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Effect of modifiers on the structure formation and properties of nickel-phosphorus coatings applied to powder steels

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Abstract. The paper shows the effect of solution temperature on the deposition rate of applying composite nickel-phosphorus coatings modified with boron nitride and polytetrafluoroethylene to powder samples made of improved P40, P40Kh and P40KhN steels obtained by hot stamping of porous sintered blanks. It has been experimentally established that within the range of 70–90 °C, the average deposition rate of modified BN and $(C_2F_4)n$ coatings is 15–19 μ m/h, while the chemical composition of the improved steels and the surface configuration of the samples have no effect on the coating build-up rate. The mechanism of the formation of the structure and properties of nickel-phosphorus coatings (NiPC) without additives and those of NiPC modified with boron nitride and polytetrafluoroethylene during deposition, sintering and running-in is revealed. It has been established that immediately after deposition, Ni-P coating has an amorphous structure with inclusions of nickel particles, and its microhardness does not exceed 380-390 MPa with no modifiers added. In the dry friction mode at the running-in stage, Ni₁₂P₅ and Ni₂P phases are formed in the modified Ni–P coatings, allowing to improve their tribological properties, and in the steady-state mode, the phase disordering of the modified NiPC proceeds. It has been experimentally revealed that the coefficient of friction and wear decrease by 1.3 times when only $(C_1F_4)n$ is introduced into Ni-P coating, these indices decrease by 1.6 times when only BN is added, and they decrease almost twice when BN and $(C_2F_4)n$ are introduced together. It has been established that upon the combined (complex) modification of NiPC with BN and $(C_2F_4)n$ after the heat treatment, there is almost no nickel oxide phase, nickel boride of NiB type is formed in the coating during running-in, and its content does not decrease when entering the stationary friction mode, thus increasing tribotechnical properties of the coating. During running-in, the coefficient of friction of Ni-P + BN + $(C_3F_4)n$ coating decreases from 0.28 to 0.19, and the wear rate of such a coating in the stationary friction mode is 1.5 mg/h. The efficiency of applying the antifriction nickel-phosphorus coatings modified with BN + (C₂F₄)n to the products made of the improved structural steels obtained by various methods has been theoretically and experimentally substantiated.

Keywords: nickel-phosphorus coating (NiPC), powder steel, modifier, tribotechnical properties, boron nitride, polytetrafluoroethylene

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Влияние модификаторов на структурообразование и свойства никель-фосфорных покрытий, нанесенных на порошковые стали

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Аннотация. Показано влияние температуры раствора на скорость осаждения композиционных никель-фосфорных покрытий, модифицированных нитридом бора и политетрафторэтиленом, на порошковые образцы из улучшаемых сталей марок П40, П40Х и П40ХН, полученных горячей штамповкой пористых спеченных заготовок. Экспериментально установлено, что в интервале температур 70-90 °C средняя скорость осаждения модифицированных BNи (C_3F_4) n-покрытий составляет 15–19 мкм/ч, а химический состав улучшаемых сталей и геометрия поверхности образцов практически не влияют на скорость их наращивания. Предложен механизм формирования структуры и свойств Ni-P-покрытий без добавок и модифицированных нитридом бора и политетрафторэтиленом в процессах осаждения, спекания и приработки. Установлено, что непосредственно после осаждения Ni-P-покрытие имеет аморфную структуру с включениями частиц никеля, а его микротвердость без добавки модификаторов не превышает 380-390 МПа. На стадии приработки в режиме сухого трения в модифицированных Ni-P-покрытиях образуются фазы Ni₁₂P₅ и Ni₂P, позволяющее повысить их трибологические характеристики, а при установившемся режиме в них протекает фазовое разупорядочивание. Экспериментально выявлено, что при введении в Ni-P-покрытие только (C_3F_4) и коэффициент трения и износ снижаются в 1,3 раза, при добавлении одного BN – в 1,6 раза, а при совместном введении ВN и $(C_2F_4)n$ – почти в 2 раза. Установлено, что при совместном (комплексном) модифицировании Ni–Pпокрытий BN и $(C_2F_4)n$ после термообработки никель практически не окисляется, в процессе приработки в покрытии образуется борид никеля типа NiB, содержание которого при выходе на стационарный режим трения не уменьшается, что стабилизирует триботехнические характеристики покрытия. В процессе приработки коэффициент трения состава покрытия $Ni-P + BN + (C_2F_4)n$ снижается с 0,28 до 0,19, а скорость изнашивания в режиме стационарного трения составляет 1,5 мг/ч. Теоретически и экспериментально обоснована эффективность нанесения антифрикционных никель-фосфорных покрытий, модифицированных $BN + (C_2F_4)n$, на изделия из конструкционных улучшаемых сталей, полученных различными методами.

