The Effect of B_4C Nanoparticles on the Corrosion and Tribological Behavior of Electroless Ni-B-B_4C Composite Coatings

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In this study, the electroless method was successfully used to deposit composite coatings containing B_4C nanoparticles on Ck45 carbon steel. The characteristics of coatings were investigated with the X-ray diffraction (XRD) and scanning electron microscopy (SEM). The hardness of coatings was measured by Vickers micro-hardness test with a load of 1 N. The hardness of the composite coating of Ni-B-B_4C was about 870 Vickers, which increased to 1350 Vickers after heat treatment at 400°C for 1 hour, which was much more than for Ni-B coating and Ck45 steel. The wear test was carried out using the pin-on-disk test technique. The results indicated an improvement in the wear resistance of Ni-B-B_4C composite coatings compared to that of Ni-B and Ck45. The results obtained from the Tafel polarization test indicated an increase in the corrosion resistance of Ni-B-B_4C composite coatings compared to that of Ni-B coatings and Ck45 steel.

Keywords: nano-B_4C, electroless deposition, composite coating, tribological behavior, corrosion.

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INTRODUCTION

Corrosion and wear are among the most important reasons for destruction of industrial parts. As a low price and accessible metal, CK45 steel has applications in industry, which are numerous but still limited due to its wear and corrosion resistance [1]. Hence, extensive bodies of research have been carried out in order to decrease the costs resulting from corrosion and wear. The electroless method is one of the best and most favorable methods in decreasing corrosion and increasing wear resistance as well as increasing the lifetime of the parts [2–4]. In the electroless coating method, metal sedimentation is done by the reduction of metal ions in the bath containing a reducing agent, without employing an external current [3]. Due to their unique properties such as high adhesion to the substrate, the uniformity of thickness, hardness, and high wear resistance, nickel–phosphorus electroless coatings have occupied an important and extensive position in industrial applications [5–8]. Today, the nickel-boron electroless coatings have become more common than nickel-phosphorus coatings due to higher hardness and wear resistance [9–11]. The obtained results of other researchers show that while electroless coatings have a higher hardness and wear resistance in comparison with Ni-P coatings, their corrosion resistance is lower due to higher degrees of porosity [11].

Inserting particles to electroless coatings is done in order to improve their chemical and mechanical properties [12–15]. In the past, composite electroless coatings were produced by adding micron particles to the coatings, but those coatings were often unable to meet the industrial requirements. The conducted research into the composite coatings containing particles such as B_4C, SiC and Si_3N_4 illustrated that although composite coatings generated by micron-sized particles have higher hardness and wear resistance compared to those of non-composite coatings, there can be seen a dramatic decrease in the corrosion resistance of composite coatings because of particles known as impurities [16–18].

With the developments in nano-science and the production of nanoparticles, the production of electroless coatings containing nanoparticles with a prolonged lifetime and higher hardness and corrosion resistance was taken into consideration [19–20]. The composite coatings developed by other researchers comprise particles such as TiO_2, Al_2O_3, ZnO and CNT that not only create a hard and wear resistant surfaces but also have a higher corrosion resistance than non-composite coatings [19, 21–23]. With its unique properties such as high hardness (*about 9.3 Mohs scale*), excellent chemical resistance, high melting point and low density, B_4C has a high potential to be used in composite coatings [14, 16, 24]. By filling the pores in electroless coatings, nanoparticles cause a considerable increase in hardness and wear resistance in addition to an increase in the corrosion resistance [19].

To date, there have been very limited bodies of research with regard to Ni-B composite coatings, this is why the objective of the present study was to investigate the impact of boron carbide nanoparticles

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on the hardness, the wear and corrosion resistance of Ni-B coatings.

EXPERIMENTAL

Specimens of Ck45 steel with the dimensions of 15×15×5 mm were prepared and sandblasted by silicon particles with an average size of 100 microns in order to increase the adhesion of the coating to the substrate before the coating process. To deposit Ni-B-B_4C composite electroless coatings, a bath with chemical composition according to Table 1, containing 1.5 g/l B_4C powder with an average size of 100 nano-meters, was used.

