni-Ni_2B composite resulted from subsequent heating to 400 °C. This composite exhibited better corrosion and wear resistance and improved mechanical properties compared to nickel or the electroless Ni-B composite without heat treatment. The properties of heat-treated electroplated Ni-B composites were similar to that of heat-treated electroless Ni-B composites. Electrodeposition of the composite Ni-B coatings in stirred heterogeneous system was reported in our earlier work [28]. The effect of deposition conditions as well as amount of boron powder in the plating bath on the boron content in composite Ni-B coatings was examined. The results showed that the content of incorporated boron particles increases with increasing amount of boron in the plating bath. It was also found that both the cathodic polarization potential of the composite electrolyte and the fraction of β-nickel (nickel hydride β phase) in the composite Ni-B film increased with increasing content of B microparticles in the plating bath. The potentiodynamic deposition method was more suitable for production of the composite coatings with high content of boron particles than the potentiostatic one. The composite films showed a uniform and homogeneous distribution of boron particles in nickel matrix without coagulation or sedimentation. The feasibility to fabricate the composite Ni-B coating with a uniform distribution of boron particles by electrochemical deposition was reported by Fedorchenko et al. [29]. The effect of heat treatment on wear resistance of Ni-B electrodeposits was examined. The formation of qualitatively new structures in Ni-B composites subjected to the diffusional annealing and enhancement of their physicomechanical characteristics was detected.

Since the studies on the electrodeposition of Ni-B composite coatings are few, the deposition behavior and various properties of electrodeposited Ni-B composites are not sufficiently understood yet. Surface modification is a well known way how to improve the performance of ordinary powder metallurgy parts. For this purpose, coating can provide materials with various combinations of surface-layer and core-region properties. Based on our previous study, the optimal conditions for electrodeposition of uniform composite Ni-B coatings with high content of boron were selected [28]. In the present work, the study is focused on investigation of the boron powder amount in plating bath on the corrosion resistance and hardness of composite Ni-B coatings. Moreover, the effect of heat treatment in a reducing atmosphere at three different temperatures (400 °C, 875 °C and 1120 °C) on the corrosion properties and microhardness was analyzed. Corrosion behavior of iron cylinders coated with nickel was considered as a reference.

2. EXPERIMENTAL

2.1 Electrolytical deposition of composite Ni-B coatings

The electrodeposition experiments of composite Ni-B coatings were carried-out using a Watts nickel plating electrolyte of following composition: 1.2 mol L^{-1} $NiSO_4.7H_2O$, 0.6 mol L^{-1} NaCl, 0.6 mol L^{-1} H_3BO_3 (pH = 2 ± 0.02). Crystalline boron powder particles (mesh: less than 40 μm) of Sigma Aldrich production in concentration of 2; 6 and 8 g L^{-1} in the plating electrolyte were used as the dispersion particles. Electroplating process was realized using cyclic voltammetry in 10 cycles within the potential range from – 350 mV to – 1500 mV (vs. Ag/AgCl (3 mol L^{-1} KCl)) at a polarization rate 12.5 mV/s at room temperature with rate of mechanical stirring 300 rpm.

All cyclic voltammetry experiments were carried out with an EcaStat potentiostat, model 110 V (Istran, Slovak Republic). The electrochemical cell consisted in a classical three-electrode set-up with an Ag/AgCl electrode (with 3 mol L^{-1} KCl solution) as a reference electrode, a platinum sheet as the counter electrode and a cylindrical iron compact as the working electrode. Cylindrical samples with diameter 1 cm and height 1 cm were prepared from iron powder material (water-atomized iron powder ASC 100.29, Höganäs, Sweden) of size fraction 63-200 μm by cold pressing at 600 MPa. The uncoated cylindrical iron samples were sintered for 60 minutes at 1120 °C in Marsh furnace in an atmosphere consisting of 90 vol.% N_2 and 10 vol.% H_2. To obtain adherent coatings, the surface of iron cylinders was before the coating deposition chemically activated and simultaneously degreased by etching in 10% aqueous solution of hydrazinium dihydrochloride for a period of 5 minutes, then rinsed by distilled water and acetone.

The boron content of the electrodeposited composite film was determined gravimetrically after dissolution of coated samples in diluted nitric acid (1:1) and boron micro-particles isolation whereas the nickel content was analyzed utilizing atomic absorption spectrophotometry (AAS) by atomic absorption spectrophotometer (Perkin Elmer).

2.2 Sintering of coated samples

The cylindrical iron samples coated with nickel or composite Ni-B films were isothermally sintered for 30 minutes at 400 °C, 875 °C and 1120 °C in Marsh furnace in a reducing atmosphere containing 90 vol.% N_2 and 10 vol.% H_2.

2.3 Analysis of the Ni–B coatings

Microscopic observations of the composite Ni-B films surfaces were made by the use of scanning electron microscopes (SEM, Tesla BS 340, Czech Republic, with EDX LINK ISIS microanalyser and JEOL JSM-7000F, Japan with analytical units EDX and EBSD Oxford Instruments), which provide unique qualitative and quantitative datasets suitable for chemical/elemental and phase compositions.

Microstructural analysis of cross-sections of the coated cylindrical samples was carried out by optical microscopy technique. Compacted samples for metallographic examination were cross-sectioned, mounted, ground, and polished using well established practices. Images were obtained with a light optical microscope (LOM, Neophot 32, Germany).

2.4 Electrochemical study of corrosion properties

Conventional three-electrode arrangement was used for potentiodynamic polarization experiments in 1 mol dm^{-3} NaCl solution (pH = 5.6). The electrolyte was de-aerated with gaseous argon for 10 minutes before measurement. Polarization curves were obtained by varying the applied potential from –1800 mV up to +100 mV (vs. Ag/AgCl (3 mol L^{-1} KCl)) at a scan rate 25 mV/s. The working electrode was a coated iron cylinder, the reference electrode was Ag/AgCl with 3 mol L^{-1} KCl solution and the counter electrode was a Pt sheet.

2.5 Determination of microhardness of composite Ni-B coatings

In a usual, macroscopic hardness test, the response of a large volume of material is investigated. This provides information on the effective, averaged properties of the material as a whole. On the other hand, measurements of microhardness may supply valuable data on local mechanical properties of microscopic volumes of material, or even of distinct material phases in multi-phase materials (individual material components). Here, the Vickers microhardness (HV 0.01) of samples was investigated using a micro hardness tester LECO LM-700AT.

If the indent’s mean diagonal is d, its depth is $d/7$ [30]. In the present experiment, the maximum value of diagonal was around 10 μm, hence the indentation depth was around 1.4 μm. It may be seen that the depth of indention is very low compared to the thickness of the coating. This implies that the measured value represents the hardness of the coating itself, with no effect of the substrate material.

