

## CERAMIC LAYERS AS THERMAL BARRIER

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*Straturile barieră termică sunt utilizate pentru creșterea performanței turbomotoarelor. Prin urmare, această lucrare prezintă un studiu efectuat în scopul de a îmbunătății proprietățile straturilor barieră termică. Deoarece deteriorarea straturilor barieră termică apare datorită creșterii unui strat de oxid la interfața strat de acroșaj / strat ceramic, s-a investigat o nouă soluție folosind un strat intermediar  $MeCrAlY + Al_2O_3$ , pentru creșterea rezistenței la oboseală termică și oxidare.*

*Thermal barrier coatings are used for increasing the turbo engines performance. This paper presents the performed studies on used materials to improve the thermal barrier layers properties. Because the failure of the thermal barrier coatings occurs by reason of growing an oxide layer at bond coat/ top coat interface, we have investigated a new solution using an intermediate layer  $MeCrAlY + Al_2O_3$ , for increasing the oxidation and thermal fatigue resistance.*

**Keywords:** thermal barrier coatings, bond coat, thermal grown oxide

### 1. Introduction

Thermal barrier coatings are used to protect metallic components used in aeronautics from high temperatures. The main process used for the TBC deposition is air plasma spray and the layers have low thermal conductivity and are durable. [3] The APS (air plasma spray) is chosen because it is necessary to have high temperature for deposition (melting point for ceramics are very high) and protection of the obtained layer against oxidation. The deposition with APS allows preheating of the metallic component and obtaining a good adherence because the recrystallization and diffusion. [5]

Thermal barrier coatings increase the lifetime of metallic components by increasing their resistance to thermal fatigue. Zirconium ceramic materials, stabilized with magnesium and calcium, were replaced in the last 20 years with zirconium stabilized with yttrium. This last ceramic material has superior mechanical, chemical and thermal properties. [1, 2]

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Typical TBCs have a two layered structure consisting of an oxidation protective bond coat and thermally insulating yttria stabilized zirconia (YSZ) topcoat. [6]

In air plasma spray the ceramimc powder is injected in high velocity plasma jet and is melted on the metalic substrat. Upon impact, the molten particles solidify and form „splats”. The splat interface contains porosity and is the cause for exfoliation initiation.

The current researches in this field are focused on improving the ceramic layers. One solution for diminishing these disadvantages is the employment of multilayer coatings, coatings which, when applied on the metallic materials, effectively constitute a thermal barrier and are proved to offer, at the same time, protection against corrosion at high temperatures, oxidation and erosion. [4]

The goal of our study was to improve the properties of the ceramic protective layer current used through a new protective system.

The APS TBC's obtained were characterized regarding the structure by XRD, metalography and microstructure by SEM analyses. To establish the thermal properties of the TBC's were performed the thermal shock tests.

## 2. Materials and methods

Six types of protection layers for the metallic support of the samples were made. Coatings were deposited using plasma spray technology, METCO 7M.

The metallic support was a Ni base alloy as a bond coat was used MeCrAlY and as a top coat was used ceramic layer on ZrO<sub>2</sub> base.

Technological parameter for APS TBC's are:

Table 1

APS deposition parameter

Bond layer	Ceramic layer
<ul style="list-style-type: none"> <li>• 7MB plasma jet torch;</li> <li>• deposition distance - 120 mm;</li> <li>• Ar 80/H<sub>2</sub> 15</li> <li>• electric arc 500 A, 70 V</li> <li>• Carrier 37.</li> </ul>	<ul style="list-style-type: none"> <li>• 7MB plasma jet torch;</li> <li>• deposition distance - 70 mm;</li> <li>• Ar 80/H<sub>2</sub> 15;</li> <li>• electric arc 500 A, U=60–65 V</li> <li>• Carrier 37.</li> </ul>

We present the following properties of the coatings in correspondence with the wear solicitation of the components:

**MeCrAlY** is a composite material with maximal properties for adherence, corrosion resistance and resistance to high temperatures (900-1000°C);

**Duplex MeCrAlY/ZrO<sub>2</sub>, 20% Y<sub>2</sub>O<sub>3</sub>** has a higher potential at thermal shock tests than stabilized zirconium with 8% Y<sub>2</sub>O<sub>3</sub> or CaO, MgO;

**Triplex of type FGM** (functionally graded materials) with an intermediary layer between the bond layer and the ceramic layer, with a mediated composition diminishing the difference effect of expansion coefficients of the two materials and the stress induced in thermal shock time.