Ключевые слова: никель-фосфорное покрытие (НФП), порошковая сталь, модификатор, триботехнические свойства, нитрид бора, политетрафторэтилен

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Introduction

Various methods of modifying and coating structural, tool and special materials to improve their functional properties are known [1–3]. Numerous papers are devoted to studying the effect of the chemical composition, methods and technological parameters of coating of steel products [4–8]. Particular attention is given to the development of new materials and technologies for coating the products of complex configuration, modified with various micro- and nano-additives [9–11]. From a technological point of view, composite nickel-phosphorus coatings (NiPC), which are obtained by chemical deposition [6; 7; 11–14] and characterized by high wear resistance, a relatively low coefficient of friction, the abi-

lity to resist significant cyclic contact loads, as well as the possibility of introducing solid lubricants and other modifiers [8–12; 15–17] into the matrix, are attractive.

However, the works devoted to the development of technology for the production of composite NiPC do not sufficiently research the kinetics of structure formation, which is formed both during deposition and sintering and during friction, and will make it possible to predict their properties, develop new materials and explain the physicochemical processes occurring at all stages of the technological process of coating and operation [13–18].

The analysis of the operating conditions of steel products coated with composite NiPC, as well as scientific and technical developments in the field of structural



adaptability of materials and coatings upon friction, developed during the creation of self-lubricating materials and coatings, revealed that the structural states of substances, which predetermine the phenomenon of selforganization in dissipative tribological systems, must be considered when developing the ones [10–13; 19–21].

The purpose of this paper was to study the mechanism of structure formation and tribological properties of composite nickel-phosphorus coatings modified with boron nitride and polytetrafluoroethylene $(C_2F_4)n$ applied to the improved powder steels.

Research methods and technology for obtaining samples

Samples 25 mm in diameter and 5 mm in thickness were obtained by sintering and hot stamping of porous blanks of improved P40, P40Kh and P40KhN steels using the technology specified in work [22]. For the purpose of coating, the surface of the steel samples was prepared in accordance with the requirements described in [10-13]. The working solution for the deposition of NiPC composites Ni-P + BN, Ni-P + $(C_2F_4)n$ and $Ni-P+BN + (C_2F_4)n$ was prepared in the sequence described by the authors [11–13].

The thickness of the composite coatings was determined by means of Konstanta K6 thickness gauge (Russia) with ID1 transducer with a maximum error of $\pm 0.01T + 1 \mu m$. The adhesive strength of NiPC was evaluated by random testing of reference samples in accordance with GOST 9.302-88 "Control Methods: Bending and Tension", using TME-10 tensile machine (Russia). The loading rate was 2 mm/min.

The X-ray studies of the samples were performed by means of DRON-1.5 diffractometer. The phase composition of the samples was identified using X-ray data published in the reference literature [23] and the methods described in paper [24]. In order to analyze the amorphous component in the coatings, the samples were taken at a rate of 2 °C/min and with a more optimal scale along the intensity axis. The required reference diffraction patterns were obtained by "smearing" of diffraction lines in the patterns of the corresponding crystalline phases, assuming their ultradispersity [24]. During the qualitative phase analysis, in all cases we attempted to describe the composition of the sample by a minimum number of phases.

