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Structure and properties of multilayer coatings based on CoCrAlY/Al_2O_3 obtained by detonation spraying

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Ceramic coatings are used to protect against high-temperature oxidation of metal products. The efficiency of the technology of detonation spraying of two-layer coatings of aluminum oxide (Al_2O_3) and a heat-resistant alloy (CoCrAlY) on the surface of a sample made of steel 12X18H10T was studied. A multi-chamber detonation unit was used in the work, providing high speed (up to 1000 m/s) and a 60–80% utilization rate of the sprayed material. We used an oxygen-neutral combustible mixture based on propane-butane. The coating material has a smooth gradient of properties from ceramic to sample substrate The complex of the obtained structural and physical-mechanical properties of the coating material makes it possible to predict its high performance under conditions of high-temperature oxidation.

Keywords: detonation spraying; hardness; CoCrAlY; roughness; Al_2O_3 ; phase composition; multilayer coating

Introduction

Current trends in the field of thermal spraying are the creation of multifunctional protective coatings that combine several performance properties, such as wear resistance and corrosion resistance, high electrical conductivity, low coefficient of friction, thermal barrier properties, abrasion resistance, etc. It is often not possible to achieve the desired versatility with single layer coatings. In order to achieve a specific functional property or a set of different properties of the coating, several materials should be selected and placed in the appropriate position within the coating. This means that a strong and logical relationship must be established between the coating composition and the coating design (the latter can also be understood as the coating structure). The design of the coating usually implies the development of gradient multilayer structures and their combinations [1–4].

To protect products made of heat-resistant alloys from adverse operating conditions, heat-shielding coatings (HSC) are widely used [5, 6], which are a multilayer system and consist of an external thermal barrier ceramic layer and a metal layer made of a heat-resistant alloy. The heat-resistant layer provides protection against oxidation of the product material [7]. CoCrAlY alloy coatings are widely used as protective materials and as heat-resistant bonding layers between the heat-shielding ceramic coating and the surface of metal products.

The main disadvantage of the classical methods of gas thermal spraying is that oxide inclusions are present in the microstructure of the coating material, i.e., there is a high gas saturation. In work [8], heat-resistant layers of heat-protective coatings based on MCrAlY were investigated. The oxide content in the coating was 0.16; 0.94 and 1.8% (by weight) for LPPS, HVOF and APS methods, respectively. The results of tests for isothermal heat resistance showed that coatings with a higher initial content of oxides have increased rates of oxide growth in the coating material, thereby promoting the growth of cracks and chipping of the ceramic layer of the heat-protective coating.

Studies show that the formation of a partially nanoscale structure improves the oxidation resistance of CoNiCrAlY coatings [9–12]. The improvement in antioxidant properties is mainly explained by the fact that nanocrystallization leads to the formation of structures with a smaller grain size, which increases the volume fractions of boundaries. With a decrease in the volume fraction of the boundaries, oxides grow at the boundary, which can lead to the formation of cracks, and the presence of an oxide film prevents further oxidation.As noted above, the creation of a multilayer coating with an outer ceramic layer of low gas permeability also slows down the oxidation processes. At the same time, the requirements for the quality of the coating and the technology of their application are high. One of the reasons for the destruction of the ceramic layer under the influence of high-temperature gases is the formation of oxides at the "ceramic layer–heat-resistant layer" boundary part, the thickness of which continues to grow during thermal exposure [13]. The rapid and uneven growth of oxides leads to localized stress concentrations, which can lead to cracks initiating destruction. The presence on the surface of a dense and homogeneous oxide film consisting of Al_2O_3 is considered optimal, since it prevents further oxidation due to its low diffusion permeability [14].

The evolution of the microstructure and oxidation in the heat-resistant layers of the coating occurs under prolonged high-temperature exposure and significantly affects the thermomechanical properties of HSC and their service life. Thus, in order to reduce the rate of degradation and destruction of HSC, it is necessary to use technologies for the deposition of dense, defect-free multilayer coatings with high adhesion and cohesion and the presence of nanoscale structures.

