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Development of Plasma-Sprayed Copper Alloy–Nickel-Clad Graphite Composite Coatings with Enhanced Tribological Properties

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Abstract

This study is focused on the development of composite plasma-sprayed coatings with a low coefficient of friction based on copper alloys with additions of nickel-clad graphite and on the investigation of their physicomechanical and tribological properties. Composite coatings were produced by atmospheric plasma spraying (APS) from agglomerated powders of copper alloys with the following compositions: BrONG-30 (70 wt.% BrOF10-1 + 30 wt.% nickel-clad graphite), BrOSNG-30 (70 wt.% BrOCTS5-5-5 + 30 wt.% nickel-clad graphite), and LNG-30 (70 wt.% L63 + 30 wt.% nickel-clad graphite). The application of graphite in a nickel shell improves its wettability by the metallic matrix and enhances adhesion. The obtained coatings exhibit high adhesion strength to the substrate (33–38 MPa) and density (94–97%). Tribological tests demonstrated that the LNG-30 – steel 45 friction pair showed the best performance. The inclusion of nickel-clad graphite reduced the friction coefficient by up to 1.5 times and increased wear resistance by up to 3.8 times. Using EDS and Auger spectroscopy, it was established that during friction in the LNG-30 – steel 45 pair, a film consisting of graphite (16–17 nm thick) and oxides of copper, zinc, nickel, and iron is formed on the counterbody wear track. The presence of such oxide films indicates a predominantly oxidative mechanism of friction, with minor adhesive interaction. The proposed coatings are promising for application in friction units, particularly under conditions where the use of liquid lubricants is limited or impossible.

Keywords: nickel-clad graphite, copper alloy, composite coatings, thermal spray coatings, friction and wear

Introduction

In modern mechanical engineering, friction units made of composite materials produced by powder metallurgy and containing solid lubricants are widely used. Such materials include iron–graphite and bronze–graphite composites. The areas of application and fabrication technologies of these materials are described in detail in a number of studies [1–3]. Bronze–graphite components are generally produced from tin bronze containing 88–92 wt.% copper and 8–11 wt.% tin with an addition of 1–4 wt.% graphite. These types of materials are used in friction units operating under low loads (3–4 MPa), sliding speeds (1–2 m/s), and temperatures (60–80 °C) in the presence of lubrication. They are widely used for the production of parts in instrument making, mechanical engineering, automotive engineering, as well as in equipment for light industry [4]. Impregnation of porous bronze–graphite products with lubricating oils (up to 2 %) allows the friction coefficient to be reduced to 0.03–0.06. Research is underway on the possibility of increasing the graphite content in such composites up to 25 % by powder metallurgy methods without decreasing their strength [5,6]. However, there are a number of engineering tasks that require components to operate under dry sliding conditions, where the use of conventional bronze–graphite materials is not feasible due to their low strength and inability to operate at elevated temperatures, loads, and sliding velocities.

It is known that for certain high-load and high-speed special friction units, virtually pure copper or tompac (a copper–zinc alloy containing 10 or 20 % zinc) has been used [7,8]. Tompac is characterized by high corrosion resistance and increased plasticity, and it can be readily processed by hot and cold deformation. However, it also has a tendency to adhere to steel, which may lead to an undesirable adhesive wear mechanism and consequently to rapid wear of the tribocouple. Adhesion during sliding friction can be prevented by forming a composite that exhibits a low friction coefficient due to the presence of a solid lubricating phase. In the present work, an innovative approach for extending the service life of friction units is proposed through the use of composite coatings with a low coefficient of friction based on copper alloys containing nickel-clad graphite. The proposed coatings are characterized by high run-in ability in friction against steel and by a self-lubricating effect. The use of nickel-clad graphite as a solid lubricant is justified by the fact that graphite in its pure form is not wetted by copper and its alloys (wetting angle $\Theta \approx 140°$) [9]. Poor adhesion of graphite to the metallic matrix in a composite coating results in its pull-out during operation and a deterioration of the functional properties of the coating. Moreover, during thermal spraying, unprotected graphite undergoes high-temperature oxidation and burns out in the plasma jet [10]. This leads to uncontrolled changes in the phase composition of the coating and poor stability and repeatability of results [11]. The wettability of graphite by nickel ensures the adhesion of the nickel film during cladding, while nickel, in turn, is well wetted by copper and its alloys [12]. As a result, graphite protected by a nickel shell does not burn out during spraying and remains well retained in the coating, ensuring a stable and controlled phase composition.