Table 1. Bath chemical composition and operating conditions of electroless Ni-B-B_4C composite coating

Bath composition	Quantity
Nickel Chloride	20 g/l
Sodium Borohydride	1 g/l
Ethylenediamine (98%)	64 ml/l
Sodium Hydroxide	40 g/l
Thallium Acetate	1 mg/l
Parameter	Conditions
pH	12
Temperature	90 ± 1°C

The bath was placed in an ultrasonic for 2 hours in order to make the particles even. The pH of the electroless bath was 12 and the coating temperature was 90°C. In order to prevent the sedimentation of B_4C particles and to distribute them uniformly in the bath, two stirrers with different turning directions were used. Before adding the B_4C powder to the bath, it was necessary to pre-treat the powder. The preparation stages are shown in Fig. 1.

In order to study the effect of the heat treatment on Ni-B-B_4C composite coatings, a number of coated samples were heat-treated at 400°C for 1 hour in the argon atmosphere. In order to survey the surface morphology and phases of samples, the scanning electron microscopy (SEM) and X-Ray diffraction (XRD) were used. The hardness of coatings was measured by the Buehler-Vickers micro-hardness test with a load of 1N. For the evaluation of tribological behavior of samples, a pin-on-disc wear set was used. In all tests, a 52100 steel pin with a hardness of about 65RC and a diameter of 5mm was used as the abrasive. The wear test was conducted in the air atmosphere with a slippage velocity of 0.1 $m.s^{-1}$, under a force of 5N and maximum slippage distance of 1000 meters. The corrosion resistance was studied by the Tafel polarization test in 3.5% NaCl solution. The samples were in contact with the electrolyte at a surface of 1 cm^2. The platinum electrode was used as the reference electrode and the saturated calomel electrode (SCE) was used as the reference electrode. Via the extrapolation method, the Tafel potential and corrosion current density were extracted from the Tafel curves. The duration for equilibrium was chosen as 1 hour for all samples.

RESULTS AND DISCUSSION

Coating morphology and structure

Figures 2a and 2b show the morphology of the electroless Ni-B and Ni-B-B_4C composite coatings deposited on the Ck45 steel substrates. These Figures illustrate the cauliflower structure of the coatings. The electroless Ni-B coatings have many pores. The existence of B_4C particles causes new nucleation areas, which, in turn, makes the structure finer and the porosity less. Figure 2c is indicative of B_4C particles and their distributions in the Ni-B coatings.

Figure 2d shows the cross section of the Ni-B-B_4C composite coating layer on the surface. As seen in this Figure, the coating deposited on the substrate is very uniform and well adhered to the substrate.

The thickness of the Ni-B-B_4C composite coating layer is 30 µm. The dark areas on the coating are indicative of B_4C particles accumulated in the coating in the form of agglomerations.

Figure 3 illustrates the XRD patterns of the Ni-B-B_4C composite coatings in as-deposited and heat-treated states at 400°C for 1 hour. This Figure shows that the Ni-B-B_4C composite coating has an amorphous and semi-crystal structure before heat treatment [24]. The peaks obtained for the as-deposited state have been obtained from overlapping a wide matrix peak in dispersion angles from 35 to 55 and two smaller peaks. The wide peak is related to the amorphous phase of the coating and small peaks are related to the nano-crystal phase of the nickel. The results of the XRD of the heat-treated Ni-B-B_4C composite coating indicated a complete change in the structure of this coating compared to that in the as-deposited state; that is, instead of the amorphous phase, clear peaks are noticed from the nickel-crystal phase (with the FCC lattice) and Ni_3B (with the orthorhombic lattice) along with B_4C peaks in the diffraction pattern.

Hardness of coatings

The hardness of the electroless Ni-B-B_4C composite coating in the as-deposited state is equal to 870 Vickers, which means a considerable increase compared to Ni-B coating (620 Vickers) and Ck45 steel (325 Vickers), as a result of adding B_4C particles to the matrix. Apart from very high inherent hardness, B_4C particles serve as an obstacle in the coating and cause a decrease in the plastic deforma-

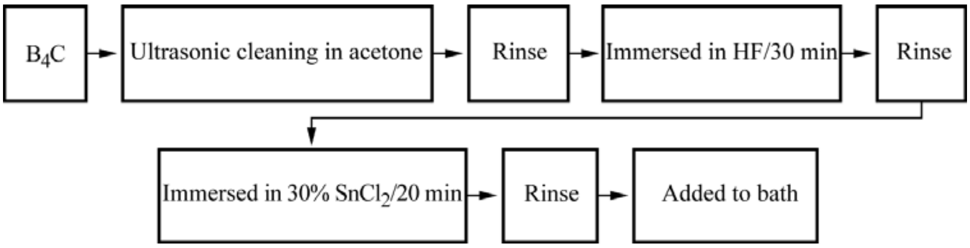


Fig. 1. Steps of preparation of B_4C.

