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Modifying NiAl intermetallic powder by phosphorus cladding for plasma-sprayed coatings and studying their structure and tribological properties

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Abstract

This article examines the impact of adding phosphorus to NiAl intermetallic powder on the structure, microhardness, and tribological properties of plasma-sprayed coatings, which are suitable for use under dry friction conditions. A composite powder designated NiAl+P was obtained by cladding NiAl powder with phosphorus-containing compounds. It was found that the addition of phosphorus promotes the formation of phosphate phases in the coatings, which reduces microhardness but significantly increases wear resistance. In the NiAl+P coating, a protective phosphate film forms on the friction surface during tribological tests, acting as a solid lubricant that reduces the wear rate by almost 2.5 times. The results demonstrate the effectiveness of phosphorus as an alloying element for enhancing the service life of NiAl-based coatings in tribological assemblies.

Keywords: NiAl intermetallic, phosphorus cladding, plasma spraying, phosphate film, tribological properties, wear resistance, solid lubricant, microstructure.

Introduction

Nickel–aluminum intermetallic alloy (NiAl) is widely used to produce thermal spray coatings for high-temperature service [1–6]. Owing to the formation of a dense protective aluminum oxide (Al_2O_3) film on the NiAl surface upon heating, such coatings exhibit excellent heat resistance and serve as an effective barrier against oxidation of the base material [3, 7–8]. NiAl-based coatings have been successfully used as heat-resistant and thermal barrier coatings under high-temperature conditions [1–5, 7]. However, expanding NiAl coatings to friction conditions (tribological units) is promising, but another problem arises in such applications. Under frictional loads, the protective Al_2O_3 oxide film breaks down, allowing direct contact with the counterface material, resulting in surface seizure (galling) and, consequently, catastrophic adhesive wear [3, 9–11]. According to the phenomenological model of fatigue tribological damage accumulation in the surface layer under friction [12], the durability of friction units is primarily governed by the kinetics of surface damage accumulation and the possibility of forming protective secondary structures on the contact surfaces. It is known that to improve wear resistance and provide a low friction coefficient in a contact pair of materials, it is advisable to introduce specific components into the coatings that can form films during friction, acting as solid lubricants [3, 5, 9, 10, 13–18]. This approach enables the coatings to perform effectively at both room and elevated temperatures without experiencing severe wear. In this work, phosphorus oxide-based compounds are introduced by cladding the initial NiAl powder, proposed for forming solid lubricant films within the coating material. This research aims to study the structural features of NiAl intermetallic powder after cladding with phosphorus-containing compounds and to determine the effect of phosphorus addition on the microstructure and tribological properties of composite plasma-sprayed coatings based on the NiAl intermetallic.

Materials and methods

For obtaining the plasma-sprayed coatings, NiAl intermetallic powder grade PN70Yu30 (composition Ni–Al with ~30.5% Al, Fe < 0.2%, C < 0.07%, Ni – balance) with a particle size up to 63 µm (ISO 7530-7:1992) was used as the base material without additives. A NiAl+P powder, containing phosphorus, was used as the composite material, manufactured by the “Composite Systems” company in Zaporizhzhia. The NiAl+P powder was obtained by phosphorus cladding of the original NiAl powder: the NiAl intermetallic particles were uniformly coated with a layer of phosphorus-containing compounds by mixing the powder with a solution of orthophosphoric acid (H_3PO_4), followed by heating, drying of the resulting agglomerate, and crushing. As a result of this process, a composite powder was obtained whose particle surfaces contain phosphorus compounds (phosphorus oxides and other derivatives of phosphoric acid). The resulting NiAl and NiAl+P powders were then used for spraying the coatings. Coatings were deposited by plasma spraying using a UPU-3D plasma unit. Steel cylindrical specimens made of St3 steel (10 mm diameter, 17 mm height) were used as substrates. Spraying was carried out in an argon atmosphere at a plasma arc current of 425–450 A and an arc voltage of 65 V. The spray distance was 160 mm. To increase coating adhesion to the substrate and to clean and roughen the substrate surface, the samples were pre-treated by abrasive blasting with electrocorundum to achieve a surface roughness of $Rz \leq 80$. The porosity of the resulting coatings did not exceed 5%. The microstructure of the obtained powders and coatings was examined by metallography and by scanning electron microscopy (Philips XL30 ESEM). The chemical composition and elemental distribution were determined by energy-dispersive X-ray spectroscopy (EDS) on powder samples and polished cross-sections of the coatings. Coating microhardness was measured with a PMT-3 microhardness tester (Vickers indenter, load $P = 50$ g). Tribological tests were performed on an M22-P friction machine in a “shaft (counterbody) – segment insert (specimen)” configuration. Tests were conducted under dry sliding conditions at room temperature. The counterbody (shaft) was made of 45 steel (HRC 48–50), and the specimen was a steel cylinder with the NiAl-based coating deposited on its end face. The normal load on the specimen during testing was 10 kg, corresponding to a contact pressure of 1.27 Mpa (contact area 0.785 cm^2). The sliding speed was 4 m/s. The wear intensity was evaluated by the mass loss of the specimen and counterbody, normalized per sliding distance (mg/km). After the tribological tests, the wear track surfaces were analyzed by optical microscopy using a Keyence VHX-7000 digital microscope and by scanning electron microscopy with EDS of the worn surfaces to determine the phase composition of wear products. Additionally, using the digital microscope software, profilograms of the wear tracks were obtained, which allowed measurement of the geometric parameters of the worn layer (depth and width of the wear tracks) to identify the wear patterns of the developed thermal spray coatings.

