Enhancing thermal barrier coatings performance through reinforcement of ceramic topcoat

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Abstract. This paper studies structure of thermal barrier coatings applied to hot gas path components in gas turbine engines and produced in a number of ways, and its impact on performance. Methods of structural reinforcement for ceramic topcoat in thermal barrier coatings are considered.

1. Introduction
At present, increasing component life for hot gas path in gas turbine engines (GTE) is inherently dependent on development of highly efficient system of thermal barrier coatings (TBC). Recent years have witnessed a growing interest therein, as advanced GTE appeared with gas temperature approaching to or exceeding the operating maximum of existing heat-resistant alloys, more advanced equipment was designed, and spray materials for industrial applications were produced. TBC are being successfully used for protection of first stage GT nozzle and rotor blades, liners, and combustion chambers [3,9]. Available capacities for enhancing TBC performance, however, still have a long way to go to be fully mobilized. One of such capacities lies in controlling TBC structure during coating formation and following treatment of the finished item.

Among multi-layer TBC, the most efficient system proved to be the one consisting of an external ceramic coating (CC) layer, composition ZrO$_2$–Y$_2$O$_3$, and intermediate one or two-layer damping metallic ceramic coating, composition Me–Cr–Al–Y with different proportions of components. In course of research, this coating system was deposited by electron beam and plasma thermal spraying techniques (ceramic and metallic ceramic coatings), as well as by plasma-enhanced vacuum deposition technology with high-energy ions (metallic ceramic coatings).

2. Impact of coating technique on its structure
Studies revealed significant impact of coating technology used in TBC formation on component life and also demonstrated a contradiction in requirements applicable to its structure. On one hand, increase in density and cohesive strength of coating materials augments the overall system resistance to high-temperature gas corrosion, on the other hand, reduces its thermal endurance and endurance limit. Findings showed that the external oxide layer produced by different techniques has distinct degree of "transparency" for ions of oxygens and does not prevent exchange processes on the border between CC and MCC. This is conditioned by the fact that microstructure of the coating produced by electron-beam technique is columnar (Figure 1 and Figure 2). Each single column contains several crystallites (Figure 1) (column boundaries are marked with a solid line, crystallite boundaries, with a...
dotted line) that have a relatively strong adhesive connection with metallic ceramic coating along the bases and a weak cohesive connection with other columns.

**Figure 1.** Diagram of a thermal barrier coating produced by atomic layer deposition technique (a) and its alteration in case of elimination of continuous intercrystalline boundaries (b) and heat pulse modulation of the external surface (c)

**Figure 2.** Structure of a thermal barrier coating produced by atomic layer deposition technique (a) and its alteration in case of elimination of continuous intercrystalline boundaries (b) and heat pulse modulation of the external surface (c), x500

Boundaries between columns and crystallites that originate on the external surface of ceramic coating and end on the border with metal base, serve as channels for entry of oxygen ions. Formation of such boundaries is determined by technological legacy when coatings are being grown from atomic layers [4]. At the same time, all techniques aimed at elimination of continuous intercrystalline boundaries within ceramic coating (Figure 1b) increase the system resistance against high temperature gas corrosion, and in case of thick coating layers significantly reduce the endurance limit of the system [1].

In coatings produced by plasma spraying, intergranular boundaries have an essentially different structure (Figure 3), therefore, speed of oxygen ions penetration to the oxide - metal border is reduced. Besides, due to their microstructure, plasma sprayed coatings [1,2] provide much better thermal protection. Pores in coatings produced by plasma spraying, are relatively large, disk-shaped and located parallel to the base surface [6,8]. Pores in coatings produced by atomic layer deposition, are small, elongated and located perpendicular to the base surface. Experiments have shown that plasma sprayed coatings have less thermal conductivity than TBC produced by atomic layer deposition.
It was also shown that increase in density of coatings and in strength of intergranular boundaries overall through the system results in reduction of thermal endurance and endurance limit due to weakening of damping properties in thermal barrier coating layers. Therefore, a certain consensus shall be maintained within the system structure in order to enhance its resistance against volumetric high temperature gas corrosion and to increase its resistance to multi-cycle intermittent thermal and mechanical loads.

With due regard to promising potential of the described TBC system in aviation applications for new generations engines experiencing considerably higher temperatures in combustion chamber, as well as to the exposed mechanisms that reduce the coatings service life, a series of further studies on plausible directions for improvement have been performed. The underlying idea for this research and development was essential feasibility of considerably enhancing coatings resistance against high temperature gas corrosion by creating a denser fine-grained topcoat with no continuous boundaries (Figure 1c, Figure 3b). At the same time, structure of the other layers within ceramic or metallic ceramic coating shall not undergo any significant changes, otherwise the coating would lose its damping properties.

Such a structure of thermal barrier coatings might be created on top of a formed base coat by potent thermal impulses (Figure 1c), and on top of a forming base coat - by using of finer-grained powders for plasma thermal (Figure 3b), or by using ions with variable kinetic energies in order to reduce the negative technological legacy while growing coatings from atomic layers (Figure 1b) [1,4,5].