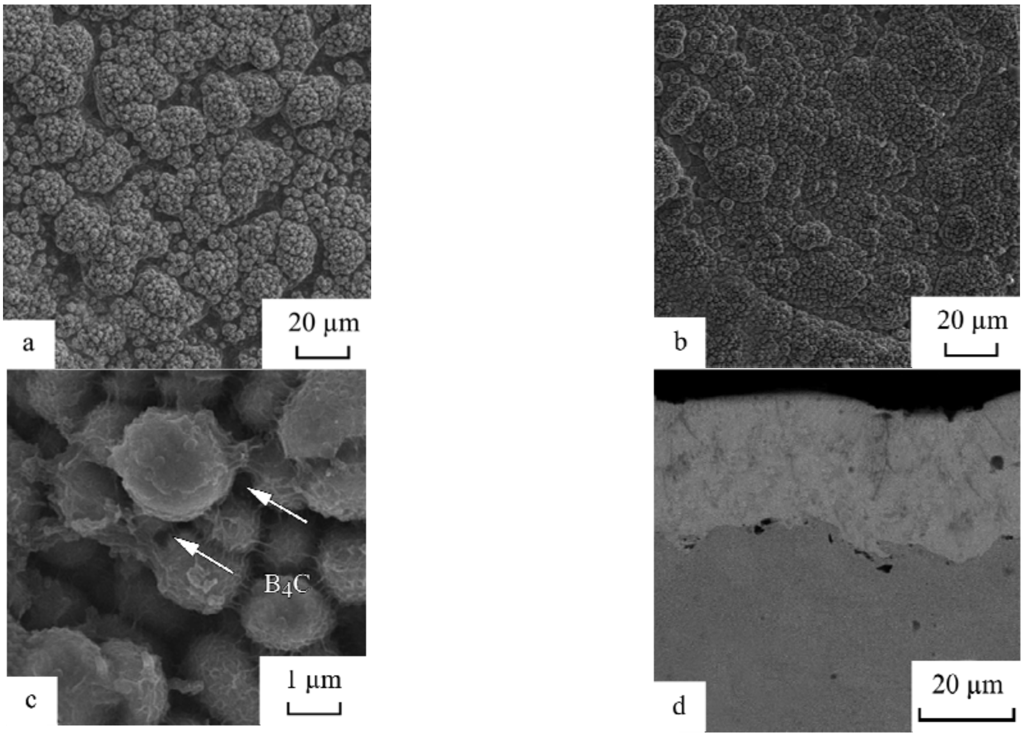


Fig. 2. SEM surface images of Ni-B and Ni-B-B_4C coatings:
(a) Ni-B; (b and c) Ni-B-B_4C; (d) Ni-B-B_4C cross-section morphology.

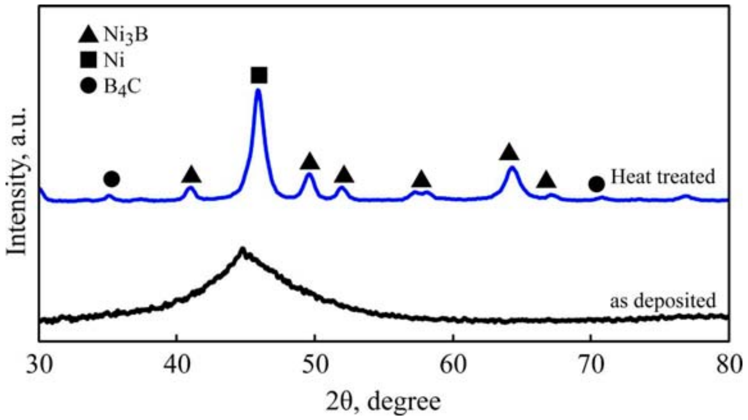


Fig. 3. XRD patterns of Ni-B-B_4C composite coatings.

tion in the Ni-B coating matrix ultimately increasing hardness of the coating. Moreover, heat treatment of the Ni-B-B_4C composite coating at 400°C for 1 hour has caused an increase of hardness up to 1350 Vickers. This increase in hardness is related to the precipitation of the Ni_3B inter metallic table phase during the crystallization of the amorphous phase. It has been reported that Ni_3B phase has a high firmness and shear module, which brings about some effect on the electroless coating hardness [10]. The image of the microhardness test is presented in Fig. 4.