Results and discussion

Microstructure and composition of the initial powders. NiAl powder consists predominantly of equiaxed particles of various sizes (up to 63 μm) with smooth surfaces (Fig. 1a). Metallographic examination of a cross-section of the particles revealed a single-phase, uniform structure of the NiAl intermetallic (Fig. 1b).

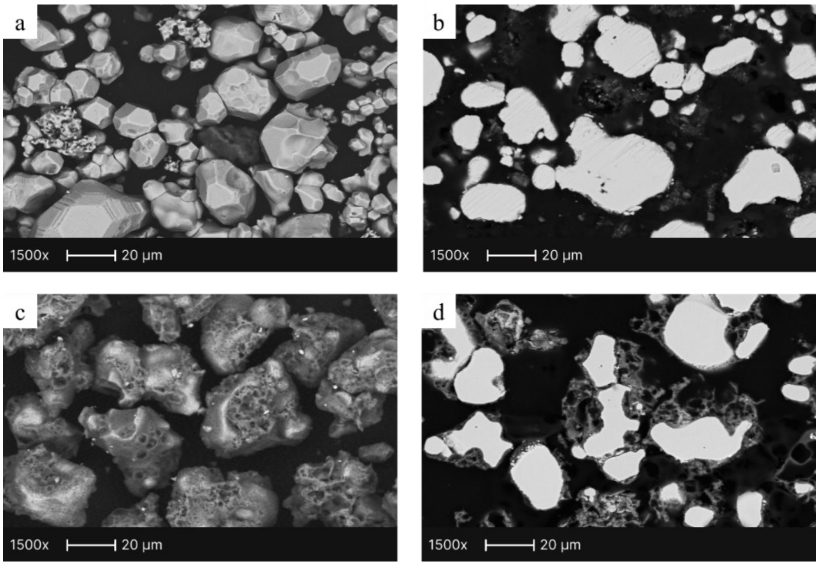

Fig. 1. Morphology of the initial powders: NiAl (a, b) and NiAl+P (c, d).

After cladding with phosphorus-containing compounds (NiAl+P, Fig. 1c, d), the powder particles retain their overall shape. Still, a layer of reaction products from the interaction with orthophosphoric acid is observed on their surface. This surface layer imparts increased roughness to the particles and can cause several particles to agglomerate, coalescing together during the heat treatment. Chemical analysis of the powders (Table 1) confirms the presence of phosphorus in the composite NiAl+P powder.

A significant oxygen content in the NiAl+P powder indicates that phosphorus is present in the form of oxide compounds (likely nickel phosphide Ni_3P and aluminum phosphate $AlPO_4$) coating the particles. Figure 2 shows the elemental distribution map for the NiAl+P powder: phosphorus and oxygen uniformly cover the particle surfaces, forming a shell, whereas nickel and aluminum are concentrated primarily on the particle cores.

Table 1

Chemical composition of the initial powders (EDS, wt.%)

Powder	Ni (wt.%)	Al (wt.%)	P (wt.%)	O (wt.%)
NiAl	69,50	30,50	–	–
NiAl+P	48,67	7,40	24,83	19,03

This confirms that, as a result of the cladding process, a NiAl core coated with a layer of phosphorus-containing compounds was obtained.

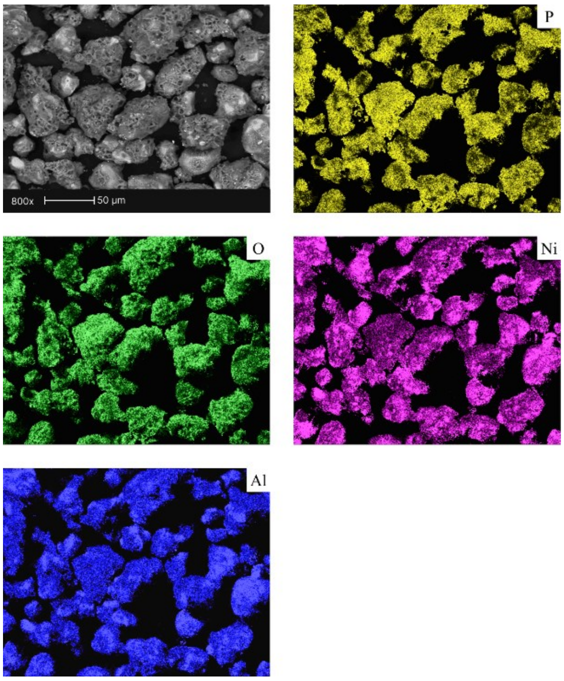

Fig. 2. Elemental distribution map in NiAl+P powder

Structure of the plasma-sprayed coatings. Plasma-sprayed coatings were obtained from both the original intermetallic powder and the phosphorus-clad powder. The cross-section of the coating from the original NiAl (Fig. 3a, b) shows a typical lamellar structure characteristic of thermally sprayed materials. The melted NiAl particles are bonded together and separated by thin oxide boundaries that formed during spraying. Pores and minor defects are uniformly distributed throughout the coating's thickness, and their number is low. The average thickness of this NiAl coating is about 360 µm.

