EFFECT OF ANNEALING ON THE MICROSTRUCTURE AND PROPERTIES OF COATINGS ON Al_2O_3 AND TI BASIS FORMED BY A NEW MULTI-CHAMBER GAS-DYNAMIC ACCELERATOR

PROZOROVA Mayya[1*], KOVALEVA Marina[1], ARSEENKO Mariia[1], YAPRYNTSEV Maxim[1], VAGINA Olga[1], NOVIKOV Vseslav[1], TYURIN Yurii[2], KOLISNICHENKO Oleg[2], SIROTA Viacheslav[3]

[1.]Belgorod National Research University, Belgorod, Russian Federation, prozorova@bsu.edu.ru

[2]Paton Institute of Electric Welding, National Academy of Sciences of Ukraine, Kiev, Ukraine

[3]Belgorod State Technological University named after V.G.Shoukhov, Belgorod, Russian Federation

Abstract

The main problem to the use of aluminum oxide as a coating material is its brittleness due to low toughness and low bending strength. The combination of high hardness, strength, fire resistance inherent in aluminum oxide, with plasticity and thermal conductivity, characteristic for titanium causes interest in coatings obtained on the basis of a composite of Al_2O_3 and Ti. A five series of nanostructure coatings from composite the titanium and aluminum oxide powders have been prepared on a corrosion-resistant steel substrate by a new multi-chamber gas-dynamic accelerator (MCDS) with different powder composites Al_2O_3/xTi (x = 3 %, 13%, 25%, 40%, 50%). It was found that the addition of Ti powder to the Al_2O_3 powder leads to changes in the structural-phase composition and the hardness of the coatings obtained, the namely contributes to the formation of the intermetallic phase of $AlTi_3$, which causes an increase in hardness (by 1.2 ... 1.3 times) of such coatings. To improve the structural characteristics it was conducted annealing of the obtained coatings. It was found that coatings from a composite of Al_2O_3/Ti powders contain twice as many particles of phase separations of nanoscale type as compared with Al_2O_3 coatings

Keywords: Alumina-titanium coatings, multi-chamber gas-dynamic accelerator, microstructure, porosity, hardness, wear resistance, heat resistance, annealing

1. INTRODUCTION

Metal products are widely used for engineering applications and constructions and are exposed to wide range of conditions and environments, e.g., in process industries. The ductile metallic base material can be subjected to different types of wear by the surrounding operation environment. The hard thermal spray coatings can be use to improve the wear resistance of the metallic surface, in such cases [1].

Alumina and titanium has attracted much attention due to their excellent high temperature strength as well as to their low density for aerospace, textile, pulp and paper, pump industries and automotive applications. Alumina is a hard and relatively cheap material with high hardness, good wear, and corrosion and thermal resistance [2,3]. It has also high electric resistance, which has made Al_2O_3 attractive for coating applications where electric insulation and high breakthrough voltage is sought. Fracture toughness of Al_2O_3 coatings can be increased by small addition of TiO_2 or Ti, which is mechanically blended with Al_2O_3 particles [1].

During the last decade, nanostructured powders have been gaining increasing attention and improved coating properties, e.g., higher toughness, adhesion, and wear resistance, have been reported [4]. Typically, Al_2O_3+Ti powders have been manufactured by blending Al_2O_3 and Ti fused and crushed powders.

One approach to improve the Al_2O_3 coatings has been the use of a new multi-chamber gas-dynamic accelerator (MCDS) [5-7]. Feature of multi-chamber gas dynamic accelerator is that for acceleration and heating the powder used cumulated flow of combustion products that are generated within the detonation chamber and the precise dosage and timing input of the sprayed powder.

This work aims at studying the influence composition of the powder Al_2O_3/xTi (where x = 3%, 13%, 25%, 40% and 50%) on the structural characteristics, hardness and wear resistance of the powder coating.