**Triplex of type MeCrAlY/ MeCrAlY 90%+Al<sub>2</sub>O<sub>3</sub>10%/ZrO<sub>2</sub>Y<sub>2</sub>O<sub>3</sub>** - incorporation of metallic, ceramic or cermets lead to an increasing thermal fatigue resistance of the thermal barrier layers with one, two or three factors.

### 3. Results and discussion

#### 3.1. Thermal shock results

The thermal shock tests distinguishing the number of shocks – heating, cooling – clearly seen modification which appears after the tests – fissure, exfoliations, etc.

The thermal shock tests were performed in the INCAS laboratories from Bucharest and AMTT laboratories from Seibersdorf, Austria.

The thermal cycling tests were performed at 900°C, 950°C, 1000°C, 1050°C, 1100°C, 1150°C and 1200°C. Each cycle consisted of 5 min in the furnace followed by 1 min cool down with air jet. The weight changes of the samples were measured. The sample were defined as failed when losing 20% ceramic surface.

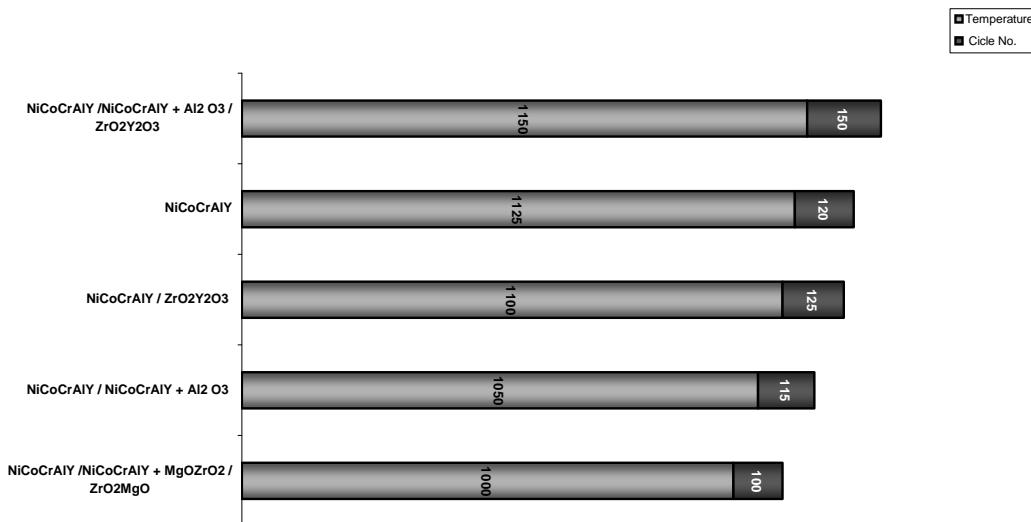


Fig. 1. The thermal shock tests results (INCAS)

The results of thermal shock tests are presented in Fig. 1. They reveal the superiority of NiCoCrAlY/NiCoCrAlY+Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>Y<sub>2</sub>O<sub>3</sub> samples in comparison with the other ceramic ones; they resisted to the aggressive thermal shock conditions, at the melting point of the base materials.

The NiCoCrAlY/NiCoCrAlY + ZrO<sub>2</sub>Y<sub>2</sub>O<sub>3</sub> / ZrO<sub>2</sub>Y<sub>2</sub>O<sub>3</sub> microstructure, after 1100 grade Celsius and 1200 grade Celsius cycles, tested at AMTT, are showed in Fig. 2 and Fig. 3. There is a spallation at the border area of the coating at 1100°C. (Fig.2) A severe spallation occured for the top coat at 1200°C (Fig. 3).