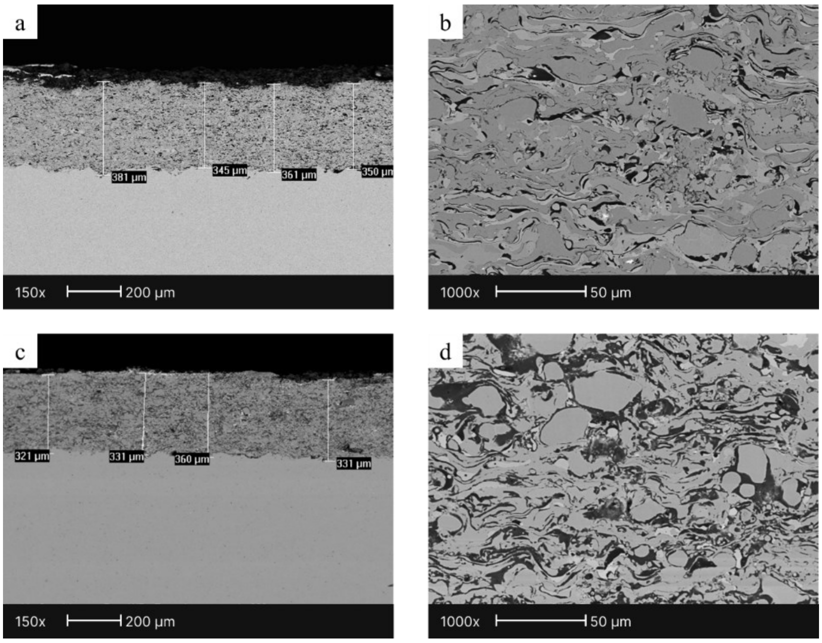

Fig. 3. Plasma-sprayed coatings from NiAl powder (a, b) and NiAl+P powder (c, d)

The NiAl+P coating, with an average thickness of 330 µm (Fig. 3c, d), also exhibits the general lamellar structure. Still, some differences are observed: the material contains inclusions and interlayers of light and dark contrast, indicating the presence of new phases. These inclusions are likely oxide-phosphate phases introduced from the clad powder. The increased fraction of dark oxide layers in the NiAl+P coating is consistent with the EDS chemical composition data (Table 2).

Table 2

Chemical composition of the plasma-sprayed coatings (EDS, wt.%)

Coating	Ni (wt.%)	Al (wt.%)	P (wt.%)	O (wt.%)
NiAl	66.57	26,51	0	3,93
NiAl + P	60,6	24,02	6,87	8,5

In particular, the NiAl+P coating was found to contain ~6.9 wt.% phosphorus and an elevated oxygen content (8.5 wt.% compared to 3.9 wt.% in the pure NiAl coating). Accordingly, the nickel and aluminum contents in the composite coating are slightly lower (approximately 60.6% Ni and 24.0% Al, versus 66.6% Ni and 26.5% Al in NiAl). This means that during spraying, the phosphorus-containing components from the powder were transferred into the coating, forming a separate phase and enriching the coating with phosphorus and oxygen. The elemental distribution in the coatings (Figs. 4 and 5) confirms the absence of phosphorus in the pure NiAl coating and its homogeneous presence throughout the NiAl+P coating. On the elemental map of the NiAl coating (Fig. 4), only Ni and Al are observed, along with a few isolated oxide areas containing O (plus minor Fe impurities near the interface with the steel substrate).

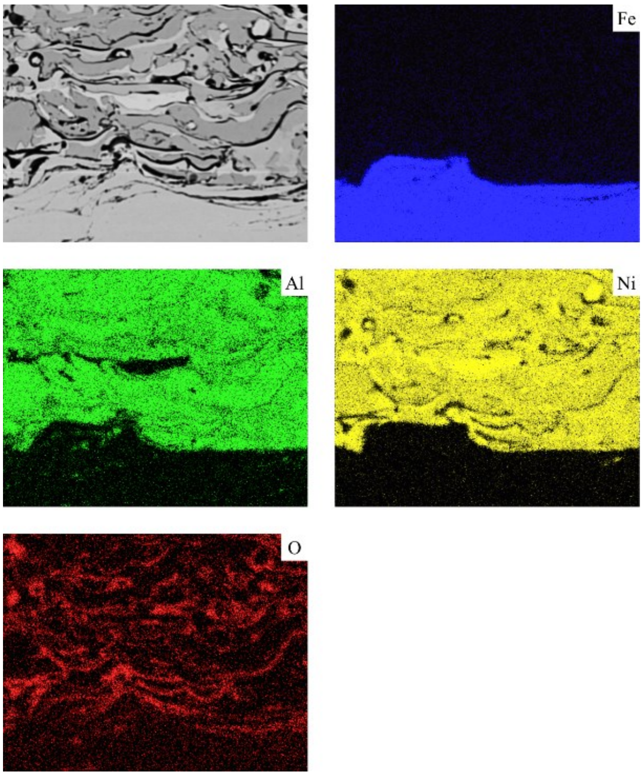

Fig. 4. Microstructure and elemental distribution maps of the NiAl coating

By contrast, the elemental maps of the NiAl+P coating (Fig. 5) clearly record the presence of phosphorus throughout the structure together with increased oxygen content, indicating the uniform incorporation of a phosphate phase between the intermetallic lamellae.

