I. Rusu, Dc. Sc. (Eng.), Ass. Prof.; S. Georgescu, C. Baciu, Dc. Sc. (Eng.), Prof.; B. Aurelian

MULTILAYER THERMAL BARRIERS OBTAINED THROUGH APS- AND HVOF- TECHNIQUES

The paper presents in brief the technological parameters used for plasma spray deposition. It is also describe the hanging layer deposition (100% metal) with the HVOF device and the other layers deposition in argon-hydrogen atmosphere using plasma jet generated by a METCO7M device. There are analyzed microscopy images performed on deposits of thermal ceramic barriers at Diesel engine pistons.

The paper also presents the analysis of the chemical composition of the multilayer thermal barrier of Me/MeCrAlY type. There are shown some EDAX images for quality analysis of stabilized zirconium layers with Y and Mg_4O_2, X- ray diffraction and chemical distribution for the deposited layers.

Key words: *multilayer thermal barrier, mixed covering method.*

1. Introduction

A multilayer protection is performed through successive deposits of metallic and ceramic simple powders or in a mixture. Five different layers are usually deposited starting from the pure metal and ending with pure oxide. The bigger the number of the layers the more efficient is the thermal protection. During deposition we have in view the decrease of the metal quantity from 100% up to 0% and the rise up to 100% of the ceramic oxides. This is a technique that avoids the cracking of the deposited layer due to the different dilatation coefficients when the guide mark is heated.

2. Important technological parameters associated with the microionized powders within the plasma jet deposition technique

The plasma spraying technology is a complex one, considering the multitude of the parameters that are implied in the process. The material transfer on the holder is performed through the deposition of the powder particles that are injected perpendicularly or against the current in the plasma jet at the exit from the burnet through a carrying gas. They must be injected in the middle of the plasma jet before obtaining a total fusion (melting) of the powder. After some milliseconds in the middle of the heat source, the particles are sprayed under the shape of small drops, that get a speed of almost 2 Mach and reach in impact with the surface the underlayer, generating very soft layers.

The superior characteristics of the deposited layers are determined by numerous parameters, as it follows: metallization distance; cooling of the flame; powder granulometry; injection speed; number of piston passing; ma parameters.

The main parameters of the metallization process are as it follows:

- Plasma: air dilution; gas composition; plasma jet composition; speed;
- Flame: moving speed; spraying distance;
- Injector: carrying gas flow; powder flow;
- Powder: distribution, size, shape of the grains; injection speeds distribution; plasma take over time;
- Underlayer: temperature; residual tension control; particle impact speed.

The coating through plasma jet spraying device we used, METCO7M, has the following characteristics: 7MB type plasma pistol; GH (3) type nozzle; powder orifice = 2; depositing distance 4÷7 inch; argon pressure in primary 80 psi; oxygen pressure in secondary 20 psi; electric arc 500 A, 70 V; deposit efficiency 60%.

3. Hvof and aps mixed covering method

We had in view the hanging layer deposition (100% metal) with the HVOF device, the other layers being deposited in argon-hydrogen atmosphere using plasma jet generated by METCO7M device. This method of mixed covering, HVOF and APS permits a maximum adherence of the hanging layer, with a minimum porosity by using the HVOF method and ensures the melting of the ceramic materials through APS.

The order of the technological operations is the following:

degreasing;

blasting;

deposition through HVOF of the hanging layer;

depositing through plasma jet of the ceramic layers.

Blasting is an operation that is necessary for the mechanical anchorage of the deposited layer. It has been performed in the specialized enclosure of the METCO metallization device. The pressure of the air is under 3,5 bars and the shots are made of corundum EF with the size of 60÷80 mesh. The projection angle of the shot jet is of 0÷30°. To prevent the corrosion of the metallic blasted surface it is recommended the beginning of metallization after maximum 2 h.

Table 1 synthetically shows the powder types that can be potentially used.

Table 1

Powder types

	Powder type	Commercial naming	Typical characteristics and applications
1.	Co32Ni21Cr8A10,5Y	AMDRY 995C	Aero spatial applications
2.	ZrO220Y2O3	Metco 202NS	For stable layers at high temperatures
3.	65MgZr03,26Ni 7Cr 2A1	M441NS-1	Used as intermediate layer
4.	24Mg0ZrO2	METCO210	
5.	NiCr 80/20	MTS 5644	

It is known the low adherence of the hanging layers of MeCrA1Y type at ceramic layers of partially stabilized zirconium that are obtained through plasma jet metallization process. In order to raise the adherence of the hanging layers, especially under thermal shock conditions, we used the supersonic jet metallization that is the HVOF type device. The adherence layer will have a double adhesion if HVOF technique is used, as compared to APS technique-plasma jet metallization and a much diminished porosity.

