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FORMATION OF COMPOSITE COATINGS BY THE METHOD OF SUPERSONIC PLASMA SPRAYING OF POWDERS BASED ON TiAl INTERMETALLIC WITH NON-METALLIC REFRACTORY COMPOUNDS SiC AND Si_3N_4

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ABSTRACT

Studies of the structural-phase state, erosion and corrosion resistance of coatings of TiAl-SiC and TiAl–Si_3N_4 systems, produced by the method of supersonic air-gas plasma spraying, are presented. As materials for spraying, composite powders, produced by the method of mechanic and chemical synthesis based on TiAl intermetallic with the addition of non-metallic refractory compounds SiC and Si_3N_4 were used. Comparison of the phase composition of the produced coatings of TiAl-SiC and TiAl–Si_3N_4 systems with the phase composition of the composite powder after mechanic and chemical synthesis indicates proceeding of processes of interaction of TiAl with non-metallic refractory compounds, as a result of which the phases of SiC and Si_3N_4 are not observed in the coating. Due to the presence of strengthening phases in the coatings, the erosion resistance of the composite coatings increases by 1.3–1.5 times as compared to TiAl intermetallic coating. Electrochemical tests found that the coatings of TiAl—SiC and TiAl–Si_3N_4 systems are capable to provide the protection of steel, aluminium and titanium base in the environment containing sodium chloride with an increase in resistance by 5–155 times. On the basis of the conducted studies of functional properties of the developed composite coatings, the possibility of their use for the protection of parts subjected to erosive wear and corrosion is shown.

KEYWORDS: intermetallic, non-metallic refractory compound, supersonic air-gas plasma spraying, structure, phase composition, erosive wear, corrosion resistance

INTRODUCTION

Owing to low density, high specific strength, resistance to environmental impact, heat strength and heat resistance, titanium aluminides are used as materials in the manufacture of some components in automotive and aircraft industries, such as turbocompressors, cars turbocharges, blades of low-pressure turbines, etc. [1]. However, the main disadvantages that limit the widespread practical use of titanium aluminides, are their brittleness, low plasticity and crack resistance in a wide temperature range, and increased ductility complicates the use of TiAl alloys in the conditions of friction of surfaces being in contact [2].

In order to increase the physical and mechanical properties of products, composite materials are developed based on TiAl systems — non-metallic refractory compound (NRC) (e.g. B_4C, SiC, etc.), for whose production mainly the methods of powder metallurgy — hot isostatic pressing, reaction sintering and high-temperature synthesis are used [3, 4].

To produce TiAl-based coatings, vacuum deposition methods, such as magnetron, cathode-arc, electron beam and ionic deposition, have become the most widespread. Magnetron coatings of TiAl-BN system increase the wear- and heat resistance of a product as compared to TiAlN coatings [5]. Coatings of TiAl–SiC system, produced by electron beam deposition, have an increased resistance to cyclic oxidation due to a high adhesion between the coating and the base [6]. Coatings of TiAlSiN system, produced by cathode-arc, magnetron and ionic deposition, have high strength, microhardness and wear resistance [7, 8].

A challenging direction in producing protective coatings based on TiAl intermetallic is thermal spraying, which, unlike vacuum methods for deposition of coating, allows depositing coatings with the thickness of few millimeters. In addition, thermal spraying methods allow repairing local damages of parts that failed prematurely as a result of corrosion, erosion, abrasive wear or fatigue.

TiAl-based thermal coatings are produced by the methods of plasma, supersonic plasma, high-velocity oxyfuel and cold gas dynamic spraying [9]. It is possible to increase the resistance to oxidation and mechanical properties of coatings based on TiAl binary alloy by adding alloying elements such as Cr, Si, V, Nb, W, Mo or Ta, [9]. The use of composite coatings based on TiAl alloy with the addition of non-metallic refractory compounds such as SiC and Al_2O_3 components as strengthening components, allows increasing the hardness and wear resistance of titanium alloy parts, while the wear resistance of composite coatings is 2.5 times higher than the resistance of TiAl intermetallic [10]. As spraying materials, composite powders are used, produced by mechanical alloying.

