***Problems of Tribology**, V. 27, No 1/103-2022,34-40*

Problems of Tribology
Website: http://tribology.khnu.km.ua/index.php/ProbTrib
E-mail: tribosenator@gmail.com

DOI: https://doi.org/10.31891/2079-1372-2022-103-1-34-40

Influence of heat treatment on tribocorrosion properties of Ni-B composite coatings

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Received: 11 January 2022: Revised: 13 February 2022: Accept: 2 March 2022

Abstract

Various surface protection technologies, in particular, electrochemical, are used to increase the wear and corrosion resistance of steels and alloys. Composite electrochemical coatings (CEC) technology is more promising than "pure" galvanic coatings. Application of CEC increases the wear, corrosion and fatigue failure resistance of metals. Nickel often is chosen as a CEC matrix because it easily forms uniformly filled defect-free composite structures with many particles of the dispersed phase (DP).

Physical and mechanical properties of metal coatings determine practical application of such composition. The characteristics of nickel-based CEC are: high hardness and strength, significant corrosion resistance in atmospheric environment, as well as in alkali and mild acidy environments. An effective composition coating with tribological designation can be CEC Ni-B, received in the process of electrolysis from suspension of amorphous boron in nickel electrolyte. A new composite structure of matrix filled type Ni-Ni_3B is formed after heat treatment. Composition and structure of coating is determined by regimes of diffusion annealing. Ni-B coatings increase wear resistance of steel in chlorine-based environments. The influence of low-temperature thermal treatment of Ni-B CEC on steel 09Mn2Si on their tribocorrosion behavior is investigated. It is shown that the structural factor has a decisive influence on the efficiency of such friction pairs. The CEC has the least wear and the most positive compromise electrode potential after vacuum annealing at 450°C, when the initial stage of solid-phase interaction of coating components with the formation of Ni-Ni_3B occurs.

Key words: composition electrochemical coating, low temperature thermal treatment, tribocorrosion, friction coefficient.

Introduction

Various surface protection technologies, in particular, electrochemical, are used to increase the wear and corrosion resistance of steels and alloys. Composite electrochemical coatings (CEC) technology is more promising than "pure" galvanic coatings. Application of CEC increases the wear, corrosion and fatigue failure resistance of metals. Nickel often is chosen as a CEC matrix because it easily forms uniformly filled defect-free composite structures with many particles of the dispersed phase (DP). Nickel-Boron CEC is an effective composite coating for tribotechnical application. It is obtained by electrolysis of a suspension “amorphous boron - the nickel electrolyte” [1]. A new composite structure Ni-Ni3B of matrix-filled type is formed in the process of subsequent thermal treatment (TT) [3,4]. The composition and structure of composite are determined by the diffusion annealing parameters. The wear resistance of steels with Ni-B CEC after TT at 900… 1000˚C increases by 1.5… 3 times compared to solid galvanic chromium or diffusion boride coatings [4]. It is due to formation of Ni3B boride grains with high microhardness (9… 12.5 GPa). It is shown, that Ni-B CEC in the initial state also increase the wear resistance of steels under conditions of corrosion and mechanical wear in chloride-containing environments, but the effect is smaller due to increased electrochemical activity of solutions [5,6].

Ni-B coatings after low-temperature TT can also be promising for surface protection of alloys [7, 8]. Therefore, the aim of the work was to investigate the influence of low-temperature thermal treatment parameters on the structure, hardness and tribocorrosive behavior of Ni-B CEC on steel 09Mn2Si.