The aim of this work is to obtain multilayer coatings based on CoCrAlY/ Al_2O_3 and to study their structure and properties. The CoCrAlY/ Al_2O_3 combination is characterized by high resistance to oxidation and corrosion, has high physical and mechanical properties such as hardness, resistance to wear and aggressive environment. The coatings were obtained by the detonation method on a multi-chamber detonation device (MCDD) [15].

Materials and research methods

To spray the substrate under the ceramic layer, CoCrAlY powder with a fineness of 45–125 µm was used as the sprayed material. The ceramic layer was sprayed with Al_2O_3 powder (H.C. Starck: AMPERITR 740.0) with a fineness of 5.6–22.5 µm. The coatings were deposited on 12X18H10T steel specimens by detonation spraying on a multi-chamber detonation device MCDD developed at the E.O. Paton Electric Welding Institute (Ukraine). Figure 1 shows a general view of a multi-chamber detonation device mounted on a robot arm.

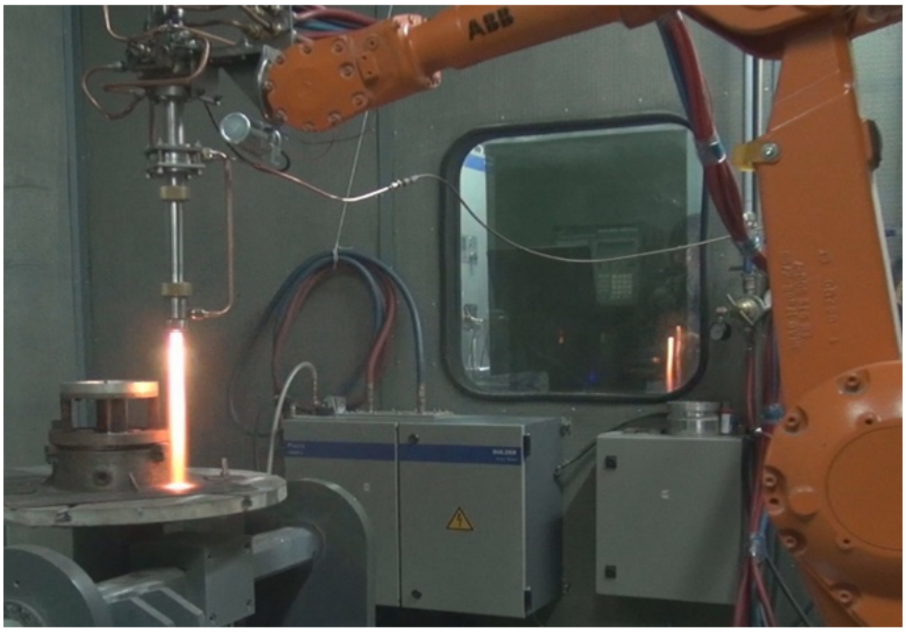

Figure 1. Multi-chamber detonation device for coating.

One of the key parameters that determine the physicochemical processes of interaction of materials and the very possibility of forming high-quality coatings are the speed and temperature of the particle at the moment of collision with the substrate. For this purpose, the MCDD implements the mode of overcompressed detonation combustion of the gas mixture in specially profiled chambers. The accumulation of combustion energy from two chambers in a cylindrical barrel provides the formation of a high-speed jet of detonation products, which accelerates and heats up the sprayed powder. In this case, the speed of a powder, for example Al_2O_3, reaches 1000 ± 200 m/s [16]. This provides the possibility of forming submicrocrystalline, dense coating materials, without oxidation and with high parameters of adhesion and cohesion. The detonation repetition rate was 20 Hz. The supply of gases and powder was carried out continuously. The powder consumption for spraying a layer of a metal heat-resistant alloy was 0.9 kg/h. The composition and consumption of the components of the combustible gas mixture for spraying the first layer (CoCrAlY) are shown in Table 1. For the spraying of the upper ceramic layer (Al_2O_3), the powder consumption was 0.6 kg/h. The composition and consumption of the components of the combustible gas mixture for spraying the upper layer are shown in Table 2. The coefficient of use of the powder in this case reached 80% for CoCrAlY and 60% for aluminum oxide.