The aim of this work is to obtain composite plasma anti-friction coatings based on copper alloys with additions of nickel-clad graphite and to investigate their physico-mechanical and tribological properties.

Materials and equipment

For the purposes of this study, experimental batches of composite agglomerated powders were produced at the Institute for Problems of Materials Science of the NAS of Ukraine using industrial powders of the following copper-based alloys:

- tin bronze BrOF10-1 (with composition 89 mas. % Cu; 10 mas % Sn; 1 mas.% P) – agglomerated powder BrONG-30;
- tin–lead bronze BrOZS5-5-5 (with composition 85 mas. % Cu; 5 mas % Sn; 5 mas.% Zn; 5 mas. % Pb) – agglomerated powder BrOSNG-30;
- brass L63 (with composition 63 mas. % Cu; 37 mas.% Zn) – agglomerated powder LNG-30.

Each agglomerated composite powder composition contained 30 wt.% nickel-clad graphite powder (NPG-50). The particle size of the developed composite agglomerated powder materials for plasma spraying was in the range of –100 +80 μm.

The composite clad powder NPG-50 (produced by "Composite Systems Ltd.", Zaporizhzhia, Ukraine) consisted of graphite coated with a nickel shell, the amount of nickel in the powder being 50 wt.%.

To increase adhesion, all coatings were deposited onto samples made of steel 45 (equivalents – AISI 1045, JIS S45C, DIN C45) through a bond coat formed from the thermoreactive powder material PTU5N containing 95 wt.% Ni and 5 wt.% Al (analogue – Metco 450NS).

Prior to deposition, the surface of the samples was subjected to grit blasting with electrocorundum powder grade 14A with particle size F22–F24 (ISO 8486-86) in order to clean, activate, and roughen the surface (Rz 63–Rz 80). The treatment was carried out at a distance of 90–150 mm and an angle of 60°–90°, using compressed air at a pressure of 0.5–0.7 MPa. The composite coatings of the above compositions were applied by atmospheric plasma spraying (APS) using an UPU-3D unit in a protective chamber equipped with a 15VB manipulator and an F4-MB plasma gun (Metco, USA). A mixture of argon and hydrogen was used as the plasma-forming gas. For comparative assessment of the influence of graphite on the tribological characteristics of the composite coatings, control test samples of plasma-sprayed L63 brass coatings were also prepared. The microstructure of the obtained plasma coatings and metallographic analysis were carried out using a REM-106 scanning electron microscope. Micro-X-ray spectral analysis (EDS) was performed on a JEOL JAMP-9500 microanalyzer.

The porosity of the coatings was determined using the intercept method (Rozival's linear method). The principle of this method is that the volume fraction of phases comprising the structure of the material under examination can be determined from the relative area of the phases in the obtained microstructural images [13]. The adhesion strength of the coatings to the substrate was determined by a pin-test method as the arithmetic mean of five measurements. Tribological tests were carried out using an M-22M friction machine (designed at the I.M. Frantsevich Institute for Problems of Materials Science of the NAS of Ukraine) according to the "shaft – partial bearing" scheme, at a sliding speed of 4 m/s and a specific load of 2.5 kg/cm² (0.25 MPa); the sliding distance was 3 km. The counterbody was a steel 45 roller with a diameter of 40 mm and hardness of HRC 45–48.

The tests were performed at room temperature in open air under dry sliding conditions.

Results and their discussion

To optimize the technological parameters of plasma spraying for the composite powder materials BrONG-30, BrOSNG-30, LNG-30, as well as the reference coating from L63 brass powder, the argon flow rate, arc voltage

(U, V) and current (I, A) were used as variable parameters, and the spraying distance was adjusted accordingly. The powder materials employed in the study exhibit similar physico-mechanical properties, comparable morphology, granulometric distribution and close melting temperatures; therefore, the optimum spraying parameters obtained for each powder were found to be similar (Table 1).