At present, the problems of increasing the reliability of operation of parts of gas turbine engines and elements of gas-compressor units, which during operation are prone to damages of both from the physical, in particular, erosion exposure of the dust-gas flow as well as from chemical effects: corrosion at high (turbine parts) and low temperatures (compressor parts, engine harness).

The aim of the work is the study of structure, phase composition and properties (erosion and corrosion resistance) of composite coatings based on titanium aluminides of TiAl–SiC and TiAl–Si_3N_4 systems, produced by the method of supersonic air-gas plasma spraying.

RESEARCH MATERIALS AND PROCEDURES

For supersonic air-gas plasma spraying (SAGPS) of coatings, powders based on TiAl intermetallic of TiAl–SiC and TiAl–Si_3N_4 systems were used. Composite powders were produced by the method of mechanochemical synthesis (MChS) of TiAl (PVT65Yu35), SiC and Si_3N_4 powders in the planetary mill within 1.5 h. The composition of initial mixtures of powders was chosen on the basis of thermodynamic calculations with the determination of the most probable reactions of interaction of titanium intermetallic with non-metallic refractory compounds (SiC and Si_3N_4):

- $88\ TiAl + 12\ SiC = 18\ TiC + 32\ Ti_5Si_3 + 50\ TiAl_3$ (wt.%);
- $83\ TiAl + 17\ Si_3N_4 = 8\ TiN + 40\ Ti_5Si_3 + 15\ AlN + 37\ TiAl_2$ (wt. %).

To provide a uniform feed of powder to the plasma jet before spraying, the powders were conglomerated by a 5 % solution of polyvinyl alcohol with a subsequent screening of particles with a size range of 40–63 μm. For comparison, a coating from initial TiAl powder was also sprayed. The characteristics of the powders used in the work are given in Table 1.

The spraying was carried out in the installation Kyiv-S for supersonic air-gas plasma spraying using the following technological parameters: current I = 230 A, voltage U = 380 V, consumption of plasma forming gas (air) $Q_{pg} = 20$ m^3/h, spraying distance L = 160 mm. The coatings for investigations were deposited on the specimens made of St3.

Table 1. Characteristics of powders for SAGPS-coatings

Composition, wt.%	Particle size, μm	Phase composition
65Ti–35Al	<80	TiAl, Ti_3Al
88TiAl–12SiC	40–63	TiAl, Ti_3Al, SiC, TiC, Ti_5Si_3, Ti_3AlC, amorphous phase
83TiAl–17Si_3N_4	40–63	TiAl, Ti_3Al, Si_3N_4, Ti_5Si_3, AlN, TiN, amorphous phase

When conducting metallographic examinations, an optical Neophot-32 microscope with a digital photography device was used; the measurements of microhardness were carried out in the PMT-3 device. X-ray structural analysis (XRD) of the coatings was performed in the installation DRON-UM-1 in a monochromatized CuK_α-radiation.

The studies of the coatings to erosion wear resistance were performed in a centrifugal accelerator of solid particles of the TsUK-3M model at a rotation frequency of the installation rotor of 3000 ± 50 rpm/min. As an abrasive material, quartz sand with 0.2–0.4 mm particles was used, which corresponds to the real size of particles in the pumped gas flow and the size of particles, coming into the air and wearing blades of aircraft gas turbine engines [11, 12]. The studies were performed at fixed angles of the abrasive attack: 30° (tangent flow) and 60° (frontal collision). As an index of wear resistance, the intensity of wear in milligrams per kilogram (average weight loss of specimens per 1 kg of abrasive got into the specimen) was taken. The total amount of abrasive spent for each series of specimens was 2 kg, a number of specimens with a coating of one type (thickness of coating is approximately 500 μm) is 3 pcs. For comparison, the tests of specimens of titanium VT6 alloy and aluminium AMg3 alloy were conducted.