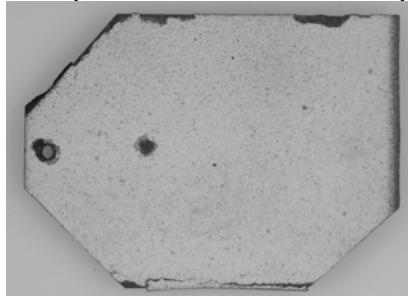


Fig. 2. NiCoCrAlY/NiCoCrAlY+ZrO<sub>2</sub>Y<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>Y<sub>2</sub>O<sub>3</sub> optical micrograph after thermal shock test at 1100°C (x300)

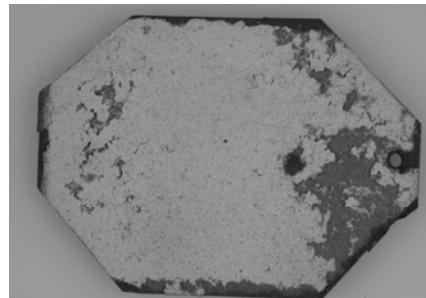


Fig. 3. NiCoCrAlY/NiCoCrAlY+ZrO<sub>2</sub>Y<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>Y<sub>2</sub>O<sub>3</sub> optical micrograph after thermal shock test at 1200°C (x300)

In this temperatures interval (1100-1200 grade Celsius) the ceramic materials degrade because of structural transformations.

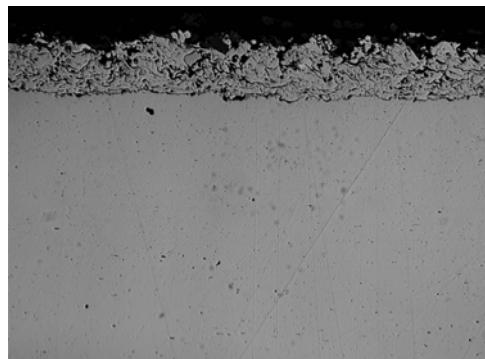
The thermal shock, which has detrimental effects on the protection layer's adherence, shows the limitations of tested ceramic layers.

### 3.2. Metallographic investigation results

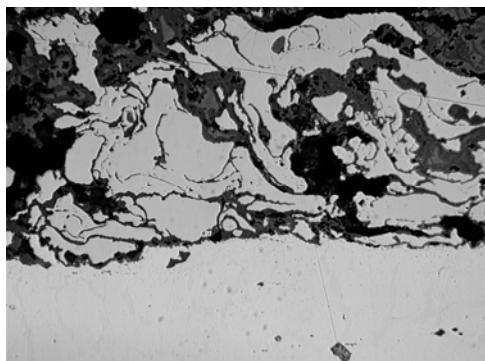
The investigations of the samples with metallic base were accomplished before and after thermal cycles, have like target, the establishing of much more parameters measured and layers characteristics. Thickness and porosity measurements have been made. We have used the Buhler Omnimet analyzing line

from the Materials Science Faculty laboratories, Bucharest – digital video camera of high resolution, Brichert Univac optical microscope.

The measures have been accomplished on one representative area. The oxidation which appears at the sample surface during the thermal shock have diminished the layer thickness. The high temperatures have diminished the porosity from 30% ( $T=1100$  grade C) to 22% ( $T=1200$  grade C) (Fig 5).

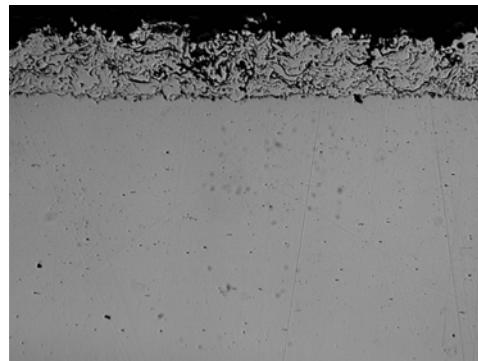


Captured image

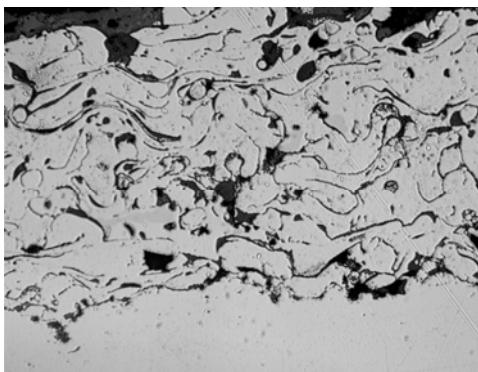


Detected image

Fig. 4. Cross section of NiCoCrAlY sample after thermal shock, at a temperature of 1000°C



Captured image



Detected image

Fig. 5. Porosity of NiCoCrAlY sample after thermal shock, at a temperature of 1100°C

### 3.3. X-ray diffraction

X-ray diffraction patterns for coatings deposited on metallic support after thermal shock are shown in Fig. 6 and Fig. 7. The structural modification for the sample at the bond layer surface and ceramic one has been investigated by X-ray diffraction.