The X-ray microanalysis was conducted by the methods of electron probe research in the Resource Sharing Center of South Russian State Polytechnic University (NPI) named after M.I. Platov, using VEGA II LMU scanning electron microscope (Tescan, Czechia) equipped with INCA ENERGY 450/XT energy-dispersive microanalysis system (OXFORD Instruments Analytical, Great Britain), providing the opportunity of elemental analysis in the range from Na to U.

The pattern of distribution of modifiers in the coating matrix, as well as the particle sizes and phase morphology were studied by means of Epiquant metallographic microscope (Karl Zeiss Jena, Germany).

Microhardness was measured at a load of 0.0981 N (10 Gs) applied for 15 s, using PMT-3 device (Russia) under GOST 9450-76. For the purpose of a more reliable determination of this characteristic, the number of measurements was 30–50 at a coating thickness of 20 μm.

To determine the tribotechnical properties of NiPC, an end friction machine (FGUP OKTB Orion, Russia) was used, allowing to develop the specific loading on the surface of the studied material up to 300 MPa at a sliding speed of 0.048 m/s. The friction area temperature was measured with a thermocouple inserted into the sample at a distance of 0.5 mm from the friction surface track. The overlap coefficient of the rubbing surfaces of the sample and the counterbody was 0.2. The washers made of steel 45 with a hardness of 48–52 HRC and a roughness of $R_a = 0.25 \,\mu\text{m}$ were used as a counterbody.

Research findings and discussion

The operational reliability of the parts of friction units, to which the composite coatings are applied, largely depends on the uniformity of their thickness and adhesion to the substrate. As shown by the experimental results presented in Figure 1, the process of NiPC formation is initiated when the samples (solution) are heated above 35-40 °C, the coating growth rate increases more intensively with increasing temperature from 60 to 90 °C and reaches 14–18 µm/h depending on the chemical composition (see Figure 1). The highest deposition rate (18– 19 μ m/h) is observed when applying Ni–P + BN + (C₂F₄) n coating at a temperature of 900 °C.

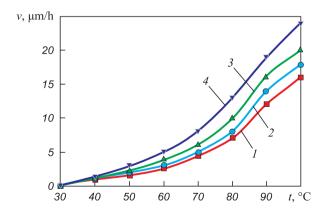


Fig. 1. The dependence of the coating deposition rate on the solution temperature and chemical composition $1 - \text{Ni-P}, 2 - \text{Ni-P} + (\text{C}_2\text{F}_4)n, 3 - \text{Ni-P} + \text{BN}, 4 - \text{Ni-P} + \text{BN} + (\text{C}_2\text{F}_4)n$

Рис. 1. Зависимость скорости осаждения покрытия от температуры раствора и химического состава $1 - \text{Ni-P}, 2 - \text{Ni-P} + (\text{C}_2\text{F}_4)n, 3 - \text{Ni-P} + \text{BN}, 4 - \text{Ni-P} + \text{BN} + (\text{C}_2\text{F}_4)n$



The studies revealed that Ni–P coating exhibits an amorphous structure immediately after deposition, and its microhardness reaches the maximum of 380–390 HV (Table 1) without modifying additives. When introducing $(C_2F_4)n$, the microhardness of the coating slightly decreases, since it is lower for this polymer than for NiPC. If the coating is modified with boron nitride, its microhardness increases up to 490–500 HV (see Table 1). This can be explained by the nature of the disperse BN phase, which is characterized by a higher hardness than Ni–P coating. The microhardness of Ni–P + BN + (C_2F_4) n composition is slightly lower than that of NiPC modified with BN.

To improve the tribotechnical properties of NiPC and the strength of adhesion to the steel substrate, the coated samples were heated within the range of $t = 50 \div 700$ °C with a spacing of 50 °C for 1 h. At the first stage, the effect of heating temperature on the microhardness of the samples was studied. As can be seen in Fig. 2, the HV behavior is the same for all types of coatings, depending on the sintering temperature of the samples.