Microhardness of the coatings. The introduction of phosphorus slightly changes the hardness of the coating material. According to the measurements, the microhardness of the plasma-sprayed coating from pure NiAl is 3.68 ± 0.25 GPa, whereas for the composite NiAl+P coating, it decreases to 3.10 ± 0.17 GPa. Thus, the addition of phosphorus results in a decrease in microhardness of approximately 15%. This reduction in microhardness may be related to the formation of relatively soft oxide-phosphate phases or to a slightly higher level of porosity in the NiAl+P coating.

Tribological properties. The tribological test results showed that the NiAl+P coatings perform significantly better under dry friction conditions than the coatings from the original NiAl powder. The quantitative indicators of wear resistance are given in Table 3.

Table 3

Tribological characteristics of the coatings (dry friction, 20 °C)

Parameter	NiAl	NiAl+P
Mass wear of the sample (mg/km)	186,6 ± 5,3	97,0 ± 3,9
Counterbody mass change (mg/km)	+0,85 ± 0,04	+3,6 ± 0,18
Linear wear of pair (µm/km)	222 ± 13	93,8 ± 9,4

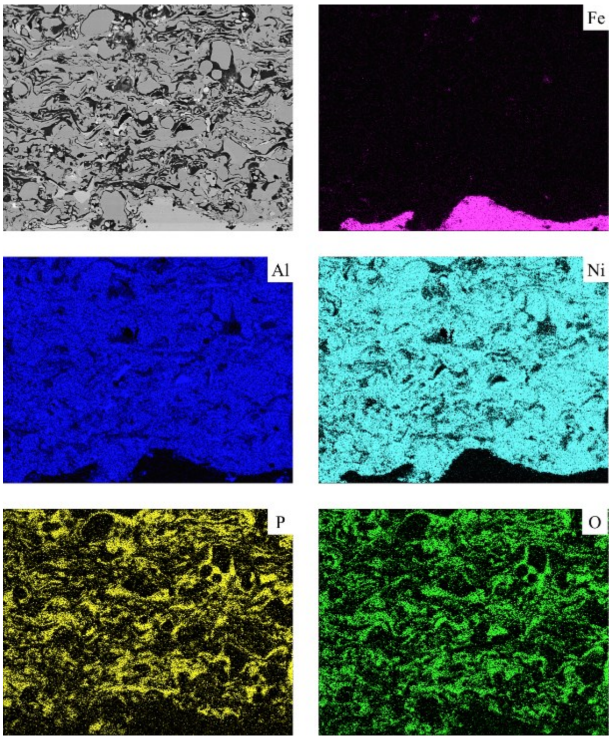

Fig. 5. Microstructure of the NiAl+P coating and its elemental distribution maps.

The mass loss of the NiAl-coated sample (without phosphorus) was 186.6 mg per 1 km of sliding, whereas for the sample with the NiAl+P coating, it did not exceed 97 mg/km, i.e., almost half as much. The total wear of the friction pair (specimen + counterbody) with the NiAl coating was 222 µm/km, while for NiAl+P it was only 93.8 µm/km, which is 2.4 times lower. Thus, the addition of phosphorus significantly reduced the wear rate of the plasma-sprayed coating (by more than a factor of 2), representing a substantial improvement in tribological performance.

The wear profiles of the coatings obtained from the original and clad powders were studied using profilometry. In the case of the pure NiAl coating (Fig. 6), the wear track is relatively deep and wide, with clearly pronounced irregularities in the profile. Significant variations in depth, reaching about 12–15 µm, were observed, indicating an intense adhesive wear mechanism. The surface is characterized by deep, ragged grooves and pronounced peaks and valleys, pointing to a non-uniform wear process.