As a method of corrosion resistance of coatings, a potentiostatic method was selected. The coatings with 500 μm thickness were deposited on the specimens of St3. The tests were performed in the P-5827M potentiostate at a scanning rate of 20 mV/s, and a temperature of 18–20 °C. As an electrolyte, 3 % NaCl solution was used. Stationary potentials were measured relative to the chlorine-silver electrode. The rate and potential of corrosion of the coatings were found by the graphic method from polarization curves. Using the values of corrosion currents that were determined from the polarization curves, a deep corrosion index (K_c) was calculated [13]. For comparison, under the same conditions the corrosion resistance of St3 steel, VT6 and AMg3 alloys was conducted.

RESULTS OF STUDIES AND THEIR DISCUSSION

STRUCTURE AND PHASE COMPOSITION OF COATINGS

Metallographic analysis (Figure 1) found that as a result of spraying of composite powders TiAl–SiC and TiAl–Si_3N_4 by SAGPS method as in the case of

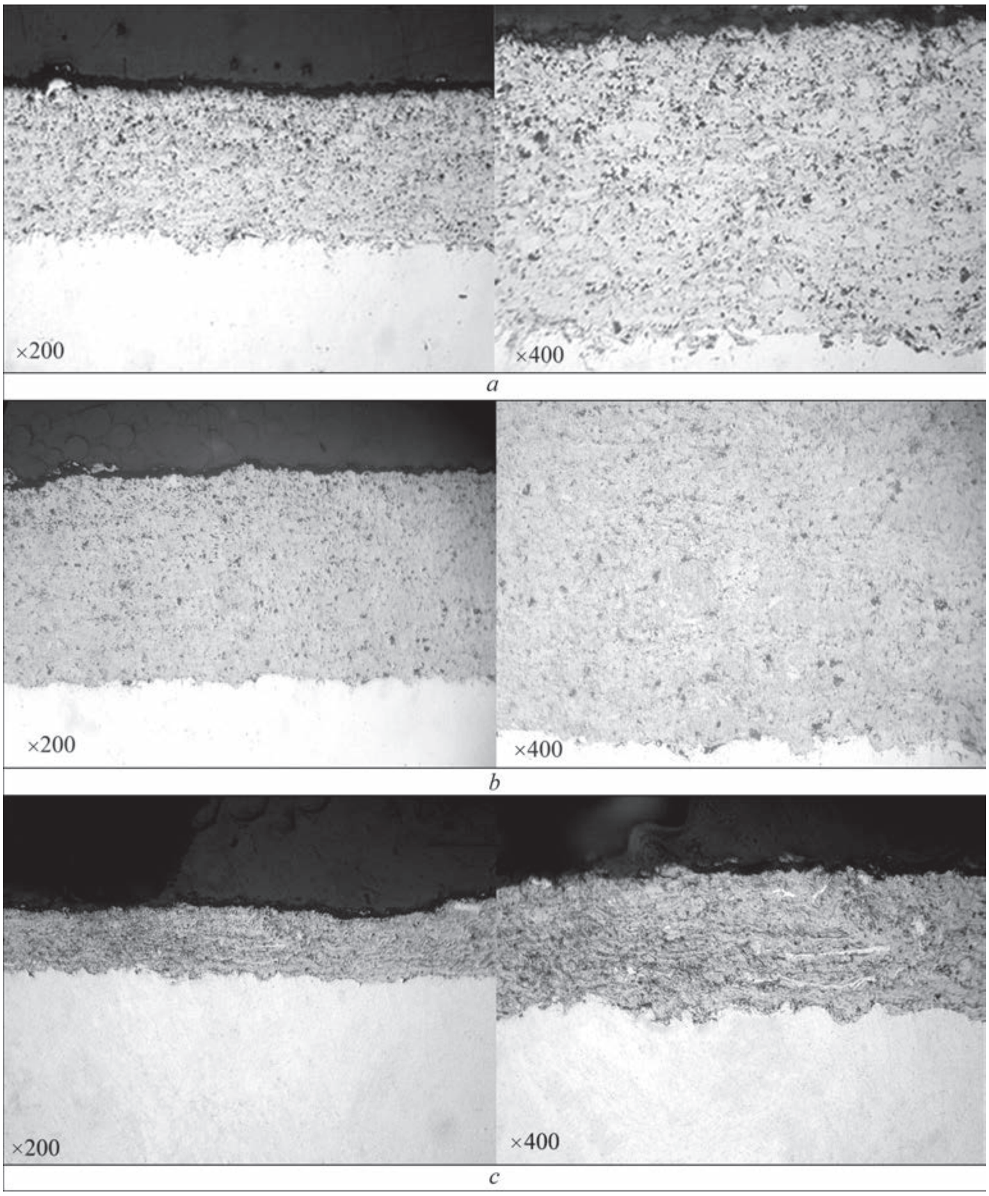

Figure 1. Microstructure of SAGPS-coatings: *a* — TiAl; *b* — TiAl–SiC; *c* — TiAl–Si_3N_4

spraying of initial TiAl powder, the coatings with a homogeneous dense structure are formed, consisting of lamellas, formed from particles completely molten and deformed during particle layer formation. The structural elements in the coatings are indistinguishable. The porosity of TiAl–SiC and TiAl–Si_3N_4 coatings amounts to 3–4 %, and in TiAl coating it is 8 %.

The data obtained from XRD (Figure 2) show, that as a result of physicochemical processes during spraying of coatings from composite powders, some changes in the phase composition are observed. In the process of spraying coatings of TiAl–SiC and TiAl–Si_3N_4 systems, the interaction of the components of TiAl composite powders with non-metallic refractory compounds and, unlike the powders after MChS, in the coatings there are no initial phases of SiC and Si_3N_4. This indicates the proceeding of exothermal reaction (according to thermodynamic calculations) in the spraying process that makes an additional heat input to the heating of powder particles. As a result of that, the end of the process of interaction of TiAl with the components of SiC and Si_3N_4 in spraying occurs, which did not proceed to the end in the process of MChS of powders. Due to proceeding of exothermic reaction and an increase in thermal energy of TiAl–SiC and TiAl–Si_3N_4 particles, in spraying the fraction of particles being in a completely molten state increases, and thus, a dense structure of coatings with lower porosity is formed than in spraying of the initial TiAl powder.

In the coatings of both systems, an amorphous phase disappeared as a result of passing the composite particles in the plasma jet of the heating zone to the transition into the melting stage with a subsequent cooling of the melt with the formation of crystalline phases. In the coatings during spraying, the oxides of

