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EFFECT OF STRUCTURE ON PROPERTIES OF Al_2O_3 AND Al (OR Ti) MECHANICAL MIXTURE COATINGS PRODUCED BY MULTICHAMBER DETONATION SPRAYING METHOD

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Effect of structure and phase composition of cermet coatings of Al_2O_3–Ti (Al) system produced using a unit for multichamber detonation spraying was investigated. Analysis of structure peculiarities of investigated coatings was performed applying optical metallography, analytical scanning as well as transmission microdiffraction electron microscopy. It is shown that dispersion of grain and subgrain structures as well as distribution of forming hardening phases of dispersion size make the most significant contribution in the indices of strength, ductility and crack resistance of the investigated coatings. 21 Ref., 2 Tables, 7 Figures.

Keywords: *cermet coatings, multichamber detonation spraying, aluminum oxide, structure, phase composition, dislocation density, hardening, fracture toughness, local internal stresses, crack resistance*

Modern industry, namely aircraft, automobile, power machine building, chemical industry, etc. uses the products, serviceability of which depends on surface quality characteristics. For example, these are piston heads and surfaces of combustion chambers, end sealings of gas turbine units, end sealings on output shafts of mining machines, surfaces of rolls and cylinders for paper industry, spinning nozzles, bars for guiding and processing of raw yarns, sealing surfaces of stop valves, etc. A relevant task is a rise of safety and life of such products, service properties of which are determined by properties of their working surfaces and allow using them for operation under extreme conditions (high temperature and pressure, intensive friction wear, alternate load, etc.). There is a number of different engineering solutions (thermal and thermal-chemical treatment, coating deposition, hardening surface treatment et al.). They provide necessary properties of functional surface layers depending on the requirements to final products under different operation conditions. These engineering methods differ to significant extent on their nature as well as effect on products and its structural-sensitive properties.

One of the most widespread and at the same time perspective methods for increase the service properties and life of the products is deposition on their surface of coatings using various spraying technologies [1–4]. E. O. Paton Electric Welding Institute of the NAS of Ukraine has developed a technology and equipment for multichamber detonation spraying (MDS). It results in formation of high-quality coatings with high coefficient of material application and productivity. Among the peculiarities of the present technology are presence of several specially profiled detonation chambers and increased detonation frequency (20 Hz) of combustible mixture, which virtually level the negative effect related with discreteness of detonation spraying methods [5].

Essential direction of application of multichamber detonation method is spraying of aluminum oxide (Al_2O_3) powders with different additives for obtaining cermet coatings [6]. Investigation of cermet coatings with different phase compositions is very important from point of view of getting a complex of physical-mechanical properties that make their application perspective in different fields of engineering. The interest to Al_2O_3–Al (Al_2O_3–Ti) cermet is provoked by the fact that it can provide a combination of high hardness, strength and refractory property typical for aluminum oxide with ductility and heat conductivity typical for Al (Ti).

Now, however, information on effect of various MDS technological parameters on structure-phase state of sprayed in such a way coatings and, respectively, on their service properties is insufficiently reliable and unambiguous.

Aim of the present work is evaluation of effect of composition of sprayed mechanical mixture of Al_2O_3 + Al and Al_2O_3 + Ti powders on structure and phase composition of the coatings produced with