For each sample, 50 indents were performed; the dwell time was kept 10 s. The indents were arranged in a grid pattern 5 x 5 with indent separation 40 µm at two distant locations on the surface of samples. Microhardness measurements made at different points of the specimen's surface enabled us to study the distribution of hardness values throughout the sample and to determine the range for these values, which reflects the microstructure of the examined material.

3. RESULTS AND DISCUSSION

3.1 Content of boron in composite Ni-B coating

The boron particles were entrapped between nickel layers gradually deposited during voltammetric cycles. The cross-section of the iron sample covered with the bare Ni and composite Ni-B coating gives Fig. 1. The amount of boron particles in the plating bath during the Ni-B coating deposition was 8 g L^{-1}. The samples in Fig. 1 were not heat treated.

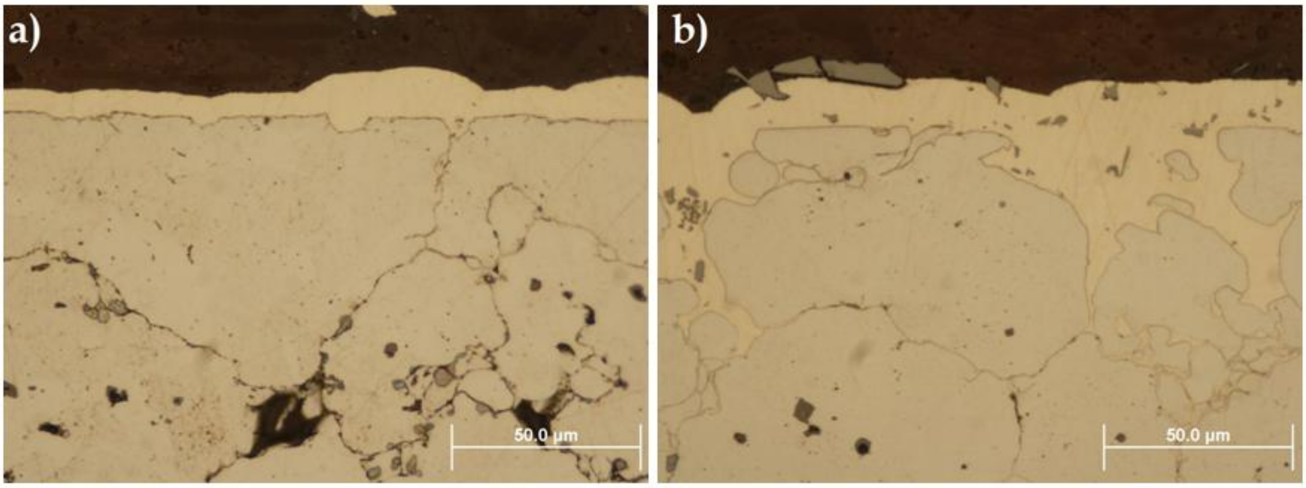

Figure 1. Optical micrograph of cross-section of the compacted cylindrical sample covered with the as-deposited bare Ni (a) and as-deposited composite Ni-B coating layer (b). The amount of boron particles in plating bath during the Ni-B coating deposition was 8 g L^{-1}.

Image in Fig.1b confirms the presence of boron particles embedded into the composite matrix. Some of boron grains were not covered completely and remained protruded over or situated on the surface of composite layer. The films are adherent and continuous. The pores on the surface of the iron substrate obviously facilitated the fixation of coating layer. The final thickness of the composite layers at given experimental conditions is about 10-20 µm. The composite coating layer filled the pores on the surface of iron substrate and sporadically reached the thickness up to 100 µm.

Content of boron and nickel in composite Ni-B coating as a function of boron micro-particles concentration in plating bath is listed in Table 1. The boron content of the electrodeposited composite film was determined gravimetrically and the nickel content was analyzed by AAS.

Both percentual content and total amount of boron particles included into the composite Ni-B deposits increased with increasing amount of boron micro-particles suspended in the plating bath. The total amount of deposited composite coating layer diminished slightly with increasing amount of boron particles in electrolyte solution indicating some inhibition effect of the boron particles on the nickel electrodeposition. The boron content in prepared composite Ni-B films was in the range from 12.8 wt.% to 24.3 wt.% depending on amount of boron micro-particles dispersed in plating bath during electrodeposition.

Table 1. Composition of composite Ni-B coating layers as a function of suspended boron micro-particles amount in plating bath. The boron content was determined gravimetrically after dissolution of coated samples and boron micro-particles isolation whereas the nickel content was determined by AAS.

Amount of B micro-particles in plating bath [g L^{-1}]	Amount of deposited composite Ni-B coating [mg]	Composition of composite Ni-B coating film			
		Ni		B micro-particles	
		[mg]	[wt.%]	[mg]	[wt.%]
2	3.9	3.4	87.2	0.5	12.8
6	3.8	3.0	78.9	0.8	21.1
8	3.7	2.8	75.7	0.9	24.3

3.2 Effect of heat treatment

The effect of heat treatment on the surface morphology, structure and the properties of the electrodeposited composite Ni-B films was analyzed and compared with characteristics of bare Ni film.

3.2.1 Surface morphology

The effect of heat treatment on the composite film structure is illustrated in Fig. 2. The SEM micrographs in Fig. 2 show the surface morphology of as-deposited Ni-B coating (Fig. 2a) on iron substrate and coating treated at 400 °C (Fig. 2b), 875 °C (Fig. 2c) and 1120 °C (Fig. 2d) in reducing atmosphere. The addition of boron particles did not affect the surface appearance of nickel coating layer, thus the bare nickel layer surface is not presented. The nodular like appearance of as-prepared Ni-B composite coating and coating heated at 400 °C is shown in Fig. 2b. The coating layer effectively reduced the surface inhomogeneity and porosity of the iron cylindrical substrate typical for powder metallurgy samples. Whereas the more rugged surface appearance of coated samples may be seen after heat treatment at higher temperatures 875 °C (Fig. 2c) and 1120 °C (Figs. 2d). The coating layer melts to some extend during the heat treatment and moves into the interparticle pores deeper inside the iron substrate, leading to the coating of individual powder particles on the surface of the cylindrical substrate that may be detected under the coating layer.