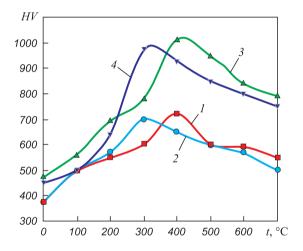


Fig. 2. The dependence of microhardness of NiPC on P40KhN steel on sintering temperature and composition $I - \text{Ni-P}, 2 - \text{Ni-P} + (\text{C},\text{F}_4)n, 3 - \text{Ni-P} + \text{BN}, 4 - \text{Ni-P} + \text{BN} + (\text{C},\text{F}_4)n$

Рис. 2. Зависимость микротвердости НФП на стали П40XH от температуры спекания и состава $I-\text{Ni-P}, 2-\text{Ni-P}+(\text{C},\text{F}_4)n, 3-\text{Ni-P}+\text{BN}, 4-\text{Ni-P}+\text{BN}+(\text{C},\text{F}_4)n$

Table 1. The microhardness of coatings in amorphous state
Таблица 1. Микротвердость покрытий
в аморфном состоянии

Coating composition	Micro- hardness $HV_{0.01/15}$	Standard deviation, %
Ni–P	380-390	7
$Ni-P + (C_2F_4)n$	370-375	9
Ni-P + BN	490-500	8
$Ni-P + BN + (C_2F_4)n$	450-460	9

Table 2 provides the critical sintering temperatures and holding time at which the coatings modified with various additives exhibit the maximum microhardness.

In particular, the microhardness of the samples made of P40KhN steel coated with Ni–P+(C_2F_4)n, sintered at $t=360\,^{\circ}\mathrm{C}$ for 1 h, was 700 HV (Fig. 2, curve 2), while the microhardness of the samples made of P40KhN steel coated with Ni–P+BN+(C_2F_4)n increased up to 980–990 HV (Fig. 2, curve 4). The maximum HV values were obtained for Ni–P and Ni–P–BN coatings after the sintering of the samples at $t=400\,^{\circ}\mathrm{C}$ (Fig. 2, curves I and I).

The studies revealed that composite NiPC are brittle and flake off easily after deposition, and the strength of their adhesion to the substrate is very low. Upon sintering, the samples coated with NiPC within the range of $t = 500 \div 700$ °C, nickel and steel interdiffusion occurs at steel—coating interface and a transitional diffusion layer, contributing to an increase in the strength of adhesion of the coating to the substrate, forms (Fig. 3). Upon that, the chrome content of NiPC does not exceed the measurement error (see Fig. 3, b).

The qualitative assessment of the adhesion strength of composite NiPC was performed by bending method (10 samples for each coating). The studies showed no flaking of the coating on the surface of P40KhN steel at the point of fracture, however, noticeable cracks appeared in Ni–P+(${\rm C_2F_4}$)n coating on the surfaces of P40 and P40Kh steels upon bending.

The results of studies performed by means of UMM-5 tensile machine (Fig. 4) showed that the mass loss of coatings of all non-sintered samples without sintering was as follows, g: Ni–P – 0.085; Ni–P + (C_2F_4)n – 0.092; Ni–P + BN – 0.045 and Ni–P + BN + (C_2F_4)n – 0.050. The flake off masses of the samples with Ni–P + BN + (C_2F_4)n coatings are virtually identical, but they are 30–35 % less compared to those with Ni–P.

Upon an increase in the temperature of sintering of the samples made of P40Kh steel from 50 to 350 $^{\circ}$ C with the holding time of 1 h, the amount of flaking off Ni–P coating decreases from 90 to 25 mg, and the one of Ni–P + BN decreases from 42 to 9 mg (see Fig. 4,

Table 2. The modes of sintering of samples made of P40Kh steel coated with different compositions

Таблица 2. Режимы спекания образцов из стали П40X с покрытиями различного состава

Coating composition	t, °C	Heat treatment time, min
Ni–P	400	90
$Ni-P + (C_2F_4)n$	360	60
Ni–P + BN	400	90
$Ni-P + BN + (C_2F_4)n$	360	90