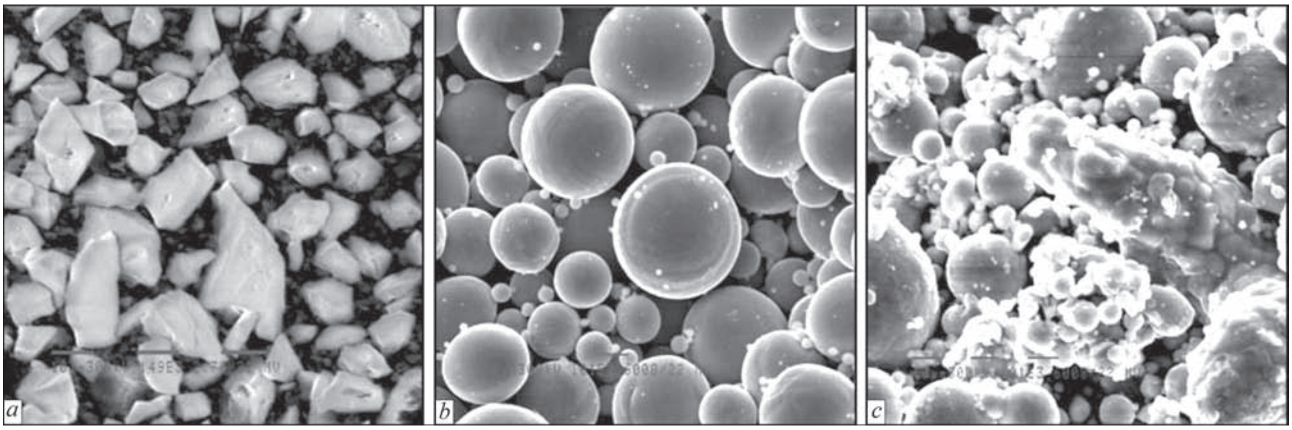

Figure 1. Appearance of sprayed powders: initial powder Al_2O_3 (*a*, x1490); additive of Ti (*b*, ×1010) and Al (*c*, ×1010) powders

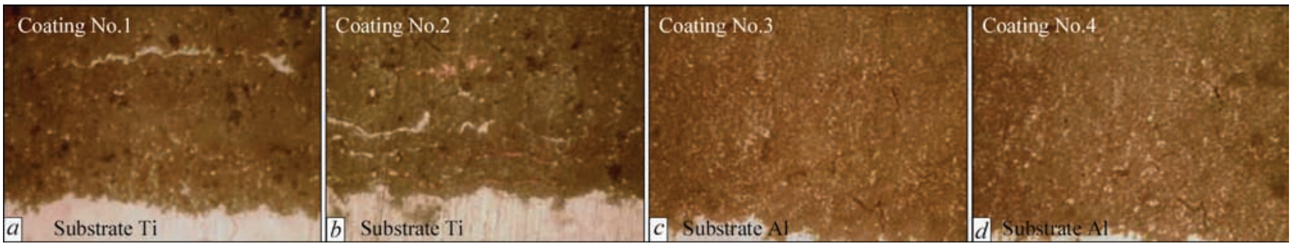

Figure 2. Microstructure (x800) of coatings: Al_2O_3 + 3 % Ti (*a*); Al_2O_3 + 5 % Ti (*b*); Al_2O_3 + 3 % Al (*c*); Al_2O_3 + 5 % Al (*d*)

MDS and structural factors on strength properties and crack resistance of investigated coatings.

Materials and investigation procedures. The coatings were sprayed using mechanical mixture of initial Al_2O_3 powder (H.C. Starck Company: AMPERIT® 740.0), fraction composition d_{fr} ~ 5–22 μm with additives (3 and 5 %) of pure powders of Al and Ti, d_{fr} ~ 5–60 μm (Figure 1). Detonation spraying mode was the following, i.e. detonation frequency 20 Hz, distance to specimen 55 mm, movement rate 1500 mm/min with similar number of passes; relationship of length (l)/diameter (d) of gun shank l/d = = 500/16 mm and combustible gas to oxidizer (β) 5.0; 5.8 (Table 1). Specimen size was 15×10×3 mm.

Examination of structural-phase state of the coatings (microhardness, volume fraction of pores, phase composition, distribution of dispersed phases, nature of grain, subgrain and dislocation structures, etc.) were carried out at all structural levels using complex technical approach, including optical metallography (Versamet-2, Japan; Leco-M400, USA), analytical scanning electron microscopy (Philips SEM-515, Netherlands), X-ray structural phase analysis (DRON-UM1) as well as transmission microdiffraction electron microscopy (JEM-200CX of JEOL Company with accelerating voltage 200 kV, Japan). The results of carried work were experimental data on full complex of structural-phase parameters of coatings in MDS.

Table 1. Parameters of technological MDS mode

Gas flow, m³/h			β	Level of chamber filling
Chamber 1	O_2	4.4 (140)	5.8	0.82
	Air	0.14 (5)		
	C_3H_8	0.77 (60)		
Chamber 2	O_2	4.0 (125)	5.0	1.13
	Air	0.325 (10)		
	C_3H_8	0.82 (55)		
Feeder	Air	1 (80)	–	–
Note. Powder flow 600 g/h.				

Examination results. Four groups of coatings, sprayed on Ti (VT1-0) and Al (AD0) base of up to 250 μm thickness δ (Table 2, Figure 2), were produced. The examinations using optical metallography method showed that porosity of such coatings is at the level of 0.7–2.5 %, volume fraction of lamellae ($V_{f/l}$, %) in them makes 1.5–5.0 %. At that, the minimum porosity (P, %) and the maximum integral microhardness *HV*0.3 are typical for coatings Nos 1, 2 produced using Al_2O_3 powders with 3 and 5 % of Ti additives.