Fig. 6 presents the X-ray diffraction pattern for the NiCoCr AlY + Al<sub>2</sub>O<sub>3</sub> layer. A Cr<sub>3</sub>O<sub>4</sub> tetragonal phase grown at high temperatures through metal elements oxidation of metal matrix was ascertained. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> recrystallisation gives well defined peaks for the (104), (122) and (208) reflection at 1000°C.

Fig. 7 shows the X-ray diffraction of ZrO<sub>2</sub> Y<sub>2</sub>O<sub>3</sub>. The high peak of c-Y<sub>2</sub>O<sub>3</sub> phase for the (431) reflection. (006) peak of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is evident in the X-ray pattern of this sample because the oxidation which appears at high temperatures.

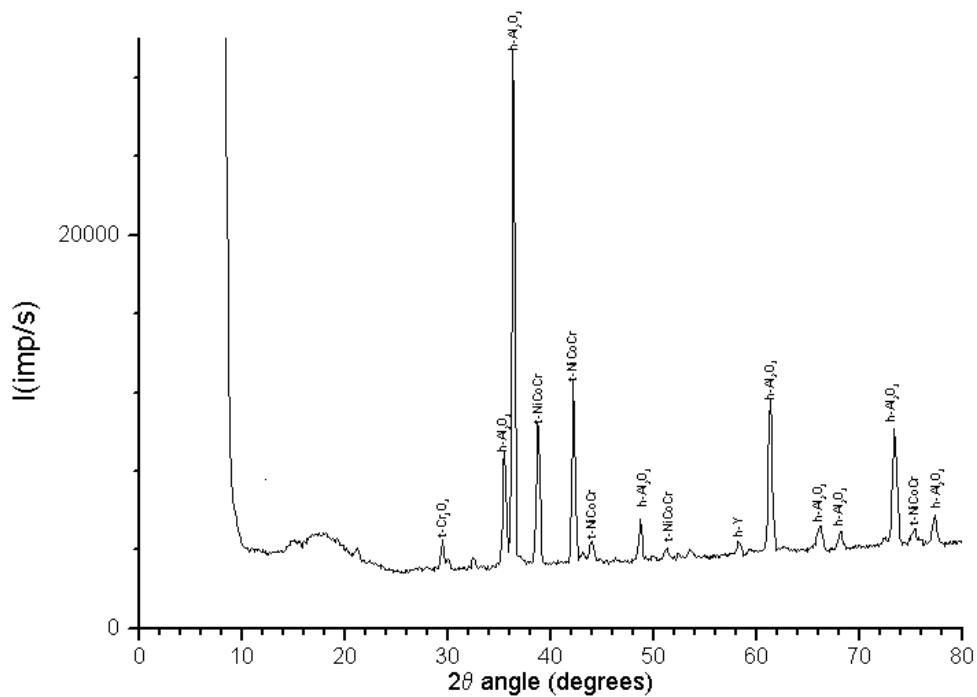


Fig. 6 X-ray difraction pattern for the NiCoCr AlY + Al<sub>2</sub>O<sub>3</sub> coating