Table 1.
Consumption of components of a combustible gas mixture for spraying a substrate.

Components of combustible mixture		Gas consumption, m^3/h
1 chamber	O_2	3.13
	air	1.27
	C_3H_8+C_4H_{10}	0.69
2 chamber	O_2	2.97
	air	1.19
	C_3H_8+C_4H_{10}	0.67
Transporting gas		1

Table 2.
Consumption of components of combustible mixture for spraying the layer of ceramic.

Components of combustible mixture		Gas consumption, m^3/h
1 chamber	O_2	4
	air	0.12
	C_3H_8+C_4H_{10}	0.75
2 chamber	O_2	4
	air	0.12
	C_3H_8+C_4H_{10}	0.68
Transporting gas		1

The surface morphology was studied by scanning electron microscopy (SEM) using backscattered electrons (BSE) on a JSM–6390LV scanning electron microscope (Jeol, Tokyo, Japan). The roughness of the surface of the coatings Ra was estimated using a 130 model profilometer (JSC "Zavod PROTON", Moscow, Russia). Micrographs of the coating surface were obtained using a metallographic microscope (Altami MET 5S model; Altami LLC, St. Petersburg, Russia). Nanoindentation was carried out on a NanoScan–4D nanohardness tester (FGBU TISNTsM, Moscow, Russia) in accordance with GOST R 8.748–2011. With a Berkovich indenter, 15 indentations were performed at a load of 100 mN. Young's modulus and hardness were determined by the method of Oliver and Pharr. The adhesion strength of the coatings was measured on an automatic adhesive meter Elcometr 510 model T.

Results and discussions

For spraying, 2 types of powders were chosen (Figure 2): CoCrAlY powder (Figure 2 a) and Al_2O_3 (Figure 1 b). Table 3 shows the characteristics of the powders.

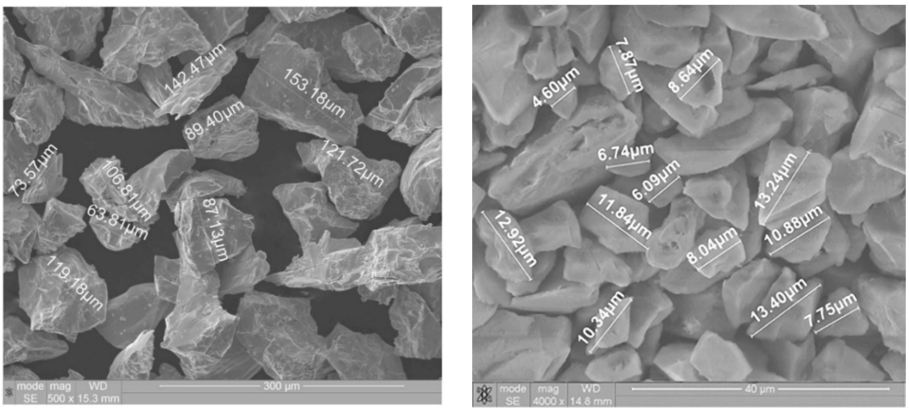

Figure 2. Morphology of powders a)–CoCrAlY [17] and b)– Al_2O_3 [18].

Table 3 shows the chemical, phase composition and particle size of powders used for detonation spraying of two-layer heat-resistant coatings.

Table 3.
Chemical, phase composition and particle size of powders.