2. EXPERIMENTAL PROCEDURE

Al_2O_3/xTi (where x = 3 %, 13%, 25%, 40% and 50%) mixing powder was used as the starting material to deposit a dense ceramic coating on the corrosion-resistant steel substrate (C~0.12 Si~0.08 Mn~2 Ni- 9-11 S~0.02 P~0.035 Cr-17-19 Fe~67, all in wt pct). The annealing was carried out in a muffle furnace Nabertherm to the parameters presented in **Table 1**. The alumina-titanium coatings were prepared according to the parameter values presented in **Table 1**.

Table 1 Spraying parameters and properties of the coatings of composite powder

Parameters		Composites % Ti/Al_2O_3				
		3/97	13/87	25/75	40/60	50/50
Flow rate of fuel mixture components (m3/h)	Oxygen	*0.99 / **1.26				
	Propane (30%) + butane (70%)	*0.22 / **0.28				
	Air	*0.48 / **0.6				
Barrel length (mm)		500				
Barrel diameter (mm)		16				
Spray distance (mm)		65				
Frequency (Hz)		20				
Powder feed rate (g/h)		800				
Annealing parameters (ºC/ heating time h/ annealing time h/ cooling time h)		800/5/3/10	750/5/3/10	700/5/3/10	600/5/3/10	550/5/3/10
Porosity (%) / after annealing		0.17/0.11	0.19/0.12	0.41/0.35	0.69/0.47	0.46/0.45
Microhardness, HV0.2 / after annealing		677±101/684±92	657±70/699±45	603±83/621±103	594±61/617±45	524±87/528±60
Wear factor, ($\times10^{-5}$)$mm^3(m\cdot N)^{-1}$/ after annealing		0.83/1.50	0.91/1.07	1.28/1.51	0.82/0.81	0.56/0.53
Heat resistance (number of cycles to failure) / after annealing		404/396	397/402	392/387	384/391	377/356

The microstructure and elemental composition of the powder and coatings were determined using scanning electronic microscopes (SEM, Quanta 200 3D FEG) equipped with an X-ray detector of the PEGASUS 2000 system and optical microscopy (OM, Olympus GX 51), transmission microdiffraction electron microscopy (TEM, JEM-200CX, accelerating voltage 200 kV, JEOL, Japan) Observations of the samples with coating were carried out on the polished cross-sections that were normal to the surface. Porosity was determined by the metallographic method with qualitative and quantitative analysis of pore geometry using an inverted optical microscope (Olympus GX51). X-ray diffraction analysis of the alumina powder and ceramic coatings was carried on the X-ray diffractometer (Rigaku Ultima IV) in the pseudo-parallel beam mode in an angle range of 18-100° 2-theta. Crystalline phases were identified using the ICDD PDF-2 (2008) powder diffraction database.

The tribological evaluations of the coated substrates under dry conditions were performed using a ball on disc tribometer that was manufactured by CSM Instruments (Switzerland) according to ASTM wear testing standard G-99. All tests were performed at 25ºC with a relative humidity of approximately 50%. A 6 mm in diameter Al2O3 ball was used as a counter body. Specimens from all series were tested under a 6 N normal load, a radius of the wear circle of 5 mm, a 0.15 m·s -1 sliding speed and a total sliding distance of 1200 m. During testing the friction coefficient was recorded as a function of the sliding distance. The total wear volume was calculated by measuring the track cross-sectional area with a stylus profilometer (Taylor-Hobson) at ten different locations along the wear track. The ASTM G-99 standard determines the amount of wear by measuring the appropriate linear dimensions of both specimens (ball and disk) before and after the test [8].

Microhardness was measured with an automatic microhardness tester (DM-8B, Affri) using a Vickers test with a 200 g test load. Indentation was carried out on cross-sections of the samples of the coatings; the distance between the indents was 20 µm. On average, 10 tests were used as an indicator of coating hardness. Ten samples were obtained by different operation cycles under the same conditions.