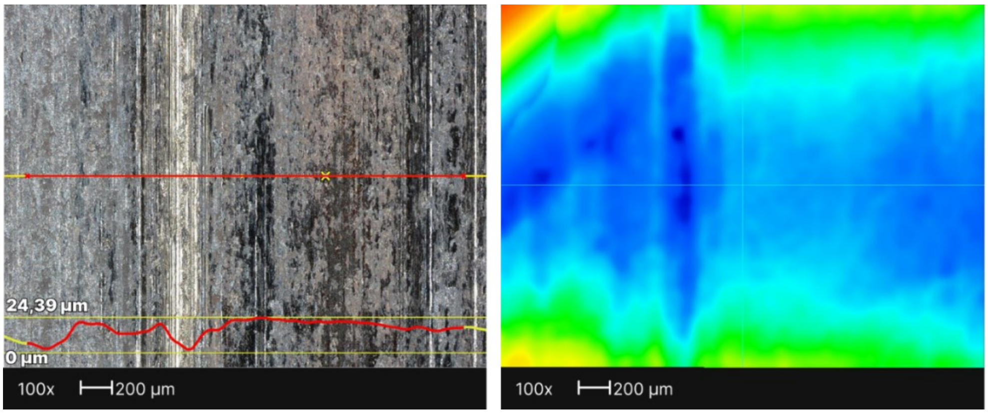

Fig. 6. Profilogram of the NiAl coating after tribological testing.

For the NiAl+P coating (Fig. 7), the wear track profile exhibits significantly more minor depth variations, not exceeding 5–7 µm. The worn surface exhibits a much more uniform character, lacking sharp depth differences, which indicates a significant reduction in the intensity of the wear process compared to pure NiAl.

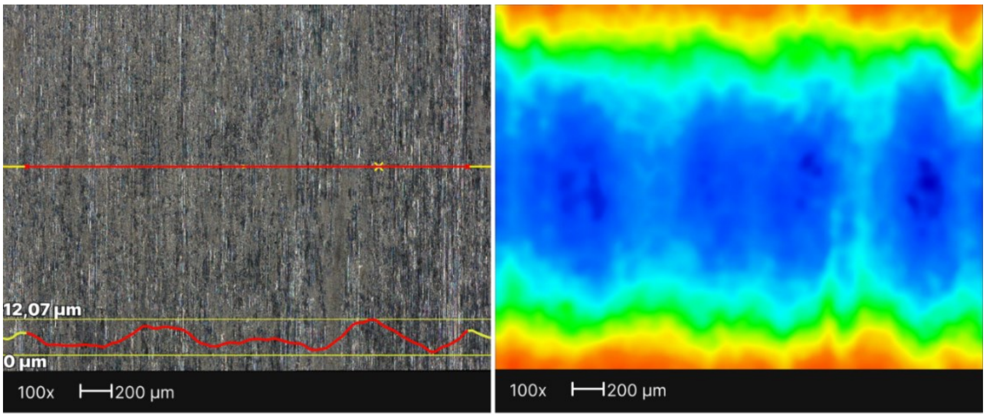

Fig. 7. Profilogram of the NiAl+P coating after tribological testing.

Visual analysis of the wear tracks further confirms the changes in wear mechanisms. On the surface of the original NiAl coating (Fig. 8), characteristic signs of severe adhesive wear are observed, in particular, deep, torn grooves. This is associated with a galling (seizure) process between the contact surfaces, which significantly increases wear and leads to highly non-uniform material removal.

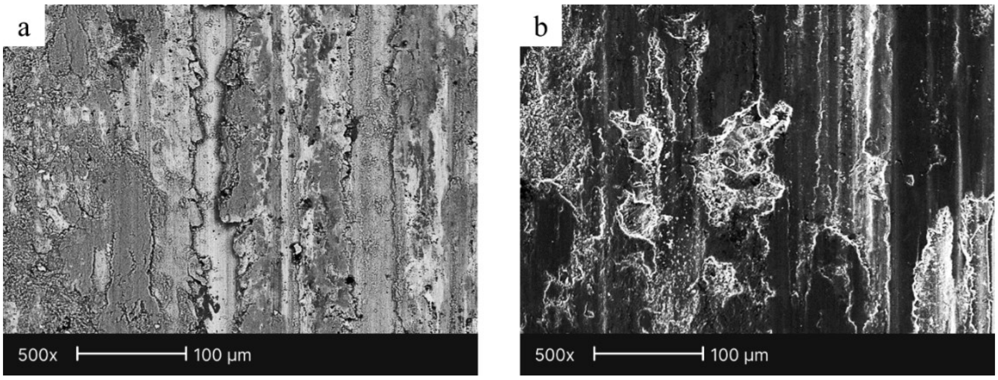

Fig. 8. Wear tracks of the NiAl coating after tribological testing: (a) microstructure (SEM/BSE) and (b) topography (SEM/SE).

In the case of the NiAl+P coating (Fig. 9), the dominant wear mechanism is altered compared to the pure NiAl coating. While the NiAl coating exhibited intense adhesive wear, the addition of phosphorus altered the wear mechanism: the intensity of adhesive interaction decreased, indicating a change in the friction conditions. Thin phosphate or oxide-phosphate films are likely formed on the wear surface, acting as a protective layer and partially serving as a solid lubricant. As a result, the tendency toward adhesion (surface seizure) is diminished, and hence the overall wear intensity is reduced.

Thus, adding phosphorus to the coating effectively prevents surface seizure during friction. Consequently, a significant improvement in tribological characteristics is achieved in both mass and geometric terms: the mass wear is reduced by more than twofold, and the geometric characteristics of the worn surfaces become much more uniform.