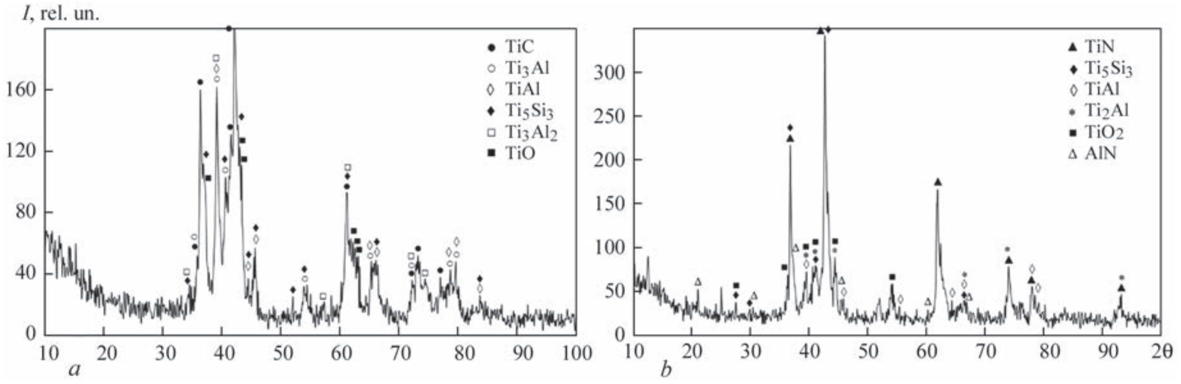

Figure 2. X-ray patterns of SAGPS-coatings: *a* — TiAl–SiC; *b* — TiAl–Si_3N_4

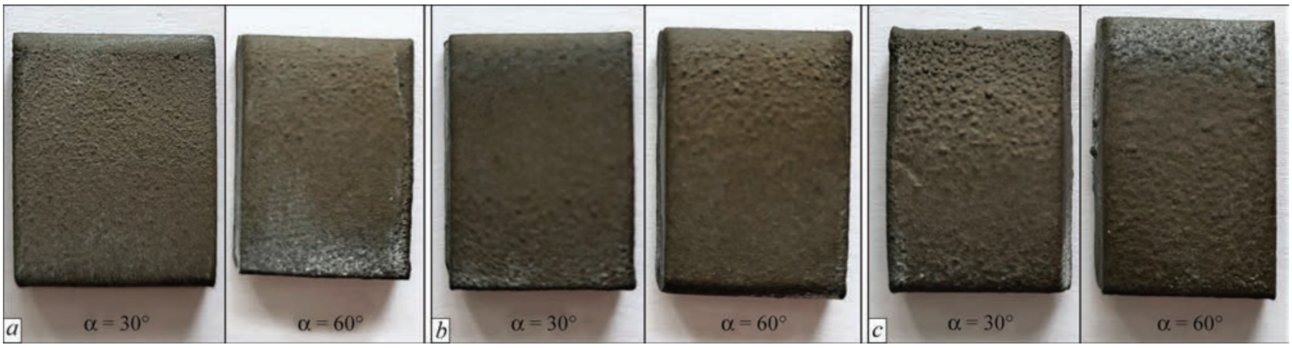

Figure 3. Appearance of the surface of specimens with SAGPS-coatings after tests for erosion resistance: *a* — TiAl–SiC; *b* — TiAl–Si_3N_4; *c* — TiAl

TiO and TiO_2 are formed, which is predetermined by interaction of the material that is sprayed with oxygen of the environment. In spraying TiAl–SiC coating as a result of phase transformations, instead of the triple phase of Ti_3AlC carbide, which was present in the powder, MACh-phase of Ti_3AlC_2 is formed.

Other changes in the phase composition of the coatings as compared to the composition of the initial composite TiAl-NRC powders, produced by MChS (Table 1) were not detected. In the coatings, the phase of initial TiAl powder maintains, as well as the phases foreseen by thermodynamic calculations (Ti_5Si_3, TiC, AlN, TiN).

The microhardness of TiAl—SiC and TiAl—Si_3N_4 coatings, which is 6610 ± 1070 and 6280 ± 950 MPa, respectively, due to the presence of solid phases of carbides, silicides, and nitrides in them, exceeds the microhardness of the TiAl coating by an average of 1300 MPa, the hardness of which is 5150 ± 670 MPa.

Table 2. Summarized results of tests on erosion resistance of SAGPS-coatings TiAl–SiC, TiAl–Si_3N_4, TiAl and VT6 and AMg3 alloys

Coating/alloy material	Average coating wear (mg/kg) at different angles of abrasive attack	
	30°	60°
TiAl–SiC	7.1 ± 1.1	10.8 ± 0.9
TiAl–Si_3N_4	8.0 ± 0.8	12.2 ± 1.2
TiAl	10.3 ± 1.2	15.3 ± 0.9
VT6 alloy	6.2 ± 0.6	5.2 ± 0.7
AMg3 alloy	7.7 ± 1.1	5.4 ± 0.4

EROSION RESISTANCE

As a result of studies of the resistance of the coatings under the conditions of erosive wear, it was found that the wear resistance of the developed TiAl–SiC and TiAl–Si_3N_4 coatings exceeds the wear resistance of the TiAl intermetallic powder coating by 1.3–1.5 times (Table 2), which is explained by the presence of strengthening phases in these coatings, that increase their strength and hardness.