	Powder		
	Element	CoCrAlY	Al_2O_3
Chemical content, all in wt. %	Co	58.88	-
	Cr	23.24	-
	Si	2.66	0.12
	Fe	1.13	1.10
	Al	13.10	54.94
	O	-	35.84
	C	-	8.00
Particle size distribution, microns			
d(0.1)		6.6	7.6
d(0.5)		62.7	15.8
d(0.9)		123.4	29.4
Main phases are determined		$Al_{0.94}Co_{1.06}Cr$	γ-Al_2O_3, α-Al_2O_3 Fe_2O_3, SiO_2

Figure 3 shows a microimage of the surface and the results of measuring the roughness of coatings based on CoCrAlY/ Al_2O_3. The surface of the coating has a heterogeneous structure with pores. As the main parameter for evaluating the surface roughness of the coating, the value of R_a was chosen, which is the arithmetic mean deviation of the profile. The roughness parameter of the obtained coatings is R_a =12 μm.

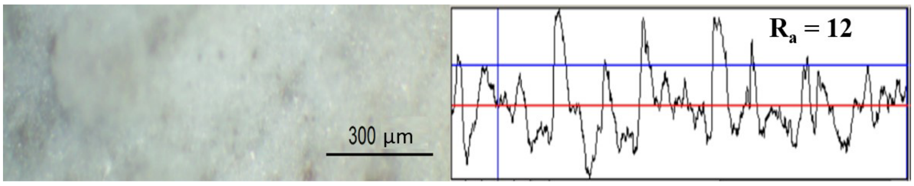

Figure 3. Photo and surface roughness of a multi-layer coating.

Figure 4 shows a cross-sectional view of the heat-resistant coating material. The coating consists of an upper ceramic layer based on an alumina ceramic. The coating has minor pores, typical for detonation coatings. The boundary of the ceramic coating with a heat-resistant metal alloy has a developed surface with visible traces of mixing of materials. The material of the heat-resistant layer of CoCrAlY powder is dense, consists of thin lamellas, which are well mixed. The heat-resistant layer adheres tightly to the material of the product, filling in all the cavities of the unevenness on the surface of the product.

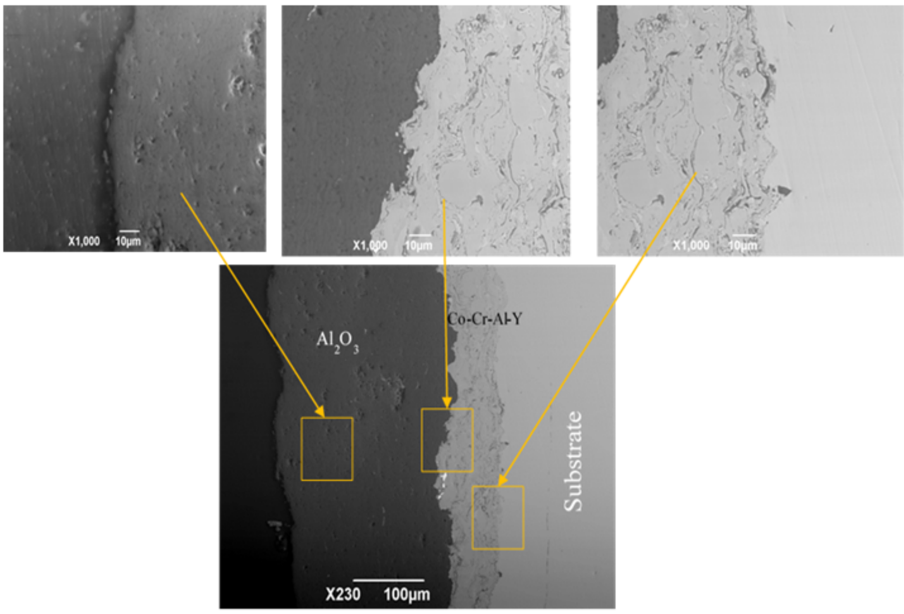

Figure 4. SEM images of a cross-section of a multilayer coating based on Co-Cr-Al-Y/ Al_2O_3 .

The study of the morphology of the cross-section of the multilayer coating was carried out by scanning electron microscopy (SEM) using backscattered electrons (BSE) on a JSM-6390LV scanning electron microscope, Figure 5.

