Advanced study of thermal behaviour of CSZ comparing with the classic YSZ coating

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Abstract. Thermal barrier coatings (TBC) are advanced materials typically applied to metal surfaces subjected to extreme temperatures to protect them and increase their lifetime. Ceria stabilized zirconia ceramic layer (CSZ) is increasingly used as an alternative improved as replace for classical TBC system - yttria stabilized zirconia - thanks to superior properties, including mechanical and high resistance to thermal corrosion. The paper describes the thermal shock testing of two types of thermal barrier coatings used to protect a nickel super alloy. For the experimental procedure, it was used plate samples from nickel super alloy with a bond coat and a ceramic top coat. The top coat was different: on some samples, it was used YSZ and on others CSZ. Ni based super alloys have good corrosion resistance in reducing environments action, but poor in oxidizing conditions. Extreme environments can lead to loss of material by oxidation / corrosion, along with decreased mechanical properties of the substrate due to damaging elements which diffuses into the substrate at high temperatures. Using laboratory equipment, the TBC systems were exposed repeatedly to extreme high temperatures for a short time and then cooled. After the thermal shock tests, the samples were morph-structured characterized using electronic microscopy to analyze the changes. The experimental results were compared to rank the TBC systems in order of performance.

1. Introduction
The last decades’ challenge for industrial gas turbines and aircraft engines is to increase the maximum operating temperature without overheating the metal parts during operation. In this way, the life of the materials used in turbine must be raised by increasing the resistance to corrosion at high temperatures, such improvement reducing the cost of the turbine. "Hot parts" of co-generative systems, and the turbo aircraft are subject to tribological demands from erosion, at speeds over Mach 3, thermal shock, abrasive wear, etc. The efficiency of gas turbines, for either industrial production of energy or marine propulsion for aircraft applications, has improved constantly for years. These advances have occurred, largely because they have been found means to operate the gas generator section of the engine at higher temperatures. The need for performance increasingly higher advanced turbine engines will continue asking the operating efficiency even higher, higher operating life duration and reduced emission levels [1].
Of all the wear factors acting simultaneously, thermal shock acts the most disruptive. In the case of hot parts of turbo engines, its temperature varies depending on the operating conditions at takeoff, landing, cruising speed, landing failure, in-flight engine shutdown, etc. Successive transition from one operating mode to another, lead to changes between 5-20%, in terms of thermal parameters. Variation of temperature produce high tensions in parts material and it can eventually lead to the plastic deformation of them, to the delamination of protective layers and to the damaging of the components and subassemblies.

One of the solutions consists in coating of combustion chamber and turbine blades with a thermal barrier coating (TBC). It protects and isolates the metal components of the gas turbine engine hot gas flow allows for higher combustion temperatures and improving engine efficiency. In the case of thermal shock, for testing materials were innovated and built on international level specific installations that simulate actual working conditions keeping in this way the similarity for working conditions and the processes involved.

2. Experimental procedure

2.1. TBC systems

A classic thermal barrier coatings (TBC) is consists in two ceramic layers (the bond coat and the top coat) deposited over metallic parts in order to provide their thermal insulation from the combustion gases. In this way, thermal barrier coatings allow the substrate metallic parts to achieve higher efficiency of combustion engines (internal combustion engines and gas turbine engines) due to an increase of their operating temperature [2].

**General structure of TBC**

Usually, thermal barrier coatings have four layers (Figure 1):

- **a. the external ceramic layer (Top Coat)** - ensures low thermal conductivity. Classic candidate for this layer is oxide ZrO₂ stabilized with Y₂O₃ (YSZ - yttria stabilized zirconia) material as this material solution shows one of the lowest values of thermal conductivity at high temperatures: 2.3 Wm⁻¹K⁻¹ at 1000° C and a thermal expansion coefficient value of 10.7 × 10⁻⁶ K⁻¹, which reduces thermal stress [3]. Usually, the thickness of a ceramic external layer is between 250 and 375μm [4].

  Intensive research [5], [6], have demonstrated over the time that, of the terms of thermal expansion coefficient, a better alternative to the YSZ ceramic layers are the ones of zirconia doped with ceria and yttria (CSZ). Expansion coefficient of YSZ is 10.7×10⁻⁶ K⁻¹ recorded values at room temperature for up to 1000°C, and the same coefficient for typical super alloys used as substrate and for the classic Bond Coat (NiCrAlY) registered values of 16×10⁻⁶ K⁻¹, respectively 17.5×10⁻⁶ K⁻¹ for the same temperature range [5]. This notable difference coefficient values recorded at the three components of the TBC can lead to high thermal tensions that have the ability to degrade over time the protective system. Thus, these tensions could influence the life of TBC systems. An alternative is adding CeO₂ as a stabilizing factor, which would also result in obtaining a coefficient of thermal expansion closer than the recorded value of to the substrate and Bond Coat. Sodeoka et al. [6] observed that by adding CeO₂ is obtained a coefficient of thermal expansion amounting to 12.5×10⁻⁶ K⁻¹ in the temperature range of 25-800°C which helps to reduce the tensions.