Materials and research methods

Preliminary preparation of steel 09Mn2Si samples was performed according to the requirements [9]. CEC Ni-B was precipitated from a suspension of amorphous boron in the sulfate chloride electrolyte of nickel plating at a cathode current density of 5 A/dm2, temperature 40...45°C and hydrodynamic electrolysis regimes, recommended in [10]. Sodium dodecyl sulfate was used as an anti-pitting agent and suspension stabilizer. The thickness of the coatings was 45...50 µm, and the boron content in them was 4.8 ... 5.2 wt.%. Samples with coatings were annealed in vacuum at temperatures of 200, 300 and 450°C for 2 h. X-ray diffraction analysis of the coatings was performed on a DRON-3M diffractometer in Cu-Kα radiation. The parameters of the fine structure (the size of the coherent scattering regions, the magnitude of the microdeformation and the dislocation density) were calculated by the method of approximation of the expansion of the diffraction line profile (111) and (222) [11]. Electron microscopic studies of the coatings were performed on a scanning electron microscope EVO-40XVP (Carl Zeiss) with an X-ray microanalysis system INCA Energy. The microhardness of the coatings was determined on a microhardness tester PMT-3M. Tribocorrosion studies of coated samples were performed according to the scheme rotating disk–counter-body in the form of a segment (block) on the SMC-2 test rig at a contact load P = 280 N. The sliding speed was 0.67 m/s, the test time was 1 h. Coatings were applied to the cylindrical surface of the "disk" specimens made of steel 09Mn2Si. Counter body - "pad" of steel ШХ 15 (100Cr6), HRC 60…63. Electro-insulating coating was applied to the non-working surfaces of the disks. Working environment - glycerin with the addition of 10% NaCl (pH = 5.9). The change in the electrode potential of the friction pairs was measured using a chlorine-silver reference electrode. Measurements of the friction moment were performed with a non-contact inductive sensor mounted on the shaft of the installation. Electrical signals (mV), from the measurement of these parameters, were transmitted to an analog-digital device and simultaneously recorded by a personal computer with a recording step of 0.2 s. The wear of the samples after the tests was determined gravimetrically with an precision ± 0.0001 g.

Results and discussion

Structure and microhardness of CEC after TT. Thermal treatment significantly changes the properties of CEC. TT is carried out to increase adhesion to the substrate material, to do partial dehydration and to reduce the level of residual stresses. TT is even more effective for CEC Ni-B, because annealing is accompanied by diffusion interaction of components with partial or complete dissolution of boron particles in the matrix and the formation of solid solution and nickel borides. In addition, the newly formed structural components occupy a larger volume in the matrix, than the dispersed particles in the initial state. Therefore, TT is an additional factor, that increases the content of the reinforcing phase in the coating. Electrochemical deposition without TT does not provide optimal volumetric filling of the matrix by the dispersed phase (30… 50%) to ensure high tribotechnical characteristics. CEC Ni-B, obtained by the above modes of electrolysis, have significant filling of the matrix with boron particles and their uniform distribution in the layer (Fig. 1a). Only diffraction lines of nickel are presented on the coating diffraction pattern. The absence of boron lines - indicates the amorphous state of its structure (Fig. 1 b).

The dislocation structure of the electrodeposited coating is formed in the presence of inclusions. Stress fields of inclusions are an effective barrier to dislocation displacement and cause higher (50… 60%) microhardness of CEC, compared to "pure" nickel coating (Fig. 2). The hardness is affected by effect of dispersed hardening of the matrix by boron particles. The hardness also depends on crystal structure, due to the new conditions of crystallization in the electrolyte suspension. The stress state of the CEC is evidenced by the results of diffractometric studies of fine crystal structure parameters. The magnitude of lattice microdeformation and dislocation density increase 1.6 and 4 times, respectively, compared to values for galvanic nickel, and substructure block sizes decrease from 54… 57 to 30 … 32 nm.

Low-temperature thermal treatment of nickel and composite coatings causes similar structural changes. Kinetics of these process is different, therefore development and the degree of conversion at certain temperatures occur differently. A polygonized structure with 50… 70% higher microhardness is formed after the heating of the nickel coating at 200… 230°C, due to the migration of point and linear defects to the grain and subgrain boundaries. The lattice microdeformation decreases after annealing at a temperature of 300°C, due to annihilation of dislocation, and the size of subgrain blocks increases to 94 nm, which affects the decrease in microhardness. When the heating temperature exceeds 360°C, recrystallization transformations start in nickel. Corresponding changes of fine structure cause a significant decrease in hardness [11,12].