Table 1

Modes of sputtering of plasma coatings

№	Coating material	Arc current, A	Arc voltage, V	Argon flow rate, l/min.	Hydrogen consum-ption, l/min.	Spraying distance, mm	Coating thickness, mm	Adhe-sion, MPa	Poro-sity, %
1	BrONG -30	450	60	45	7	150	0,4	35	3-5
2	BrOSNG -30	450	60	45	7	150	0,6	33	4-6
3	LNG -30	450	65	45	9	160	0,6	38	3-5
4	L63	450	65	45	9	160	0,6	40	3-4

The optimum spraying regimes were determined based on the following criteria: microstructure, density, and adhesion to the substrate. All coatings exhibited a density of 94–97 %, and the adhesion strength to the substrate was in the range of 33–38 MPa.

The obtained composite coatings possess a multiphase lamellar microstructure typical of plasma-sprayed coatings. In order to increase adhesion to the substrate, the coatings were deposited through an intermediate layer of Ni + 5 wt.% Al thermoreactive powder. All coatings adhere tightly to the substrate, and no delamination was observed in any case (Fig. 1).

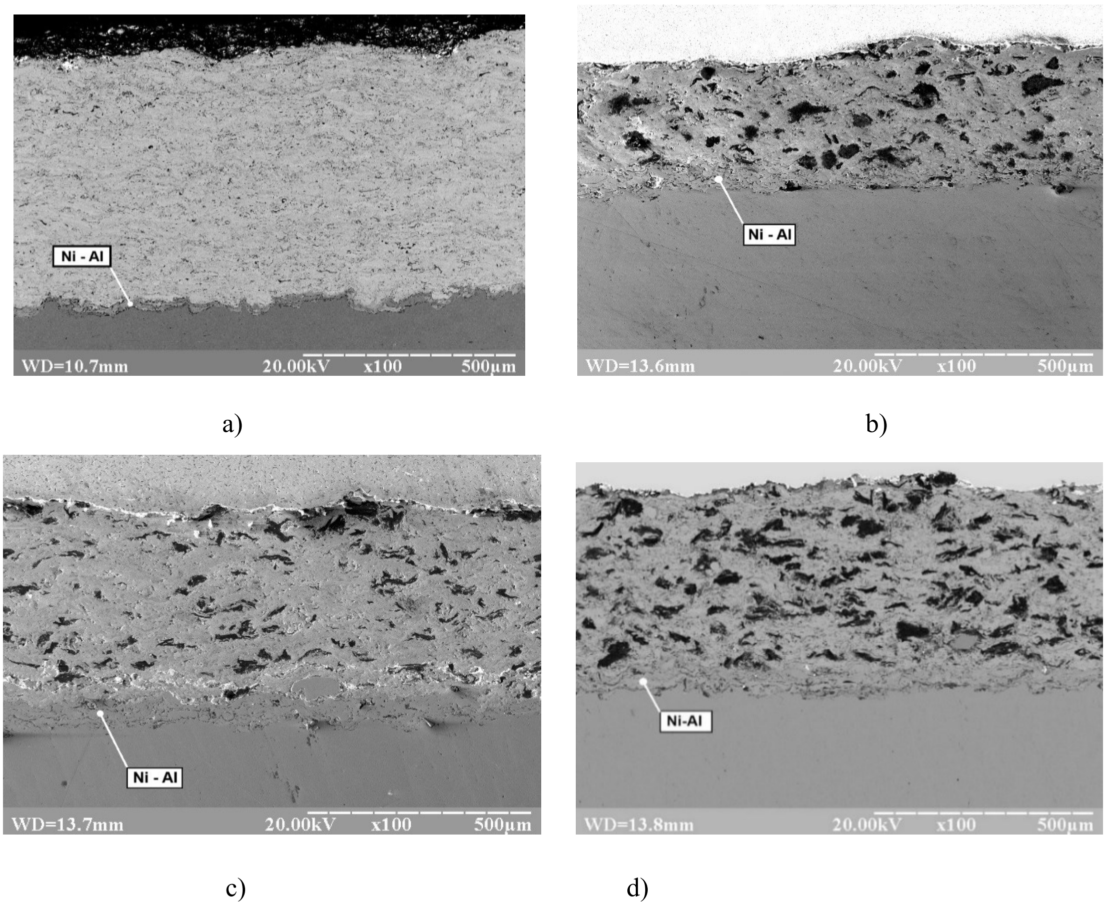
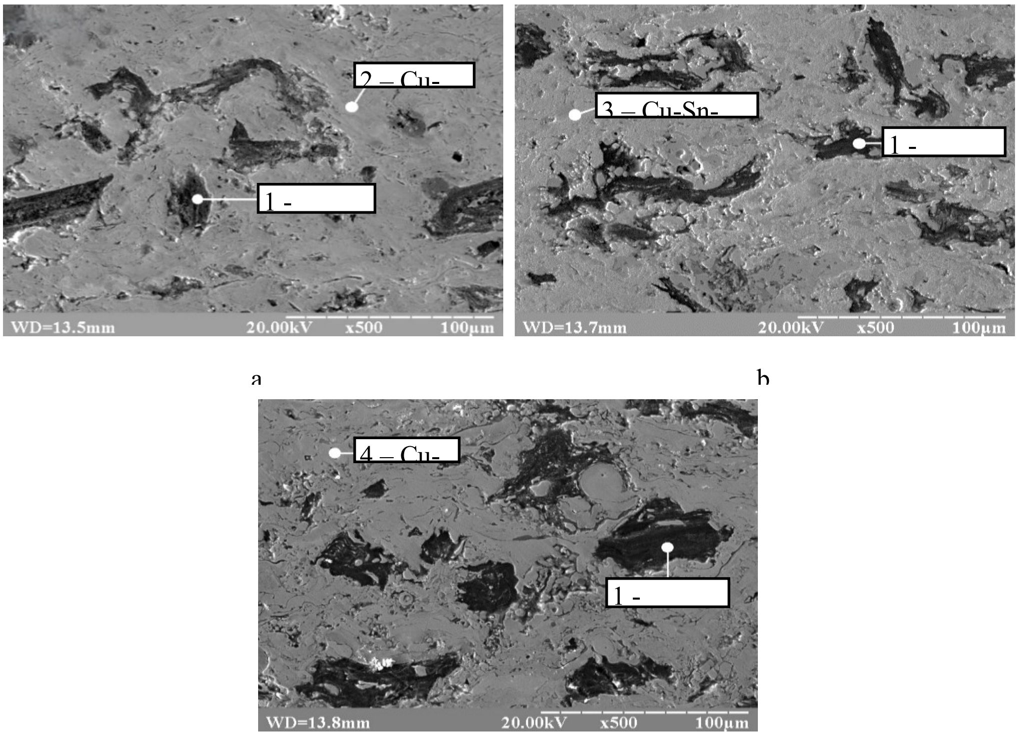