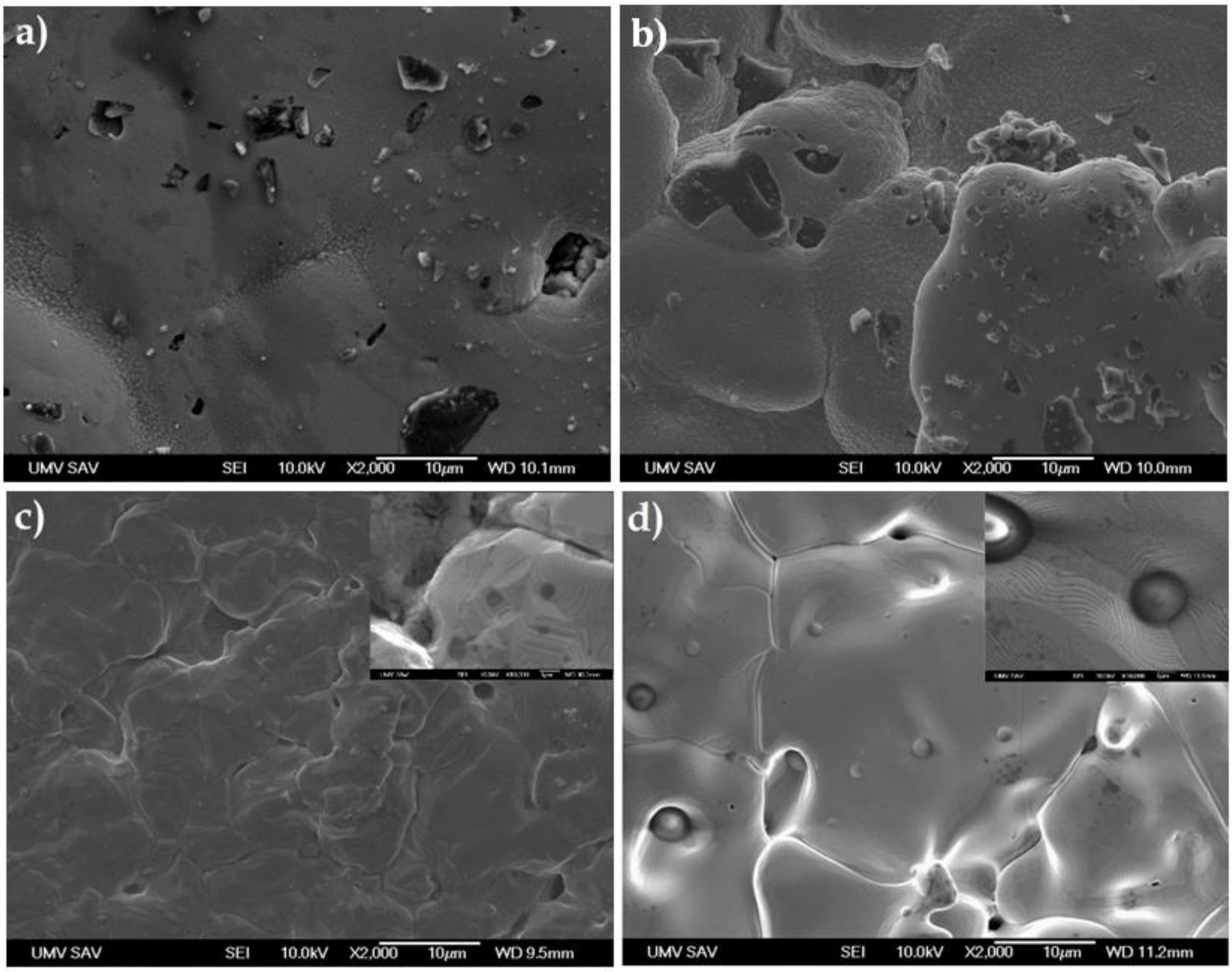

Figure 2. SEM micrographs of as-deposited Ni-B coatings (a, b) on iron substrate and coatings treated at 400 °C (c, d), 875 °C (e, f) and 1120 °C (g, h) in reducing atmosphere at lower (a, c, e, g) and higher magnification (b, d, f, h). The amount of boron particles in plating bath during the Ni-B coating deposition was 8 g L^{-1}.

The high temperature surface etching along crystallographic planes can be observed at higher magnification on the surface of samples heated at 875 °C and 1120 °C (inserts in Figs. 2c, d).

In the SEM micrographs of the coating layers a uniform distribution of isolated B micro-particles on the composite surface was obtained for as-deposited layers and heat treatment conducted at 400 °C (Figs. 2a, 2b). Relatively homogeneous distribution of boron particles in nickel matrix could be associated to electrochemical fabrication method in stirred heterogeneous system. On the contrary, the boron particles were not observed on the surface of deposits heated at higher temperatures (875 °C (Fig. 2c) and 1120 °C (Fig. 2d)). With increasing temperature the deeper sinking of boron particles into the nickel matrix was assumed. This indication was proved by SEM micrographs and line EDX analyses of cross-sections of coated cylindrical samples (Fig. 3).

