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THE STRUCTURAL TRANSFORMATION OF THE CERAMIC LAYER $ZrO_2/20\%Y_2O_3$, OBTAINED BY THERMAL SPRAYING AFTER HEAT TREATMENT

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Abstract: *In this paper presents a new concept of thermal barrier coating which consist of a ceramic layer of $ZrO_2/20\%Y_2O_3$ and an adherent layer of Ni-22wt% Cr-10wt% Al-1wt% Y, deposited by atmospheric plasma spraying (APS), on samples of Ni super alloy used for the manufacturing of turbine blades. In this paper a heat treatment is applied on the layer obtained by atmospheric plasma spraying, by cooling it with a jet of air at a pressure of 100 bar after maintaining it a a temperature of 1000°C for intervals of 5, 10 and 15 hours. After the heat treatment the surfaces were analyzed microstructurally and morphologically using electronic microscopy and in terms of the phase composition by X-ray diffraction. After the heat treatment an increase in grain size on the surface layer can be observed which is caused by the formation of "bridges" between neighboring splats that had the effect of closing the initial micro cracks produced during spraying.*
Keywords: *SEM, X-ray, heat treatment, $ZrO_2/20\%Y_2O_3$*

1. INTRODUCTION

Plasma spray is one of the most important achievements in the field of surface engineering, a field in which remarkable progress has been made in recent years. Since gas turbine power units used in aeronautics work at very high temperatures, the thermal barrier coatings have become essential for increasing the lifetime of the gas turbine. This coating is designed to isolate components also protecting them from corrosion, erosion, thermal and mechanical stresses that occur on their surfaces in operating conditions. Using these thermal barrier coatings allows an increase in the maximum operating temperature of the gases without increasing the temperature of the material and reducing the amount of air necessary for cooling while keeping the temperature of the turbine.
Heat treatments applied on the superficial layers obtained by plasma spray jet are aimed at structural changes and removal of defects caused during spraying. Through heat treatment is aimed at acquiring physical-mechanical, chemical or technological imposed by the terms of use.

2. EXPERIMENTAL PROCEDURE

Thermal barrier coatings (TBCs) used on turbine blades consist of a two-layer system. First deposited layer is relatively thin and is called adherent layer and the second layer is sprayed over the first layer and called thermal barrier. The intermediate layer is of a MCrAlY alloy. The purpose of this layer is to protect the substrate from oxidation and corrosion and also to improve the adhesion between the substrate and insulation. The standard material used in aerospace industry as thermal insulator is zirconia stabilized with yttria. The ceramic powder which was sprayed on the samples was $ZrO_2/20\%\ Y_2O_3$ using the Sulzer Metco 7MB type installation produced by METCO.
The spray parameters used for the plasma jet deposition are presented in Table 1.

Table 1: Technical parameters

Powder	NiCrAlY	YSZ (202NS)
Spraying distance (mm)	120	120
Injector	1,8	1,8
The intensity of the gas Plasma, (A)	600	600
Electrode voltage (U)	62	65
Velocity of rotation (rot/min)	55	55
Composition of plasma (m^3/h)	50%Ar 13,51%H	40%Ar 13,51%H

3. EXPERIMENTAL RESULTS

This paper presents the thermal treatment applied to the layers obtained by plasma jet spraying. They were cooled with a jet of air at a pressure of 100 bar, after keeping them at a temperature of 1000 °C at intervals of 5, 10 and 15 hours. Average furnace heating speed in the first 10 minutes is 100 °C. After the first 10 minutes the oven heats up with 20 °C at every 10 minutes until the temperature reaches 1000 °C.
The heat treatment goal is to analyze the effect of sintering of the layer in morphology and phase transformations terms. After the heat treatment the microstructure and surface morphology were examined by electron microscopy and in terms of the phase composition by X-ray diffraction.