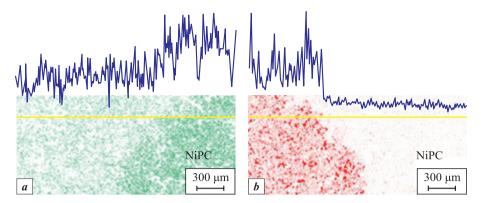


Fig. 3. The distribution of nickel (a) and chrome (b) at the interlayer boundary "P40KhN steel – Ni–P coating" after sintering at t = 700 °C for 2 h

Рис. 3. Распределение никеля (a) и хрома (b) на межслойной границе «сталь П40XH – Ni–P-покрытие» после спекания при t = 700 °C в течение 2 ч

curve I and 2). The studies demonstrated that the samples modified with boron nitride and polytetrafluoroethylene (Fig. 4, curve 4) exhibited the minimum mass loss of coatings, whereas the samples with (C₂F₄)n-modified coatings (Fig. 4, curve 3) had the largest losses. The mass loss decrease after sintering at t = 400 °C for 1 h is approximately the same for the $(C_2F_4)n$ -modified coatings (Fig. 4, b, curves 1 and 2).

As can be seen in Fig. 2 and 4, the microhardness and mass loss behavior, depending on the sintering temperature, coincides, and that is associated with the kinetics of coating microstructure formation.

According to the X-ray phase analysis, immediately after the chemical deposition, the boron nitride-modified NiPC exhibited an amorphous structure, which can be called an X-ray amorphous structure.

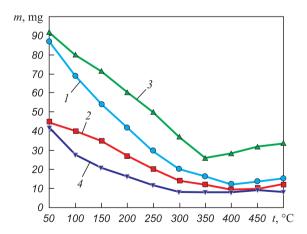


Fig. 4. The dependence of flake off mass on the sintering temperature and the composition on the samples made of P40Kh steel 1 - Ni-P, 2 - Ni-P + BN; $3 - \text{Ni-P} + (\text{C}_2\text{F}_4)n$, $4 - \text{Ni-P} + \text{BN} + (\text{C}_2\text{F}_4)n$

Рис. 4. Зависимость отслоившейся массы покрытия от температуры спекания и состава на образцах из стали П40Х

 $1 - \text{Ni-P}, 2 - \text{Ni-P} + \text{BN}; 3 - \text{Ni-P} + (\text{C}_2\text{F}_4)n, 4 - \text{Ni-P} + \text{BN} + (\text{C}_2\text{F}_4)n$

It should be noted that the number of centers for the nucleation of NiPC inclusions virtually does not depend on the surface geometry of the powder samples, while the surface roughness and the presence of microand macropores impact the morphology (Fig. 5, a and b). In those areas of the surface of the sintered samples where the micropores are located, the content of nickel and phosphorus is noticeably lower than on the end surface of the samples made of hot-stamped P40Kh steel.

After sintering Ni-P + BN-coated samples made of P40Kh steel obtained by hot stamping of porous blanks within the temperature range of 350-370 °C for 1 h, β-Ni, Ni₂P, BN phases and a small amount of NiO, being well-identified in diffractograms (Fig. 6, a), were found. At the running-in stage during testing, the Ni₂P and BN phases are dispersed and their characteristic reflections are smeared, therefore they can only be approximately identified in X-ray patterns (Fig. 6, a, curve 2 and 3). Furthermore, Ni₁₂P₅, Ni₂P and NiB highly dispersed phases arise during friction, and their content in the surface layers of the coating increases upon entering the stationary friction mode. The nickel oxides appeared to dissociate and disperse at the running-in stage and in the stationary friction mode, therefore, they could not be identified in the diffraction patterns.

The coefficient of friction (in the dry friction mode) slightly decreases from 0.29 at 20 °C to 0.22 at 300 °C upon temperature increase in the contact area of "steel 45-P40Kh with NiPC" pair, while the temperature increases (Table 3). However, the wear rate increases significantly from 0.21 to 3.8 µm/h at the indicated heating temperatures of the coatings (Table 3). Upon modifying NiPC with boron nitride, the coefficient of friction (f) and wear rate (I) are slightly lower than those of the samples containing no additives (see Table 3). This can be explained by the fact that during the running-in of the coating surface, the dispersed NiB inclusions appear, and their conЩербаков И.Н., Гасанов Б.Г. Влияние модификаторов на структурообразование и свойства никель-фосфорных ...