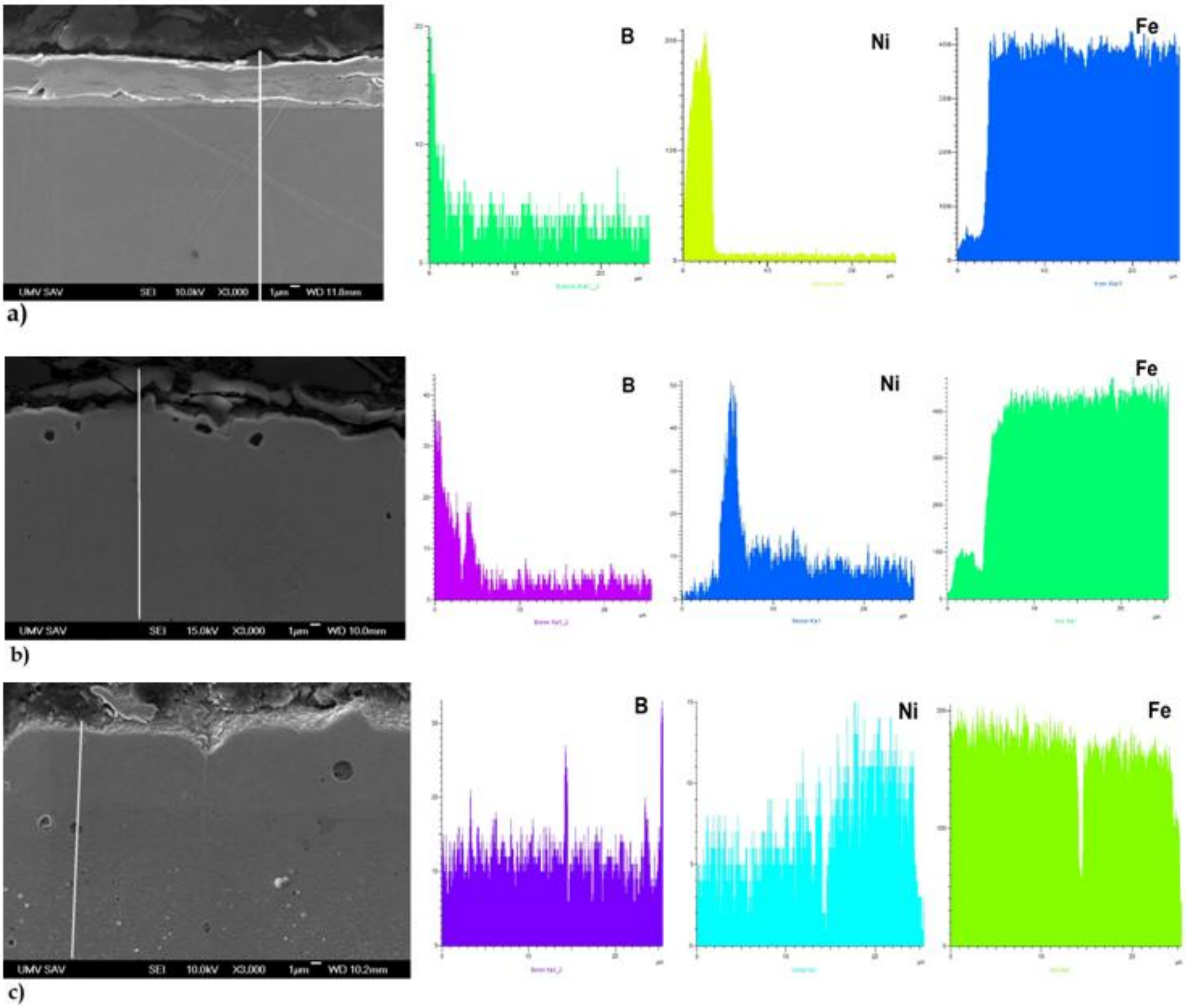

Figure 3. SEM micrographs of cross-sections of iron sample covered with composite Ni-B coating layer heat treated at 400 °C (a), 875 °C (b), and 1120 °C (c), together with X-ray line analyses of B, Ni and Fe in the marked line. The amount of boron particles in plating bath during the Ni-B coating deposition was 8 g L^{-1}.

3.2.2 Surface composition

The EDX mapping and point analysis of the composite Ni-B coatings proved the composite structure with presence of isolated B micro-particles in nickel matrix on the surface of as-plated coating and layer treated at 400 °C. The content of boron in composite coatings ranged between 14 wt.% and 20 wt.%. The change of boron content on the surface of the deposits heated at higher temperatures (875 °C and 1120 °C) was indicated. The boron content over the whole surface was significantly lower (up to 5 wt.%), but locally it reached 15-20 wt.%, indicating the presence of B particle in subsurface layer covered with a thin metallic layer. With respect to the coverage of EDX analyze, the thickness of this layer should be less that 3 μm. Higher boron content was detected also in the lines at the grain boundaries. The average compositions of the composite coatings as a function of the temperature of heat treatment are summarized in Table 2. Approximately 30-40 EDX point analyses were made on each sample, at the different regions of the substrate, to compute the average composition listed in Tab. 2.

Uniformly distributed Ni and Fe were detected in the surface layer of all samples. The amount of Fe increased with increasing temperature of thermal treatment. The highest oxygen content was detected in as-deposited sample. The content of oxygen in heat treated coating layers was lower due to the reduction atmosphere during sintering.

Table 2. Average composition of composite Ni-B coating over the whole surface as a function of the heat treatment temperature. The amount of boron particles in plating bath during the Ni-B coating deposition was 8 g L^{-1}. The average composition was computed from EDX point analyses (approximately 30-40) taken from different regions on the sample surface.

Temperature [°C]	Composition of composite Ni-B coating film [wt.%]				
	Ni	Fe	B	O	Ni : Fe
0	67.3	9.90	17.7	5.10	6.8 : 1
400	67.6	14.4	16.2	1.90	4.7 : 1
875	42.7	51.2	4.70	1.50	0.8 : 1
1120	31.6	62.3	4.90	1.30	0.5 : 1

SEM observation and EDX analysis indicate that B is not dissolved in the Ni or Ni-Fe matrix and still keeps the morphology of the particles even at higher alloying temperatures. The SEM micrographs of cross-sections of iron samples with composite Ni-B coating layers heat treated at 400 °C, 875 °C and 1120 °C together with EDX line analyses are presented in Fig. 3. The adherent composite Ni-B layer on the surface of iron cylinder with evident interface between the coating layer and substrate is shown on the cross-section of sample heated at 400 °C (Fig. 3a). The thickness of composite layer is 4-5 μm. Change in composition of Ni-B layer is presented by EDX line analysis (Fig. 3a). Although the major component of composite layer is nickel with its maximal content at 4-5 μm from the surface, high boron content was detected on the top surface of composite layer, approximately 1 μm thick, which corresponded to the boron particle on the SEM image. Iron content increased rapidly along with decrease in nickel content. SEM micrographs as well as EDX line analyses on cross-sections of iron samples with composite Ni-B coating layers heat treated at 875 °C (Fig. 3b) and 1120 °C (Fig. 3c) show the above mentioned sinking of boron particles into the substrate and indicated that iron diffused during the heat treatment into the nickel and nickel diffused into the iron substrate. While the boron particles could be detected on the surface as well as in the depth of about 4-5 μm from the surface on the sample heated at 875 °C, the sharp boron maxima in the depth of about 14 μm and 25 μm were observed in the case of sample heated at 1120 °C. Moreover, increased boron content was registered in the whole analyzed region of the sample (approximately 25 μm) indicating partial dissolution and/or diffusional annealing of boron in substrate during heat treatment. Formation of nickel boride inclusions of varying sizes after diffusional annealing of composite Ni-B electrolytical coatings in the temperature range 950-1000 °C was reported by Fedorchenko et al. [29]. But structural analysis would be necessary to prove this assumption. The interface between the coating layer and substrate was less apparent for samples heat treated at elevated temperatures (875 °C and 1120 °C). The maximum nickel content in the depth about 6-7 μm and 18 μm from the surface was registered on the samples heated at 875 °C and 1120 °C, respectively. The presence of iron in the whole analyzed region was detected in the case of sample heated at 1120 °C, however the content of iron was lower as compared to other heat treated samples.