The appearance of the specimens with the coatings after the tests (Figure 3) shows that the mechanisms of fracture of coatings of TiAl–NRC systems and TiAl coatings under the same influence of gas abrasive flow are slightly different. This is explained by the inner structure of the deposited coatings, in particular, by the presence of pores in the coatings. The effect of porosity on the nature of material wear can be considered from two positions. Firstly, pores and discontinuities, reducing the live cross-section of the deposited layer and being concentrators of local stresses, can significantly reduce strength properties of the coatings. Secondly, due to the peculiarities of the microrelief, which are associated with the presence of surface defects, the wear conditions of the specimens vary.

Table 3. Results of electrochemical studies of SAGPS-coatings in a 3 % NaCl solution

Coatings	Electrochemical characteristics			
	E_{st}, V	E_c, V	i_c, A/cm^2	K_c, mm/year
TiAl–SiC	–0.44	–0.40	$4.2{\cdot}10^{-7}$	0.019
TiAl–Si_3N_4	–0.42	–0.38	$4.8{\cdot}10^{-7}$	0.023
TiAl	–0.48	–0.42	$6.4{\cdot}10^{-6}$	0.045
Note. i_c (A/cm^2) for St3 steel — $6.5{\cdot}10^{-5}$; AMg3 alloy — $2.6{\cdot}10^{-5}$; VT6 alloy — $2.4{\cdot}10^{-6}$.				

At each point, the angle of attack of the abrasive is determined by the size and shape of pores and cavities. As a rule, the conditions of wear of the specimens in the area of surface defects are more tough than in defect-free plane areas. As a result of the effect of the mentioned factors, a more intense chipping of larger TiAl coating blocks is possible under the action of the gas abrasive flow, which are observed on the surface of the specimens after the tests.

The intensity of wear of the investigated coatings is 1.5 times higher when examining the specimens at an angle of attack of the abrasive of 60°. It is known that according to the degree of resistance to gas-abrasive effect (depending on the angle of attack of abrasive particles), the powder materials and coatings are conditionally divided into two groups [14]: $\alpha < 35°$ — maximum wear for plastic and $\alpha > 45°$ — for brittle materials. Thus, TiAl–SiC and TiAl–Si_3N_4 coatings wear as brittle materials. Therefore, it will be rational to use the developed coatings at angles of attack of the abrasive that do not exceed 30°, which corresponds to the actual attack angles of the particles on the blades surface of centrifugal wheels in the compressors of oil and gas equipment [11].

It was also found that at an angle of abrasive attack of 60°, the wear resistance of TiAl–SiC and TiAl–Si_3N_4 SAGPS-coatings is 2.0–2.4 times lower than the wear resistance of the specimens made of VT6 and AMg3 alloys. In turn, at an angle of abrasive attack of 30°, the wear resistance of composite coatings is lower than the wear resistance of VT6 and AMg3 alloys by only 1.1–1.3 times, and in TiAl–SiC coating it slightly exceeds the wear resistance of AMg3 alloy (by 1.1 times).

CORROSION RESISTANCE

Electrochemical studies showed that the corrosion of SAGPS-coatings occurs with hydrogen depolarization with inhibition of anodic dissolution. The absence of passivation of the coatings is predetermined by the fact that a 3 % NaCl solution refers to an aggressive environment with a high content of Cl-, in the presence of which oxygen is removed from the surface of the electrode and the formation of a passive film on the surface of the coatings is prevented.