Heat resistance test for samples was performed by thermal shock method by RU standard 9.312-89. Tests were carried out on samples which were fixed in holders (**Figure 1**.). The thermal movement arose as a result of cyclic heating and cooling of the central part of the sample. The thermal shock as is known not only sharp single heating, but also a few heating of high-intensity (up to several tens or hundreds). Therefore tests on thermal stability under heat shock were conducted according to the scheme: heating up to the set temperature - holding time 5-10 minutes - abrupt cooling to the set temperature (the diagram is shown for one cycle). The flat square sample with a sufficiently thick wall heated with one hand and cooled with the other hand. The thermal stresses arising as a result will be to lead to cracking.

The criterion is the magnitude of the temperature gradient with a single cycle use:

$$\Delta t = \frac{t_1 - t_0}{h} \quad (1)$$

where t_1 and t_0 - heat (t_1) and cool (t_0) temperature of the surface; h - the thickness of the wall on which detected the initial crack or a crack of given length.

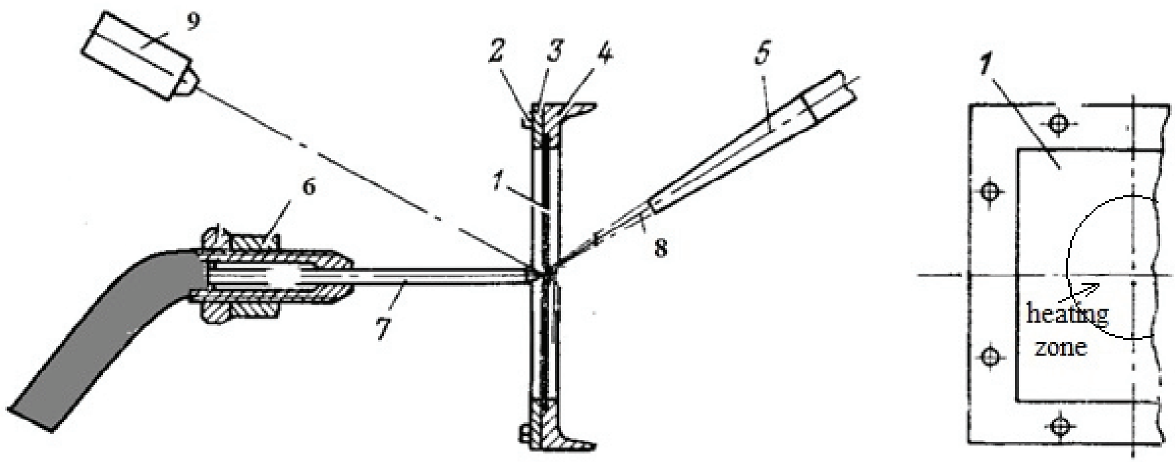

Figure 1 Scheme fixing for heating and cooling sample: (1) sample; (2) screw for fastening clamp; (3) clamp; (4) frame for mounting the sample; (5) nozzle for the supply of cooling water; (6) acetylene burner; (7) gas-flame jet; (8) water jet; (9) laser pyrometer

The destruction of the sample or the number of cracks evidencing of its destruction is criterion for the stop of the cyclic thermal shock test. Al_2O_3/Ti coatings on the steel substrate were tested by the above procedure to complete destruction of the coating on the sample. The water jet was 4°C; the coatings were heated to 550 ± 15°C. Cooling the sample to ambient temperature was carried out using water jets.

All of the obtained samples are characterized by almost the same microstructures, microhardness and heat resistance, before annealing the coatings from a composite of Al_2O_3/Ti powders contain twice as many particles of phase separations of nanoscale type as compared with Al_2O_3 coating. After annealing Arbitrary selected data are presented in the paper.

3. RESULTS AND DISCUSSION

The cross-sections of the coatings were studied with Quanta 200 3D FEG (SEM). General views of the coating structures are presented in **Figure 2** and **Figure 3**. All coatings are relatively dense. The coatings sprayed from fused and crushed powders showed typical coating structure with evenly distributed porosity (**Table 1**). **Figure 3** shows a more dense structure of coatings, which is associated with a decrease in porosity. The composite coating 60%Al_2O_3/40% Ti coating showed higher porosity co pared to other coatings. The porosity was found to result from pull-outs and removal of completely unmelted particles in the structure.