Research was started along the three plausible lines: in topcoat structure refinement through impulse plasma deposition, works have advanced up to the pilot production stage; as for laser surface enhancement, studies are still going on in laboratories; and research on fine-grained powders introduction has reached its final stage. In what follows we consider some of the findings.

3. Topcoat structure reinforcement through impulse plasma deposition
The first challenge of creating a dense fine-grained layer within the formed thermal barrier coating on the item was to determine whether such technology is technically feasible. This is explained by the fact that the temperature of fused external surface on the ceramic topcoat shall exceed its melting temperature $T_{M,1} = 2910$ K. At the same time, temperature on the border between CC and MCC shall not exceed the approximate value of $T_{C,2} = 0.8 \cdot T_{M,2} = 1500$ K ($T_{M,2}$ being the temperature when MCC material starts to melt). This restriction for $T_{C,2}$ is conditioned by the fact that at higher temperatures, processes of gas release and sublimation begin on the MCC surface, which results in a cohesive failure of ceramic coating continuity. As the literature review revealed no data on analysis of similar situations, we developed a specific mathematical model and analyzed, on the basis of a numerical
simulation, the potentiality of matching thermal impulse parameters \((t_i - \text{time interval for which an impulse acts, } q - \text{density of energy flux})\) that would make the situation above possible. The mathematical model was conceived in terms of a unidimensional, flat, nonlinear problem of thermal conductivity within a three-layer composite body, while its external surface is being exposed to a thermal impulse, and it is being cooled via heat radiation and evaporation of material. Heating, melting, crystallization, and cooling stages were sequentially calculated.

Numerical simulation showed that heating time \(t_m\) of the oxide surface up to melting temperature \(T_{M,1}\) is more or less proportional to \(q^2\) (Figure 4). At time point \(t = t_M\), thermal impact depth of an impulse is concentrated in a narrow layer adjacent to the surface. Starting from the time point \(t_M\), a molten mass is formed on the surface, and its melting front drifts into the depth of the material. At the same time, the temperature of the oxide surface is rising rather quickly, but as it approaches the oxide boiling temperature \(T_B = 4573\ K\), its rising rate slows down and the temperature is stabilized around that value. Temperature distribution per system thickness during the impulse effect is characterized by a steadily decreasing function (Figure 4).

![Figure 4](image-url)

Figure 4. Temperature distribution per system thickness \((\text{ZrO}_2 + \text{Y}_2\text{O}_3) - (\text{NiCoCrAlY}) - (\text{base})\) with pulse effect \(q = 10^8\ W/m^2\) (a); \(q = 10^9\ W/m^2\) (b) and \(t_i > 9.2 \cdot 10^{-3}\) at time: (a): \(1 = \text{4.2} \cdot 10^{-3}\ s,\ 2 = \text{7.8} \cdot 10^{-3}\ s,\ 3 = \text{9.4} \cdot 10^{-3}\ s\) and (b) \(1 = \text{7.8} \cdot 10^{-3}\ s,\ 2 = \text{5.1} \cdot 10^{-3}\ s,\ 3 = \text{7.8} \cdot 10^{-3}\ s,\ 4 = \text{9.4} \cdot 10^{-3}\ s\)

Numerical analysis of the exposed situation allows to choose \(q\) and \(t\) parameters for a pre-set system thickness, so that maximum or set CC melt-through value would be reached, while temperature on the border between CC and MCC rests below the pre-set critical value. At the same time, as the grain size in the crystallization zone decreases along with the solidification rate increase and molten mass zone reduction, it was suggested to treat the thermal barrier coating by several sequential impulses. The first impulse shall provide for penetration of \((20 - 50)\%\) of the CC depth, and the next impulses, for a more reduced penetration, which shall create a finer-grained structure adjacent to the external surface of the TCC without altering the rest of its structure.

This treatment technique was implemented in an impulse plasma coaxial accelerator for gas plasma. Turbine blades, blades simulators and witness samples with thermal barrier coatings were placed into the vacuum chamber, assisted by special tools, and treated with an impulse flow of gas plasma with energy flux density of \((2 \cdot 10^8 \ldots 2 \cdot 10^9)\ W/m^2\). Blades were treated sequentially from both sides with two impulses, with a pause between them lasting 12 minutes.

Studies of TBC specimens produced by electron-beam technique confirmed the hypothesis about alterations in ceramic topcoat structure resulting from impulse plasmadynamic treatment. Adequacy of the mathematical model was assessed by comparing theoretical calculations of penetration depth and thickness of structurally altered coating zone in cross-sections.
Studies showed that surface roughness is reduced after treatment, from $R_a=1.25 \, \mu m$ down to $R_a=(0.8\ldots0.63) \, \mu m$; open channels along the column boundaries within the structure disappear, and partially reduced zirconium oxide produces zirconium on the surface. Color of the coating surface changes from matte white into lustrous dark metallic. Depending on the treatment mode, cross-section demonstrates substantial alterations in the layer adjacent to the surface; alteration zone width varies from 20 to 60 $\mu m$. At the penetration depth of the oxide layer, columns and crystals boundaries, characteristic for the surface, disappear. The very structure of the layer has the appearance shown in Figure 1c, and demonstrates fine-grained equiaxial pattern, with no trees nor pronounced directions of solidification. Maximum grain size within the structure varied in the range of $(1\ldots3) \, \mu m$. Presence of such a structure implies predominantly volumetric solidification of the molten mass zone.