Coating wear

Results obtained from wear tests as the weight loss are summarized in Fig. 5. The data are indicative of improvements in the wear resistance of Ck45 steel after the employment of Ni-B and Ni-B-B_4C composite coatings with a thickness of 30 µm. The attained results show that electroless Ni-B-B_4C composite coatings have a higher wear resistance compared to that of Ni-B coatings under two conditions: both as-plated and at heat treatment.

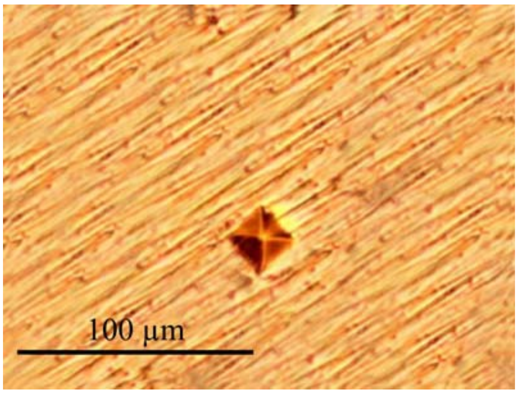


Fig. 4. Image of microhardness of Ni-B-B_4C-HT.

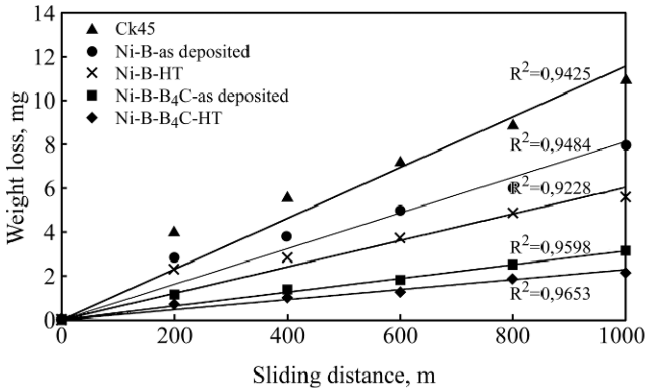


Fig. 5. Weight loss vs. sliding distance for Ck45 steel, Ni-B and Ni-B-B_4C coatings.

The presence of the Ni-B-B_4C composite coating, because of its high hardness, and of B_4C particles cause an increase in the wear resistance. B_4C Nanoparticles, firstly, have a strong effect on preventing the movement of the existing cracks in the whole coating matrix,ng nomaki the change in the plastic form. Secondly, B_4C particles cause a separation between the coating and the metal while the wear test is being carried out; the B_4C particles cause a decrease in the load from the pin side on the coating surface preventing the destruction of the coating by the pin to a large extent. Moreover, heat treatment causes an increase in the wear resistance of the Ni-B-B_4C composite coating, which is due to the complete permutation of the amorphous phase to crystal and an increase in the coating hardness.

SEM pictures of the worn surfaces of the samples are illustrated in Figs. 6a–6c. As can be seen in Fig. 6a, the worn surface of Ck45 steel has deep scratches confirming the dominance of a wear mechanism of the abrasive wear. This is why the scratches on the worn surface of the Ni-B-B_4C composite coating (Fig. 6b) have become less pronounced and the composite coating surface has not been destroyed as a result of the pin contact; certain (limited in number) parts of the coating have been crushed as a result of the load caused by the pin. In the heat-treated Ni-B-B_4C composite coating (Fig. 6c) the scratches and crush have decreased due to an increase of the coating hardness. The microscopic picture of the pin surface prior to and after wear is provided in Fig. 7. The pictures mentioned above illustrate that, according to the wear test, a part of the wear has been separated from the surface and got stuck to the surface of the steel pin. The obtained results were also proved by the EDX test. The presence of a high level of nickel on the surface is an eloquent proof of this fact.