The inclusion of boron particles in the CEC slows down the relaxation processes at the stage of pre-recrystallization annealing at 200… 300°C. Slight change in the parameters of the fine structure is observed. In contrast to the nickel coating, the size of the substructure blocks increases to only 33… 34 nm, the microdeformation of the lattice decreases from 1.5 10^{-3} to 1.2 · 10^{-3}, and the density of dislocations - from 0,29·10^{12} to 0.24·10^{12} sm^{-2} after annealing of the CEC at 300°C. Heating within 400… 450°C determines the initial stage of solid-phase interaction of components, which is confirmed by the results of differential-thermal [12] and X-ray diffraction methods of analysis (Fig. 1 d). The development of the interaction between boron particles and the nickel matrix, which is carried out by the type of reaction diffusion, leads to a marked change in the microstructure of the coating (Fig. 1 c).

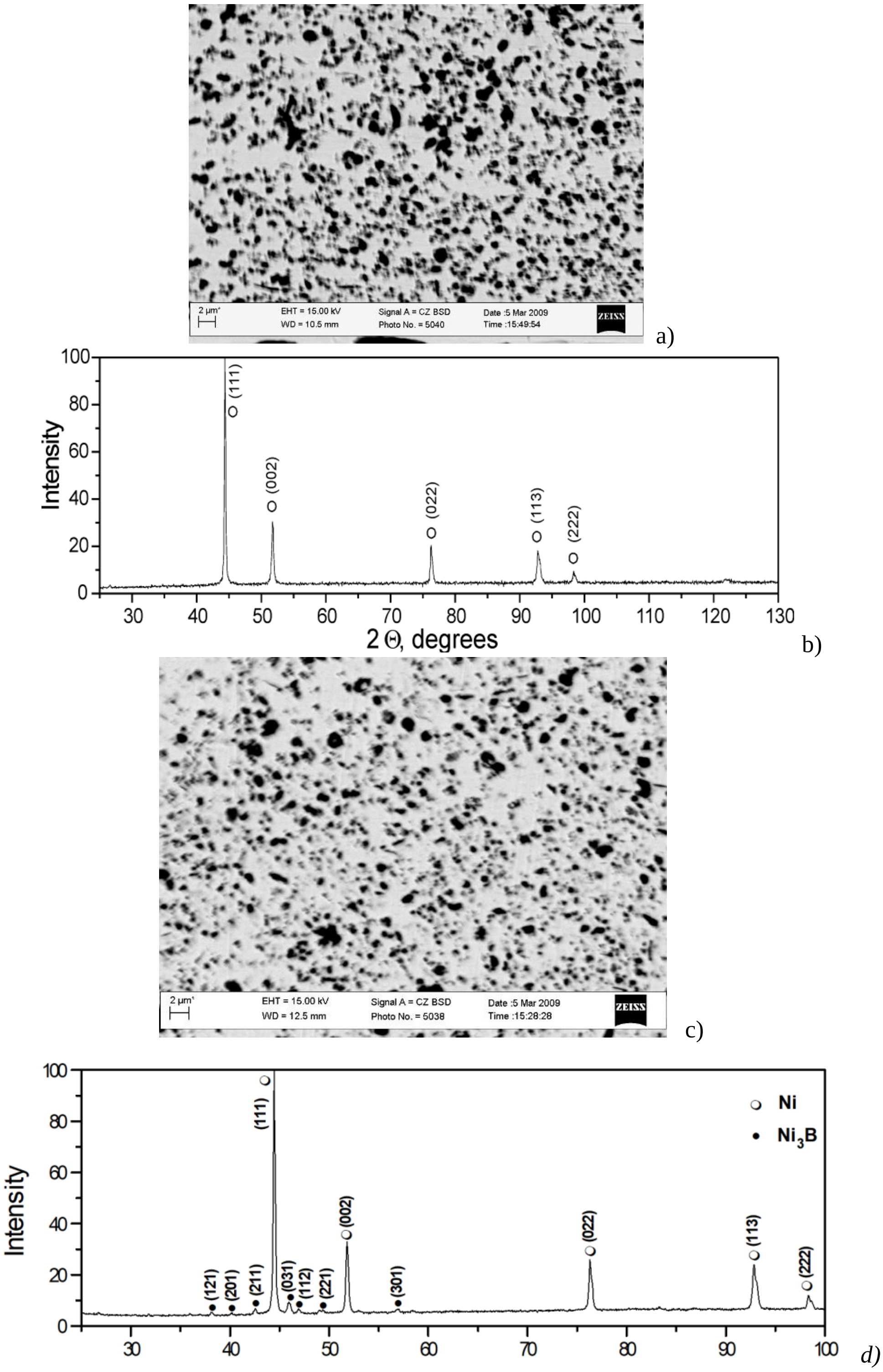


Fig.1. Microstucture (a, c) and X-ray diffraction patterns of CEC Ni-B in initial state (a, b) and after thermal treatment at 450°C (c, d)