3.2.3 Corrosion behavior

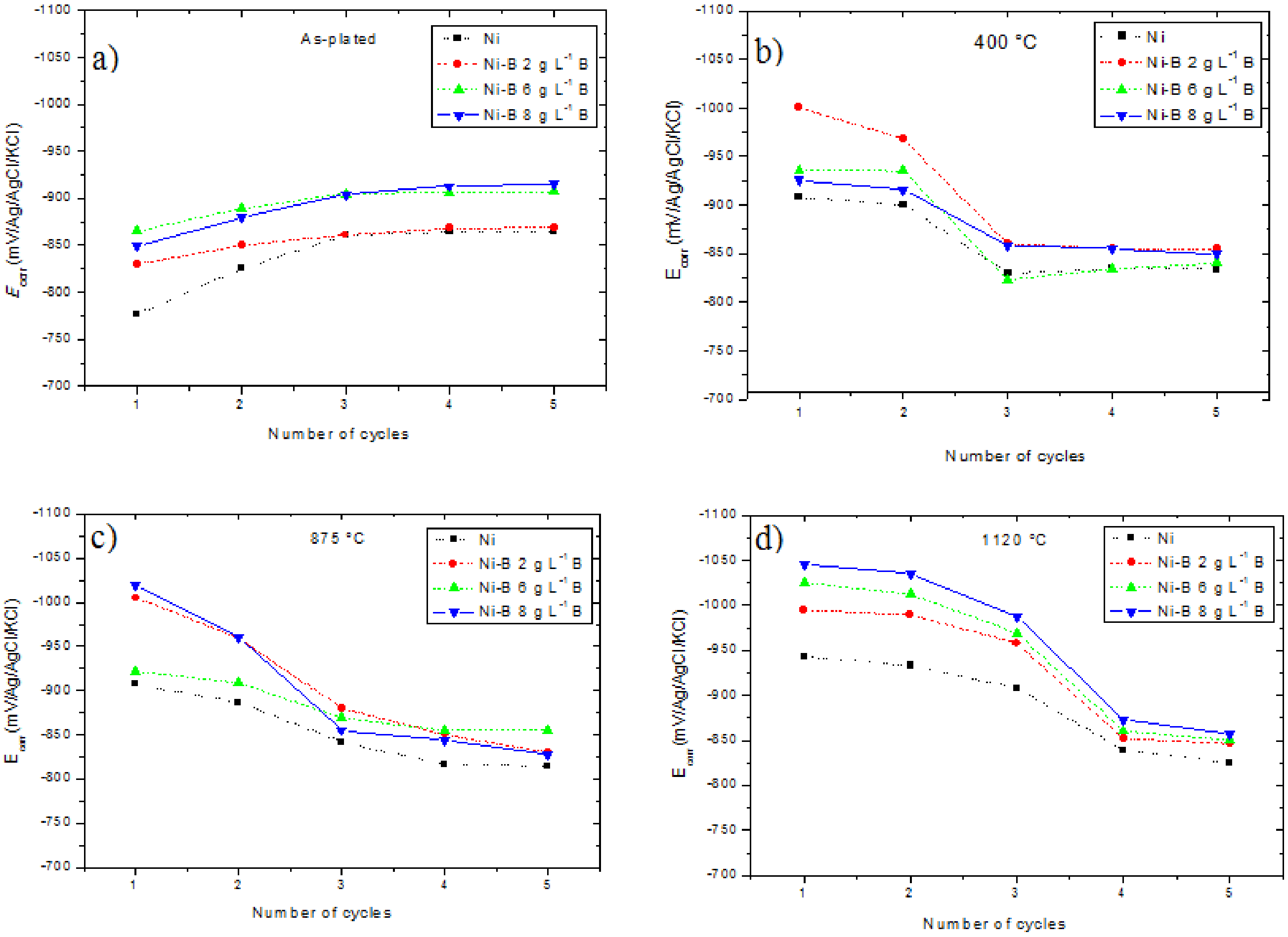

Figure 4. The values of corrosion potentials (vs. Ag/AgCl (3 mol L^{-1} KCl)) of bare Ni and composite Ni-B coating determined from potentiodynamic polarization curves in 1 mol L^{-1} NaCl solution as a function of boron content and heat treatment temperature: as-plated (a), heat treated at 400 °C (b), 875 °C (c) and 1120 °C (d).

Effect of boron content and heat treatment on the corrosion properties of the iron cylindrical samples with composite Ni-B coatings was investigated employing potentiodynamic polarization method in 1 mol L^{-1} NaCl solution. Five cycles of anodic potentiodynamic polarization were registered for every coated sample.

First, the corrosion potentials (E_{corr}) of as-plated samples with different content of boron in plating bath: 2 g L^{-1}, 6 g L^{-1} and 8 g L^{-1} were determined. A sample coated with the nickel film without the boron particles was examined as the reference state. All values of corrosion potential for five cycles are plotted in Fig. 4a. The corrosion resistance of the samples coated by neat Ni layer was almost in all cases better than the corrosion resistance of samples coated by the composite Ni-B film. The observed results may be assigned to the incoherence of Ni film in the vicinity of boron micro-particles.

For the as-plated samples it was found, that the corrosion resistance decreases with increasing amount of boron content as well as with increasing number of cycles (Fig. 4a). The values of E_{corr} in the first cycle are in the range from -770 mV to -870 mV (vs. Ag/AgCl (3 mol L^{-1}KCl)) for the as-plated samples. The passive layer on the coating film top-surface, which protected the coated sample to some extent, was dissolved during the first two-three cycles of anodic polarization. Thereupon in next cycles the samples showed a higher tendency to corrode. Moreover, the content of iron increases in any further exposed layer of examined sample with increasing distance from the top surface.

The adverse trend was registered for the heat treated samples. The corrosion potentials for five cycles of samples heat treated at 400 °C, 875 °C and 1120 °C are plotted as a function of boron amount in the plating bath in Figs. 4b, c and d, respectively. The corrosion potentials of the coated samples shifted to more positive values with increasing number of anodic polarization cycles. This positive shift gives indication about the decreased corrosion susceptibility of the coated samples. Moreover, the noticeable negative shift of E_{corr} for heat treated samples compared to as-plated samples was observed in first and second polarization cycles, while values of E_{corr} for the last two cycles remained practically unvaried. This shift moderately rose with increasing temperature. Observed deterioration of corrosion resistance could be assigned predominantly to the increase of iron content in surface with increasing sintering temperature as well to the elimination of passive layer from the sample surface during its sintering in the reducing atmosphere. This represents the considerable distinction in initial conditions before the first cycle of anodic polarization of sintered and as-prepared samples. Moreover, the changes in microstructure of the compacted samples along with the creation of interparticle connections and diffusion interactions between Ni and Fe resulted in formation of solid solutions may be induced by the thermally activated diffusion processes during the sintering. As a consequence the residual iron may be found on a sample surface. Some precipitation processes can be supposed in course of the cooling.

These findings indicate that the composite Ni-B layer increased slightly the susceptibility of samples to be attacked by the chloride ions compared to bare Ni coating layer. Further increase in corrosion susceptibility of coated samples was associated with heat treatment. It was found that the corrosion resistance decreased with increasing temperature. Generally, no significant correlation between the amount of boron content in the plating bath and the corrosion properties of coated cylindrical samples was observed (Figs. 4a - d).

The increase in corrosion susceptibility of electroless Ni-B coating films after heat treatment at 250 °C was reported by Abdel Hamid et al. [16]. This was attributed to the transformation of the structure from amorphous to microcrystalline form. On the contrary, the decrease in corrosion susceptibility of the same samples after heating at 400 °C due to the completely formation of Ni_3B phase was observed by these authors. The improvement of corrosion resistance of electroless Ni-B coating layers with increase of boron content from 4.5 to 8 wt.% was observed by Anik et al. [20].

Typical polarization curves of the coated iron cylindrical samples in 1 mol L^{-1} NaCl solution at room temperature shows Fig. 5. Similar polarization mechanism was observed for bare Ni and composite Ni-B coatings in corrosive media for all five polarization cycles and for all temperatures. Thus only few typical polarization curves were selected for demonstration. It can be seen that co-deposition of boron particles decreased slightly the corrosion resistance of composite Ni-B coatings as compared to bare Ni coatings.

