THE STRUCTURAL CHANGES TO A ZrO_2 COATING DUE TO CYCLING THERMAL STRESSES

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Abstract: *Gas turbine aircraft engines are operating under severe thermal, mechanical and chemical conditions. The turbine technology depends on the development of suitable materials that can operate in extreme working environments. Of all the factors acting simultaneously and causing wear, the most important is thermal shock. This paper presents a concept of thermal barrier coating used to prevent exfoliation and increase the maximum working temperature. The coating consist of a $ZrO_2/20\%Y_2O_3$ ceramic layer and a Ni-22wt%Cr-10wt%Al-1wt%Y adherent layer, deposited by atmospheric plasma spraying (APS), on a Ni super alloy sample usually used for the manufacturing of turbine blades. The sample was subjected to thermal shock and after that analyzed. The highlighting and interpretation of the structural changes caused by the thermal shock were made by using modern methods of structural analysis.*

Keywords: *$ZrO_2/20\%Y_2O_3$, thermal shock, SEM, XRD*

1. Introduction

Thermal barrier coatings used in the manufacturing of turbine blades are meant to isolate the components of a gas turbine aircraft engines which are exposed to severe regimes of the temperature, thereby ensuring a good and safe functioning.[1] That would otherwise not be possible due to excessive heating of the material from which they are made. TBC layers permit lowering the temperature of the "hot parts" targeted in the energy industry and aeronautics with 100-200°C.[5] The thermal barrier coating effect allows increasing the maximum cycle temperature and along with it the turbo engines efficiency.[2]

The manufacturing of turbine blades with ceramic coatings for gas turbine aircraft engines is a usually used method for increasing the strength and durability of blades.[3]

This paper analyzes coatings deposited by atmospheric plasma spraying on a Nimonic 90 base material used in the manufacturing of turbine blades.

Parts used in aeronautics, aerospace, metallurgy, power industry, etc. are subjected to severe heating/cooling thermal cycles within a few tens of seconds.[4] For this reason a conclusive characterization of the material used to achieve a TBC demand a thermal shock test. [4]

The thermal shock is a very detrimental phenomenon to the durability and safety functioning of turbine blades.[7] Due to this reason an adequate protection for the blade is required.

For this paper the samples used in the thermal shock test were sprayed with a $ZrO_2/20\%Y_2O_3$ powder by atmospheric plasma spraying. The zirconium oxide has a polymorphic structure (multiple crystal structures of the same chemical formula) on different temperature intervals. Thus, the elementary cell is monoclinic from room temperature up to 1170ºC. This is the most stabile structure of zirconium structure. Between 1170-2370ºC the structure is tetragonal and over 2370ºC the structure becomes cubic. Because of the polymorphism, the use of the material at high temperatures is accompanied by changes in volume (3-5%) that can induce cracks and various defects in the ceramic coatings.

The transformation from tetragonal to monoclinic is a desired process, due to the improved mechanical properties, especially the tenacity of the material. It is a martensitic transformation, of shear without diffusion. The reverse transformation from monoclinic to tetragonal happens at 1170°C while the tetragonal

to monoclinic transformation occurs at cooling in the range of 850-1000°C and is dependent on the internal tensions. For this reason, pure zirconium oxide processing is not possible - cracks occur instantly. Overcoming this technological drawback is done by maintaining the tetragonal structure at room temperature by adding oxides as: yttrium, calcium or magnesium.

2. Materials, methods and instrumentation

The protection layers were obtained by successive deposition of the bonding and ceramic top layer by air plasma jet method on a 7MB METCO type installation. The parameters used for the plasma spraying deposition are presented in Table 1.

For the thermal shock test in extreme and rapid heating/cooling conditions the QTS2 installation was used. The installation was designed and built by INCAS (National Institute for Aerospace Research "Elie Carafoli") and is presented in Fig.1.