The highly developed and branched surface of boron particles in the initial state gradually acquires more rounded shapes, framed by newly formed boride zones. It is due to the diffusion of boron atoms into the adjacent volumes of the Nickel matrix. Stresses are removed insufficiently, the high level of microdeformation remains, the sizes of blocks increase insignificantly. X-ray diffraction analysis showed a significant amount of Ni_3B phase. It is the main reason for the increase in the microhardness. The coating, obtained after this mode of TT is significantly different from pure nickel coating (Fig. 2).

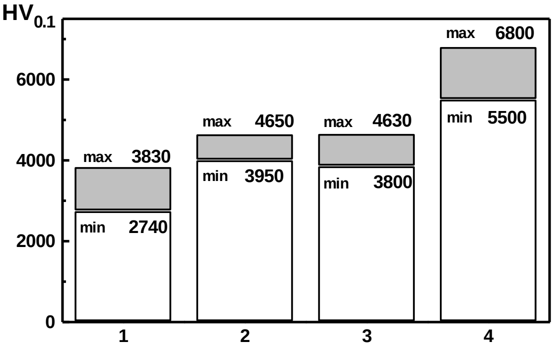
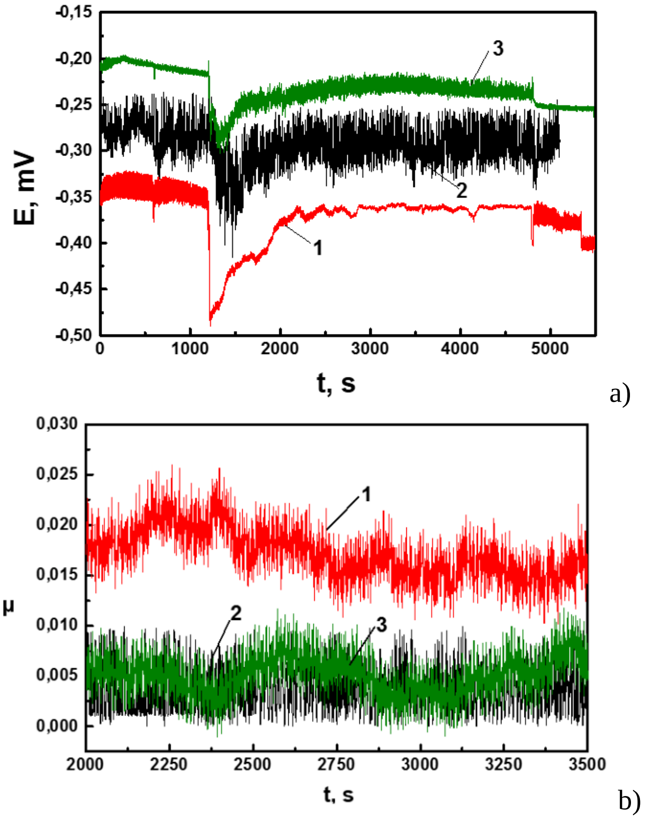


Fig.2. Microhardness of CEC Ni-B after the different thermal treatment parameters. (1) – without TT; after TT: (2) – 200°C; (3) – 300°C and (4) – 450°C. The minimum and maximum values of microhardness are given

Tribocorrosive behavior of CEC. Changes in the electrode potential and friction coefficient (Fig. 3 a, b) during frictional interactions in pairs "steel - Ni-B CEC after different TT" in glycerol + NaCl were studied. Test stages: I - 0… 600 s - contact of friction pairs occurred through a layer of work environment, without load, II - 600… 1200 s friction pairs in contact, III - 1200… 5000 s load is applied, IV - 5000… 6000 s friction pair is unloaded (Fig.3 a, b). The compromise electrode potential is the most positive in the friction pair "steel - CEC-Ni-B after TT at 450□C (E ≈ - 235 mV) (Fig. 3 a), and the most negative - without TT (E ≈ - 370 mV). The coefficient of friction is the lowest in the first case ≈ 0,005 (Fig.3 b), and the highest - in the last ≈ 0.018. The electrode potential in the friction pair "steel - CEC-Ni-B after TT at 300°C is E ≈ - 300 mV, and the coefficient of friction changes randomly from 0.005 to 0.008 during the tests.