X-ray structural phase analysis of produced coatings determined that application of Al_2O_3 + 3 % Ti (mode No.1) and Al_2O_3 + 5 % Ti (mode No.2) powders promotes formation of coatings with identical phase composition at approximately equivalent content of forming phase constituents, namely γ-Al_2O_3 (67–69 %); α-Al_2O_3 (18 %); $AlTi_3$ (13–15 %). However, in Al_2O_3 + 5 % Ti (mode No.2) coatings the integral microhardness *HV*0.3 shows 17 % rise (from

Table 2. Results of investigation of coating structure

No.	Powder (substrate)	δ, μm	P, %	$V_{f/l}$, %	*HV*0.3, MPa
1	Al_2O_3 + 3 % Ti	135–200	1.5–2.0	2.5–3.0	8900–10990
2	Al_2O_3 + 5 % Ti	100–230	0.7–1.5	4.5–5.0	9660–13770
3	Al_2O_3 + 3 % Al	115–250	1.7–2.4	1.5–2.5	8900–10520
4	Al_2O_3 + 5 % Al	90–225	1.9–2.5	1.9–2.5	7900–10250

8900–10990 to 9660–13770 MPa) in comparison with Al_2O_3 + 3 % Ti coating (mode No.1), Table 2.

Spraying of Al_2O_3 + 3 % Al (mode No. 3) and Al_2O_3 + 5 % Al (mode No.4) powders promotes formation of coatings at γ-Al_2O_3 (69 %); α-Al_2O_3 (15 %); Al (16 %) content and approximately similar level of the integral microhardness *HV*0.3 (Table 2).

As a result it was determined that (3 and 5 %) Ti additive in comparison with (3 and 5 %) Al coatings results in changes of the structural-phase composition and microhardness (*HV*0.3) of the coatings. Interaction of Al_2O_3 and Ti in formation of coating layer under conditions of detonation spraying leads to formation of intermetallic phase $AlTi_3$ that possibly stipulates rise (1.2–1.3 times) of the integral microhardness *HV*0.3 of such coatings.

Results of electron-microscopic transmission examinations allowed investigating the peculiarities of fine structure of the coatings, i.e. change of density and nature of dislocation distribution in different structural constituents (in the internal volumes and along structural boundaries); nature of forming substructure, its parameters; size of phase precipitation particles; effective distances between the forming phases, etc. In this connection the following was determined for the coatings with the most favorable (high microhardness, minimum porosity et al.) structural-phase variations, namely Al_2O_3 + 5 % Ti (mode No.2, Figure 3) and for comparison — Al_2O_3 + 5 % Al (mode No.4, Figure 4).

In the case of application of Al_2O_3 + 5 % Ti (mode No.2, Figure 4, *a*) , the size of phase precipitation particles (d_p = 100 nm) in the surface layers of the coatings