The elemental composition of the coatings was determined using EMF analysis. As shown by SEM, the coating has 2 layers. The total coating thickness is 270 μm (CoCrAlY–80 μm) (Al_2O_3 –190 μm).

Measurements of the microhardness of the coating material, Figure 6, show a gradual decrease in hardness from a maximum of 12 GPa near the surface of the ceramic coating to 6 GPa in the CoNiCrAlY heat-resistant layer and 4 GPa in the substrate.

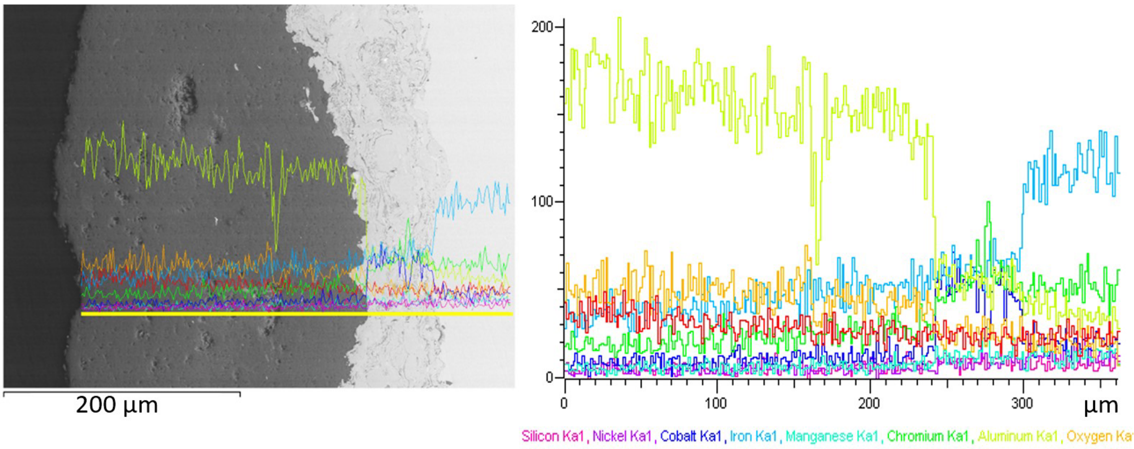

Figure 5. SEM images of the cross-sectional morphology of a multilayer coating and the distribution of elements depending on the depth of the coating.

