1 Introduction

Wear and corrosion of the aluminium skin of aircraft begin as early as after two years of operation under severe climatic conditions, despite the use of the most advanced protection methods [1]. The applied protective coatings should be guarded against mechanical damages, scratches, nicks, etc. The points of damages, as well as zones affected by exhaust engine gases, acid vapours and other aggressive environments may act as centres of initiation of corrosion, which particularly actively develops in locations of accumulation of moisture and dirt [2]. In this connection, development of wear- and corrosion-resistant coatings to be applied to the surface of the aircraft skin is an issue of primary importance. The challenge now is to protect surfaces of the aluminium parts under the most severe atmospheric conditions for a term of not less than 6-8 years [1,2].

In view of high physical-mechanical properties of titanium and its compounds, it is of interest to deposit a coating of titanium-base composite materials on aluminium. A thin layer of the titanium-base coating will have no substantial effect on weight of a structure. While applying the coating, it is necessary to take into account that aluminium structures operate under cyclic loading conditions. This imposes increased requirements not only to strength and adhesion of the coating to the aluminium substrate, but also to the probability of its weakening in realisation of the technology.

We suggest that gas jet generators providing the non-stationary detonation combustion processes should be used with thermal spraying technologies. The generators allow control of the gas jet pulse power, velocity from 2.000 to 6.000 m/s, and temperature from 5.000 to 10.000 K. Increase of up to 20-30 Hz in the detonation initiation frequency makes it possible to work in the quasi-continuous mode, which permits using standard powder feeders and gas control panels.

2 Materials and Methods

Coating was deposited by the cumulative-detonation device. The device provides a high velocity of the powder materials (>800 m/s) without its overheating. Because of a high kinetic energy, the powder material is deformed and diluted with the surface layer of the aluminium substrate. This allows formation of thin coatings and hardening of the aluminium layer under a coating. The device provides formation of quality coatings at a 20 times lower consumption of power and 5-10 times lower
consumption of fuel gas mixture components, compared with known HVOF devices [9]. An essential difference of the cumulative-detonation device from the detonation one is that it combines the energy from several, specially profiled detonation chambers. This provides an efficient energy transfer to the powder materials. In addition, it is characterised by a wide possibility of controlling the velocity and temperature of the powder materials. The device operates at a frequency of up to 30 Hz, this allowing the use of standard powder and gas control devices, simplification of the equipment, reduction of its price, and improvement of its operational reliability. Productivity – 1 kg/hour, gas mixture consumption \((C_2H_8+O_2+N_2) \sim 5 \text{ m}^3/\text{hour}\), frequency – 17 Hz, distance to surface – 30 mm, coating thickness – 130 \(\mu\)m. Coefficient of powder utilization – 80%. Material of samples - base Al, 0.3\%Mn, 8\%Mg. It is used titanium powder with fraction 50 \(\mu\)m (Raymor Industries Inc.) and the powder consisted of 100 wt.% Ti (Fig. 1).

Investigations of microstructure of titanium powder and coating were carried out by using electron ion microscope Quanta 200 3D equipped with integrated microanalysis system Pegasus 2000. Local phase and diffraction analysis of the titanium coating was conducted by using transmission electron field emission microscope Tecnai G2 20F S-T (FEI) with microdiffraction and X-ray powder diffractometer ARL X'TRA, providing integrated information on a layer of several microns thick. Plasticity of the coating material is confirmed by investigations of adhesion/cohesion strength using scratch tester REVETEST (CSM Instruments) [10]. The similar procedure was employed to determine adhesion and cohesion of thermal spray nickel-base coatings [11]. Coating was deformed by a spherical diamond indenter of the “Rockwell C” type with a rounding radius of 200 \(\mu\)m at a continuously growing load in a range of 0.9-200 N. Results of the element analysis and defects in the deformed coating were studied.

3 Results and Discussion

Cumulative-detonation technology is carried out on the air without heating of a product and allows to deposit the coatings on local surfaces of large-sized products [9]. The coating (130 \(\mu\)m thickness) is uniform, dense, with a good adhesion to the substrate. The visible boundary line has no defects. The bulk of the coating material is deformed and closely packed. However, coarse inclusions in the form of non-deformed discrete particles are detected (Fig. 2). Titanium has low thermal conductivity (22.07 W/mK), which hampers heating and deforming it in formation of a coating. It is likely that coarse particles (>30 \(\mu\)m) were not heated and, despite a high kinetic energy, were deformed only slightly. At the same time, they hardened the substrate material and consolidated the underlying coating layers. The analysis performed allows a conclusion that the fine powder particles were heated and deformed to a state of fine lamellae, and that they filled up the spacings between the coarse particles to form a dense coating (Fig. 2). Thickness of the lamellae in the coating was 100-1000 nm.