Table 2

Working technological parameters

Power of installation	35 KW
Intensity	800A
Working tension	45V
Argon gas flow	40 l/min
Hydrogen gas flow	2 l/min
Distance	7 cm
Carrying speed	226m/s
Powder taking temperature	2 800ºC

The method we used permits the obtaining of deposits in layers with high wear resistance and corrosion as well as for the deposits of layers that are resistant when applied on high precision pieces. From the technological multifunctional point of view we can consider dies and composites using aluminum that are today applied in laboratories and have some published results, as figure 1, b shows. They are used as comparative models in the investigation stage.

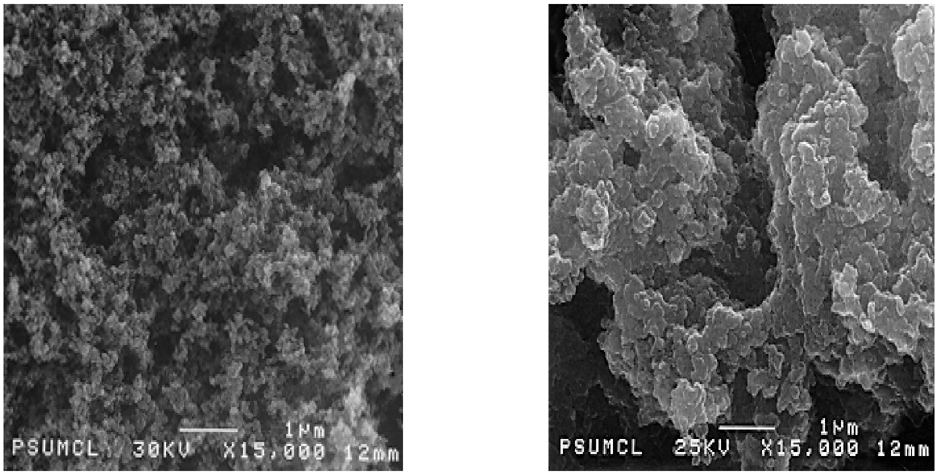

Fig. 1. Microscopy images performed on deposits of thermal ceramic barriers at Diesel engine pistons. The EUROCERAM European program; a - residual deposits of hydrocarbons agglomerated in the pores of the ceramic material deposited on the front head of the cylinder; b - softer and more homogeneous deposits on the rim of the piston in the area of the tightness segments.

The TBC barrier was performed at a thickness of about 11 microns and the size of the grains was about 0,5 up to 1 micron, in homogeneous layers and with the possibility to restrict the open porosity of the layer and a very small diffusivity of the oxygen in the deposited layer.

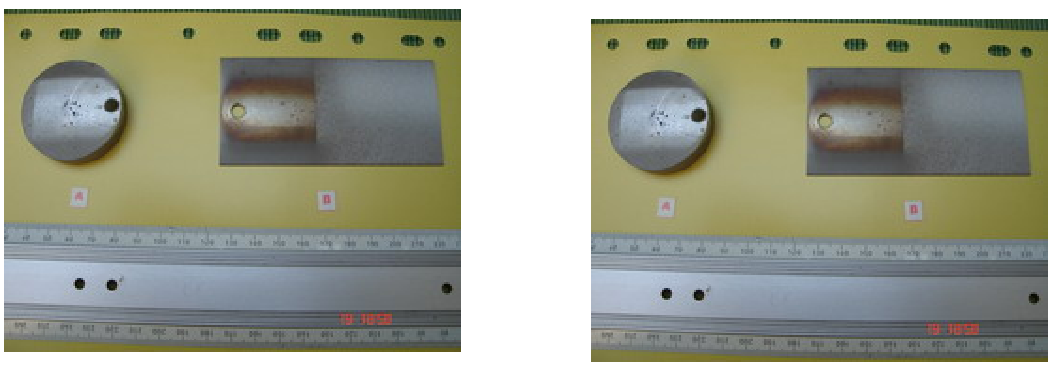

Fig. 2. The depositing tests of layers on disk type samples and on plates.