Fig.1. Microstructure of plasma composite coatings at 100x magnification: a – L63; b – BrONG -30; c – BrOSNG-30; d – LNG-30

The metallic matrix in all composite coatings is homogeneous and consists of Cu–Sn–P alloys (Fig. 2a, point 2), Cu–Sn–Zn–Pb alloys (Fig. 2b, point 3), and Cu–Zn alloys (Fig. 2c, point 4). Graphite grains are uniformly distributed within the metallic matrix (Fig. 2, point 1). During preparation of the transverse polished section of the coating, no pull-out of graphite particles was observed, indicating a high degree of cohesion, which is attributed to the use of nickel-clad graphite [14].

The results of the tribological tests of the composite plasma-sprayed coatings were determined as the arithmetic mean of five samples for each coating. Analysis of the obtained data showed that all composite coatings, when paired with steel 45, exhibit a coefficient of friction that is 1.6–1.8 times lower than that of the steel 45 – L63 coating friction pair (Table 2, Fig. 3).



c

Fig. 2. Phase composition of composite plasma coatings: a – BrONG -30; b – BrOSNG -30; c – LNG-30

Table 2

Results of tribotechnical tests of plasma composite coatings.

№	Coating material	Friction path, L, km.	Coefficient of friction, f	Linear wear of friction pair, I, µm/km	Sample temperature, T°C
1	L63	3	0.3	18.9	100
2	LNG-30		0.20	4.9	86
3	BrONG -30		0.24	7.9	92
4	BrOSNG -30		0.27	12.8	120

As can be seen, the wear resistance of the samples with composite coatings is higher than that of the sample coated with L63. The lowest wear was observed for the LNG-30 coating, whereas the wear of the BrOSNG-30 coating was more than two times higher and the total linear wear of the friction pair reached 12.8 µm/km. Thus, it can be concluded that the BrOSNG-30 – steel 45 friction pair showed the poorest performance among all the composite coatings tested.