3.1. Structural analysis by electron microscopy of the heat treated layers

In the following figures are presented secondary electron images obtained by scanning electron microscopy on the Quanta 200 3D microscope in the Low Vacuum module which is working at pressures ranging from 50 to 60 Pa and using the LFD (Large Field Detector) type detector. The voltage used to accelerate the electron beam has the value of 30kV and the working distance of the beam cannon varies from 12 to 15 mm.
From the taken SEM images of the surface layer and from the line analysis (Figure 1) it can be seen that the layer structure became more rough, peaks increasing in intensity. The same can be concluded from diffraction and X-ray diffractometry following also the performed scan and the profile of the surfaces.

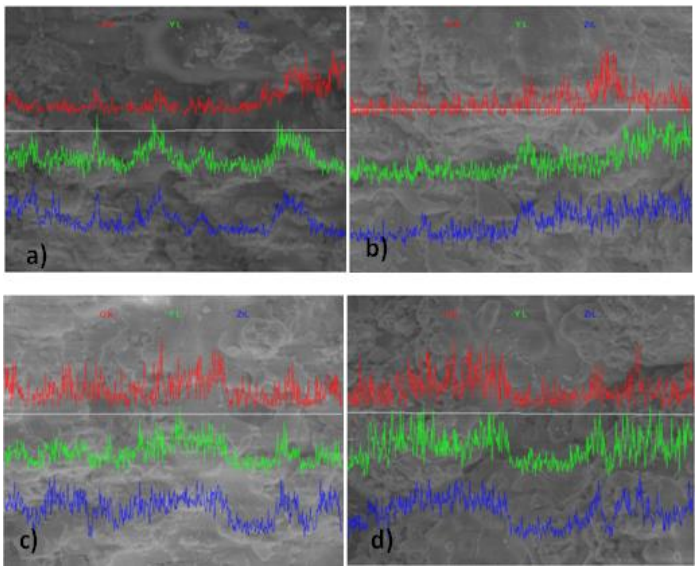

Figure 1: The SEM images show the microstructure of the ZrO_2/20%Y_2O_3deposited layer:
a) before the heat treatment; b) after the heat treatment at 1000ºC for 5 h;
c) after the heat treatment at 1000ºC for 10 h; d) after the heat treatment at 1000ºC for 15 h.

In Figure 2 are shown SEM images of the ceramic layer with the thickness of 100 µm and the adherent layer thickness of 30µm. The adherent layer has a filiform layout and a very good adherence to the base material and makes a good relation with the ceramic layer which consists of successive splats with regular geometric shape, a porous structure [1]. Also intergranular corrosion is observed due to the porous ceramic layer combined with its high temperature undergoing heat treatment (Figure 2-c). Black particles are located at the adhesion

layer/ceramic layer interface and have a high content of Al and Ni from the oxidation process of the elements which compose the adherence layer during the deposition and they rise during the heat treatment (Figure 2-d).