The Quanta 200 3D electron microscope was used to perform secondary electron images and EDAX analysis, working in the Low Vacuum module at pressures ranging from 50 to 60 Pa and using the LFD (Large Field Detector) detector. The voltage used to accelerate the electron beam had the value of 30kV and a working distance varied from 12 to 15 mm, Fig.2.

In order to perform a more complete analysis in terms of structural changes due to thermal shock, the ceramic layer was analyzed before and after the test using X-ray diffraction with the X'Pert PRO MRD installation presented in Fig.3.

Table 1: Parameters of deposition

Technological parameters	NiCrAlY	ZrO_2/ 20%Y_2O_3
Spray distance, (mm)	120	120
Injector	1,8	1,8
Plasma gas intensity, (A)	600	600
Arc voltage (U)	62	65
Speed of rotation (rot/min)	55	55
Argon flow (m^3/h)	50	40

The samples used in the test had the following characteristics:

- Nimonic 90 base material;
- Bonding layer NiCrAlY (AMDRY 962 powder);
- Top layer ZrO_2/20% Y_2O_3;
- Thickness of the TBC deposition 100 μm;
- The samples have rectangular shape with dimensions 2.15x30x50 mm.

Figure 1: *QTS2-Installation for material testing in extreme thermal conditions*

Figure 2: *Quanta 200 3D electron microscope*

Figure 3: *X'Pert PRO MRD X-ray diffraction installation*

3. The thermal shock resistance test

The aim of the thermal shock resistance test is to reveal micro structural changes of the tested samples. The thermal shock test is completed when macroscopic exfoliation appears and the damage is more than 25% of the TBC surface [1]. The

thermal cycling has been performed at a temperature of 1200ºC. The tested samples coating thickness was of 100 µm. The samples were tested to a sufficient number of cycles so the coating is exfoliated.

The oven is heated at the test cycling temperature. The sample is moved from the environment temperature into the oven. The heating speed of the specimen is variable depending on the specimen size, type of material, single layer or multilayer. The specimen is moved from inside the oven to the cooling area where is cooled till about 40°C.

In Fig. 4 is shown the resulting chart after the thermal shock test at a temperature of 1200 °C, and in Fig. 5 the images captured during the heat shock test using the Lab View software.

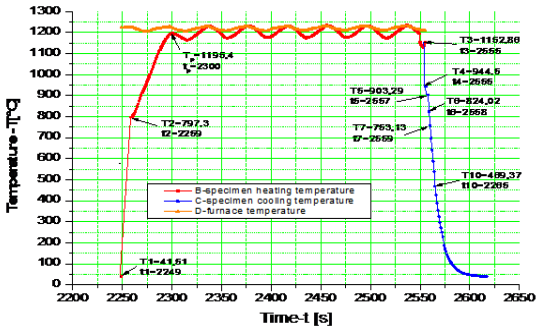

Figure 4: *The chart resulted from the thermal shock test at 1200 ºC*

The parameters used for the rapid thermal shock test are: the average speed of heating of the sample in the first 10 seconds (75,57 °C/s), the average speed of cooling of the sample in the first 10 seconds (69,34 °C/s) for 60 s of cooling, while maintaining the sample in the oven 5 minutes. The duration of the test is 6 minutes. The maximum pressure of the compressed air during cooling is of 8,7 bar and the minimum pressure has the value of 7,13 bar.

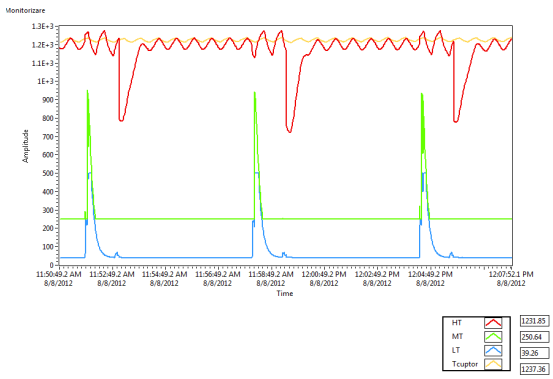

Figure 5: *Images captured with the Lab View software during the thermal shock test*

3.1 Structural analyses of the layers subjected to thermal shock by electron microscopy

Following the thermal shock test investigations by electron microscopy of the tested sample in comparison with a sample not subjected to thermal shock were made. The aim of the investigations was to determine the structural changes which occurred to the sample due to the thermal shock.