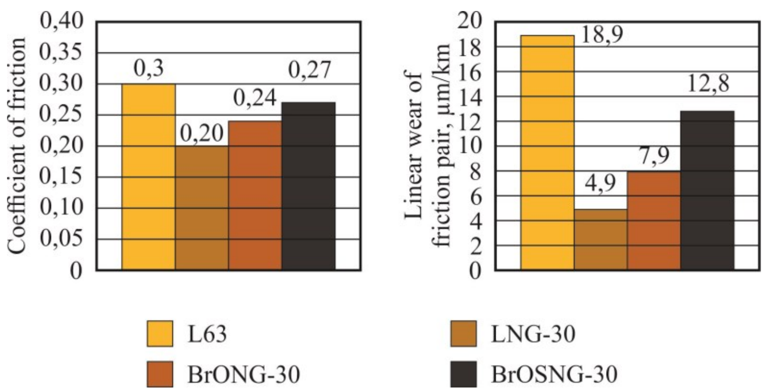
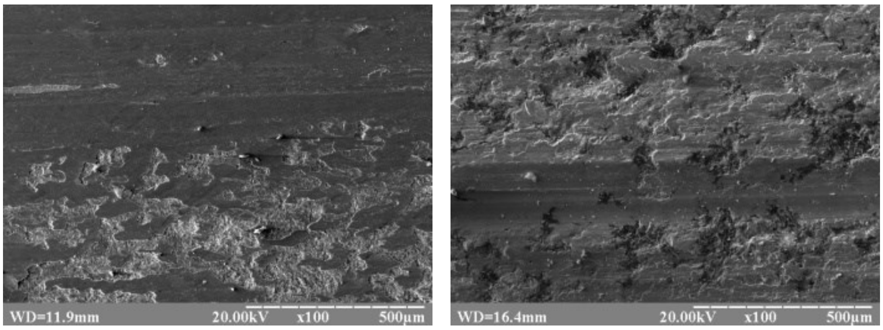


Fig. 3. Results of the study of tribotechnical properties of coating samples

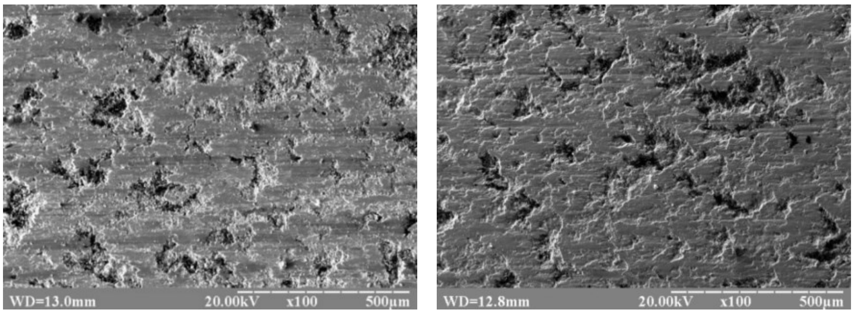
The linear wear of the BrONG-30 – steel 45 friction pair amounted to 7.9 μm/km, while that of the LNG-30 coating was 4.9 μm/km. This is the best result among all the coatings tested. For comparison, the wear of the L63 – steel 45 pair was 18.9 μm/km, which is almost 4 times higher than that of the LNG-30 coating. The highest temperature in the contact zone was observed for the BrOSNG-30 coating (120 °C), whereas the lowest was recorded for the LNG-30 coating (86 °C), which correlates well with the friction coefficient values.

No delamination, microcracking or evidence of scuffing/adhesive seizure was observed on the working surfaces of the composite coatings. However, pores and pits are clearly visible, caused by the pull-out of graphite particles from the metallic matrix during friction (Fig. 4). Considering the obtained tribological results, it can be stated that under the given test conditions, the LNG-30 composite plasma coating showed the best functional performance when paired with steel 45. Therefore, this friction pair was selected for more detailed investigation.