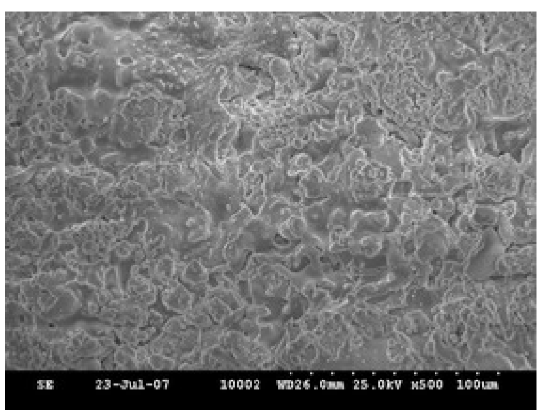

Fig. 3. Deposited layer of stabilized zirconium with Y_2O_3. SEM image x500

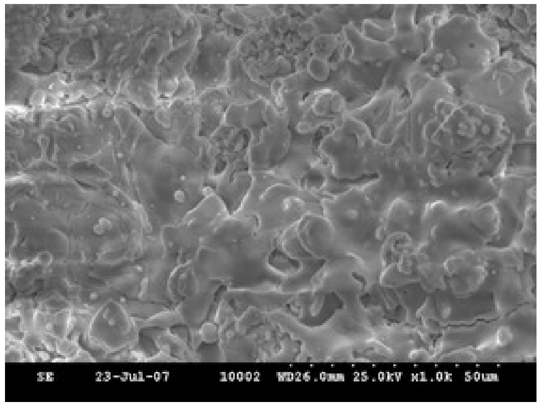

Fig. 4. Deposited layer of stabilized zirconium with Y_2O_3. SEM image x1000.

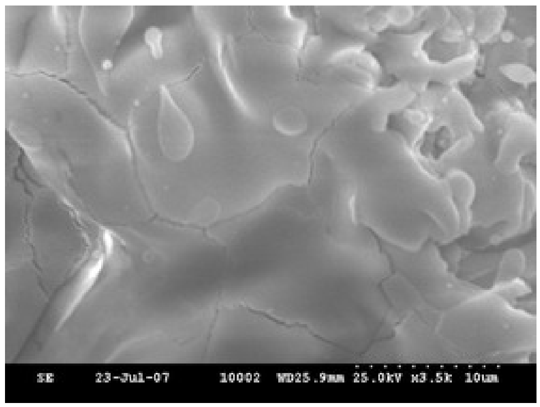

Fig. 5. Deposited layer of stabilized zirconium with Y_2O_3. SEM image x3500 (a network of microcracks in the last depositing layer can be noticed).

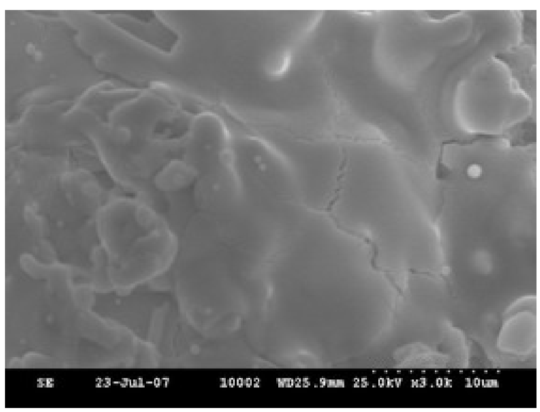

Fig. 6. ZrO_2-Y_2O_3 depositing through plasma –sprayed method. SEM image x3500. The microcracks network in the last depositing layer is of island type and covers the entire surface of the ceramic layer.

The homogeneousness of the deposited ceramic layer can be noticed in figure 3. As compared to the other available techniques, the proposed technology has thermal stability and a good mechanical resistance of the layer that can have porosity and microcracks between 10-20% from the volume of the ceramic layer.

4. The analysis of the chemical composition of the multilayer thermal barrier

In order to elaborate and test new protection layers associated with the piston heads, we should first consider those materials that can have certain characteristics to satisfy the resistance at specific wear factors, as well as the characteristic factors for the exploitation behavior of the internal combustion engines.

Therefore, we suggest, in a first stage, the ceramic bi and multilayer covering of FGM type, respectively Me/MeCrAlY. These layers can be of multiple $ZrO_2 \cdot Y_2O_3$ compositions or of MeCrAlY 90% +Al_2O_3 10% type and $ZrO_2Y_2O_3$.

These types of multilayer structures can increase the main disadvantage of the deposited ceramic layers, the thermal shock resistance. The important problem that must be solved in the case of this technological alternative is the performing of a connection layer (adherence layer) that can be applied on the aluminum holder as well as for the depositing of the ceramic layer.

The technological alternative is the production of some protection solution based on one layer, with complex alloys (Al-Ni type), compatible with the aluminum substrate and resistant in the extreme conditions within the burning chamber of the Diesel engines.

