Analysis of the ceramic layer microstructure influence on plasma spray thermal barrier coating performance

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Abstract. This paper outlines the results of analysis and describes the structure of the thermal protection coatings formed by atomic ion stream deposition in vacuum, and plasma thermal spraying method. Crystallite structure features are considered along with the crystallite dimensions, spatial orientation, and position of the boundaries between separate crystallites. Discontinuity, volume, and morphology of the pores has been evaluated. Experimental studies have been accomplished using various fractions of the powder-like material ZrO₂ – 8% Y₂O₃. The influence of the coating microstructure on the coating performance has been analyzed, such as adhesive strength, thermal stability, and thermal conductivity.

1. Introduction
Improvement of efficiency, reliability, and service life are the topical areas of the modern engine building industry. Finding solutions to these problems is provided by various design and engineering means including new materials and special coatings. Protective coatings have become popular in production of modern gas-turbine engines with high operational temperature ratings that are far beyond the potential of the heat-resistant structural materials used for the hot path parts, such as rotary blades and nozzle blades of the turbine, combustion liners, and combustion chamber [1–7]. Currently, from the viewpoint of the structural material thermal protection, the most efficient system is made of heat-resistant bonding metal-ceramic coating Me–Cr–Al–Y and external ceramic coating ZrO₂ – 8% Y₂O₃ [4, 5, 7–10]. Apart from the materials, protection capacity depends on the method and operating practices used to form the coating that predetermine its structural features and performance [10].

2. Materials used in modern thermal protection coatings
It is known [1–3,6] that the first stage gas-turbine engines blades operate in the most severe operating conditions in comparison to other components and practically determine the engine service life. Failure of cooled blades made of heat-resistant superalloys is caused by high-temperature gas corrosion that results in further intergranular corrosion and fatigue cracking under high-temperature and mechanic activation. Attempts to use oxide coatings to protect such alloys revealed a number of problems, the major one is thermal endurance. Plausible solution to this problem has been found in flattening the gradient of thermal expansion coefficient per system thickness by making use of intermediate damping layers, and resulted in creation of a coating material Me–Cr–Al–Y (where Me stands for Ni, Co, Fe or their combinations). This coating was termed metal-ceramic, and for a rather long time period was used as the main thermal barrier coating (TBC) for components with relatively low operation temperature.
To date, more than three million blades have been manufactured with such coatings and are currently being operated [1].

The material is based on heat-resistant alloy components (Ni–Cr), which minimize changes in thermal expansion coefficient, while additional components (Al–Y) are meant to produce high temperature stable oxides on the surface at the end of recrystallization annealing. Processes of diffusion, formation and reduction of yttria-stabilized aluminium oxide still continue against its erosive wear from surface during operation. Thus, this system gradually changes the value of thermal expansion coefficient from values close to the ones of the heat-resistant alloy to values close to ones of the oxide. Metal-ceramic coating service life is over when Al and Y concentration in the material goes under certain critical value below which overall oxide covering is not produced anymore, and the rest components of the material undergo intensive high-temperature corrosion. So, service life is actually specified by the thickness of the coating, as aluminum concentration increase above 13% and yttrium above 0.6% proved ineffective. However, metal-ceramic thickness increase above certain values results in reduction of endurance limit within the coating – metal base system. There exist special manufacturing methods that allow partially balancing this effect, but development of new generation engines with extreme temperatures in combustion chamber required new systems of multi-layer thermal barrier coatings.

Currently, as thermal protection coatings, the systems of metal-ceramic and ceramic layers are used; due to the gradient changing of the properties, these systems are able to provide optimal combination of the adhesive, corrosive, and thermal stability of such coating [4]. As for the ceramic layer, the most popular material is ZrO₂, stabilized 8% Y₂O₃ [7]. ZrO₂ stands out among refractory oxides because of its high melting temperature, low thermal conductivity, relatively high (in comparison to other oxides) thermal expansion coefficient, better chemical stability, structural stability, strength, and resistance to cracks, while being resistant to corrosion. When heated, it is rather stable and loses insignificant amount of oxygen even when melted [4].