In order to clarify the mechanisms of friction and determine the chemical composition of secondary structures formed on the working surfaces of the counterbody (Fig. 5), micro-X-ray spectral analysis was carried out on the wear tracks. The microstructure and composition of the wear track on the counterbody surface indicate minor transfer of coating material and formation of secondary structures consisting of complex oxides due to adhesive interaction, which is consistent with the results obtained during tribological tests (Table 2). The results of the chemical analysis of the wear track surface before ion etching (Table 3) show that the main element covering the entire surface is carbon. Its content at points 1 and 2 is the highest – 69.2 at.% and 53.2 at.%, respectively.

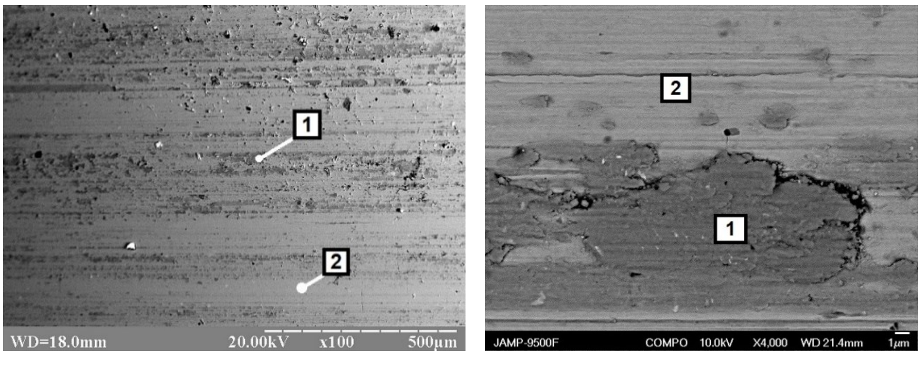


a) b)



c) d)

Fig.4. Microstructure of the friction surfaces of plasma coating samples: a – L63, b – LNG-30, c – BrONG-30, d – BrOSNG-30



a) b)

Fig. 5. Microstructure of the surface of the friction track of the counterbody (aand the places of analysis of the chemical composition of the transfer products from the composite coating sample LNG-30 (b)

This indicates that, during friction, graphite is transferred from the composite coating to the surface of the counterbody, which explains the significant reduction in the coefficient of friction (Table 2, Fig. 3). The small number of adhesive seizure areas and the presence on the surface of elements such as oxygen, copper, zinc, nickel, and iron suggest the formation of oxide films of complex chemical composition on the counterbody surface. This fact indicates that, in the steel 45 – LNG-30 coating friction pair, the oxidative wear mechanism prevails over the adhesive one.

Table 3

The content of friction track elements on the surface of the counter-body before ion etching

Analysis area	Chemical composition, at.%							
	C	N	O	Fe	Ni	Cu	Zn	S
1	69.3	1.6	13.8	2.8	1.3	9.6	1.2	0.4
2	53.4	2.1	25.3	12.9	1.1	4.0	0.8	0.4

After ion etching for two minutes at a rate of 8 nm/min, the carbon content on the surface of the wear track decreases to 2.4–3.4 at.% (zones 1 and 2, respectively) (Table 4). Thus, the thickness of the graphite film is 16–17 nm.

Table 4

The content of friction track elements on the surface of the counter-body after ion etching.

Analysis area	Chemical composition, at.%							
	C	N	O	Fe	Ni	Cu	Zn	S
1	2.4	1.5	45.8	22.5	8.7	13.8	5.3	0.0
2	3.4	0.9	1.8	93.3	0.2	0.2	0.2	0.0

The chemical composition of the secondary structure consists of complex oxides of copper, zinc, and nickel. The significant increase in iron (22.5 at.%) can be explained by the background from the substrate of the steel 45 counterbody. These oxides are absent on the surface of the counterbody (zone 2, Fig. 5a, Table 4).

Conclusions

The results of this study show that the introduction of a solid lubricant into copper-based antifriction alloys in the form of nickel-clad graphite makes it possible to obtain plasma-sprayed composite coatings with high functional performance. The microstructure of the composite coatings consists of a metallic copper-based matrix with uniformly distributed graphite grains. Graphite protected by a nickel shell does not oxidise or burn out in the high-temperature plasma jet during spraying and participates in the formation of the coating. Even with a nickel-clad graphite content of 30 wt.%, the coating exhibits a high adhesion strength to the substrate (33–38 MPa) and a high density (94–97 %).