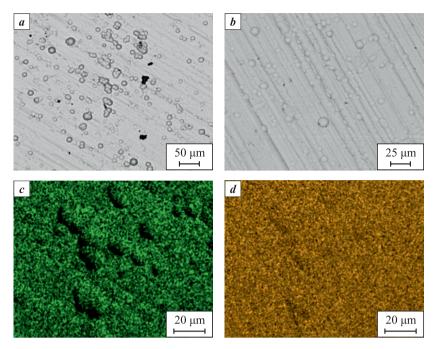


Fig. 5. The microstructure of NiPC on the surface of sintered steel before (a) and after (b) heat treatment and the behavior of distribution of nickel (c) and phosphorus (d) (light inclusions) in the coating

Рис. 5. Микроструктура НФП на поверхности спеченной стали до (a) и после (b) термообработки и характер распределения в покрытии никеля (c) и фосфора (d) (светлые включения)

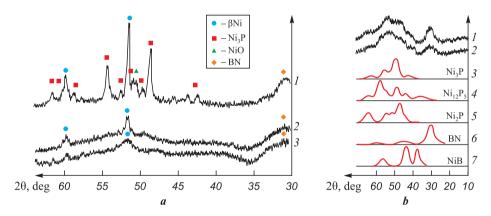


Fig. 6. The surface diffraction patterns of NiPC modified with BN a – after sintering (1) and at the running-in stage (2 and 3);
b – in the steady-state friction mode (3–7 – the reflections being typical for the specified phases)

Рис. 6. Дифрактограммы поверхности НФП, модифицированного BN a – после спекания (1) и на стадии приработки (2 и 3); b – в установившемся режиме трения (3–7 – рефлексы, характерные для указанных фаз)

Table 3. The effect of the chemical composition of the modifiers on the coefficient of friction and wear rate at different temperatures

Таблица 3. Влияние химического состава модификаторов на коэффициент трения и скорость изнашивания покрытий при разных температурах

Coating composition	f			I, μm/h		
	$t = 20 ^{\circ}\text{C}$	250 °C	300 °C	20 °C	250 °C	300 °C
Ni–P	0.29	0.24	0.22	0.21	2.5	3.8
Ni–P + BN	0.25	0.22	0.20	0.18	2.1	3.1
$Ni-P+C_2F_4$)n	0.23	0.20	0.19	0.32	2.4	3.2
$Ni-P + BN + (C_2F_4)n$	0.20	0.18	0.17	0.14	1.5	2.2



tent does not change when entering the stationary friction mode (Fig. 7, *a*).

Upon modifying NiPC with $(C_2F_4)n$ polytetrafluoroethylene in the process of sintering under the aforementioned mode, the crystals of β-Ni and Ni₃P phase are formed more actively, while nickel oxide is absent (Fig. 7, a). During running-in, nickel particles actively interact with phosphorus; phosphorus-containing Ni₁₂P₅ and Ni₂P highly dispersed phases were found on the surface of the coating along with (C₂F₄)n inclusions (Fig. 7, b). In this case, no phases formed during sintering were found in Ni-P + $(C_2F_4)n_4$ coating at the stage of the steady-state friction mode. Therefore, the diffraction patterns shown in Fig. 7, a, curve 3 and Fig. 7, b. curve I and 2 have a form being typical for materials with an amorphous-crystalline structure. Consequently, during friction, a structural-phase disorder arises on the surface of composite NiPC modified with NB and $(C_2F_4)n_4$.

Upon modifying NiPC with $(C_2F_4)n$ polytetrafluoroethylene, the coefficient of friction is slightly decreased and the wear rate in the steady state is virtually the same as that of coatings with NB additive (Table 3). The complex modification of Ni–P coatings with BN and $(C_2F_4)n$ showed the efficiency of their introduction. If, upon that, the phase composition of NiPC remains the same as that of a coating modified only with $(C_2F_4)n$ (Fig. 8, a), its tribological properties are significantly higher than after the introduction of these additives separately (Table 3). Particularly, upon adding $(C_2F_4)n$, the wear rate of NiPC at the stage of the stationary friction mode decreases by 1.3 times; upon adding BN, it decreases by 1.6 times, and it decreases virtually by 2 times upon the combined introduction of BN and $(C_2F_4)n$ (Table 3).