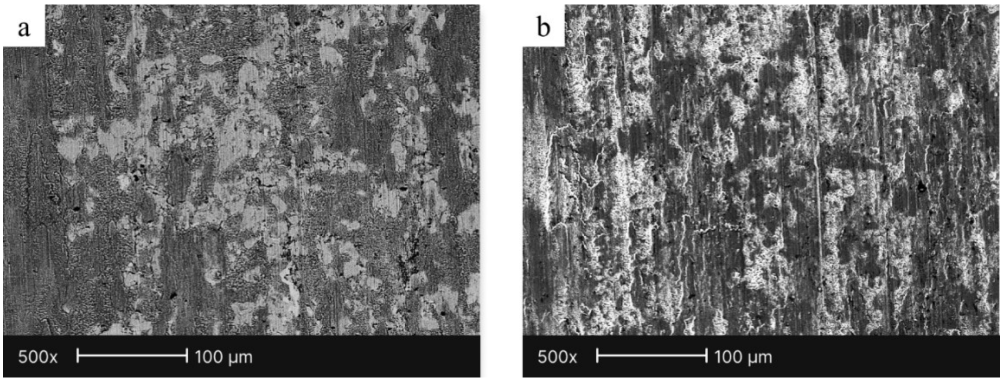

Fig. 9. Wear tracks of the NiAl+P coating after tribological testing: (a) microstructure (SEM/BSE) and (b) topography (SEM/SE).

The EDS analysis of the worn surfaces (Figs. 10 and 11) provides further evidence of the change in wear mechanism. On the worn surface of the NiAl coating (Fig. 10), in addition to the base elements Ni and Al, a considerable amount of iron was detected. This indicates the transfer of iron (as iron oxides) from the steel counterbody onto the coating's wear surface due to intense adhesive contact.

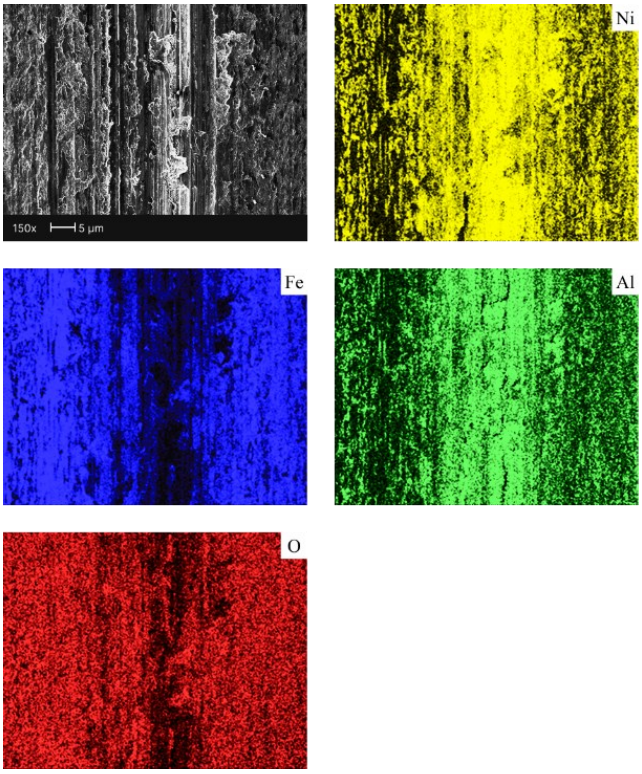

Fig. 10. Elemental distribution map of the NiAl coating after tribological testing.

By contrast, on the worn surface of the NiAl+P coating (Fig. 11), virtually no iron is detected. Instead, an increased concentration of phosphorus and oxygen is present.

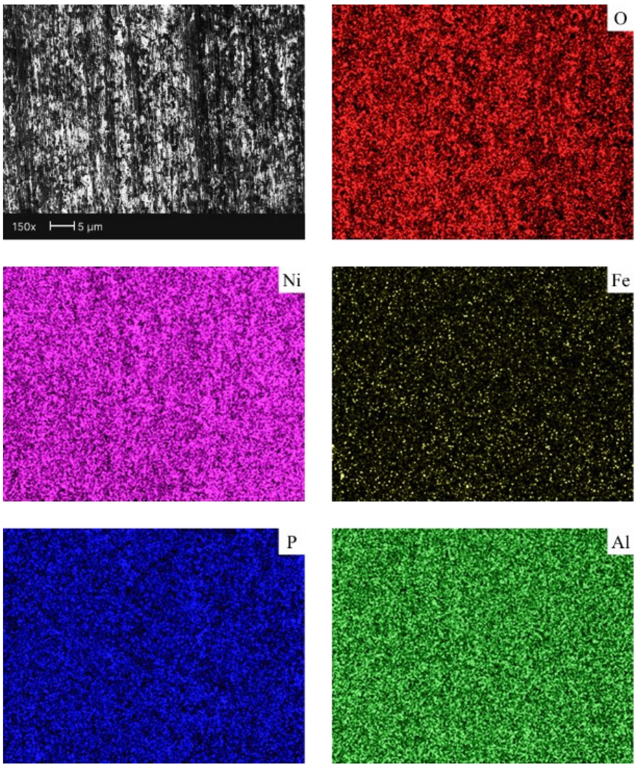

Fig. 11. Elemental distribution map of the NiAl+P coating after tribological testing.