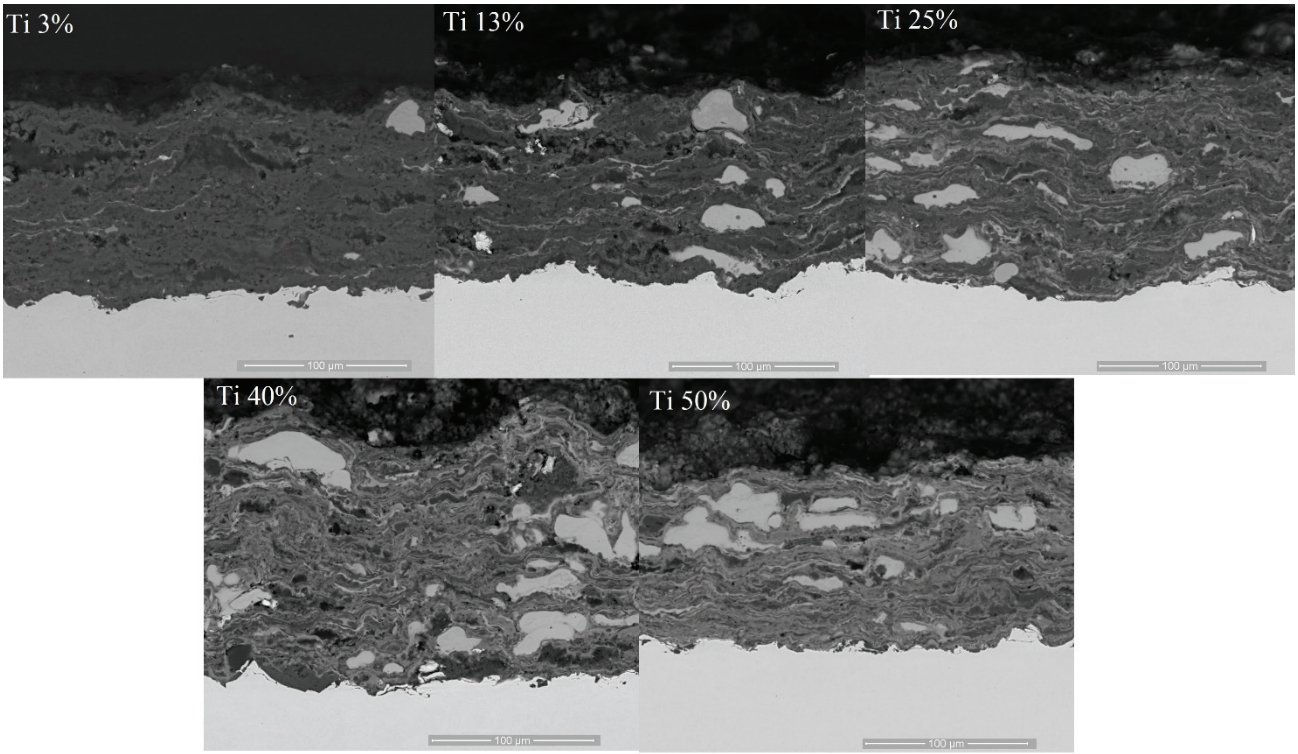

Figure 2 Structure of the Al_2O_3/xTi composite coatings before annealing

The coating is formed through the successive layering of a set of deformed particles with different temperatures, speeds and masses. The dense coating was formed through the intensive plastic deformation resulting from the impact of a particle moving with high velocity and the tamping effect on the source side of the following particles. Spraying is associated with the high temperatures and velocities of the moving powder particles, with the result that a large fraction of the powder are melted and small particles are completely melted with deposition of the appropriate alternating layers. The process of the combustion in the new multi-chamber gas-dynamic accelerator allows for increase of the of the particles velocity.