The microstructure of the deposited layer in its initial state consists of elongated grains with clear boundaries between them. The coating material has a very high porosity. The pores have different sizes, with zones of crowded arrangement, or with preferential arrangements in certain directions. These characteristics are shown in Fig. 6.a.

After the thermal shock microstructural changes occurs on the top layer (fig. 6.b). Due to thermal stresses in the heating/cooling cycles, internal tensions are formed under the effect of which micro cracks develop at the interface between grains.

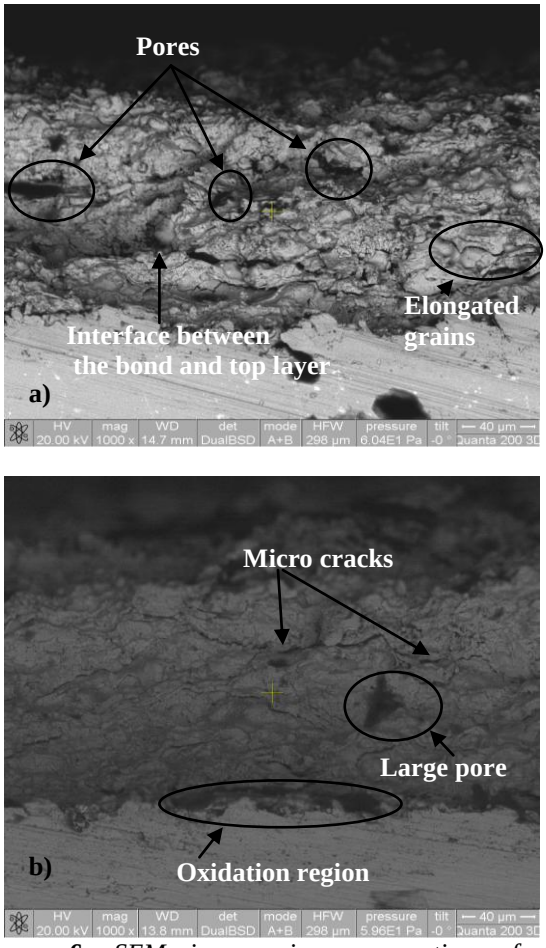

Figure 6: *SEM images in cross-section of the ZrO2/20% Y2O3 coating: a) before heat shock and b) after the thermal shock test at a temperature of 1200°C.*

In the process of micro crack propagation if it encounters an obstacle ramification of the crack will happened. Following the thermal shock at a temperature of 1200 ºC the bond layer continued to ensure a good adhesion between the base material and the ceramic coating. At the interface between the bond and top layer an oxidation region appeared, consisting of oxides of elements from the bond material.

Fig. 7-a. presents grains with a columnar structure and an overlapping preferential development. This structure formed during the cooling of the coating.