Apart from the materials, protection capacity depends on the method and operating practices applied to form such coating, they determine its structural features and performance [10].

3. Dependency of the coating microstructure and properties, and method of application

Notable structure of the coating formed by plasma thermal spraying method is layered and consists of disk-shaped crystallites located along the surface of the structural material, horizontal and vertical borders between the crystallite and micro voids (pores) in the area of the crystallites vertical borders (Figure 1). Thickness of each disk-shaped crystallite is 2 – 10 μm and 10–20 times smaller than its typical horizontal dimension. Vertical borders of the crystallites are limited from both sides by the monolithic material of the other disk-shaped crystallites. The coating has no end-to-end pores, and the percentage of the isolated porosity varies by the spraying modes within 2 – 12 % [8]. Such coatings made from the suitable materials guarantee efficient protection of the structural materials against corrosion, including the high-temperature gas corrosion. Coating adhesive and cohesive compression strength and shear strength is significantly higher than the tensile strength. However, experience has shown [1] that the coating adhesive strength for peeling 25 – 45 MPa and cohesive strength for tension, which is only 0.4 – 0.8 of the monolithic material strength, provide their performance in all known scenarios of complex heavy-duty applications because of their operation under the conditions of external compressive or shearing mechanical forces. One of the main features of this plasma thermal spraying coating structures is its high damping capacity to the alternating mechanical and temperature stresses, as well as the ability to localize the fatigue damage and microcracks inside the crystallite's seed, preventing from growth to the structural material of the substrate.
This cluster-like structure of the plasma coatings where the pores are oriented orthogonally to the thermal stream is radically different from the structure of the coatings formed by deposition of the atomic and ionic streams in vacuum (thermal, electron-beam, ionic-plasma deposition) or atomic streams in the galvanic & chemical methods. In this case, the microstructure is column-like. Each separate column of the structure consists of some crystallites with smaller diameter typically oriented normally to the surface of the substrate material (Figure 2). Borders between the columns and crystallites begin on the surface of the coating and end on the surface of the substrate, while the cohesive strength between the crystallites is much greater than the cohesive strength between the columns of the structure [7, 10].

Availability of these vertical borders results in forming of channels for penetration of oxygen ions, harmful impurities, and other chemical elements into the protected structural materials. The vertical borders of columns having thickness more than 5 – 10 µm are the reason of decreasing of endurance strength of the coated product in comparison with the uncoated product. These high-strength borders between the crystallites often contain the emissions of various phases and do not limit the growth of fatigue cracks, but only in some scenarios slow their growth down. Columns and crystallites are relatively non-elastic in the normal direction, and have unsatisfactory toughness. Since the columns are oriented in such a way where the crystallites bond with one end on the small surface area in comparison to their volume, erosion problems may occur [7, 10].

Structure of the thermal spraying coating also significantly differs from the structure of monolithic structural materials consisting of sizable crystallites with strong bonds between each other through common borders. Structure similar to the layered disk-shaped structure of the plasma coatings is often formed in the near-surface layer of the product to improve the fatigue endurance limit by processing the
surface with surface plastic deformation methods. However, the possibilities of such methods in creation of disk-shaped crystallites in monolithic materials are a lot scantier than the same of the plasma coating deposition method from powder-like materials.

Often, in the process of development of plasma thermal spraying coating, there is a viewpoint about the need to improve the plasma coatings quality by means of the densification and creation of non-porous structure. According to our experience [10], such structure stays efficient only when used as not thick layer on the typical structure of the plasma coating, since the non-porous monolithic structure results in significant reduction of its service life under alternating mechanical and thermal loads.