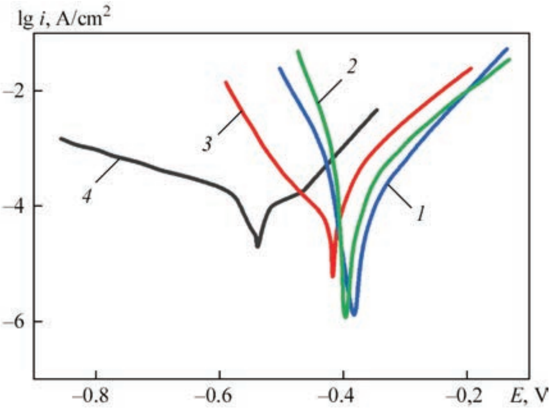

Figure 4. Polarization curves of SAGPS-coatings TiAl–SiC (curve *1*), TiAl–Si_3N_4 (curve *2*), TiAl (curve *3*) and St3 steel (curve *4*) in a 3 % NaCl solution

The kinetics of the corrosion process of the coatings of TiAl–NRC systems, unlike the coating of TiAl intermetallic, takes place with a shift of corrosion potentials in the positive direction and a decrease in corrosion currents (Figure 4).

The analysis of the results of corrosion studies showed that the corrosion resistance of TiAl–SiC and TiAl–Si_3N_4 SAGPS-coatings is superior to TiAl intermetallic coating by approximately one order of magnitude with the indices of corrosion current of $4.2{\cdot}10^{-7}$ A/cm^2, $4.8{\cdot}10^{-7}$ and $6.4{\cdot}10^{-6}$, respectively (Table 3).

An increase in corrosion resistance can be explained by the presence of titanium silicide Ti_5Si_3 in the coatings of TiAl–NRC systems, which, as is known [15], significantly increases the corrosion resistance of coatings and alloys in different aggressive environments, which is predetermined by the presence of strong covalent bonds metal–non-metal, as well as Si-Si bonds.

In addition, the corrosion resistance of the produced TiAl–SiC and TiAl–Si_3N_4 coatings exceeds the corrosion resistance of St3 by 135–155 times, AMg3 alloy by 24–62 times, and VT6 alloy by 5–6 times.

CONCLUSIONS

1. Applying the method of supersonic air-gas plasma spraying using composite powders produced by the method of mechanochemical synthesis, the coatings based on TiAl intermetallic with the additives of non-metallic refractory compounds SiC and Si_3N_4 were formed. As a result of spraying, heterophase coatings with a dense structure with a hardness of 6.3–6.6 GPa and a porosity of 3–4 % are formed.

2. It was found that in the process of spraying coatings of TiAl–SiC and TiAl–Si_3N_4 systems, the

components of TiAl composite powders interact with non-metallic refractory compounds and, unlike powders after mechanochemical synthesis, initial phases SiC and Si_3N_4 are absent in the coatings.

3. Conducted studies of erosion resistance of the coatings showed that due to the presence of solid phases in the developed coatings, the resistance under the conditions of erosive wear is 1.3–1.5 times higher than the resistance of the coatings made of TiAl intermetallic powder. According to the wear nature, the coatings TiAl–SiC and TiAl–Si_3N_4 belong to the brittle class and are recommended for using in the conditions of abrasive wear at angles of abrasive attack that do not exceed 30°.

4. Electrochemical studies showed that TiAl–SiC and TiAl–Si_3N_4 coatings, due to the presence of the titanium silicide phase in them, are superior in corrosion resistance to TiAl intermetallic coatings by approximately one order of magnitude in terms of corrosion resistance in a 3 % NaCl solution, and also exceed the corrosion resistance of St3 by 135–155 times, AMg3 alloy by 24–62 times and VT6 alloy by 5–6 times.