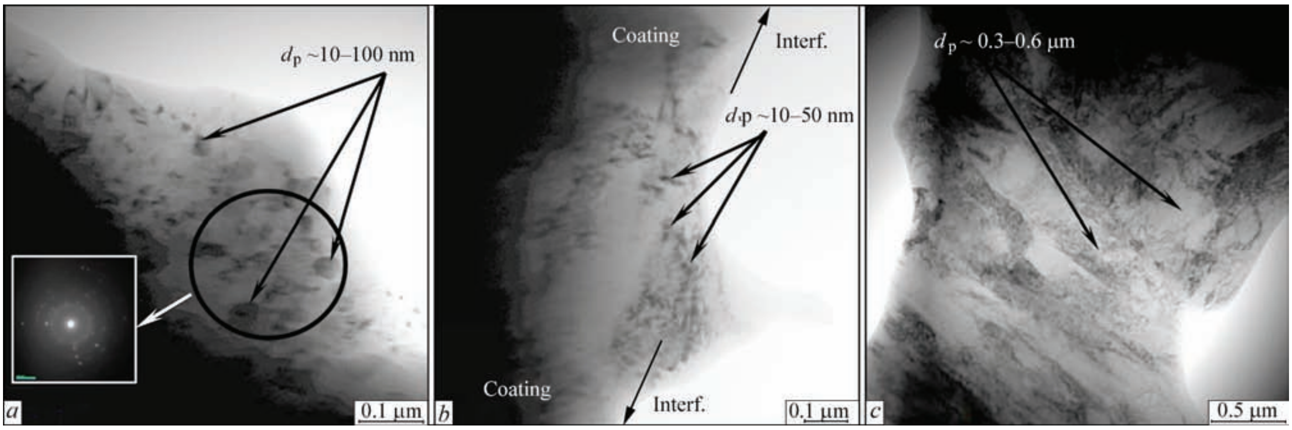

Figure 3. Fine structure of coating No.2 (Al_2O_3 + 5 % Ti) sprayed on titanium base at δ ~ 150–200 μm depth from interf. (*a*), in zone of interface (interf.) of coating-substrate (*b*) and substrate material (*c*) (O — place of examination)

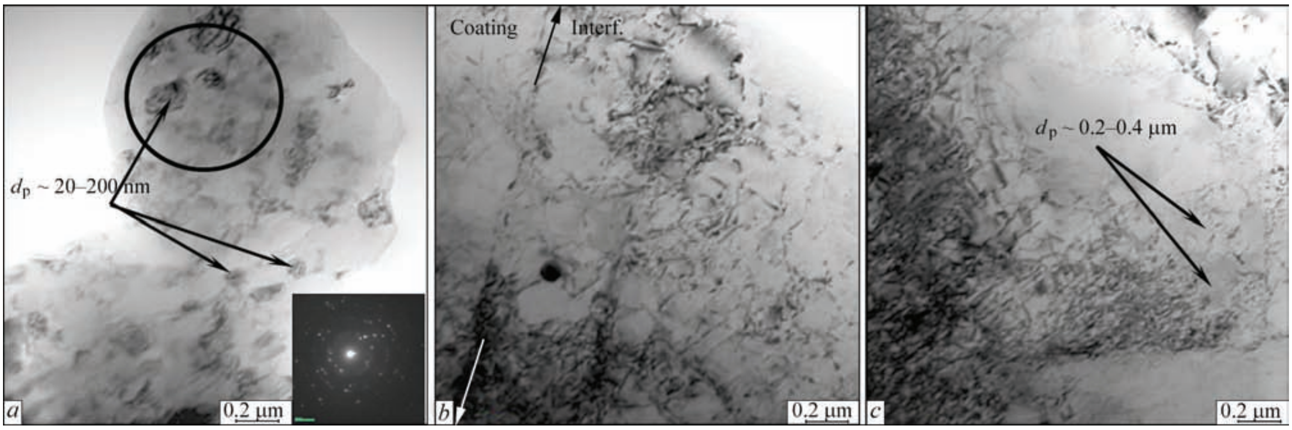

Figure 4. Fine structure of coating No.4 (Al_2O_3 + 5 % Al) sprayed on titanium base at δ ~ 200 μm depth from interface (interf.) (*a*), in zone of interface (interf.) of coating-substrate (*b*) and substrate material (*c*)