- **b. bonding layer (Bond Coat)** is typically Ni(Co)CrAlY. The thickness of this layer is between 75 and 125μm. Contact layer has a high content of aluminium and chromium which helps improve resistance to oxidation and corrosion hot. The content of yttria contributes to reducing thermal conductivity value.

- **c. oxide layer barrier TGO (thermally grown oxide layer)** - this develops as a result of the temperature rise generated on the surface. The oxide grows at the interface between the ceramic layer and bond coat, as a result of oxidation of the bond coat during the oxidation and thermal shock. Its role is to inhibit the oxidation process of bond coat.
d. nickel-based alloys and cobalt-based alloys are typically used as substrate materials. Other alloys that are suitable to be used as substrate are structures made of steel, titanium alloy or Ti-Al alloys of systems, structures made of niobium alloys etc.

![Construction of thermal barrier coatings](image)

**Figure 1.** The structure of a TBC sistem

Generally, most TBC are produced by a method of thermal spraying air atmosphere APS (Air Plasma Spray) or using HVOF, HVAF or EB-PVD methods. Thermal barrier layers deposited on the elements of turbine combustion chambers are made by thermal spraying methods with the use of plasma guns and the rotating blades are covered through technology EB-PVD. A global characterization of the thermal barrier coatings and their degradation mechanisms require a detailed description of the properties, microstructure, and the role of individual components contained in a composition of the layers of TBC, especially the bonding layer and the ceramic layer.

2.3. Deposition methods

2.3.1. APS (Air Plasma Spray). A characteristic of the thermal spraying processes is highly concentrated source of energy, wherein the coating material is supplied in the form of powder, fiber or rod. The coating material is melted and accelerated towards the substrate, forming coverage. The coating consists of several stacked flattened drops that are strengthening consecutively square and lashed each other. Due to high kinetic energy of the droplets, they spread on the substrate, forming a blanket incrementally. Plasma spray gun consists of two electrodes. Figure 2 presents a plasma spray gun with a tungsten cathode located in the interior of the anode copper which is water cooled. A gas mixture of argon and hydrogen is injected into the annular space between the two electrodes. To begin the process, a DC electric arc between two electrodes is stabilized. Arcing occurs gas ionization, atoms lose electrons become positive ions. The electrons moving at high speed at the anode, while the ions moving to the cathode. On their way, the electrons and neutral atoms collide with atoms and molecules of gas. Therefore, the electric arc continuously transforms the gas into plasma (a mixture of high-energy ions and electrons). Plasma is electrically neutral and is generally characterized by a very high temperature [7]. The kinetic energy of plasma (mostly given by free electrons) is converted into heat energy during collisions between ions, electrons and atoms. Thus, the plasma is capable of producing temperatures up to about 104 ° C [8]. The hot gas exits the gun nozzle at high speed. The powder is fed into the plasma layer. The powder particles are melted and propelled by hot gas on the substrate surface [9]. When molten particles strike the substrate surface, they form dots flattened by scattering, cooling and solidification. These dots gradually build coating.
The level of porosity of the plasma sprayed ceramic coatings is generally in the range of 3-20% [10]. For thermal barrier coating, high porosity may be desirable because the thermal conductivity of the layer decreases as the presence of porosity [11]. Certain applications require low porosity; this may be achieved by spraying conditions are controlled to speed up the droplets.

2.3.2. HVAF. During this process, the combustion gas is mixed with ambient air in a combustion chamber, the combustion causing a pressure above 10 bars. Due to this pressure, the flame velocity exceeding 600 m / s. The powder may be fed axially into the HVOF combustion chamber under high pressure or by the side of the Laval nozzle where the pressure is lower. Fuel gas (propane, propylene or hydrogen) and air are supplied at high pressure, combustion occurs outside the nozzle but in the layer of the supplied compressed air. The compressed air tightens and accelerates the flame and acts as a cooling agent for the spray gun. The material to be deposited can take the form of a powder or rod.

HVAF deposition procedure using material in powder form is using a gaseous fuel and air for projecting powder at supersonic speeds. The particles reach a speed of 800 m / sec, while remaining at a temperature below the melting point. Since the melting limit is not reached, the carbides are not damaged, nor does it undergo dissolution in the metallic binder.