Tafel polarization test

Tafel polarization test graphs for Ck45 steel, Ni-B and Ni-B-B_4C composite coatings in NaCl 3.5% solution are given in Fig. 8. Corrosion parameters like corrosion potential (E_{corr}), corrosion current density (i_{corr}), obtained from the Tafel polarization graphs by extrapolation are shown in Table 2. Ck45 steel has a very low corrosion resistance in corrosive environments, but by employing an appropriate coating its corrosion resistance can be considerably increased. As noticed in the results obtained from the Tafel polarization test, the density of the corrosion current has remarkably decreased as a result of employing Ni-B and Ni-B-B_4C composite coatings with a thickness of 30 µm.

According to the obtained results, the electroless nickel coating has demonstrated a moderate corrosion resistance in 3.5% sodium chloride solution. Additionally, the coatings developed in the framework of the present research have shown no reaction. Which is in accord with the results of other researchers [25].

Moreover, one of the reasons of the increased corrosion resistance of the Ni-B-B_4C composite coating can be the result of pressing a layer of B_4C with an excellent corrosion resistance and low chemical reactivity in the joint between the coating and electrolyte, which can act as a physical dam against corrosion. Furthermore, even distribution of B_4C particles can help in improving the corrosion resistance by limiting the corrosion area [16]. By filling the scratches and pores existing in the Ni-B coating, B_4C nanoparticles cause a decrease in the corrosion prone areas, which results in an increase of the corrosion resistance in the electroless Ni-B-B_4C composite coatings [16].

In order to investigate the effect of heat treatment on corrosion of a composite coating, a sample of it was exposed to heat treatment at 400°C for 1 hour and subsequently, under identical conditions, along with the previous samples, was placed under polarization tests. The investigation of the Tafel diagram of such a coating illustrates that the heated coating (cover) was clearly influenced by the corrosion in the saltwater zone, which led to a substantial decrease of the corrosion current density and corrosion potential of the heated sample in comparison to the