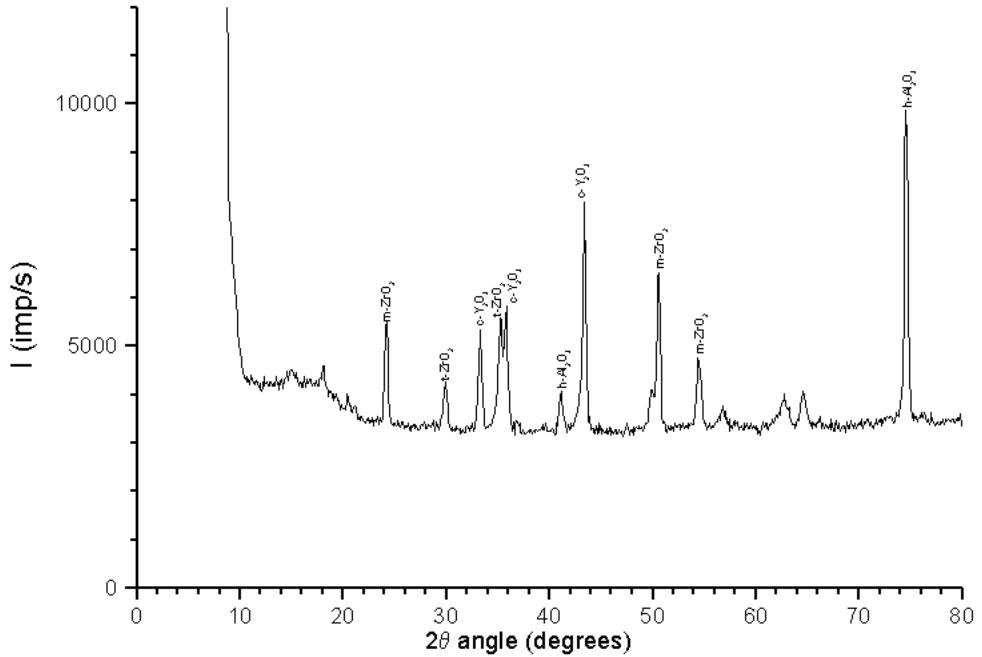


Fig. 7 X-ray diffraction pattern for the  $\text{ZrO}_2$   $\text{Y}_2\text{O}_3$  coating

### 3.4. Electron microscopy results

For the structural and compositional layers, a punctual analysis was carried out, for semi quantitative determination of the elemental distribution on the selected areas and for a surface morphology of the samples.

The layers proved to be uniform and to have a low adherence between the external layer and the base material because the extended porosity (Fig. 8 and Fig. 9).

In Fig. 8 it can be seen there are some longitudinal cracks which are initiated near by the thermal grown oxide. Fig. 9 illustrates the aluminium distribution which is non homogeneous. The growth of the oxide in the layer can be explained by the Al-depletion from the coating. At the high temperature of  $1100^\circ\text{C}$  the chromium diffusion outwards is fast enough to form chromium oxide at the layer surface.

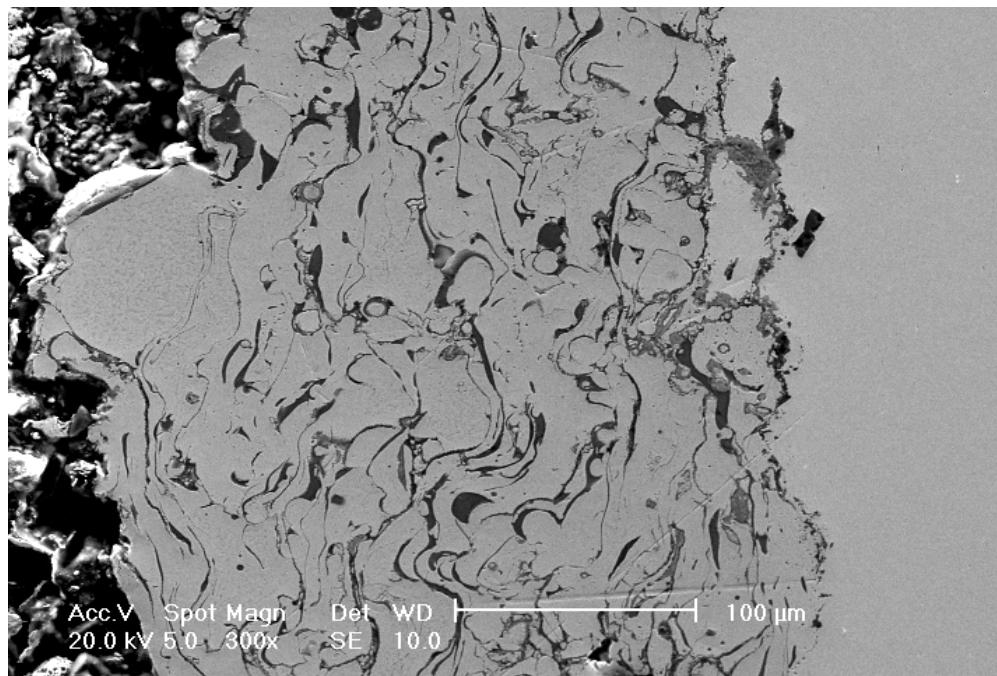


Fig. 8. SEM image of NiCoCrAlY/NiCoCrAlY+  $\text{Al}_2\text{O}_3$  sample after thermal shock (500x)