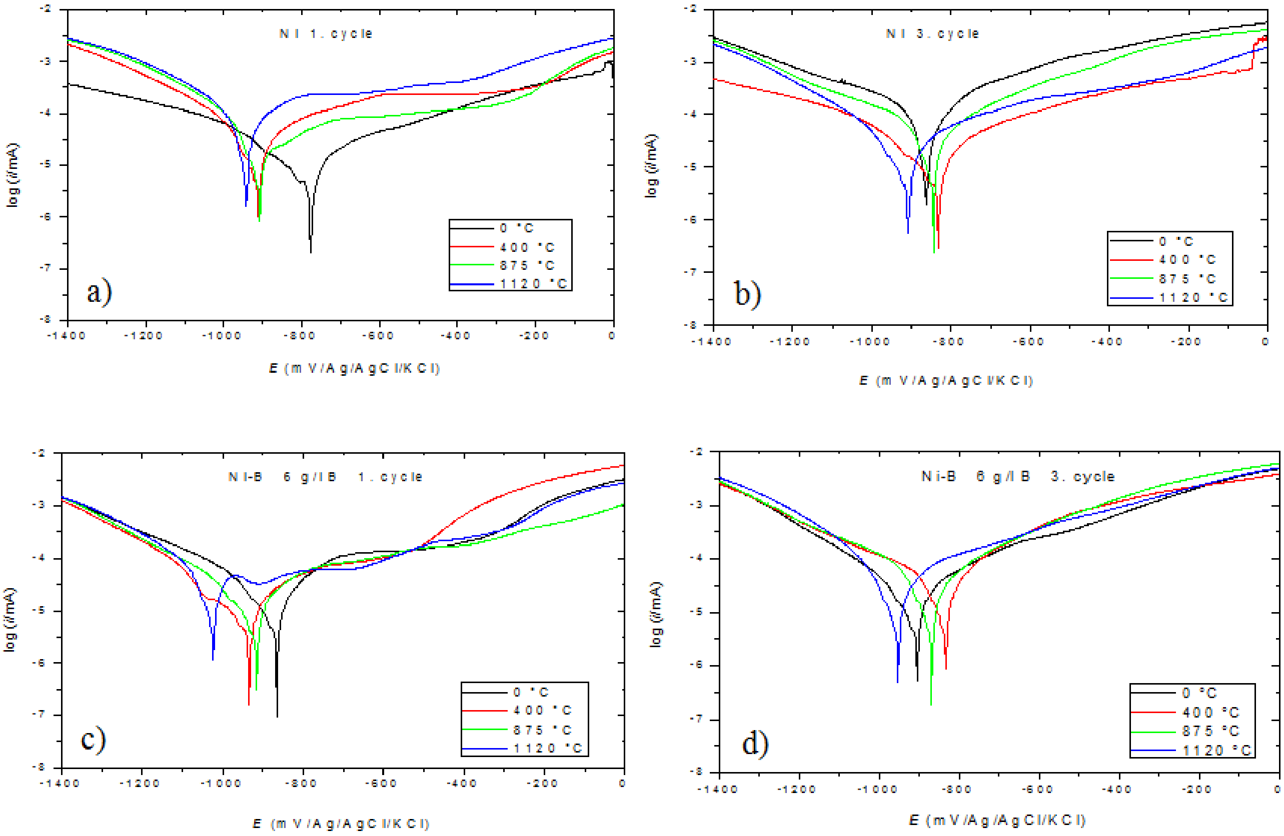

Figure 5. Typical polarization Tafel plots for bare Ni and composite Ni-B coating in 1 mol L^{-1} NaCl solution as a function of heat treatment temperature: Ni coating layer, first polarization cycle (a), Ni coating layer, third polarization cycle (b), Ni-B composite coating layer, first polarization cycle, 6 g L^{-1} B (c), Ni-B composite coating layer, third polarization cycle, 6 g L^{-1} B (d).

The plots for iron samples coated with bare Ni (Fig. 5a) and Ni-B composite layer (Fig. 5c) for first polarization cycle show that the polarization anodic and cathodic Tafel lines are shifted to higher polarization current values with increase in heat treatment temperature. No dependence of boron content or heat treatment temperature on polarization current was observed for curves for the other polarization cycles.

Low anodic current was observed for bare Ni coating (except as-plated sample) as well as for composite Ni-B coatings for all temperatures in the potential range from corrosion potential to about -400 mV (vs. Ag/AgCl (3 mol L^{-1} KCl)) on curves for first polarization cycle (Fig. 5a, c). The current increase at more positive potential indicated the slow breakdown of the passive films. No passivation tendency was observed for all polarization cycles in the measurement range.

The similar results were presented for electroless Ni-B coatings by Bekish et al. [10]. They have observed the shift of the corrosion potential to the negative direction in consequence of boron doping and the breakdown of the passive layer due to the interaction of the aggressive chloride ions with the passivated surface during the anodic oxidation of the film.

Significant increase in corrosion resistance of steel samples after electroless deposition of Ni-B coating layer was observed by A.F. Kanta et al. [18]. Further increase in corrosion resistance was obtained after heat treatment at 400 °C. The polarization curves of as-plated as well as of heat treated Ni-B layer showed no passive behavior.