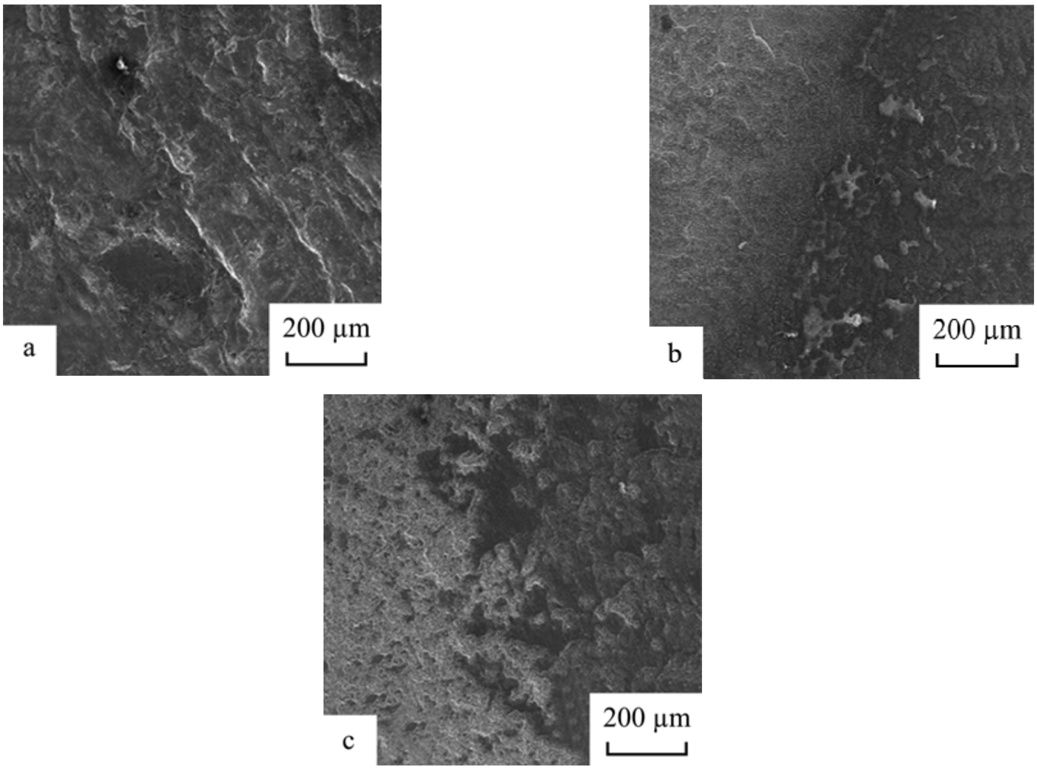
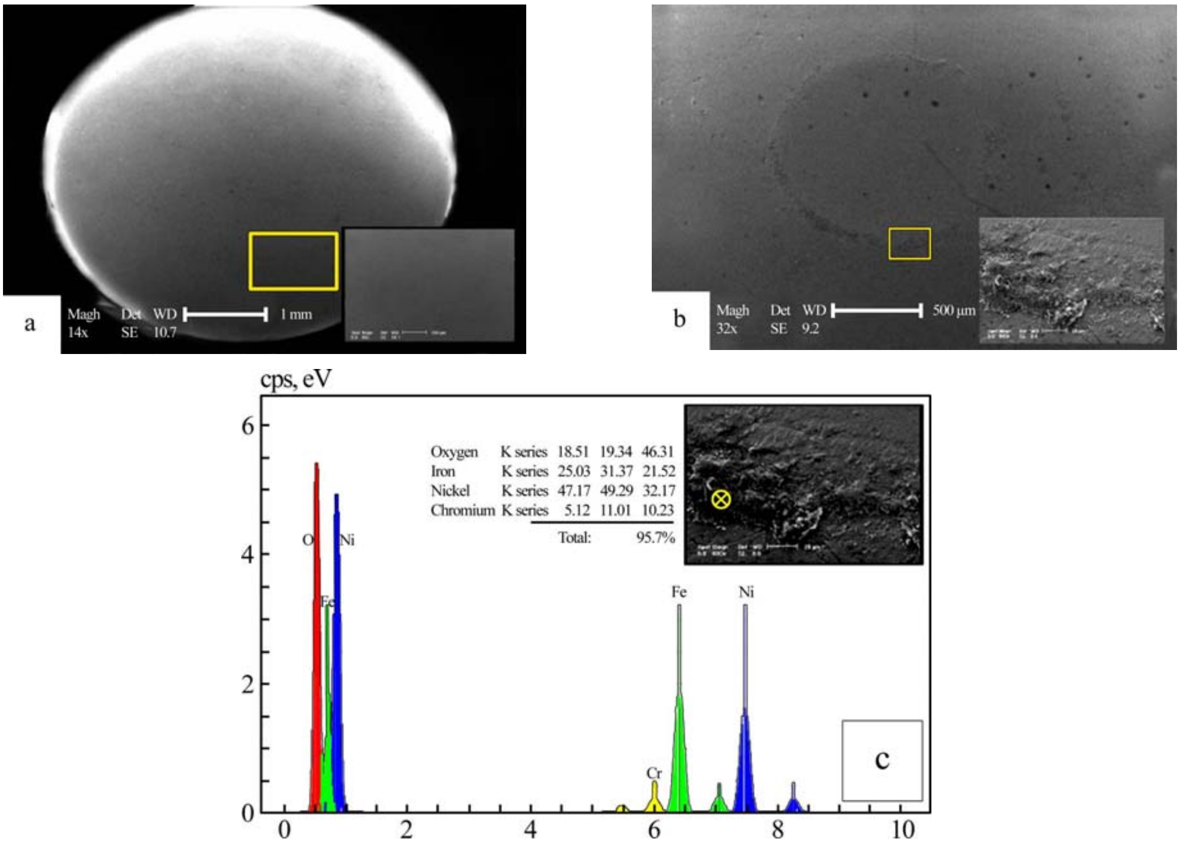


Fig. 6. Worn surface morphology of: (a) Ck45; (b) Ni-B-B_4C-as deposited and (c) Ni-B-B_4C-HT.



Oxygen	K series	18.51	19.34	46.31
Iron	K series	25.03	31.37	21.52
Nickel	K series	47.17	49.29	32.17
Chromium	K series	5.12	11.01	10.23
		Total:		95.7%

Fig. 7. Morphology of the pin surface: (a) prior to wear; (b) after wear, and (c) analysis of EDX of pin surface.