All three composite coating compositions (BrONG-30, BrOSNG-30 and LNG-30) demonstrated better tribological properties in friction against steel 45 compared with the coating deposited from L63 brass powder. The best results were observed for the LNG-30 – steel 45 friction pair. The friction coefficient in this pair was 0.20, and the linear wear was 4.9 µm/km, which is 1.5 and 3.8 times lower, respectively, than in the L63 friction pair.

XPS and Auger spectroscopy confirmed that, during friction of the LNG-30 – steel 45 pair, a film consisting of graphite (16–17 nm thick) and oxides of copper, zinc, nickel and iron is formed on the wear track of the counterbody. The presence of solid lubricant in the form of graphite in the contact area promotes a reduction in the coefficient of friction and the linear wear of the friction pair. The presence of oxide films of metals originating from both the coating and the counterbody indicates the prevalence of an oxidative wear mechanism in this friction pair.

It was also established that there are local adhesion spots on the wear track surface of the counterbody, where secondary structures containing oxides of copper, zinc, nickel and iron are formed. The presence of such adhesion spots indicates that an adhesive wear mechanism is also present in this pair. However, the small number of these areas and the significant improvement in the tribological performance of the coating allow the conclusion that the dominant wear mechanism in the LNG-30 – steel 45 pair is oxidative.

Based on the results of the conducted research, the composite coatings BrONG-30, BrOSNG-30 and LNG-30 can be recommended for use in friction units of various mechanisms operating under extreme conditions. One of the possible applications of the LNG-30 composite coating is as an antifriction coating for the driving bands of artillery shells in order to extend the service life of gun barrels.

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Author contributions

Terentjev O.: Conceptualization, Analysis, Investigation, Writing original draft; Umanskyi O.: Conceptualization, Analysis, Investigation, Methodology; Kushchev O.: Analysis, Investigation, Visualization, Writing original draft; Varchenko V.: analysis, Investigation; Konoval V.: Writing original draft, Review & editing, Bondarenko O.: Analysis, Investigation; Kurilovych V.: Review & editing.

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Терентьєв О.Є., Уманський О.П., Кущев А.В., Варченко В.Т., Коновал В.П., Бондаренко О.А., Костюнік Р.Є., Курілович В.Д. Розробка плазмових композиційних покриттів системи мідний сплав-плакований графіт з підвищенним рівнем триботехнічних властивостей

Данна робота присвячена розробці композиційних плазмових покриттів з низьким коефіцієнтом тертя на основі сплавів міді з добавками графіту, плакованого нікелем і дослідження їх фізико-механічних та трибологічних властивостей. Відпрацьовано технологію нанесення композиційних покритий методом плазмового напилення (APS) з конгломерованих порошків на основі мідних сплавів наступних складів: БрОНГ-30 (70 мас.% БрОФ10-1 + 30 мас.% графіту, плакованого нікелем); БрОСНГ-30 (70 мас.% БрОЦС5-5-5 + 30 мас.% графіту, плакованого нікелем); ЛНГ-30 (70 мас.% Л63 + 30 мас.% графіту, плакованого нікелем). Застосування графіту у нікелевій оболонці вирішує проблему підвищуення змочуваність графітової фази металевою матрицею, а також покращує адгезію. Отримані покриття мають високий адгезійний зв'язок з основою (33 - 38 МПа) і високу щільність (94 - 97%).

В результаті проведених трибологичних випробувань встановлено, що Найкращі результати спостерігалися в парі тертя ЛНГ-30 - сталь 45 покриття. Включення до складу композиційних покриттів на основі мідних сплавів плакованого нікелем графіту, забезпечує зниження коефіцієнта тертя у трибопарі до 1,5 разів та підвищує її зносостійкість – до 3,8 разів.

Методами МРСА та Оже-спектроскопії встановлено, що на поверхні доріжки тертя контртіла пари ЛНГ-30 – сталь 45 у процесі тертя формується плівка з графіту (завтовшки 16 – 17 нм) та оксидів міді, цинку, нікелю та заліза. Присутність окисних плівок металів зі складу покриття та контртіла свідчить про переважно окисний механізм тертя у цій парі тертя.

Отже, запропоновані покриття можуть бути перспективними для застосування у вузлах тертя особливо в умовах, де використання рідких змащувальних матеріалів є обмеженим або неможливим.

Ключові слова: плакований нікелем графіт, мідний сплав, композитні покриття, газотермічні покриття, тертя та зношування