a)

b)

Fig.3. General changes of mixed electrode potential (*a*) and friction coefficient (*b*) of friction couples steel – CEC Ni-B in the environment of glycerin + 10% NaCl at the contact loading 280 N. Friction couples – CEC Ni-B without thermal treatment (*1*), after vacuum annealing at 300°C (*2*) and 450°C (*3*)

After unloading, the electrode potentials of the friction pairs “steel - CEC Ni-B after TT at 450°C” and “steel - CEC Ni-B without TT” became more negative. This indicates, that the friction surfaces are in the activated state for some time after the test. The values of the compromise electrode potential of the friction pair “steel - CEC Ni-B after TT at 300°C” do not change after unloading and are at the same level for some time.

Wear resistance of CEC without TT is the worst, after TT at 300°C is slightly better, and after TT at 450°C is the best (Fig. 4).

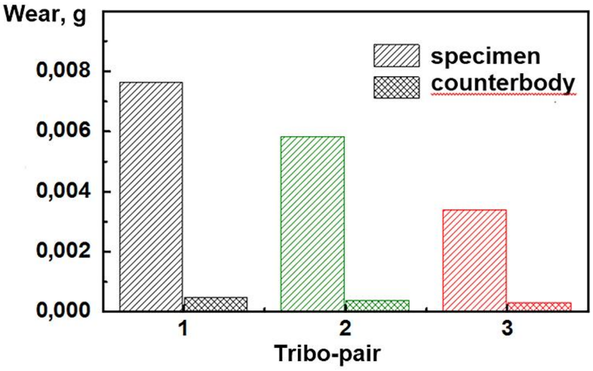
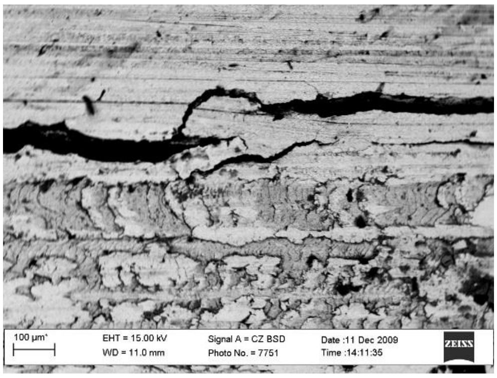


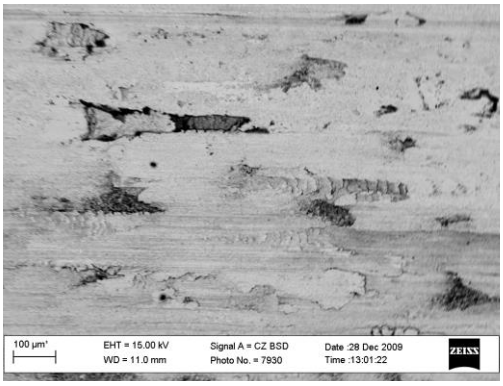
Fig.4. Wear of the friction pairs “steel - CEC Ni-B”, load 280 N. CEC Ni-B: (*1*) – without thermal treatment, after vacuum annealing at 300°C (*2*), and 450°C (*3*)

Toporaphy of friction surfases CEC Ni-B after tribocorrosin investigations was analysed. Cracks were found on the surface of the CEC without TT. Working environment penetrates through cracks during friction (Fig. 5 a), and galvanic pairs are formed between CEC and base steel. Oxide films are absent and stresses increase at the places of friction contact. It is sufficient for the development of shift processes and accumulation of the defects with the subsequent formation of surface and near-surface cracks. The growth and propagation of cracks ends with the separation of individual fragments of the coating.