Table 2. Corrosion resistance of coatings in 3.5% NaCl solution, evaluated by Potentiodynamic polarization technique

Coating	E_{corr} (mV)	I_{corr} (A·cm^{-2})
Ck45	-413	5.5×10^{-4}
Ni-B	-362	1.8×10^{-6}
Ni-B-B_4C-as-plated	-305	4.1×10^{-8}
Ni-B-B_4C-heat treated	-310	2×10^{-7}

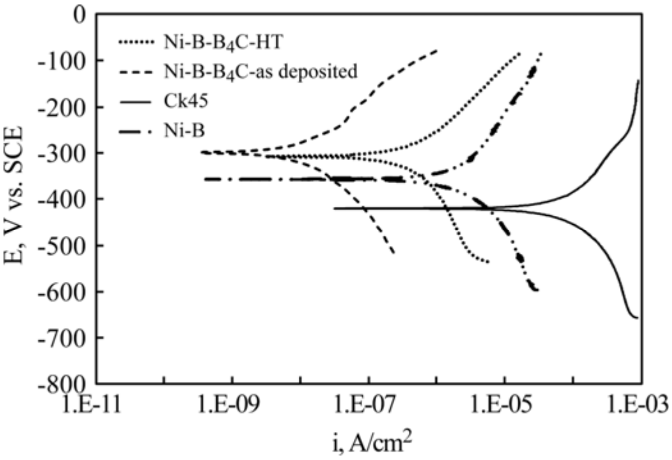


Fig. 8. Polarization curves of coatings in 3.5% NaCl solution.

as-plated sample. This phenomenon could be a result of the crystallization of the coating and the formation of grains in the coating under heat. Due to a higher energy of the grain boundaries than of the grains themselves, grain boundaries result in the creation of the areas prone to the corrosion in the coating, which are much more influenced than other parts by corrosive environments. Heat treatment and the formation of the hard phases of Ni_3B result in the reduction of the boron distribution uniformity. This process can cause the development of different areas with different corrosion potentials in the coating surface, which can result in the formation of the active/passive corrosion cells, the final result of which will be the formation of pores in the coating. However, the probability of the development of pores is really low, which was demonstrated by the polarization diagram that showed no reaction/passivity [25].

CONCLUSIONS

The aim of the present research was to improve the tribiological properties and corrosion of Ck45 steel by creating Ni-B-B_4C composite coating. The results obtained from this research are as follows.

The Ni-B composite coating containing B_4C nanoparticles was successfully created on the Ck45 steel substrate. This coating is very uniform on the substrate surface. Moreover, B_4C nanoparticles have been evenly distributed in the electroless coating matrix. The presence of B_4C nanoparticles in the electroless coating matrix caused a remarkable increase in hardness and subsequently the wear resistance of this coating compared to that of Ck45 steel. Heat treatment at 400°C for 1 hour caused an increase in hardness and wear resistance of the composite coating. The creation of the electroless coating can increase the corrosion resistance of the steel substrate. In the meantime, B_4C particles with reduced porosity of Ni-B coating and its increased coherence as well as the development of a surface with a high chemical resistance against corrosive environment resulted in the improvement of the corrosion resistance of Ni-B-B_4C composite coatings. Furthermore, the heat treatment due to the crystallization of the cover and the formation of the grains in it diminished the corrosion resistance of the cover.

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Реферат

В настоящем исследовании успешно был использован метод химического осаждения для получения композитных покрытий с включением наночастиц B_4C на углеродистой стали Ck45. Характеристики покрытий исследовали методами энергодисперсионной спектрометрии и сканирующей электронной микроскопии. Твердость покрытия измерялась с применением микротвердомра Викерса под нагрузкой 1Н. Твердость композитного покрытия Ni-B-B_4C H_V ~ 870 после термообработки при 400°C в течение 1 часа увеличивалась до $H_V = 1350$, что гораздо больше, чем твердость покрытий никель-бор и стали Ck45. При испытаниях на износ использовалась методика штифт-диск. Результаты показали улучшение износостойкости композитных покрытий Ni-B-B_4C по сравнению с покрытиями никель-бор и сталью Ck45. Результаты, полученные при использовании метода таффелевской поляризации, показали увеличение коррозионной стойкости по сравнению с покрытиями никель-бор и сталью Ck45.

Ключевые слова: наночастицы B_4C, химическое осаждение, композитные покрытия, трибологические характеристики, коррозия.