Physical nature of layered structure formation from the disk-shaped crystallites when forming the plasma thermal spraying coatings is associated with the step-by-step deposition of powder particles accelerated and heated in the plasma, which – when hitting the surface and with further plastic deformation – becomes disk-shaped [8, 9]. This mechanism of the formation of coating contributes to creation of relatively big pores parallel to the surface of the substrate structural material. Experiments have confirmed [11] that such morphology and positioning of the pores in the plasma gas and thermal coatings provides significantly less thermal conductivity unlike the coatings formed by deposition from atomic streams (Figure 3). Therefore, we can say that the plasma thermal spraying method is the best for protection of surfaces of the gas-turbine engine parts exposed to high temperature loads from the viewpoint of the control over the structure and properties in each separate layer of the coating.

4. Analysis of powder-like materials granulation influence on the plasma thermal spraying coating microstructure and thermal endurance

Currently, thermal barrier coatings on the hot gas path of the gas-turbine engines are produced in the form of the metal-ceramic layers 100 – 150 µm thick from Me–Cr–Al–Y powder and external layer of ceramic coating 150 – 350 µm thick from ZrO$_2$–8%Y$_2$O$_3$ [1–3].

Tests have been accomplished using the fractions: 20 – 40 µm, 40 – 60 µm, and 60 – 80 µm of powder material ZrO$_2$–8%Y$_2$O$_3$. The use of fine fraction 20 – 40 µm has reduced the amount of open porosity almost by three times, and reduced the amount of total porosity determined on metallographic specimens to 4 % (Figure 4, Figure 5).

Analysis of the strength of the plasma thermal barrier coatings sprayed from the powders with various granulation, with spraying distance 40 – 80 mm, have demonstrated that no matter what modes are used, the peeling strength is about 28 – 35 MPa that provides durability of the coating.

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**Figure 3.** Influence of the pores volume and morphology on the thermal conductivity of coating made of ZrO$_2$–8%Y$_2$O$_3$: a – experimental data, b – calculated data [11].
Figure 4. Microstructure of plasma thermal protection coatings formed with the following fractions of the powder material ZrO₂ – 8% Y₂O₃: a – granulation 20 – 40 μm; b – granulation 40 – 60 μm; c – granulation 60 – 80 μm

Figure 5. Dependence between the plasma thermal barrier coatings porosity and spraying distance: 1 – granulation 60 – 80 μm; 2 – powder granulation 40 – 60 μm; 3 – powder granulation 20 – 40 μm; — approximated curve; ● – experimental data.

Thermal fatigue tests have demonstrated that the specimens with the coating formed using the powder material granulation 40 – 60 μm has the best properties. This is associated with greater damping capacity of the layers formed from the powder particles of this fraction. Increase of the coating porosity to 10 – 12 % results in deterioration of the coating protective properties, and consequently to reduction of thermal fatigue properties (Figure 6).
Figure 6. Dependence between the number of cycles to failure of plasma thermal barrier coatings and spraying distance: 1 – granulation 60 – 80 µm; 2 – powder granulation 40 – 60 µm; 3 – powder granulation 20 – 40 µm; — approximated curve; ● – experimental data.

5. Results and Conclusions
Apart from materials used, protective capacity of the coating in significant extent depends on the method and operating practices that largely predetermine structural features and performance of the coating [10]. To protect the parts of the modern gas-turbine engines exposed to heavy thermal loads, the optimal way is to use the plasma thermal spraying method from the viewpoint of the possibility to control the structure and properties of each separate layer of the coating, and from the viewpoint of providing significantly less thermal conductivity coefficient in comparison to the atomic and ionic flows deposition in vacuum.

Experimental studies have been accomplished using the various fractions of the powder-like material ZrO₂ – 8% Y₂O₃. Results of the metallographic control has demonstrated that the use of fine fraction 20 – 40 µm has reduced the amount of open porosity almost by three times, and reduced the amount of total porosity to 4 %. It has been established that the increase of the coating density within the entire system leads to the better adhesion of the coating with the substrate, but leads to worse thermal endurance and thermal endurance strength because of damping properties deterioration of thermal protection coating layers. Therefore, some compromise is required in the structure of the system to improve its resistance against the high-temperature gas corrosion and increase of resistance to multi-cycle alternating thermal and mechanical loads.

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