Hardness of thin lamellae in the coating is 1590±120 HV0.01. The particles of deformed titanium has hardness 244±21 HV0.01. Hardness of boundary area in the coating has 303±12 HV0.01. The substrate under the coating is hardened. And hardness of the substrate under the coating varies to a depth of 100 \(\mu\)m from 190 HV0.01 to an average hardness of the sample material equal to 160 HV0.01. Lamellas consist of the dislocation-free titanium nanocrystalline grains 30 nm in size, separated by interlayers of the amorphous phase (C, Al), and nanocrystallites of titanium oxide and titanium carbide with a cubic lattice (Fig. 3). The phase analysis was shown that the main phase in the coating layer is Ti with face-centred close-packed structure \((a = 2.965 \text{ Å})\). The presence of other phases was determined from reflexes in an angle range of 10 to 40°. Some lines are overlapped in this range, which makes the phase analysis more difficult to conduct. The distinguished interplanar spacings calculated from reflexes make it possible to identify the following phases in the coating: TiC with cubic lattice \((a = 4.349 \text{ Å})\), and TiO with cubic lattice \((a = 4.027 \text{ Å})\) (Fig. 4).

Complex phases in interplanar spacings have an amorphous structure, which is proved by the transmission electron microscopy results. This structure could be caused by a high-temperature cycle in formation of the coating [12-13]. Therefore, it can be assumed that the values of hardness in a layer at the interface with the substrate and in fine lamellae of the coating are attributable to the absence of dislocations inside the crystalline grains and ratio of the volume contents of nanocrystalline to amorphous phases of metallic and non-metallic titanium compounds.

Strength of intermediate and near-interface layers leads to increase of deformation resistance of the
coating. The absence of dislocations inside the crystalline grains leads to increase in elasticity and, at the same time, in plasticity of the coatings. It was detected for the first time ever [14], as far back as 20-25 years ago, that ceramic materials of titanium oxides acquire superplastic properties at room temperature at the characteristic sizes of crystals equal to several nanometres.

In this study, adhesive strength was determined by optical microscope (Fig. 5), SEM (Fig. 6), critical load of Lc, which led to the destruction of the coating and the changing curves of the coefficient of friction and acoustic emission of the load (Fig. 4). Conditionally, the process of fracture of the coating in scratching can be subdivided into five stages (Fig. 4). The indenter monotonously penetrates into the coating within a load range of 0.9 to 8 N: the friction coefficient increases but very slightly, and the acoustic emission signals remain unchanged. Under a load of 8 N the indenter completely penetrates into the coating. The diamond indenter slides over the coating at a friction coefficient of 0.65-0.55. Further movement of the indenter and increasing of load (49.6-60.6 N) cause expulsion of the coating material ahead of the indenter in the form of humps and increase of the indenter penetration depth (stage I). Overcoming of humps by the indenter is accompanied by growth of the friction coefficient (up to 0.7) and formation of acoustic emission peaks (Fig. 5). Sudden change in the indenter penetration depth (~120 µm) and friction coefficient (0.8) occurs at a load in the 60.6 – 78.5 N range (stage II), this being caused by pushing off of the coating material and deformation of the substrate. Thickness of the coating was 130 µm (Fig. 2). Increasing the load to more than 78.5 N (stage III) leads to impression of the coating material into the substrate and sliding of the indenter over the groove bottom into the coating without a change in its penetration depth (no variations in the acoustic emission signals were fixed). As the load is increased, the coating is impressed into the substrate material (stage IV), which is accompanied by formation of herring-bone (transverse) cracks on the groove bottom and intensive cohesive destruction of the coating material (load ~ 93.4 N). Increasing the load from 112.5 to 184.3 N (stage V) at monotonous sliding of the indenter causes plastic deformation of the coating, thinning and impressing it into the substrate material. The almost complete absence of peaks on the acoustic emission curve confirms plasticity of the coating and its deformation without cracks and delaminations. The elemental analysis of a trace of deformation showed that the groove bottom comprised regions with a titanium content of up to 9.4 wt. %, and regions where the coating was impressed into the substrate material and which contained up to 97.6 wt. % Ti. Therefore, the loss of the cohesion strength of the coating at a load on the indenter equal to 93 N, and the loss of the coating to substrate adhesion strength at a load of 184.3 N were fixed (Fig. 5,6). It is supposed, that absence of dislocations inside of the nanocrystallines increases the elasticity and, simultaneously, plasticity of coatings [14].

4 Conclusions

The cumulative-detonation technology allows to form the nanocomposite titanium powder coatings with productivity ~ 1 kg/hour and gas mixture consumption ~ 5 m³/hour. The coating consists from the deformed titanium particles and nanocrystallites of titanium oxide and titanium carbide. It has high plasticity at average hardness 1590±120 HV0.01, low porosity <1 %, high adhesive and cohesive strength and can be used for protection of aluminium constructions against corrosion and wear.

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Fig. 3. Diffraction TEM photographs of material of lamellae in coating (a) amorphous phases (C, Ti, Al), (b) titanium oxide crystalline grains with cubic lattice.

Fig. 4. XRD analysis of titanium coating.

Fig. 5. Results of adhesion tests.

Point 1:
Ti – 5.5 at.%
Al – 87.1 at.%
Mg – 7.4 at.%

Point 2:
Ti – 95.6 at.%
Al – 3.1 at.%
Mg – 1.3 at.%

Fig. 6. Elemental composition of coating – substrate system (Lc = 190 N)

References