The presence of phosphorus on the NiAl+P friction surface indicates the likely formation of a protective phosphate film during sliding. Notably, the mass of the counterbody (steel shaft) in tests with the NiAl coating increased slightly (+0.85 mg/km, see Table 3), implying the transfer of a small amount of coating material onto the counterbody. In the pair with the NiAl+P coating, the counterbody's mass gain was higher (+3.6 mg/km), meaning a larger quantity of material from the composite coating was transferred to it. This suggests that the formed phosphate film effectively bears the load and protects the main coating from further wear — a portion of the coating material is sacrificed and transferred to the counterbody, creating a transfer film. Although this transferred film slightly increases the mass of the shaft, it serves as a solid lubricant, thereby reducing the overall wear of the tribosystem.

The results of these studies confirm that the presence of phosphorus significantly improves the wear resistance of the coating under friction due to the formation of protective phases on the surface that act as a solid lubricant.

Conclusions

1. Phosphorus cladding of NiAl powder leads to new phases in the coating: Cladding the original NiAl powder with phosphorus promotes the formation of a phase in the resulting coating based on phosphorus-containing compounds. This is confirmed by the presence of ~6.9 wt.% phosphorus and an elevated oxygen content (8.5 wt.%). The introduced phase is represented predominantly by oxide-phosphate formations uniformly distributed between the lamellae of the primary NiAl intermetallic.
2. Phosphorus changes the dominant wear mechanism: The addition of phosphorus alters the prevailing wear mechanism of the coatings. The pure NiAl coating is characterized by severe adhesive wear with pronounced grooves and significant depth variations (up to 12–15 µm). In contrast, after adding phosphorus, no adhesive wear mechanism is observed. The formation of a protective phosphate film ensures uniform wear with minimal depth variation (limited to about 5–7 µm).
3. Phosphorus markedly improves tribological performance: The use of phosphorus-containing (NiAl+P) coatings significantly improves tribological properties. The mass wear of the NiAl+P coating is more than two times lower compared to NiAl (approximately 97 mg/km vs 186.6 mg/km), and the total wear of the friction pair is reduced by a factor of 2.4. These results demonstrate the high effectiveness of phosphorus as an alloying additive for increasing the service life of NiAl-based coatings in tribological applications.

References

1. Chen, H., Luo, W. Effects of β-NiAl powder addition on the high temperature oxidation behaviour of thermally sprayed CoNiCrAlY coatings // Journal of Materials Research and Technology, 2025, Vol. 37, 1737–1747, https://www.doi.org/10.1016/j.jmrt.2025.06.140
2. Hardwicke C.U., Lau Y.-C., Advances in thermal spray coatings for gas turbines and energy generation: a review, Journal of Thermal Spray Technology 22 (2013) 564-576, https://www.doi.org/10.1007/s11666-013-9904-0
3. Hu, Q., Geng, S., Niu, X., Wang, J., Huang, Y., Wang, F. Effect of Y/Pt modification on high-temperature corrosion resistance of NiAl coatings in the environment of NaCl-humid air // Corrosion Science, 2025, Vol. 253, 113000, https://www.doi.org/10.1016/j.corsci.2025.113000
4. Ghara, T., Kuroda, S., Yanagisawa, T., Shahien, M., Suzuki, M., Inoue, T., Shinoda, K. Degradation behaviour of HVOF sprayed CoNiCrAlY coating in high-temperature ammonia environment towards its applicability in ammonia fueled gas turbines // International Journal of Hydrogen Energy, 2025, Vol. 130, 345–359, https://www.doi.org/10.1016/j.ijhydene.2025.04.277
5. Sun, H., Wan, S., Yi, G., Yang, J., Bai, L., Shi, P., Cheng, J. Friction and wear behaviors of NiAl–Bi_2O_3–Ag–Cr_2O_3 composite coating in the thermal cycle of RT–800 °C // Tribology International, 2021, Vol. 159, 106957, https://www.doi.org/10.1016/j.triboint.2021.106957
6. Zhou, X., Mukoyoshi, M., Kitagawa, H. Recent advances in high-entropy intermetallic nanoparticles: synthesis and electrocatalytic applications // Chemical Communications, 2025, Vol. 61, 10911–10930, https://www.doi.org/10.1039/D5CC00993F
7. Peng, J., Li, Z., Li, Y., Wang, Z., Tan, L., Wang, Y., Huang, L., Liu, F. Effect of in-situ growth Al_2O_3 on high-temperature oxidation performance and mechanism of NiAl // Journal of Alloys and Compounds, 2025, Vol. 1036, 181701, https://www.doi.org/10.1016/j.jallcom.2025.181701
8. Zhang, W.L., Li, S.M., Fu, L.B., Li, W., Sun, J., Wang, T.G., Jiang, S.M., Gong, J., Sun, C. Preparation and cyclic oxidation resistance of Hf-doped NiAl coating // Corrosion Science, 2022, Vol. 195, 110014, https://www.doi.org/10.1016/j.corsci.2021.110014
9. Zhang, L., Liao, X.-J., Chen, R., Luo, X.-T., Li, C.-J. Tribological behavior of NiAl coating deposited by plasma spraying of diamond-contained Ni/Al composite powder at a wide range temperature from 25 °C to 700 °C // Transactions of Materials Research, 2025, Vol. 1, 100100, https://www.doi.org/10.1016/j.tramat.2025.100100