X-ray diffraction analysis of the coatings revealed that the use of Al_2O_3 / Ti powders promotes the formation of coatings identical phase composition (α-Al_2O_3; γ-Al_2O_3; $AlTi_3$) with an approximately equal content of the emerging phase constituents. However, with increasing titanium, the content of the $AlTi_3$ phase increases, which leads to an integral decrease in the microhardness of the coating. After annealing in the coatings, the content of α-Al_2O_3 increases due to the reduction of γ-Al_2O_3, the content of the $AlTi_3$ phase remains virtually unchanged. Increase in α-Al_2O_3 is due to an increase in microhardness and a decrease in the wear resistance of coatings.

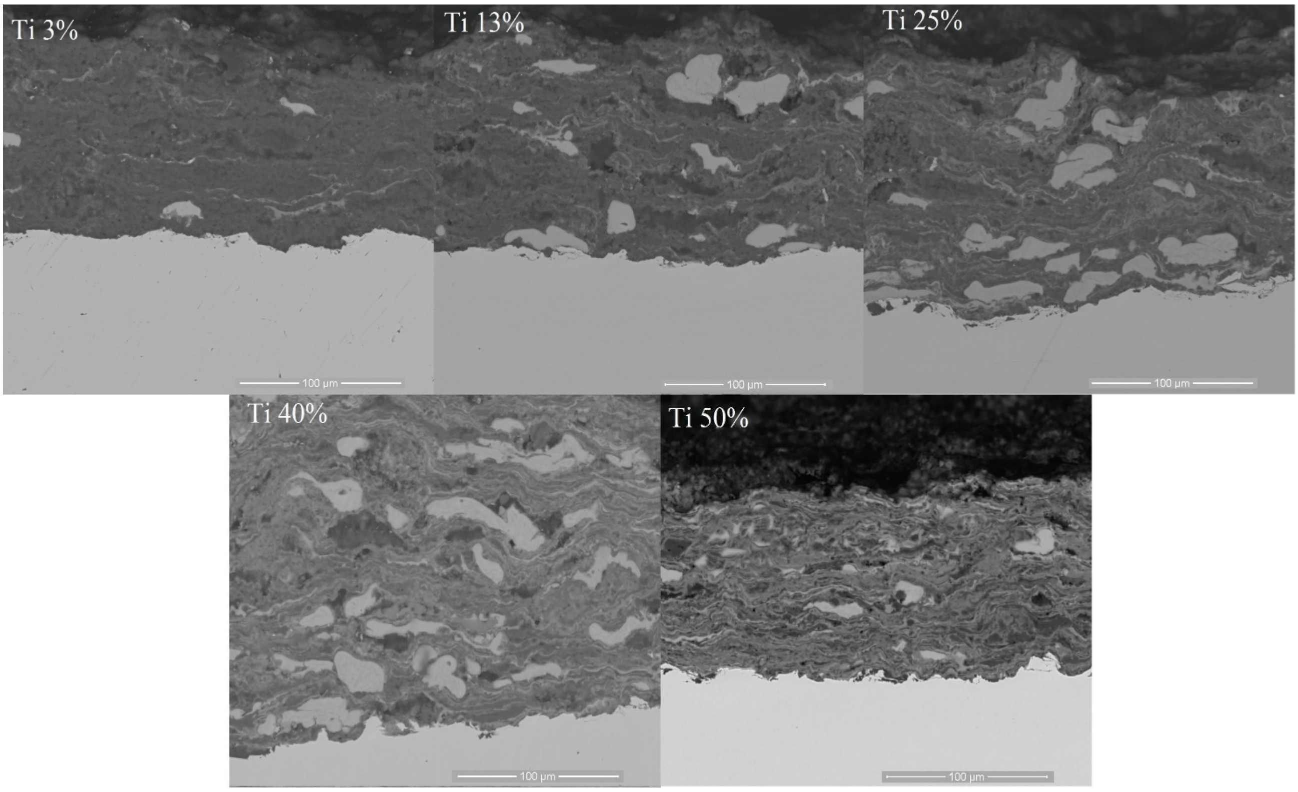

Figure 3 Structure of the Al_2O_3/xTi composite coatings after annealing

The results of TEM studies have made it possible to study the features of the fine structure of coatings and its parameters: a change in the density and nature of dislocation distribution in various structural components (in internal volumes and along structural boundaries); the nature of the emerging substructure, its parameters; the size of the subgrain; diameter of particles and phase precipitates; the effective distances between the emerging phases, and etc.