Specimens and turbine blades were tested for thermal endurance by thermal shock (heating in 3 minutes up to $T = 1404 K$, hold time of 10 minutes, cooling for 40 seconds down to $T = 473 K$), cyclical thermal loading consisting of $2\cdot10^7$ cycles ($T_{\text{max}} = 1233 K$, $T_{\text{min}} = 473 K$, cycle duration of 20 minutes), with subsequent study of structure alteration and emerging defects. Studies showed that number of cycles required for defects to emerge was at least 1.8 times higher, as compared to similar coatings or coatings of different type, but without surface reinforcement. However, testing of reinforced blades were discontinued by thermal shock after 1300 cycles, before micro and macro defects had time to emerge. Heat resistance in specimens with reinforced coating increased $1.5\ldots2.2$ times in relation to coatings without reinforcement. Long-term high temperature strength in air ($T = 1248 K$, $\sigma = 270 \, MPa$) exceeded long-term high temperature strength of the base material, and endurance limit at normal temperatures complied with the allowance range for base material endurance limit.

All the above demonstrates the potential of continuous works in this direction and future opportunities for implementing this technology in gas turbine engines manufacturing and upgrading. At the same time, industrial operation and maintenance of the impulse plasma coaxial accelerator were shown to be complicated. Therefore, research on possible use of laser technique for ceramic coatings reinforcement via dynamic focus laser beam configurations has been started.

4. Topcoat structure reinforcement through fine-grained powders introduction at the final stage of the external layer formation

Nowadays, general-purpose plasma sprayed coatings are widely used in gas turbine engines applications, including thermal barrier coatings [1,3-5]. Existing equipment, specificity of powder materials production and storage, specificity of its heating and transportation within the plasma jet, as well as specificity of its interaction with the base material surface, determined the applicable particle size range for these powders of 40...200 $\mu m$. In general, for most technical problems addressed by this technique, emphatic issue of finer-grained fractions use seems irrelevant. Therefore, the challenge formulated above is rather specific, but very important from the practical point of view. Should this technology be implemented in production, it can generate substantial economic profits, due to its simplicity, low energy consumption and high operational efficiency.

Studies of plasma coatings properties in relation to the particle size of the powder used (40...200) $\mu m$ show [3] that particle size reduction improves coating filling, increases its density, reduces porosity, and the structure generally becomes more homogeneous [7]. However, during storage, powder materials with particle size under $10 \ldots 20 \, \mu m$ form conglomerates consisting of various numbers of small particles, the reasons for which being humidity, extended surface and molecular cohesive forces. It results in unstable flow rate of powder material supplied to the heating zone. The conglomerates spend a very short time period in the plasma jet nucleus, so that the particles they contain acquire rather different velocities and temperatures, and, therefore, the coatings they grow possess a wide range of operational characteristics. Besides, due to their low inertia, small particles are carried away by the gas flow passing along the surface, so that they do not end up on the
surface, or if they do, their incidence angle is rather big. It reduces both adhesive and cohesive strength of the coating, increases its porosity, and results in low materials utilization rate.

Therefore, the challenge of ceramic topcoat reinforcement called for creation of a technique for fine powders preparation prior to the deposition, for development of specific ultrasound dosing devices and plasma guns, as well as for optimization of spraying modes, firstly in relation to flow rates of plasma forming gas and spraying distance.

Studies used fractions of (20 – 40) µm and (10 – 20) µm of ZrO₂+Y₂O₃ powder. Those fractions were applied both independently and in a mechanical mixture with a standard fraction of (40 – 60) µm. Best results were obtained in deposition of a topcoat (40 – 60) µm thick from the fraction (10 – 20) µm. Use of this fraction allowed to reduce maximum value of geometric surface deflection from 30 µm to 10 µm, reduced open porosity by almost 3 times and reduced total porosity as determined on metallographic specimens down to 4 %. The coatings have passed a series of standard tests in accordance with the above-described procedure, and thermal endurance, long-term strength and endurance limit thereof were not reduced, as compared to coatings produced by previously developed techniques, while they presented an increase in heat resistance of almost 50 %. At the same time, when spraying this fraction, materials utilization rate resulted almost twice as low in comparison to spraying of (40...60) µm fraction.

5. Results and Conclusions

Thus, we used the example of thermal barrier coatings for hot gas path components in gas turbine engines in order to show that materials with dense fine-grained crystal structure might prove to be a significant resource in increasing performance, but only in case of its justified and rational use. Rational scope of application for TBC is restricted to the external part of the ceramic layer.

Creation of a fine-grained crystal structure in the external part of the ceramic layer requires development of specific techniques: as such, impulse plasma deposition and laser surface reinforcement were used for the formed layer, and plasma spraying was used for deposition of coatings from fine-grained powders. Cited results demonstrate the promising potential of further research and development in this area.

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