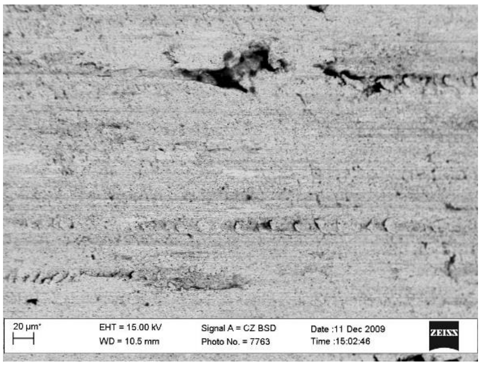
In addition, significant areas of plastic deformation were also found on the surface. Such morphological changes in the structure of CEC without TT are due to the frictional interaction of the contact surfaces in an aggressive environment and leads to a significant shift of the electrode potential towards the negative values.



a)



b)



c)

Fig.5. Toporaphy of friction surfases CEC Ni-B after tribocorrosion investigations in glycerin + 10% NaCl: (*a*) without thermal treatment, after vacuum annealing at 300°C (*b*) and 450°C (*c*)

There are no microcracks of friction surfaces of Ni-B CEC after TT at 300°C. Scores occurs mainly due to insufficient volume content of boride grains. The low hardness of the coating facilitates plastic deformation of the friction surface (Fig. 5 b). Defects in the structure are accompanied by a simultaneous shift of the compromise electrode potential toward negative values and an increase in the coefficient of friction at the local time intervals of the test.

Scores are practically not detected on the friction surfaces of Ni-B CEC after TT at 450°C, when the initial stage of solid-phase interaction of coating components with the formation of Ni-Ni_3B occurs (Fig.5 c). The friction process is stable, as it is evidenced by changes in the values of the compromise electrode potential and the coefficient of friction.

Conclusion

The influence of low-temperature thermal treatment of Ni-B CEC on steel 09Mn2Si on their tribocorrosion behavior is investigated. It is shown that the structural factor has a decisive influence on the efficiency of such friction pairs. The CEC has the least wear and the most positive compromise electrode potential after vacuum annealing at 450°C, when the initial stage of solid-phase interaction of coating components with the formation of Ni-Ni_3B occurs.

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Хома М., Мардаревич Р., Винар В., Василів Х., Ковальчик Ю. Вплив термічної обробки на трибокорозійні властивості композитних покриттів Ni-B

Для підвищення зносостійкості та корозійної стійкості сталей і сплавів застосовуються різні технології захисту поверхонь, зокрема, електрохімічні. Технологія композитних електрохімічних покриттів (КЕП) є більш перспективною, ніж «чисті» гальванічні покриття. Застосування КЕП підвищує стійкість металів до зносу, корозії та втомного руйнування. Нікель часто вибирають в якості матриці КЕП, оскільки він легко утворює рівномірно заповнені бездефектні композитні структури з великою кількістю частинок дисперсної фази (ДФ).

Фізико-механічні властивості металевих покриттів визначають практичне застосування такого складу. Характеристиками КЕП на основі нікелю є: висока твердість і міцність, , а також корозійна стійкість в лужних та слабкокислих середовищах. Ефективним композиційним покриттям з високими трибологічними властивостями є композиційне електрохімічне покриття Ni-B, отримане в процесі електролізу із суспензії аморфного з сульфатхлоридного електроліту нікелювання за катодної густини струму 5 А/дм^2, температури 40...45°С. Встановлено, що після термічної обробки формується нова композитна структура з наповненою матрицею типу Ni-Ni_3B. Покриття Ni-B суттєво підвищують зносостійкість сталі в середовищах з хлоридами. Досліджено трибокорозійну поведінку КЕП Ni-B у вихідному стані та після низькотемпературної термічної обробки. Показано, що структурний фактор має вирішальний вплив на ефективність таких пар тертя. КЕП на основі нікелю має найменший знос і найбільший позитивний компромісний електродний потенціал після вакуумного відпалу при 450°С, за якого відбувається початкова стадія твердофазної взаємодії компонентів покриття з утворенням Ni-Ni_3B.

Ключові слова: композиційне електрохімічне покриття, нікель, бор, структура, твердість, низькотемпературна термообробка, трибокорозія, коефіцієнт тертя