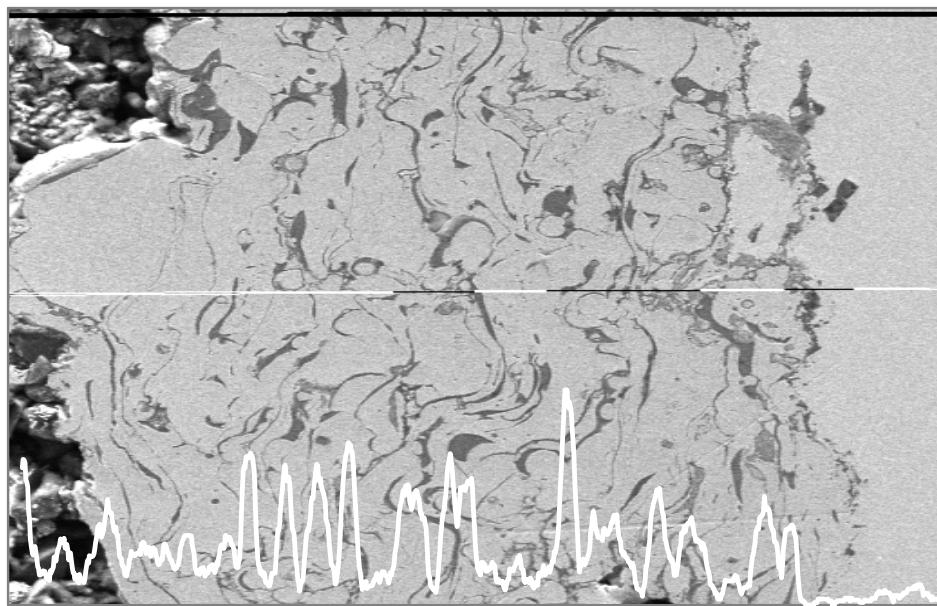


Fig. 9. Distribution of the Al element on the selected area (x 500) of Fig. 8

#### 4. Conclusions

The degradation of TBC layers on partially stabilized zirconium during the thermal cycle's solicitation is caused by the accelerated oxidation of the bonding layer. The oxidation of the bonding layer elements during the plasma spray process and the heating cycles cause cracks in the layers. The stresses on the bonding layer are adding to the induced stresses in the ceramic layer and are, together, are the causes of the exfoliations at the interface between the bond layer and the ceramic layer. The existence of pores causes the expansion of the cracks in the layer.

#### R E F E R E N C E S

- [1] *V. Manoliu, I. Pencea, R. Paunescu, I. Hritac*, "Ceramic protection layers for the furnace blast inlets" Proceeding of METAL 2000, 9<sup>th</sup> International Metallurgical Fair and Conference, Ostrava, Republica Ceha, 16 - 18 May 2000, p. 78
- [2] *V. Manoliu, N. Constantin, Gh. Ionescu, A. Ștefan*, "Protective ceramic coatings for aircraft engines", Proceeding of Int. Conf. Reliability and diagnostics of transport structures and means 2002, Pardubice, Republica Ceha, 26-27<sup>th</sup> September 2002, p. 36
- [3] *V. Manoliu, A. Ștefan* "Thermal testing (conductivity, dilatometry) and thermal shock testing of some TBC layers on super alloys and cooper alloys base", Scientific Report, FP5-Contract MRI no. HPRI-CT-1999-00024, AMTT - Aerospace and Space Materials Technology Testhouse, Seibersdorf, Austria, April 2003
- [4] *V. Manoliu, D. Gheorghe, P. Nedelcu, Gh. Ionescu*, „Ceramic layers on copper support applied at metallurgical furnaces”, European Congress on Advanced Materials and Process EUROMAT 2003, Laussane, Switzerland, 1-5 september 2003
- [5] *V. Manoliu, A. Ștefan, Ghe. Ionescu, T. Lamba*, "Straturi de protecție pentru turbomotoare", Sesiunea Nationala de Comunicari Stiintifice "Terra Dacica – Romania, Mileniul 3", mai 2006, Brașov
- [6] *C. Zhou, N. Wang, H. Xu*, „Comparison of thermal cycling behavior of plasma-sprayed nanostructured and traditional thermal barrier coatings”, Mat. Sci. and Eng. A (2006)