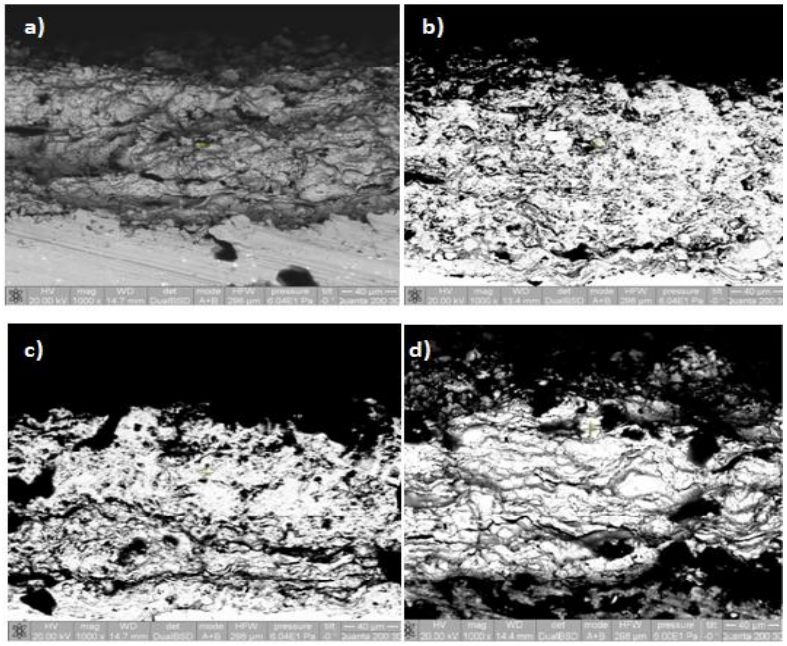

Figure 2: The SEM cross-section images present the microstructure of $ZrO_2/20\%Y_2O_3$ deposited layer in contrast Z: a) without thermal treatment; b) after the thermal treatment at 1000ºC for 5 h; c) after the thermal treatment at 1000ºC for 10 h; d) after the thermal treatment at 1000ºC for 15 h

In Figure 3 are presented the limits between neighboring splats with interlamellar cracks. The heat treatment caused an increase in grain size on the layer surface by the formation of "bridges" between neighboring splats (Figures 3-b, c, d), with the effect of closing the initial microcracks [1,2]. Large pores are maintained after prolonged heat treatment. There were no qualitative differences between the surface layer heat treated for 5 h and the one treated for 10 h (Figure 3-b, c). For the treatment carried at the temperature of 1000 °C for 15h a splitting of the grains is observed and a tendency of disappearance of the successive arrangement of the splats (Figure 3-d).

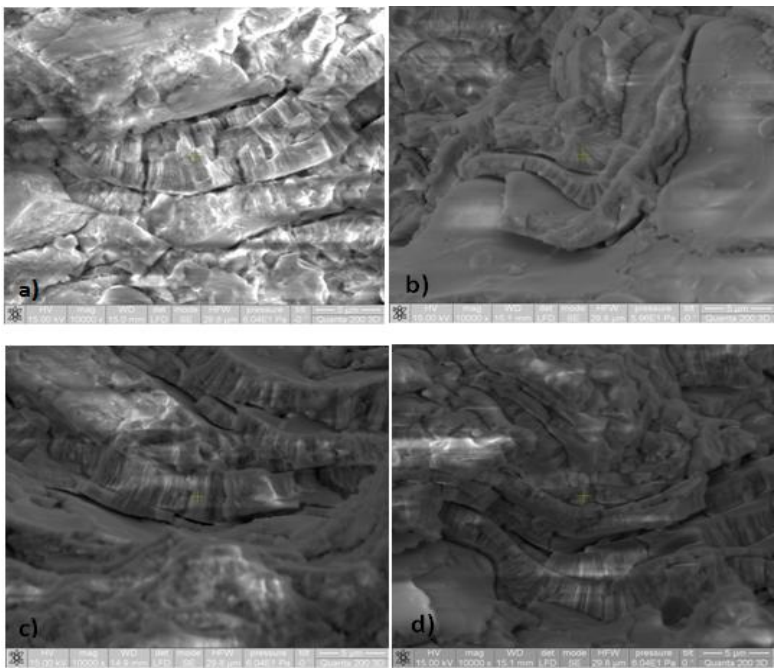

Figure 3: The SEM cross-section images which present the microstructure of the $ZrO_2/20\%Y_2O_3$ deposited layer: a) without heat treatment; b) after the heat treatment at 1000 ºC for 5 h; c) after the heat treatment at 1000 ºC for 10 h; d) after the heat treatment at 1000 ºC for 15 h.

3.2. Structural analyses using X-ray diffraction

The X-ray diffractometer is equipped with a X-ray anode tube made of Cu kα, λ = 1.54 Å, to which has been applied voltage of 45 kV with a current of 40 A, at an angle of diffraction (2θ) ranging from 25 to 130º. X-ray diffraction analysis was performed in order to observe and highlight the structural changes depending on the number of hours applied to each treatment compared with the phases that were highlighted on the untreated samples (Figure 4). [1]
Wavelengths are: K Alpha 1 [A]: 1.54060, K-Alpha 2.1,54443, K-Beta [A]: 1.39225, K-A2 / K-A1 Ratio: 0.50000.
Structural analysis were performed using a dedicated software (Xpert High Score Plus) thought which the crystallographic parameters were identified (lattice type, network constant values a, b and c and angles elementary cell alpha, beta and gamma elementary cell volume, density) and the possible compositional parameters. For the precise choosing of the stoichiometric compositions.