References

1. Noda, T. (1998) Application of cast gamma TiAl for automobiles. *Intermetallics*, **6**(7–8), 709–713. DOI: https://doi:10.1016/s0966-9795(98)00060-0
2. Lobanov, L.M., Asnis, Yu.A., Piskun, N.V., Statkevych, I.I. (2020) Improvement of mechanical properties of β-stable intermetallics of TiAl system by floating-zone refining. *Dopov. NANU*, **8**, 51–56. DOI: https://doi.org/10.15407/dopovidi2020.08.051
3. Zhang, W., Yang, Y.Q., Zhao, G.M. et al. (2014) Interfacial reaction studies of B_4C-coated and C-coated SiC fiber reinforced Ti–43Al–9V composites. *Intermetallics*, **50**, 14–19. DOI: https://doi:10.1016/j.intermet.2014.02.003
4. Liu, C., Huang, L.J., Geng, L. et al. (2015) In situ synthesis of (TiC + Ti_3SiC_2 + Ti_5Si_3)/Ti6Al4V composites with tailored two-scale architecture. *Advanced Engineering Materials*, 17(**7**), 933–941. DOI: https://doi:10.1002/adem.201400585
5. Jong-Keuk, P., Jong-Young, C., Hyeong-Tag, J., Young-Joon, B. (2009) Structure, hardness and thermal stability of TiAlBN coatings grown by alternating deposition of TiAlN and BN. *Vacuum*, 84(**4**), 483–487. DOI: https://doi:10.1016/j.vacuum.2009.10.013
6. (2003) *Study of cyclic oxidation behavior of anti-oxidation coatings on a super alloy.* Eds by Shahid M.R., Subhani T., Shengkai G., Mirza J.A. Dr AQ Khan Research Labs, Islamabad, Pakistan.
7. Li, G., Li, L., Han, M. et al. (2019) The performance of TiAlSiN coated cemented carbide tools enhanced by inserting Ti interlayers. *Metals*, 9(**9**), 918. DOI: https://doi:10.3390/met9090918
8. Fager, H., Andersson, J.M., Lu, J. et al. (2013) Growth of hard amorphous TiAlSiN thin films by cathodic arc evaporation. *Surface and Coatings Technology*, **235**, 376–382. DOI: https://doi:10.1016/j.surfcoat.2013.07.014
9. Gizynski, M., Miyazaki, S., Sienkiewicz, J. et al. (2017) Formation and subsequent phase evolution of metastable Ti–Al alloy coatings by kinetic spraying of gas atomized powders. *Surface and Coatings Technology*, **315**, 240–249. DOI: https://doi:10.1016/j.surfcoat.2017.02.053
10. Machethe, K.E., Popoola, A.P.I., Adebiyi, D.I., Fayomi, O.S.I. (2017) Influence of SiC–Ti/Al on the microstructural and mechanical properties of deposited Ti–6V–4Al alloy with cold spray technique. *Procedia Manufacturing,* **7**, 549–555. DOI: https://doi:10.1016/j.promfg.2016.12.069
11. Parajko, Yu.I. (2011) Regulations of wear of operating surfaces of gas-compressor unit and development of technologies of their service life increase. *Problemy Tertya ta Znoshuvannya,* **56**, 71–83 [in Ukrainian].
12. Mikhailov, D.A. (2014) Main features of operation of GTE compressor blades and classification of their service functions. *Progresyvni Tekhnologii i Systemy Mashynobuduvannya*, 50(**4**), 126–131 [in Russian].
13. Zhuk, N.P. (2006) *Course of theory of corrosion and protection of metals*. Moscow, LLC TID Alliance [in Russian].
14. Kulu, P. (1988) *Wear resistance of powder materials and coatings.* Tallin, Valgus [in Ukrainian].
15. Liu, L. Xu, J., Li, Zh. (2013) Electrochemical characterization of Ti_5Si_3/TiC nanocomposite coating in HCl solution. *Inter. J. Electrochem. Sci.*, **8**, 5086–5101.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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