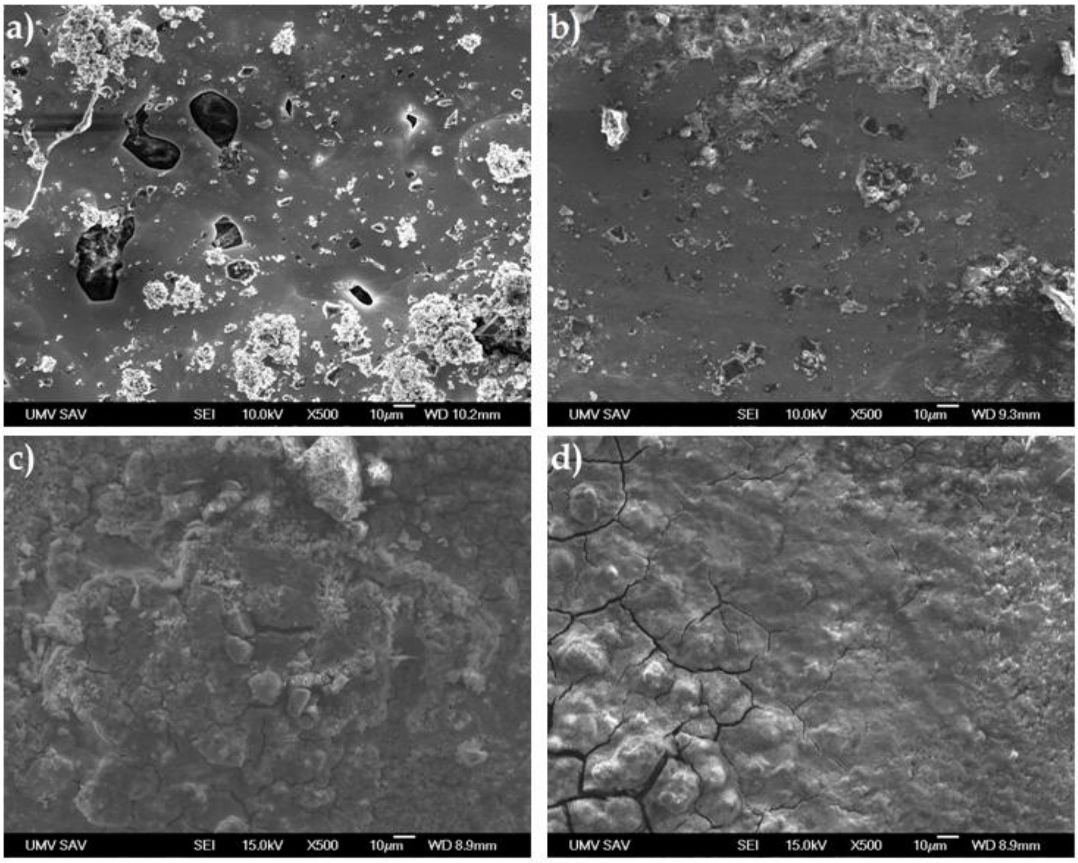

Figure 6. SEM micrographs of corroded surfaces of composite Ni-B films thermally untreated (a, b) and heat treated at 400 °C (c, d), 875 °C (e, f) and 1120° C (g, h) after 5 cycles of anodic potentiodynamic polarization in 1 mol L^{-1} NaCl solution and details of corroded surface at different magnification. The amount of boron particles in plating bath during the Ni-B coating deposition was 8 g L^{-1}.

Figure 6 shows the typical corroded surfaces of composite Ni-B films thermally untreated (Fig. 6a) and heat treated at temperatures 400 °C (Fig. 6b), 875 °C (Fig. 6c) and 1120 °C (Fig. 6d) after 5 cycles of anodic potentiodynamic polarization in 1 mol L^{-1} NaCl solution.

The corroded surfaces of as-deposited sample and the sample sintered at 400 °C are markedly smoother with lower damage than that of the heat treated samples at temperature 875 °C and 1120 °C. Only a low degree of flaking and a few fine craters were observed on the corroded surfaces of an as-deposited sample and a sample sintered at 400 °C. A higher degree of corrosion pits formation and cracking occurs on the distinctly rougher, damaged surface of coating layers heat treated at 875 °C and 1 120 °C.

The average element content of composite Ni-B coatings over the whole surface after corrosion test is listed in Table 3 as a function of the heat treatment temperature. The significantly higher amount of O and slightly lower amount of B was detected after corrosion when compared with surface composition before corrosion test (Tab. 2), meaning that there is a metal oxide forming on the corroded surface. Moreover, the considerable decrease of nickel to iron ratio was observed (Tab. 3). This could be probably associated with higher amount of iron corrosion products due to higher content of iron in the coated sample and with lower corrosion resistance of iron as compared to nickel. Furthermore, diffusion interaction of Fe and Ni may cause the formation of Fe rich phases in Fe-Ni solid solution after sintering, which represented the corrosion active sites. The formation of metallic (Ni, Fe) corrosion products such as chlorides, oxides or hydrates together with adsorption of intermediate species may occur on the particle surface.

It can be concluded that the corrosion resistance of composite Ni-B coating layers was lower than that of bare Ni coating layer and that the heat treatment significantly reduced the corrosion resistance of composite Ni-B coatings due to the Fe-Ni phase formation. The effect of boron particle loading on the corrosion properties of composite layers was not observed.

Table 3. Average compositions of composite Ni-B coatings over the whole surface after corrosion test as a function of the heat treatment temperature. The amount of boron particles in plating bath during the Ni-B coating deposition was 8 g L^{-1}. The average composition was computed from EDX point analyses (approximately 30-40) taken from different regions on the sample surface.

Temperature [°C]	Composition of composite Ni-B coating film [wt.%]				
	Ni	Fe	B	O	Ni : Fe
0	48.5	23.5	14.1	13.9	2.1 : 1
400	39.4	34.4	9.70	16.5	1.1 : 1
875	27.2	45.4	2.80	24.6	0.6 : 1
1120	12.7	55.5	3.60	28.2	0.2 : 1

3.2.4 Mechanical behavior

Microhardness values of iron cylindrical samples coated with bare Ni and composite Ni-B layer were compared.

The properties of coating from pure nickel were affected by the heat treatment only minimally (Tab. 4 and Tab. 5, Fig. 7). For all samples, as-deposited or heat treated, the observed microhardness values were lying in a very narrow interval and the frequency of occurrence of a particular microhardness value clearly peaked for microhardness around 3 GPa (Fig. 7) on the sample surface and about 1.3 GPa on the cross-section. Generally, very slight increase of microhardness with increasing temperature of heat treatment was observed.