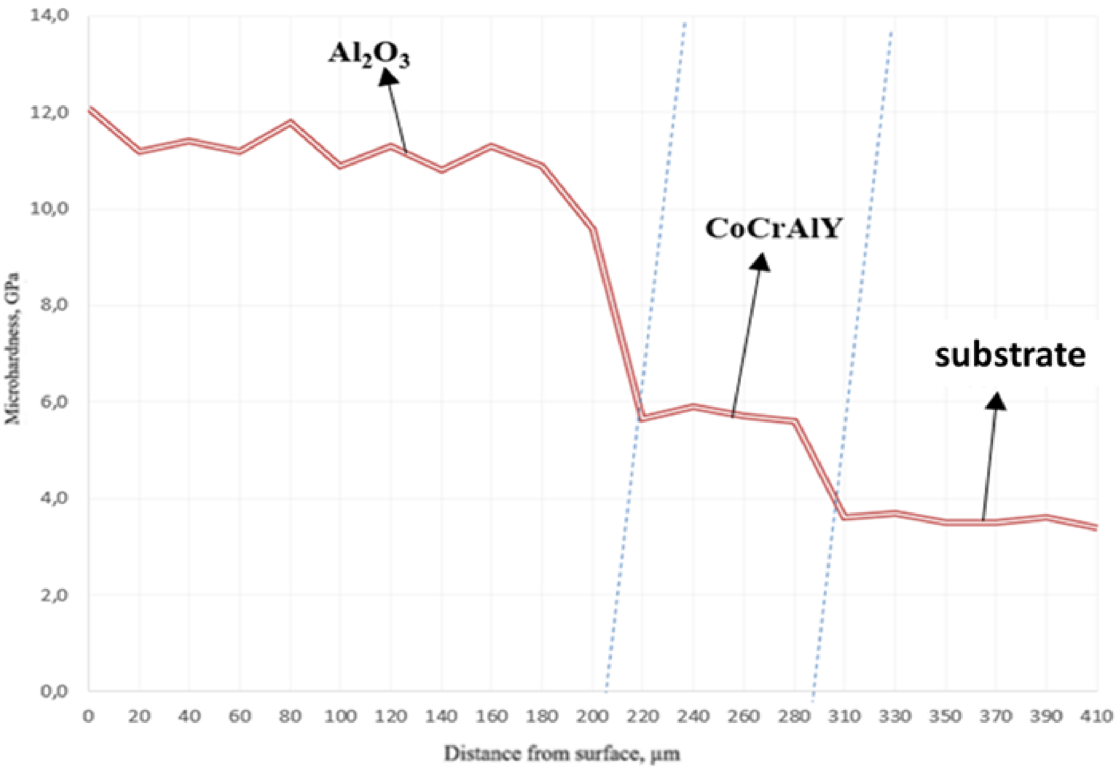

Figure 6. Microhardness of the sample cross section.

The mechanical characteristics of the obtained coatings were studied by the Oliver–Pharr method to analyze the elastic stiffness of the sprayed coating materials. Figure 7 shows diagrams of the elastic stiffness of the coating and substrate layers.

From the analysis of the loading and unloading curves, it can be seen that the penetration depth of the nanoindenter in the surface layer was less than in the second layer and substrate. According to the analysis of the curves, the hardness in the surface layer is higher (Figure 7 a) than in the second layer (Figure 7 b) and the substrate (Figure 7 c). This is due to the fact that ceramic made of Al_2O_3 powder has a higher rigidity than a layer of metal alloy and steel. A smooth decrease in hardness, stiffness, an increase in the coefficients of thermal expansion of coating materials and protection against oxidation create conditions for reliable operation of coated products in oxidizing environments, under conditions of thermal cycling.

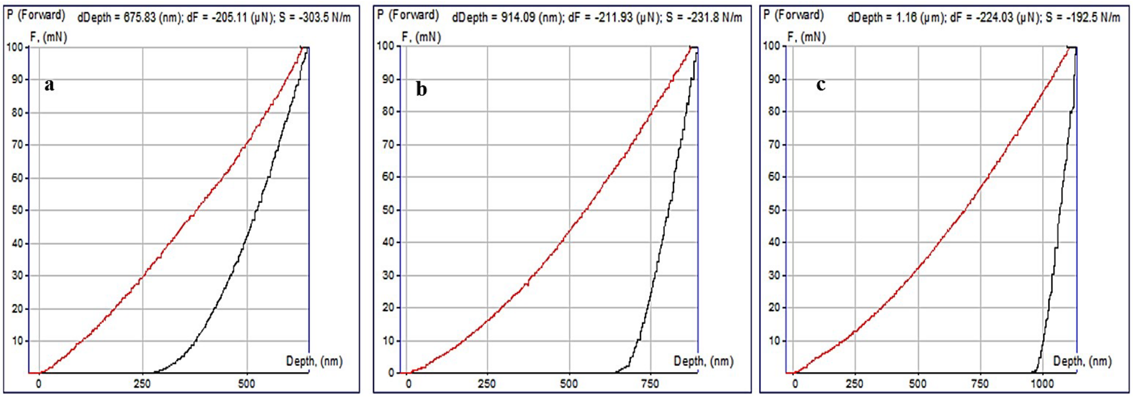

Figure 7. Graphs of force versus depth. of Co-Cr-Al-Y/ Al_2O_3 : (a) ceramic layer, (b) layer from CoCrAlY, (c) substrate.

Table 4.
Distribution of hardness (H) and elastic modulus (E) over the depth of Co-Cr-Al-Y/ Al_2O_3 .