10. Guo, H., Li, B., Yan, P., Wu, Z., Li, F., Liu, Z. Microstructures, mechanical properties and tribological behaviors of NiAl-based composite coatings with various addition of Nb // Surface and Coatings Technology, 2022, Vol. 449, 128977, https://www.doi.org/10.1016/j.surfcoat.2022.128977

11. Zhang, H., Zhu, H., Huang, J., Li, J., Xie, Z. In-situ TiB_2–NiAl composites synthesized by arc melting: Chemical reaction, microstructure and mechanical strength // Materials Science and Engineering: A, 2018, Vol. 719, 140–146, https://www.doi.org/10.1016/j.msea.2018.01.125

12. Sorokatyi, R., Chernets, M., Dykha, A., Mikosyanchyk, O. Phenomenological Model of Accumulation of Fatigue Tribological Damage in the Surface Layer of Materials // Mechanisms and Machine Science. – 2019. – Vol. 73. – P. 3761–3769, https://www.doi.org/10.1007/978-3-030-20131-9_371

13. Fan, X., Huang, W., Zhou, X., Zou, B. Preparation and characterization of NiAl–TiC–TiB_2 intermetallic matrix composite coatings by atmospheric plasma spraying of SHS powders // Ceramics International, 2020, Vol. 46, No. 8, 10512–10520, https://www.doi.org/10.1016/j.ceramint.2020.01.052

14. Bolelli, G.; Cannillo, V.; Lusvarghi, L.; Rosa, R.; Valarezo, A.; Choi, W. B.; Dey, R.; Weyant, C.; Sampath, S. Functionally graded WC-Co/NiAl HVOF coatings for damage tolerance, wear and corrosion protection // Surf. Coatings Technol. 2012, 206 (8–9), 2585–2601, https://www.doi.org/10.1016/j.surfcoat.2011.11.018

15. Sun, Y., Yuan, J., Wang, M., Wang, H., Chen, Z., Liu, X., Li, S., Zhao, W., Yang, J. Enhanced tribological performance of NiAl-based composite coatings: Design of the composition in coatings by addition of Mo and Nanodiamond // Tribology International, 2025, Vol. 203, 110405, https://www.doi.org/10.1016/j.triboint.2024.110405

16. O. Umanskyi, O.Poliarus, M. Ukrainets, O. Kostenko, M Antonov, I. Hussainova Influence of Cr, Ti and Zr Oxides Formation on High Temperature Sliding of NiAl-Based Plasma Spray Coatings // Journal “Key Engineering Materials”, Trans Tech Publications, Switzerland, Vol. 674 (2016), pp 308-312, https://www.doi.org/10.4028/www.scientific.net/KEM.674.308

17. O. Umanskyi, O. Poliarus, M. Ukrainets, M. Antonov, I. Hussainova. High Temperature Sliding Wear of NiAl-based Coatings Reinforced by Borides // Materials Science (Medžiagotyra). – 2016. – Vol. 22, No. 1. – pp. 49-53, https://www.doi.org/10.5755/j01.ms.22.1.8093

18. O.Poliarus, J. Morgiel, O. Umanskyi, M. Pomorska, P. Bobrowski, M. Szczerba, O. Kostenko. Microstructure and wear of thermal sprayed composite NiAl-based Coatings // Archives of Civil and Mechanical Engineering, 19(4), pp. 1095-1103 (2019), https://www.doi.org/10.1016/j.acme.2019.06.002

Левчук Т.О., Полярус О.М., Коновал В.П., Макаренко О.С. Модифікація порошків інтерметаліду NiAl шляхом плакування фосфором для плазмових покриттів та дослідження їх структури і триботехнічних властивостей

У статті досліджено вплив додавання фосфору до інтерметалідного порошку NiAl на структуру, мікротвердість та триботехнічні властивості плазмових покриттів, які можуть бути рекомендовані для роботи в умовах тертя без мастила. Композиційний порошок NiAl+P отримано шляхом плакування NiAl фосфоровмісними сполуками. Встановлено, що додавання фосфору сприяє утворенню в покриттях фосфатних фаз, що знижує мікротвердість, але суттєво підвищує зносостійкість. В покритті NiAl+P при трибовипробуваннях на поверхні тертя формується захисна фосфатна плівка, яка виконує роль твердого мастила та зменшує інтенсивність зношування майже в 2,5 раза. Отримані результати свідчать про ефективність фосфору як легуючого елементу для підвищення експлуатаційної довговічності NiAl-покриттів у триботехнічних вузлах.

Ключові слова: інтерметалід NiAl, плакування фосфором, плазмове напилення, фосфатна плівка, триботехнічні властивості, зносостійкість, тверде мастило, мікроструктура