For coatings with the most favorable (high microhardness, minimum porosity, etc.) structural-phase changes, namely - Al_2O_3+3% Ti (**Figure 4**) and for comparison - Al_2O_3+13%Ti (**Figure 5**) the following is established. In the case of using Al_2O_3+3%Ti powder (**Figure 4a**), the particle size of phase separations of nanosize type (dh = 10 ... 100 nm) in the surface layers of coatings decreases by a factor of 2 compared to the coatings Al_2O_3+13%Ti (**Figure 5a**). In practice, the distance (lh) between the emerging dispersed phases (up to lh = 10 ... 30 nm) also decreases practically 2 ... 2.3 times, which characterizes the increase in the volume fraction in the matrix of the phases formed. It is also observed that the substructure is reduced by a factor of 1.4 with increasing dislocation density on the outer surface of the coatings: from r ~ 2 ... 3 · $10^9 cm^2$ to r ~ 3 ... 5 · 10^9 cm^{-2}. In this case, the dislocation density (r) in coatings varies from r ~ 5 ... 6*10^9 cm^2 (**Figure 4 b, c**) to r ~ 6 ... 7*$10^{10} cm^{-2}$ (**Figure 5 b, c**).

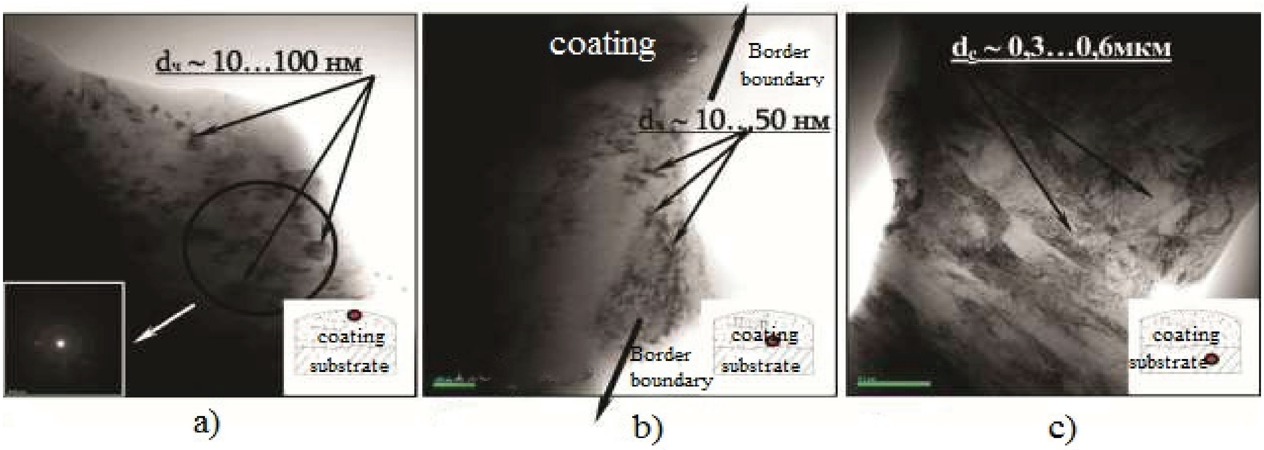

Figure 4 Fine structure: coatings Al_2O_3+3% Ti at a depth of δ ~ 150 ... 200 µm from the interface (a), in the coating-substrate interface (b) and the substrate material (c)