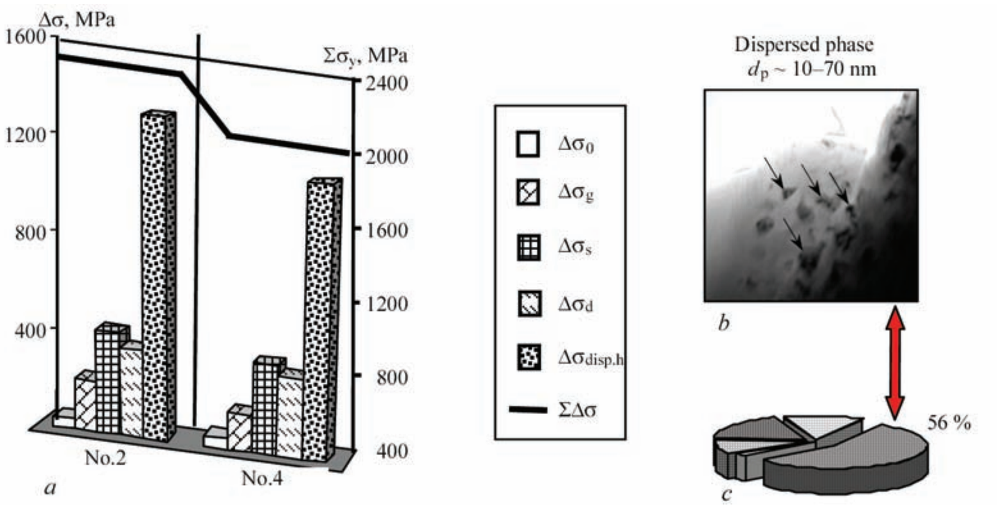

Figure 5. Histograms (*a*) showing differential contribution of grain ($\Delta\sigma_g$), subgrain ($\Delta\sigma_s$), dispersion ($\Delta\sigma_{disp.h}$) and dislocation ($\Delta\sigma_d$) hardening in variation of integral value of $\Sigma\Delta\sigma_y$ in material of coatings sprayed on different modes: Al_2O_3 + 5 % Ti (mode No.2 — Ti base) and Al_2O_3 + 5 % Al (mode No.4 — Al base) and contribution of dispersed particle phase formations (*b*, *c*) in total $\Sigma\Delta\sigma_y$ level

reduces 2 times in comparison with Al_2O_3 + 5 % Al coatings (mode No.4, Figure 3, *a*). Also, there is virtually 2.0–2.3 times decrease of a distance (λ_p) between the forming dispersed phases (to λ_p = 10–30 nm), that characterizes increase of the volume fraction in a forming phase matrix. Refinement (1.4 times) of substructure (values of subgrain d_s 0.1 ~ 0.4 μm) at increase of dislocation density (ρ) is observed as well on outer surface of the coatings from $\rho \sim 2–3\cdot10^9$ cm^{-2} (mode No.4) to $\rho \sim 3–5\cdot10^9$ cm^{-2} (mode No.2). At that dislocation density at the coatings interface makes $\rho \sim 5–6\cdot10^9$ cm^{-2} (Figure 3, *b*, *c*) and $\rho \sim 6–7\cdot10^{10}$ cm^{-2} (Figure 4, *b*, *c*).

Analytical evaluations of coating service properties. Carried complex of experimental examinations at all structural levels allows performing analytical evaluations of specific (differential) contribution of different structural-phase constituents, forming in the examined coatings, on variation of mechanical properties and determine structural factors having principal effect on nature and distribution of local internal stresses ($\tau_{l/in}$). They are potential sources of nucleation and propagation of cracks in structural microareas [7–9].

Analytical evaluations of hardening were carried out according to equation including known dependencies of Hall–Petch and Orowan et al. [10–16]:

$$\Sigma\Delta\sigma_y = \Delta\sigma_0 + \Delta\sigma_{s.s} + \Delta\sigma_g + \Delta\sigma_s + \Delta\sigma_d + \Delta\sigma_{disp.h},$$

where $\Delta\sigma_0$ is the resistance of metal lattice to free dislocation movement (lattice friction stress or Peierls–Nabarro stress); $\Delta\sigma_{s.s}$ is the solid solution hardening with alloying elements and additives (solid solution hardening); $\Delta\sigma_g$, $\Delta\sigma_s$ is the hardening due to change of grain and subgrain size (Hall–Petch dependences, grain boundary and substructural hardening); $\Delta\sigma_d$ is the dislocation hardening caused by interdislocation interaction; $\Delta\sigma_{disp.h}$ is the hardening due to dispersed particles by Orowan (dispersion hardening).

It is shown as a result that in the case of application of Al_2O_3 + 5 % Ti (mode No.2) and Al_2O_3 + 5 % Al (mode No.4), the integral values of hardening ($\Sigma\sigma_y$) for coatings make $\Sigma\sigma_y$ = 2370 MPa and $\Sigma\sigma_y$ = 2050 MPa (Figure 5, *a*). In the both cases the maximum contribution (up to 56 %) in $\Sigma\sigma_y$ value is made by coating matrix hardening due to dispersed particles of phase precipitations (dispersion hardening by Orowan): $\Delta_{disp.h}$ = 1334 MPa (mode No.2) and $\Delta\sigma_{disp.h}$ = 1070 MPa (mode No.4) , Figure 5, *b*, *c*). At that contribution of grain ($\Delta\sigma_g$), subgrain ($\Delta\sigma_s$) and dislocation ($\Delta\sigma_\alpha$) hardening for examined coatings makes 8–10 % ($\Delta\sigma_g$ = 90–200 MPa); 12–20 % ($\Delta\sigma_s$ = 100–500 MPa) and 10–15 % ($\Delta\sigma_d$ = 180–200 MPa) , respectively, Figure 5, *c*.