Name	Hardness (H), GPa	Elastic modulus (E)6 GPa
substrate	4.1	320
Co-Cr-Al-Y	7.3	243
Al_2O_3	13.4	203

The results of the adhesive strength of the coatings are shown in the Table 5. The adhesion strength of a single layer (Al_2O_3) and a multi-layer coating(Co-Cr-Al-Y/ Al_2O_3) was determined by a shear strength test in accordance with the standard ASTM F0144–99.

Table 5.
Results of the adhesive strength of the coatings.

No	Sample	Shear strenght (MPa)
1	Al_2O_3	4.49
2	Co-Cr-Al-Y/Al_2O_3	7.33

Conclusion

Based on the obtained experimental data and their analysis, the following conclusions were made:

1. The multi-chamber detonation device provides the formation of uniform dense layers from materials: alumina ceramics and CoCrAlY heat-resistant alloy.

2. Technical characteristics of MCDD provide the possibility of creating multi-layer dense coatings without cracks and delamination with properties high adhesion properties and economic indicators: the utilization rate of materials is 60-80%. Productivity is up to 1 kg/hour with a combustible mixture consumption up to 8 m^3 /hour. The adhesion strength results of the coating showed that the multi-layer coating has better adhesive strength than the single-layer coating.

3. A multilayer coating based on CoCrAlY/ Al_2O_3 was obtained. The combination CoCrAlY/ Al_2O_3 is characterized by high resistance to oxidation, since the presence on the surface of a dense and uniform oxide film consisting of Al_2O_3 is considered optimal, as it prevents further oxidation due to low diffusion permeability. In future studies, these coatings will be investigated under thermal cycling conditions as well as additional studies.

Acknowledgments

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References

[1] A.D. Pogrebnyak et al., Physics-Uspekhi **52** (2009) 29-54. [*CrossRef*]
[2] D.N. Kakimzhanov et al., Eurasian Journal of Physics and Functional Materials **5**(1) (2021) 45-51. [*CrossRef*]
[3] B. Rakhadilov et al., Coatings **11**(2) (2021) 141. [*CrossRef*]
[4] V.Y. Ulianitsky et al., Adv. Powder Technol. **29** (2018) 1859-1864. [*CrossRef*]
[5] O.I. Grishina et al., Aviacionnye materialy i tekhnologii **S6** (2014) 39-44. (in Russian) [*CrossRef*]
[6] S.A. Muboyadzhyan et al., Aviacionnye materialy i tekhnologii **1**(26) (2013) 17-20. (in Russian)
[7] P.V. Matveev et al., Aviacionnye materialy i tekhnologii **S5** (2014) 56-60. (in Russian).
[8] M. Shibata et al., Material Translations **47**(7) (2006) 1638-1642. [*CrossRef*]
[9] D. Mercier et al., Surface and Coatings Technology **205** (2011) 4162-4168. [*CrossRef*]
[10] F. Tang et al., Oxidation of Metals **61** (2004) 219-238. [*CrossRef*]
[11] Q. Zhang et al., Surface and Coatings Technology **202** (2008) 3378-3384. [*CrossRef*]
[12] Ji-yu Du et al., Surface and Coatings Technology **369** (2019) 16-30.[*CrossRef*]
[13] P.K. Wright et al., Current Opinion in Solid State and Materials Science **4** (1999) 255-265. [*CrossRef*]
[14] K. Messaoudi et al., Materials Science and Engineering **247** (1998) 248-262. [*CrossRef*]
[15] Yu. Tyurin et al., Ukraine Patent Bull **16** (2008) No 83831.
[16] O.V. Kolisnichenko et al., Avtomaticheskaya-svarka **10** (2017) 28-34. (in Russian) [*CrossRef*]

[17] M.G. Kovaleva et al., Applied Mechanics and Materials **752-753** (2015) 11-16. [*CrossRef*]
[18] M.S. Prozorova et al., Alternativnaya ehnergetika i ehkologiya **12** (2012) 45-50. (in Russian)