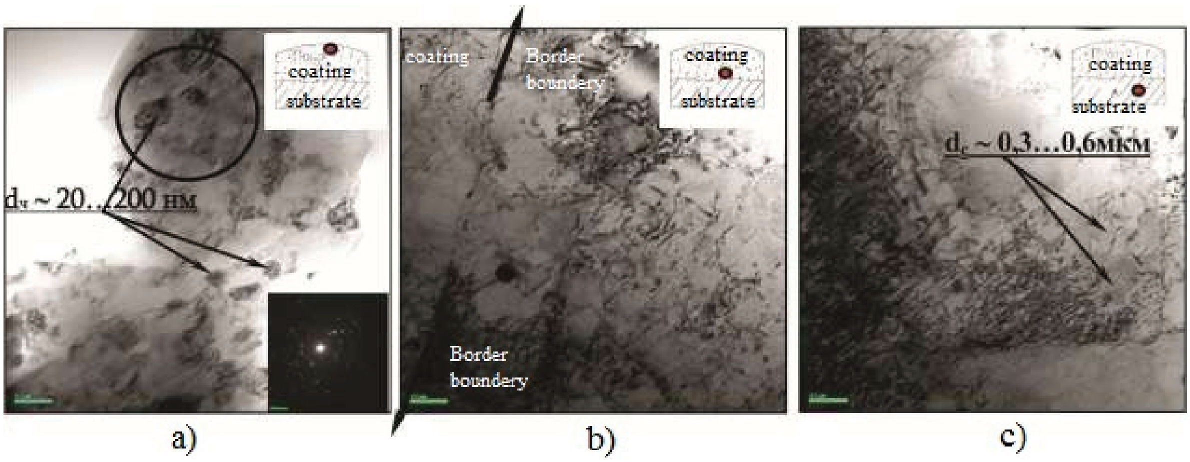

Figure 5 Fine structure: coatings Al_2O_3+13% Ti at a depth of δ ~ 150 ... 200 µm from the interface (a), in the coating-substrate interface (b) and the substrate material (c)

4. CONCLUSION

The performed complex of experimental studies at all structural levels allowed to carry out analytical assessments of the contribution of various structural-phase factors and parameters formed in the studied coatings to a change in mechanical properties and to determine the structural factors that radically affect the character and distribution of local internal forming phases. It is established that high-temperature annealing allows improving some strength characteristics of coatings due to phase-structural changes inside the coating.

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REFERENCES

[1] PAWLOWSKI, L. *The Science and Engineering of Thermal Spray Coatings; John Wiley & Sons, Inc.: Oxford, UK, 1995; 626 p..*

[2] DAVIS, J.R. *Handbook of Thermal Spray Technology; ASM International: Materials Park, OH, USA, 2004; 338 p..*

[3] BENGISU, M. *Engineering Ceramics; Springer: New York, NY, USA, 2001;. 620 p.*

[4] JORDAN, E.H., GELL, M. et.al. *Fabrication and evaluation of plasma sprayed nanostructured alumina-titania coatings with superior properties. Mater. Sci. Eng. A 2001, 301, pp. 80-89.*

[5] KOVALEVA, M., PROZOROVA, M., et.al. *Structure and properties of an Al2O3 powder coating formed by a cumulative detonation method.Russian Metallurgy (Metally), 2014, no.4, pp. 275 -278.*

[6] KOVALEVA, M., TYURIN, YU., et.al. *Deposition and characterization of Al2O3 coatings by multi-chamber gas-dynamic accelerator. Surf. Coat. Technol., 2013, no.232, pp. 719 - 725.*

[7] VASILIK, N., TYURIN, N., KOLISNICHENKO, O. Gas-Dynamic Detonation Method of Acceleration of Powders and Device for Its Implementation, RU Patent 2012. No 2506341.

[8] *Standard Methods of Preparing Metallographic Specimens, E-3-86, Annual Book of ASTM Standards, American Society for Metals, 1986,no. 0301, p. 12.*