The calculation values of fracture toughness index K_{1c} evaluated on dependence [17]: $K_{1c} = (2E\sigma_y\delta_k)^{1/2}$, where E is the Young's modulus; σ_y is the calculation value of hardening; δ_c is the value of critical crack opening (according to data of substructure parameters) as well as comparison of K_{1c} and σ_y showed the following, Figure 6.

In the case of application of Al_2O_3 + 5 % Ti powder (mode No.2), K_{1c} index (Figure 6, *a*) insignificantly (7–10 %) reduces that results in quasi-brittle intergrain fracture of coating material, Figure 7, *b*. In the case with Al_2O_3 + 5 % Al powder (mode No.4) there is a fracture nature with tough constituent (pits of disperse sizes 1–2 μm (see Figure 6, *c*)) that should provide crack resistance of produced coatings.

Calculation-analytical estimations of the level of local internal stresses ($\tau_{l/in}$) allowed evaluating crack resistance of examined coatings taking into account nature of the dislocation structure, which is clearly observed at transmission examination of fine structure using thin foil ion thinning procedure [18].

Evaluation of $\tau_{l/in}$ exactly based on the dislocation theory of crystalline solid bodies, binding the processes of local internal stresses formation with nucleation and rearrangement of the dislocation structure [7, 19–21] was taken following the analysis of the different approaches to determination of mechanisms of crack nucleation and material fracture. The field of internal stresses, developed by dislocation structure (dislocation density ρ) and peculiarities of formation of $\tau_{l/in,}$ namely sources of nucleation and propagation of cracks (their level, extension, interaction with structural peculiarities of the coatings) were determined on dependence [20]:

$$\tau_{l/in} = Gbh\rho / [\pi(1-\nu)],$$

where G is the shear modulus; b is the Burgers vector; h is the foil thickness equal $2\cdot 10^{-5}$ cm; ν is the Poisson's ratio; ρ is the dislocation density.

It is shown that all investigated modes of MDS provide formation of low level (without rapid gradients) of local internal stresses (Figure 7). The maximum $\tau_{l/in}$ are observed at coating-substrate interface in the case of application of Al_2O_3 + 5 % Ti powders (mode No.2, Figure 7, *b*). At that their level does not exceed 600 MPa (or $\tau_{l/in} = 0.14\tau_{theor}$ from the level of theoretical shear strength of material). This provides sound coatings with low susceptibility to crack formation and, respectively, optimum service characteristics.

Thus, the results of experimental-analytical evaluations of the service properties of coatings determined that high level of mechanical properties and crack resistance is provided due to fine grain and subgrain structure at uniform distribution of dispersed hardening phases and dislocation density. Rise of coating crack resistance is promoted by absence of the extended dislocation accumulation-concentrators of local internal stresses.

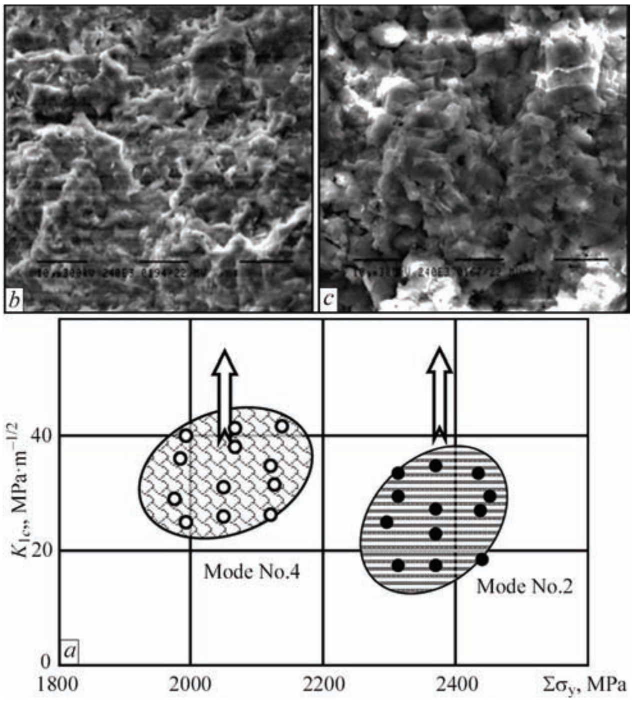

Figure 6. Change of calculation values of strength ($\Sigma\sigma_y$) and fracture toughness (K_{1c}) of coating material (*a*) and fracture patterns of tough (*b*) and quasi-brittle fracture (*c*) in material of coatings sprayed at different modes: Al_2O_3 + 5 % Ti (mode No.2 — Ti base) and Al_2O_3 + 5 % Al (mode No.4 — Al base)