It should be noted that the performance of P40, P40Kh and P40KhN powder steels obtained by hot stamping of porous blanks coated with the Ni-P + BN + $(C_2F_4)n$

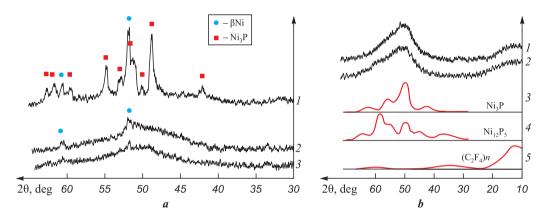


Fig. 7. The surface diffraction patterns of Ni–P + $(C_2F_4)n$ composite coating a – after sintering (1) and at the running-in stage (2 and 3); b – in the steady-state friction mode (3–5 – the reflections being typical for the specified phases)

Рис. 7. Дифрактограммы поверхности композиционного покрытия состава Ni–P + $(C_2F_4)n$ a – после спекания (1) и на стадии приработки (2 и 3); в установившемся режиме трения (3–5 – рефлексы, характерные для указанных фаз)

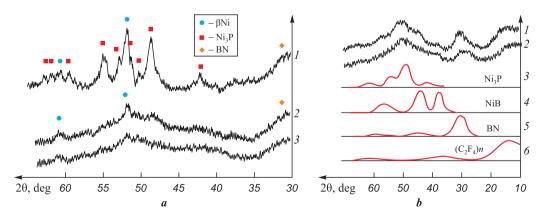


Fig. 8. The surface diffraction patterns of Ni–P + BN + $(C_3F_4)n$ coatings a – after sintering (1) and at the running-in stage (2 and 3); b – in the steady-state friction mode (3–6 – the reflections being typical for the specified phases)

Рис. 8. Дифрактограммы поверхности покрытий Ni–P + BN + $(C_2F_4)n$ a – после спекания (1) и на стадии приработки (2 и 3); b – в установившемся режиме трения (3–6 – рефлексы, характерные для указанных фаз)

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composition remained active for some time upon the appearance of traces of the base metal, while the samples with Ni–P-coating, which does not contain these additives, did not exhibit such a phenomenon.

Conclusion

It has been experimentally established that the process of formation of modified nickel-phosphorus coatings is initiated when the solution is heated above 35–40 °C. Upon temperature increase from 60 to 90 °C, the rate of coating build-up on the powder samples made of P40, P40Kh and P40KhN steel increases more intensively and reaches 14–19 $\mu m/h,$ depending on the chemical composition of the coating. The microhardness of coatings of different chemical composition is largely effected by the mode of the subsequent heat treatment.

It was newly revealed that composite NiPC are rather brittle and flake off easily after deposition; upon sintering the powder samples with such coatings in the range of $t=500-700\,^{\circ}\text{C}$, nickel and steel interdiffusion occurs at steel—coating interface and a transitional diffusion layer, contributing to an increase in strength of adhesion of the coating to the substrate, forms. During friction, Ni_{12}P_5 , Ni_2P and NiB highly dispersed phases, improving the tribological properties, arise. The contents of these phases in the surface layers of the coating increase when entering the stationary friction mode.

It has been theoretically and experimentally substantiated that the complex modification of nickel-phosphorus coatings with BN and $(C_2F_4)n$ allows to reduce the coefficient of friction and the wear rate at the stage of the stationary mode. When only $(C_2F_4)n$ polytetrafluoroethylene is added to NiPC, the coefficient of friction and the wear rate decrease by 1.3 times; upon adding BN, they decrease by 1.6 times, and upon the combined BN and $(C_2F_4)n$ modification they decrease virtually by 2 times.

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