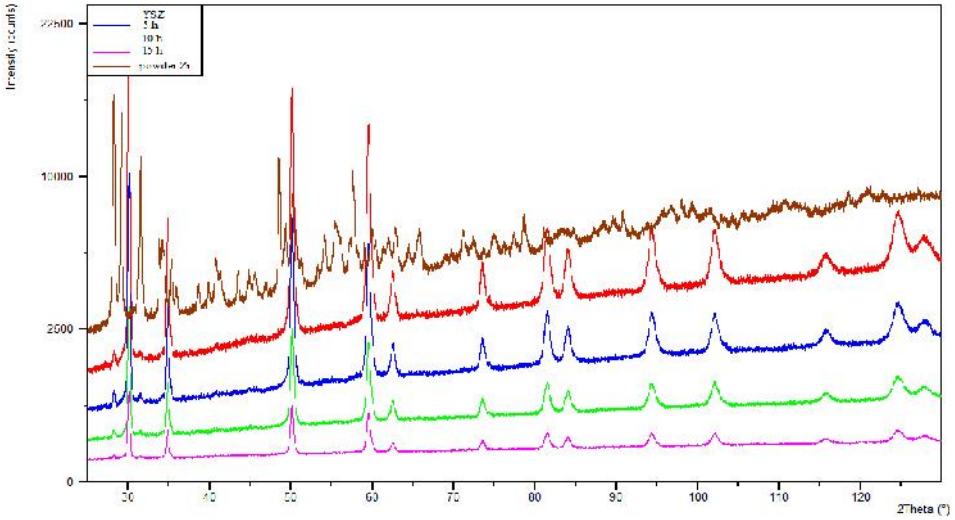

Figure 4: The X-ray diffractogram for the ZrO_2/20%Y_2O_3 deposited layer, at an diffration angle of 2θ = 25…130°

On the cumulative diffractogram was also inserted the specific one for the initial powder. Since the initial powder is a mixture of Zr, Y, O, peaks for all the specific crystallographic planes are present. The XRD patterns of the samples have a smaller number of peaks, on one hand due to the formation of new compounds with new types of crystallographic networks, on the other hand due to the reduced exposure of some crystallographic planes, mainly due to the influence of the substrate and texturing[3].
The determination of the elementary cell parameters is showing the appearance on the substrate of a modified network from the original zirconium oxide. The changes are due to the inclusion in the network of yttrium atoms of the stabilizer.
The original tetragonal monocrystalline lattice of the zirconium oxide has the following parameters a = 5.1240 A and c = 5.1770 A. For the sample with the coating thickness of 100 μm, the new network has the following parameters a = 3.6120 and c = 5.2120. All the networks are monoclinic, but after 15 hours of heat treatment the networks relocate presumably by the migration of the yttrium atoms in the place of the missing oxygen atoms, so the network is tetragonal, with monoclinic precipitates. The new tetragonal network has different parameters from the original zirconium oxide, namely a = 3.6260 and c = 5.2350.

Table 2: Stoichiometric structures occurring for different types of heat treatment

Parametre	ZrO_2/20%Y_2O_3	ZrO_2/20%Y_2O_3/ 5 h heat treatment	ZrO_2/20%Y_2O_3/ 10 h heat treatment	ZrO_2/20%Y_2O_3/ 15 h heat treatment
a	5,1484	5,1507	5,1507	3,6260
b	5,2067	5,2028	5,2028	3,6260
c	5,3154	5,3156	5,3156	5,2350
alfa	90,0000	90,0000	90,0000	90,0000
beta	99,2290	99,1960	99,1960	90,0000
gama	90,0000	90,0000	90,0000	90,0000

The XRD patterns with indexed crystallographic planes are shown in the following figure:

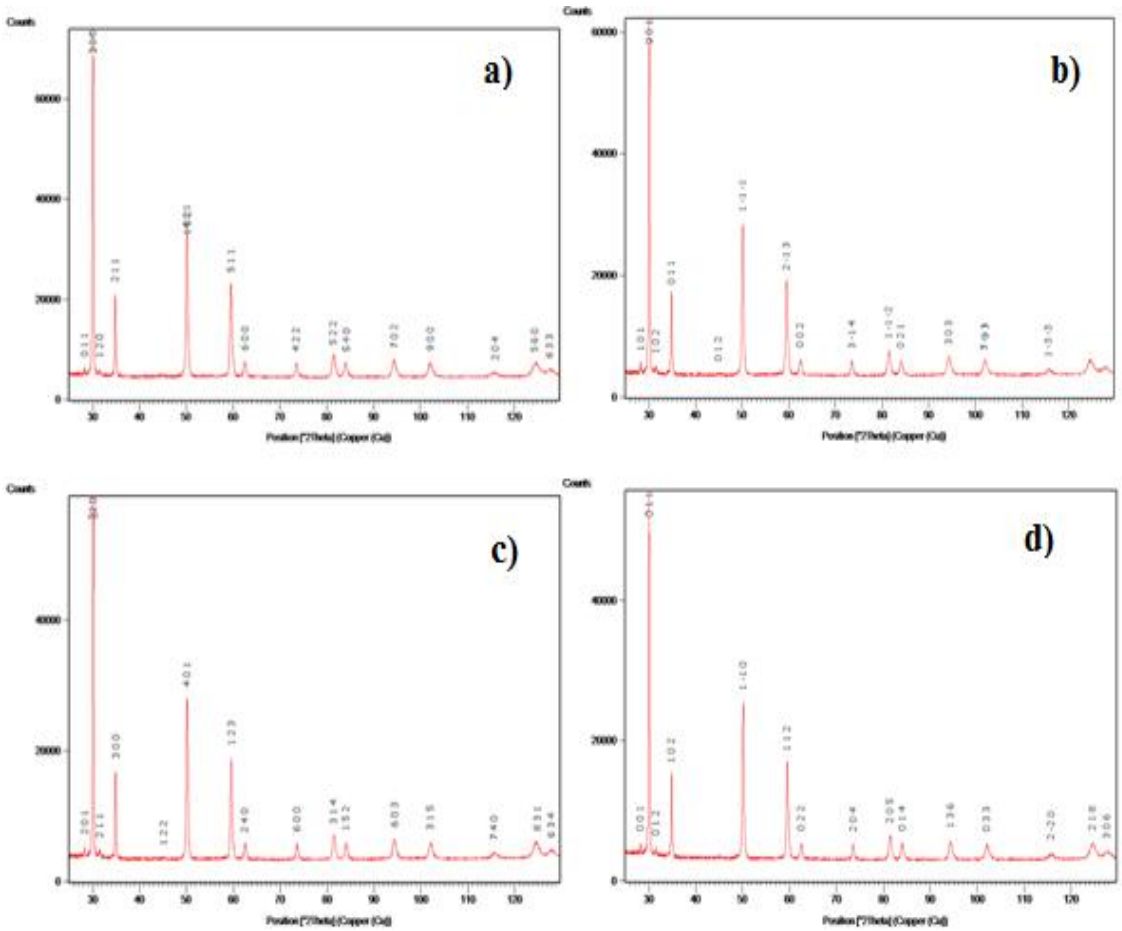

Figure 5: The crystallographic planes for the ZrO2/20%Y2O3 deposited layer, with a diffraction angle of: 2θ = 25…130:
a) without heat treatment; b) after the heat treatment at 1000ºC for 5 h;
c) after the heat treatment at1000ºC for 10 h; d) after the heat treatment at 1000ºC for 15 h.