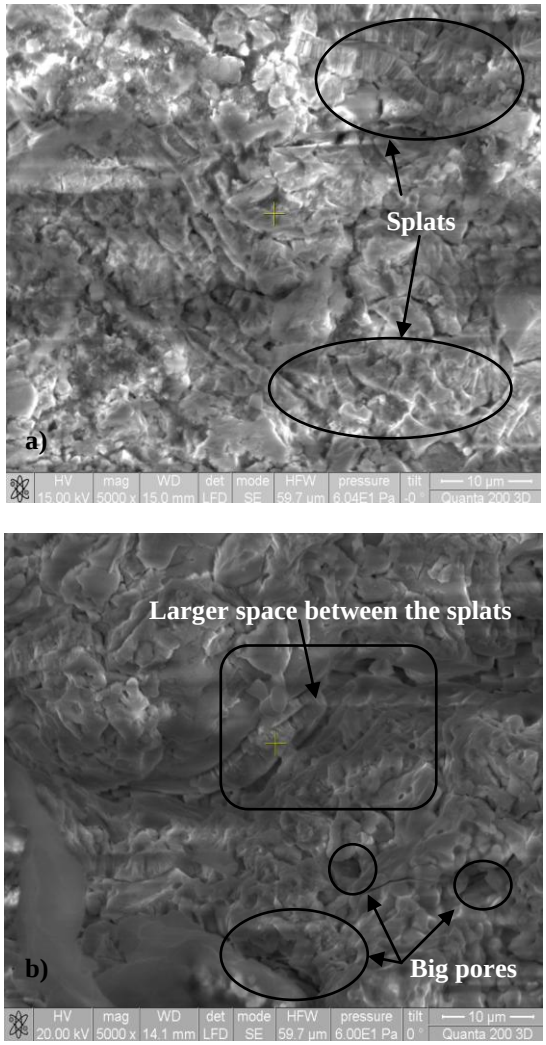

Figure 7: *SEM images in cross-section of the ZrO2/20% Y2O3 coating: a) before heat shock and b) after the thermal shock test at a temperature of 1200°C.*

Doing a comparison between the witness sample and the samples subjected to thermal shock at a temperature of 1200°C, the second one suffered a sintering of the splats (Fig. 7-b). Also a larger space between the splats is present and bigger pores formed during the process.

3.2 Structural analyses by X-ray diffraction of the layer before and after thermal shock

In order to perform a complete analysis in terms of structural changes after the thermal shock test, the ceramic layer was analyzed before and after the test.

The initial powder is a mixture of Zr, Y, O and in Fig. 8 are presented all the specific peaks characteristic to the crystallographic planes. The difractograms of the samples with ceramic coating and subjected to thermal shock have a smaller number of peaks, on one hand due to the formation of new compounds with new types of crystallographic lattices, on the other due to reduced exposure of some crystallographic planes, mainly because of the influence of substrate and texturing.

The elementary cell parameters of the layer show the appearance of a modified lattice different from the original zirconium oxide one. The changes in the lattice were due to the inclusion of yttrium atoms in the network.

The original lattice of the monocrystalline tetragonal zirconium oxide has the network parameters a = 5.1240 Å and c = 5.1770 Å (Fig. 8). After the process of plasma spraying, the new network has the parameters a = 5.1484 Å, c = 5, 3154 Å and β = 99.229 ° (fig. 9) and after the heat shock (fig. 10) at a temperature of 1200 °C, it is observed that the peaks attributed to the ZrO_2 phase were transformed from monoclinic to tetragonal with new lattice parameters a = 3.6292 Å, c = 5.1973 Å and β = 90.000 °.