In the technique HVAF of electric arc and the material in the form of rods, the wire is melted by the operation of an electric arc and a feed supersonic combustion air (propane, propylene, LPG) for atomization of the molten metal and to increase the speed to give the fines. Cape gun contains a toroidal combustion chamber with a ceramic area insertion for controlling catalytic combustion process where propylene is burned. The flue gases without oxygen forms a supersonic flow (which will not oxidize the molten metal), which is placed in the direction of the arc (Figure 3).
2.4. Thermal shock testing

Testing procedure

In the experimental campaign were carried out tests of thermal shock on dedicated QTS2 facility (Figure 4) the property of the Materials Compartment laboratory of INCAS Bucharest (National Institute for Aerospace Research and Development "Elie Carafoli") on various samples with protective ceramic layers. Thermal shock test consists essentially of a fast heating (less than 2 minute) from room temperature to the test temperature (1200°C), maintaining the temperature of the specimen at this level for 3-4 minutes after which it is rapidly air cooled to ambient temperature, with compressed air (~ 9 bar) for 1 minute. The data acquisition in the time of the tests is performed by Lab VIEW program (Figure 5).

Materials

There were tested two types of ceramic layer: no. 7 YSZ specimen – APS deposition (ZrO$_2$8% Y$_2$O$_3$) and no. 34 CSZ specimen – HVAF deposition technique (ZrO$_2$24% CeO$_2$2.5% Y$_2$O$_3$).

For the deposited ceramic layers, it was used a bond coat of NiCoCrAlY (deposited by APS technique) on a metallic support of Nimonic 90. Number of cycling has been counted up to exfoliation of about 20-30% of the deposited area, above which is considered the ceramic surface can no longer perform thermal protective function.

![Figure 4. QTS2 thermal shock facility](image)

| Time (PM) | HT (°C) | MT (°C) | LT (°C) | Toven (°C) |
|---------|--------|--------|--------|-----------|
| 9:51:22 | 1200   | 1200   | 1200   | 1200      |
| 9:52:13 | 1200   | 1200   | 1200   | 1200      |
| 9:53:04 | 1200   | 1200   | 1200   | 1200      |
| 9:53:55 | 1200   | 1200   | 1200   | 1200      |
| 9:54:46 | 1200   | 1200   | 1200   | 1200      |
| 9:55:37 | 1200   | 1200   | 1200   | 1200      |
| 9:56:27 | 1200   | 1200   | 1200   | 1200      |
| 9:57:18 | 1200   | 1200   | 1200   | 1200      |

![Figure 5. The temperature Lab VIEW representation during a thermal shock test (heating – dwell - cooling)](image)

Following are the few specimens tested in the conditions above.
Thermal shock tests were observed better behavior of the specimens with the CSZ (Figure 7) compared with YSZ specimens (Figure 6).

Figure 6.a) The no. 7 specimen initially appearance (before thermal testing)  
Figure 6.b) The no. 7 specimen appearance after the testing program (75 thermal cycler)

Figure 7.a) The no. 34 specimen initially appearance (before thermal testing)  
Figure 7.b) The no. 34 specimen appearance after the testing program (100 thermal cycler)

2.5. Microstructure analysis
Microscopic analysis was performed in the case of thermal shock test specimens in areas where no macroscopic delamination was observed.
For the microscopic characterize were choose sections presenting all protection systems components, after that the samples were specifically embedded and processed for analysis.
Can be notice the formation of cracks due to temperature differences the specimens are repeatedly subjected during thermal tests. Also, seen in Figures 8, 9.a and 9.b, is an increase of porosity of ceramic layers.

Qualitative and quantitative analysis of protection systems highlights the formation of the fourth layer component present in TBC structures: TGO - thermally growth oxides, which form at the top coat/bond coat interface having a protective role. Further qualitative analyses are given for two types of protection systems in the two cases: before and after exposure to temperature specimens to observe changes that occur in the material structure due to thermal shock tests.

It is noticed that the aluminium migrates from bond coat layer and focuses on interface between the bond coat and ceramic layer after the sample have been exposure to temperature (Figures 10.a and 10.b). So, the main element that forms the growing thermal oxide layer (TGO) is aluminium. It reacts with oxygen to form Al₂O₃. Comparing sizes of TGO layer in case of the two test pieces it is notice an increase of the TGO layer size proportional to the number of exposures to temperature. The oxide layer form develops once with prolonged exposure to high temperatures.
3. Conclusions

Tests carried out on the installation QTS2 are reproducible, safe and helps assess the TBC layers for high-tech applications (aeronautics, space, energy, etc.). In the course of our experiments we used two types of ceramic layers with the use of the same substrate - Nimonic 90 and the same Bond Coat NiCrAlY. For ceramic layers were used two types of powders based on zirconia (ZrO2): yttria partially stabilized zirconia YSZ and ceria stabilized zirconia (CSZ).

Comparing test results for those two types of TBC structures observed a higher resistance of CSZ (YSZ structures have shown the protective structure degradation after 75 thermal shock tests and the structures suffered delamination after about 100 tests).

After analysing the microstructure is observed in both cases forming an oxide layer (TGO) following exposure to the temperature, this being proportional to the number of tests. From qualitative analysis, it appears that this oxide is largely in the form of aluminium oxide. Another observation after microscopic analysis is good adhesion between layers.

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