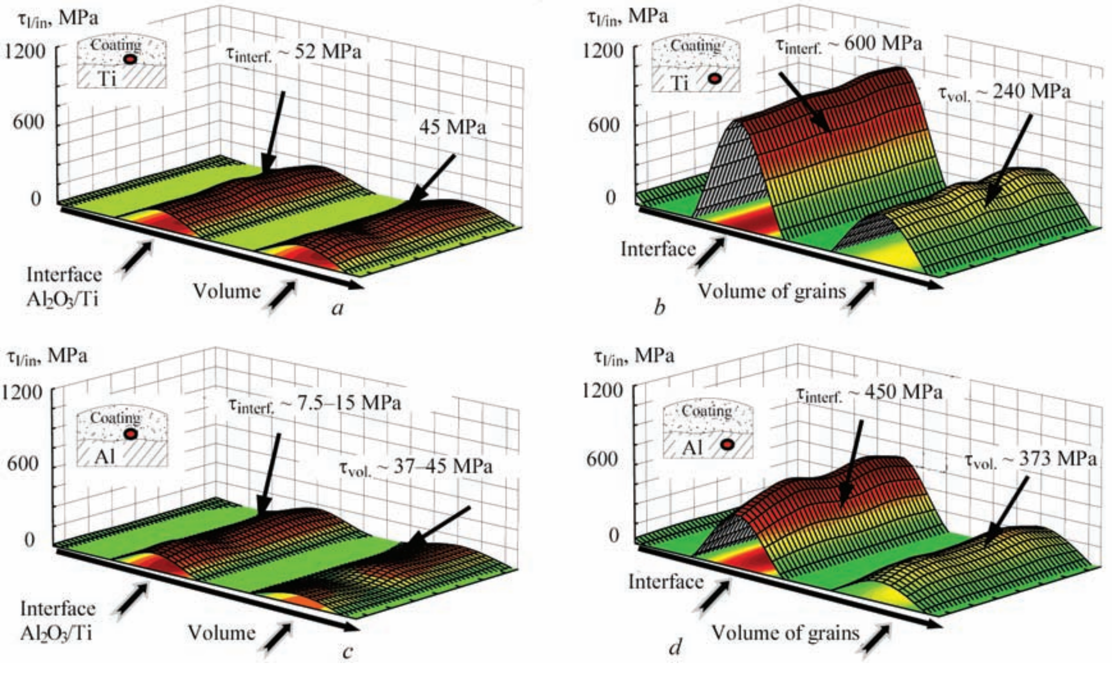

Figure 7. Distribution of local internal stresses ($\tau_{l/in}$) in material of coatings (*a, c*) and substrate (*b, d*): *a, b* — coatings No.2 (Al_2O_3 + 5 % Ti) sprayed on titanium base; *c, d* — coatings No.4 (Al_2O_3 + 5 % Al) sprayed on aluminum base

Conclusions

The results of complex examination of the coatings, produced by multichamber detonation spraying, at different structural levels (grain, subgrain, dislocation) showed:

● approximately similar content of base phase constituents, such as γ-Al_2O_3 (67–69 %) and α-Al_2O_3 (18–15 %), the rest are $AlTi_3$ and Al, respectively, in the coatings of initial powder Al_2O_3 with additives of (3 and 5 %) of Ti or Al sprayed on different bases (Ti and Al). Ti additive (3 and 5 %) promotes formation of intermetallic phase $AlTi_3$(18 %).

● Al_2O_3 + 5 % Ti (Ti base) coatings are characterized with the largest (1.2–1.3 times) values of integral microhardness (*HV*0.3 = 9660–13770 MPa), refinement (per 10–15 %) of grain, subgrain structure and size (2 times) of phase precipitation particles, gradients on dislocation density are virtually absent;

● analytical evaluations showed that the most significant contribution in the service properties (strength, fracture toughness, crack resistance) of the examined coatings have uniform distribution of forming hardening phases of dispersed size, refinement of grain and subgrain structures in absence of extended and dense dislocation accumulation-concentrators of local internal stresses.

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