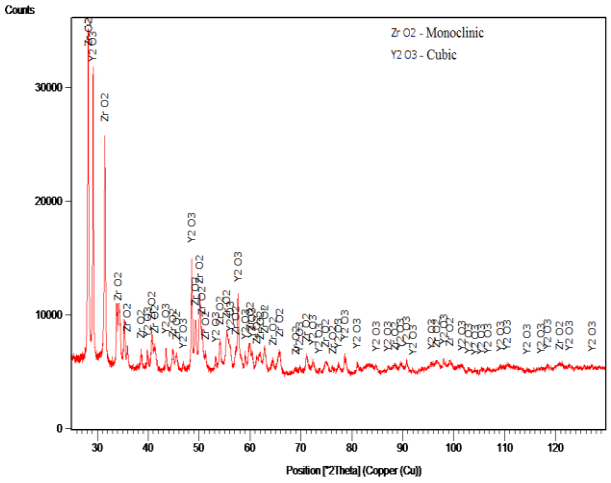

Figure 8: *XRD spectra in 2θ range of 25…130° of the ZrO_2/20%Y_2O_3 powder*

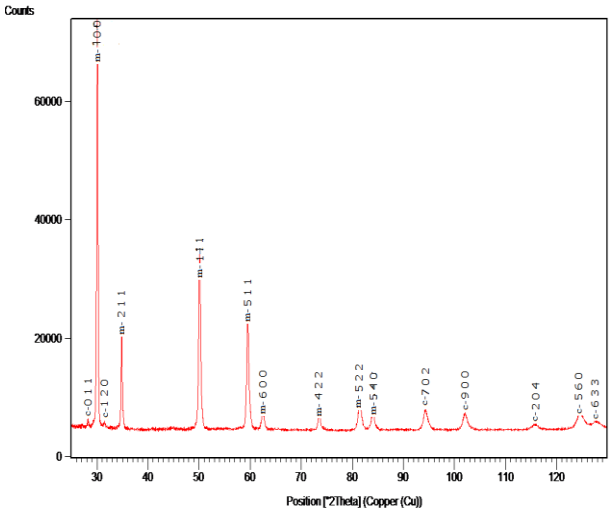

Figure 9: *The crystallographic planes of the samples with layer thickness of 100µm before heat shock*

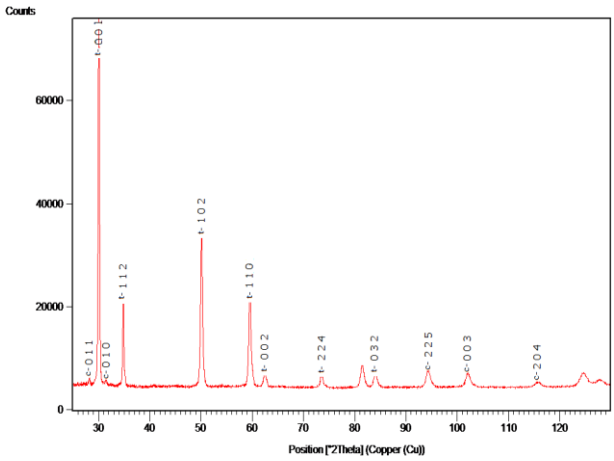

Figure 10: *XRD spectra in 2θ range of 25…130° of the ZrO_2/20%Y_2O_3 top coat, for the sample with the coating thickness of 100µm, after heat shock*

Conclusions

The samples subjected to the thermal shock test have withstood a total of 14 heating cooling cycles. The thermal shock test cause changes in the deposited layers microstructure.

Because of the thermal stresses caused by the heating/cooling cycles, internal tensions are formed in the ceramic material, under the effect of which a rapid development of microcracks is produced at the boundaries between grains. In the propagation process of the microcracks, if they encounter obstacles a ramification of the cracks is produced.

At the interface between the bond coating and the top layer an oxidation zone has appeared consisting of the elements contained in the bond layer. Similar behavior has been reported in the research made by Manoliu V. (2008) and Kobylañska–Szkaradek K.

Following the X-ray diffraction on the ZrO_2/20%Y_2O_3 ceramic layer obtained by plasma spraying it can be observed that it has a monoclinic structure for the ZrO_2 phase and the crystallographic parameter of the lattice were determined.

From the structural point of view, after the thermal shock test at a temperature of 1200 °C, changes have occurred in the structure of ZrO_2 from monoclinic to tetragonal.

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Acknowledgements

We thank to the INCAS (National Institute for Aerospace Research "Elie Carafoli") reserch center for their support in performing the thermal shock tests.

We thank to SC Plasma Jet SA for the support in the plasma jet deposition of the analysed layer from this paper.

I give thanks to the Faculty of Mechanics for the support and for making available the science of materials and Materials Science laboratories for performing the necessary tests for the paper.