3.3. The determination of the surface roughness

The surface roughness measurements for the layer sprayed with the $ZrO_2/20\%Y_2O_3$ ceramic powder were made using the Form Talysurf Intra system.
In Figure 7 is presented the roughness analysis on the four profiles using the LS-Line module. The arithmetical mean deviation of the profile roughness measured for the sample with the layer thickness of 100 µm without heat treatment (Figure 7-a) is: R_a = 6,4238 µm, the standard deviation of the assessed profile roughness R_q = 8,1743 µm and the average height roughness R_z = 40,1180µ.
Arithmetical mean deviation of the roughness profile measured for the sample with the layer thickness of 100 µm after a 5 hours heat treatment (Figure 7-b) is: R_a = 5,9197 µm. The standard deviation of the assessed profile roughness R_q = 7,6334 µm and the average height of roughness profile measured R_z = 38,4407 µm.
In the case of the roughness profile measured on the sample with the layer thickness of 100 µm subjected to heat treatment for 10 h (Figure 7-c) the parameters are: R_a = 6,0821 µm, the standard deviation of the assessed profile roughness R_q = 7,4465 µm and the average height roughness R_z = 32,464.

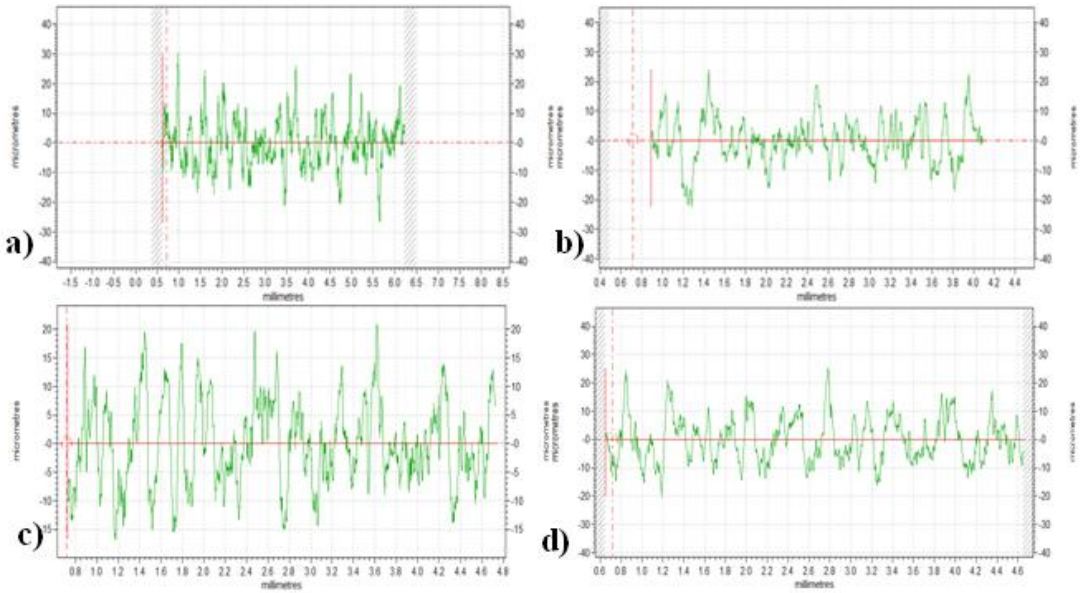

Figure 7: The roughness values: a) without heat treatment; b) for the samples subjected to heat treatment for 5 h; c) for the samples subjected to heat treatment for 10h; d) for the samples subjected to heat treatment for 15 h.

The roughness profile measured on the samples with the layer thickness of 100 μm and subject to a 15h heat treatment (Figure 7-d) is: R_a = 6,5547 μm, the standard deviation of the assessed profile roughness R_q = 7,9397 μm and the average height of roughness profile measured is R_z = 34,9909 μm.

4. CONCLUSIONS

After the heat treatment at a temperature of 1000 ºC the matrix becomes more compact. The grain size increases due to the formation on the surface layer of "bridges" between neighboring splats.
Following the heat treatment carried out at a temperature of 1000 °C with a 15 h maintenance, a division of the grains appears and a tendency of disappearance of the successive arrangement of the splats.
Following the X-ray diffraction investigations it is revealed that the spraying of the ceramic powder under high temperature, a multiphase structure coating is obtained. The structure consists of elementary monoclinic cell particles for the heat treatment from 5 to 10 hours.
For the 15 hour heat treatment, multiphase changes were revealed in the assembly. Particles with a tetragonal crystalline structure appear, stable at room temperature and which, according to the literature, show superior thermo-mechanical properties for technological applications.

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