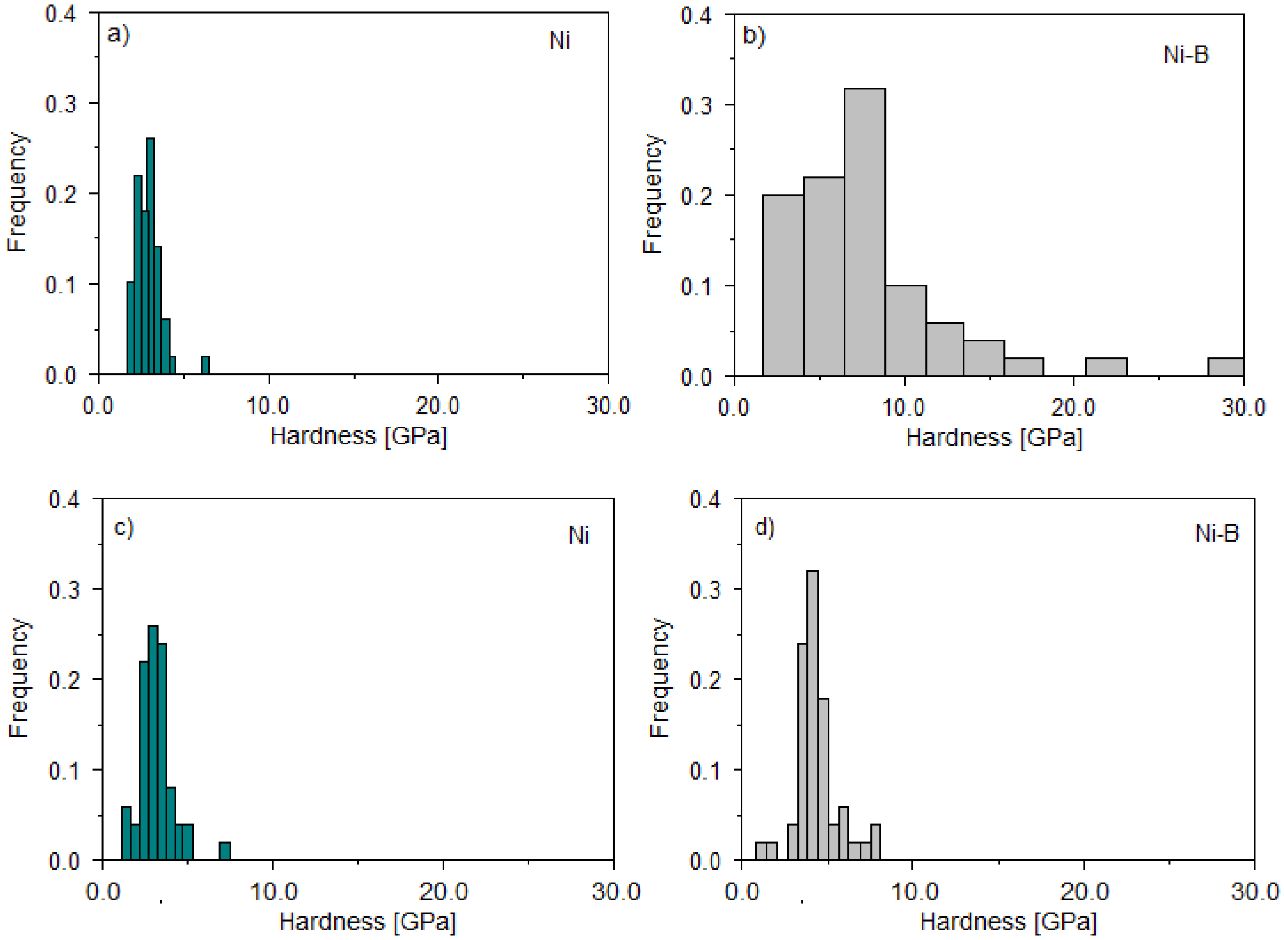

Figure 7. The values of microhardness HV 0.01 on the surface as a function of frequency of occurrence for as-deposited samples: bare Ni (a), composite Ni-B (b), and heat treated samples at 1120 ^{o}C: bare Ni (c), composite Ni-B (d). The amount of boron particles in plating bath during the Ni-B coating deposition was 6 g L^{-1}.

The properties of composite Ni-B coatings were affected by the heat treatment significantly (Tab. 4 and Tab. 5). For as-deposited coating, the interval of observed microhardness values was quite wide and the most often occurring microhardness value was about 7 GPa on the sample surface (Tab. 4) and about 1.4 GPa on the cross-section (Tab. 5). The heat treatment significantly narrowed the range of observed microhardness values and the most frequently occurring microhardness value on the sample surface lowered to about 3~4 GPa. This could be attributed to the mentioned sinking of boron particles into the nickel matrix due to the heat treatment. The effect of the value of used temperature was moderate. The values of microhardness on the cross-section for pure Ni coating were not affected by the heat treatment (Tab. 5).

Table 4. Characteristics of the distribution of hardness values measured on the surface of coated samples for loadings of indenter of 10 g (0.1 N). The amount of boron particles in plating bath during the Ni-B coating deposition was 6 g L^{-1}.

Coating layer	HV [GPa]			
	0 °C	400 °C	875 °C	1120 °C
Ni	2.9 ± 0.8	3.0 ± 0.7	3.0 ± 1.0	3.2 ± 1.0
Ni-B	7.8 ± 5.0	3.3 ± 1.3	4.6 ± 1.0	4.4 ± 1.3

The value of microhardness on the cross-section for composite Ni-B coating remained nearly unchanged for sample heated at 400 °C (about 1.2 GPa) and next increased to about 2.4 GPa, and about 2.8 GPa for samples heat treated at 875 °C and 1120 °C, respectively (Tab. 5). This could be associated with increased boron content over the cross-section of samples heated at 1120 °C observed in Fig. 3c.

Table 5. Characteristics of the distribution of hardness values measured on the cross-section of coated samples for loadings of indenter of 10 g (0.1 N). The amount of boron particles in plating bath during the Ni-B coating deposition was 6 g L^{-1}.

Coating layer	HV [GPa]			
	0 °C	400 °C	875 °C	1120 °C
Ni	1.3 ± 0.1	1.4 ± 0.1	1.4 ± 0.2	1.3 ± 0.2
Ni-B	1.4 ± 0.3	1.2 ± 0.1	2.4 ± 0.4	2.8 ± 0.6

These findings indicate that the increase in microhardess of coating layer resulted from the presence of boron microparticles together with the heating at higher temperatures.

It was reported by several researchers that the maximum hardness of electroless Ni-B deposits can be attained in 1 h at about 400 °C or in 10 h at 260 °C. The ability to maintain their hardness under elevated-temperature service conditions increases with increasing boron content, but decreases rapidly above 385 °C [8,12,21,23,31]. The increase in coating hardness of electroless Ni-B coatings with annealing temperature was observed by Abdel Hamid et al. [16] with the highest value for annealing temperature of about 300 °C.

The significant effect of heat-treatment on the hardness of electrodeposited Ni-B films was reported by Ogihara et al. [27]. They found that the heat-treatment at lower than 300 °C enhanced the film hardness because of the formation of Ni_3B and Ni_2B alloy structure. Hardness of Ni-B films heat-treated at higher than 350 °C decreased since crystallization of Ni metal occurred.

4. CONCLUSIONS

The effect of the boron powder amount in plating bath on the corrosion resistance and hardness of composite Ni-B coatings produced by electrodeposition in stirred heterogeneous system was investigated. Moreover, the effect of heat treatment in a reducing atmosphere at 400 °C, 875 °C and 1120 °C on the corrosion properties and microhardness was evaluated.

The microscopic observations revealed that the heat-treatment influenced the surface appearance of the layers obtained. The semispherical shape of nodules in as-plated film and in coating heated at 400 °C changed to the rather edginess, protrusive appearance after heating at 875 °C and 1120 °C. The relatively homogeneously distributed boron particles may be observed on the surface of as-prepared Ni-B composite coating and coating heated at 400 °C.

The surface composition of heated deposits changed. The proportion of iron to nickel increased with increasing sintering temperature. Moreover, it was found that the heat treatment resulted in broadening of coating layer with formation of Fe-Ni phases causing the reduction of corrosion resistance due to the higher iron content in the surface layer.

The corrosion resistance of composite Ni–B films was not affected by the boron content.

The improvement of microhardness due to the presence of boron particles in coating layer was observed. The highest increase in composite Ni-B coating microhardness as compared with bare Ni coating microhardness was detected for as-plated sample. The heat treatment of samples with composite coating layer caused the lowering of microhardness values on the surface while the increasing of microhardness values on the cross-sections.

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