Starting from the deposited layers we shall present some difractographycal analysis and quality analysis.

Figures 7 and 8 show the characteristic drops from the quality analysis of zirconium layers stabilized with yttrium and MgO_2 that are deposited during the tests. Figure 9 shows the relatively uniform distribution of the elements in respective layers.

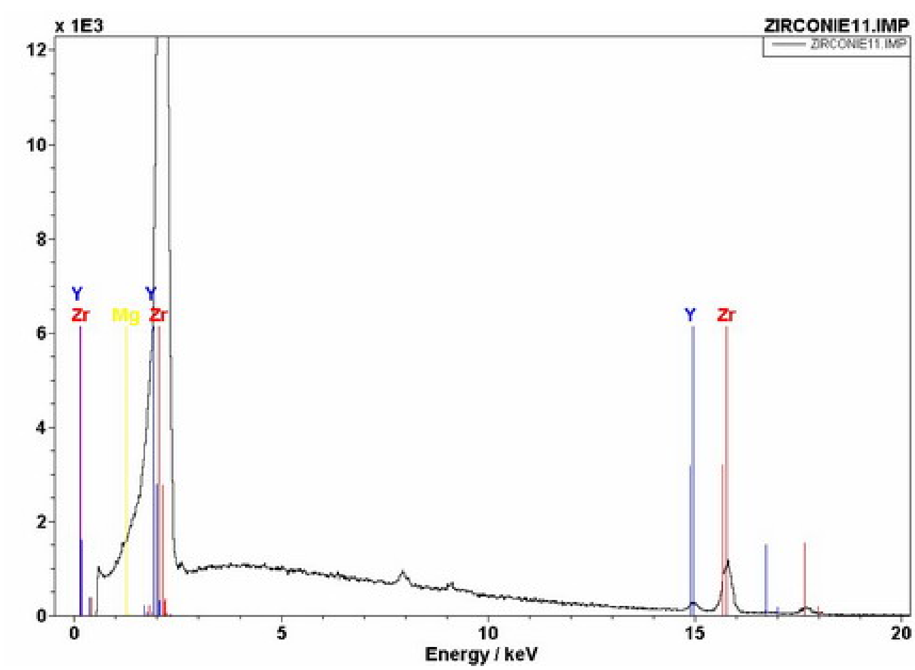

Fig 7. Emphasize of the characteristic drops. EDAX image for quality analysis of stabilized zirconium layers with Y and MgO_2, obtained from the SEM images.

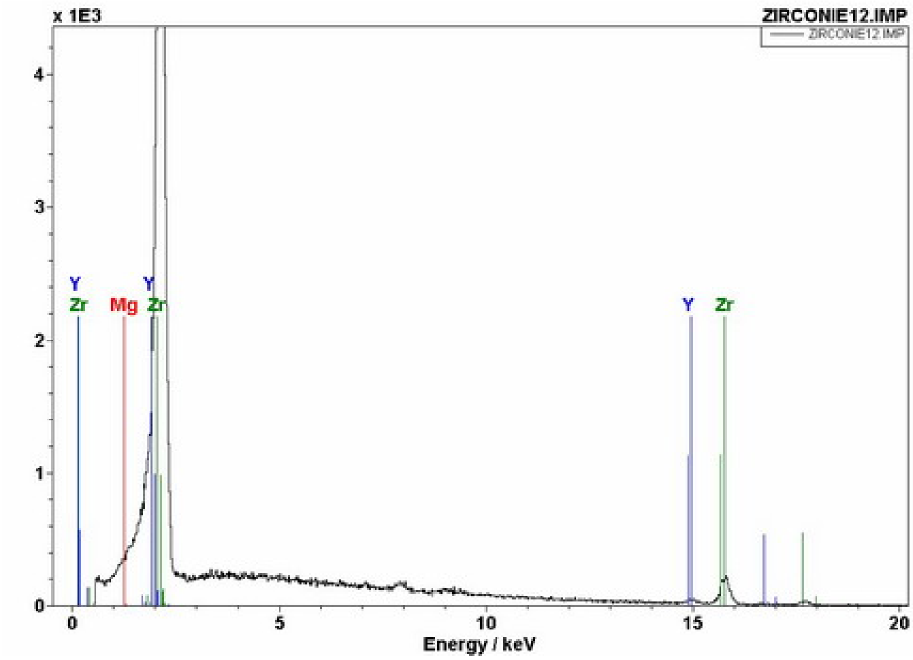

Fig. 8. Emphasize of the characteristic drops. EDAX image for quality analysis of stabilized zirconium layers with Y and MgO_2, obtained from the SEM images.

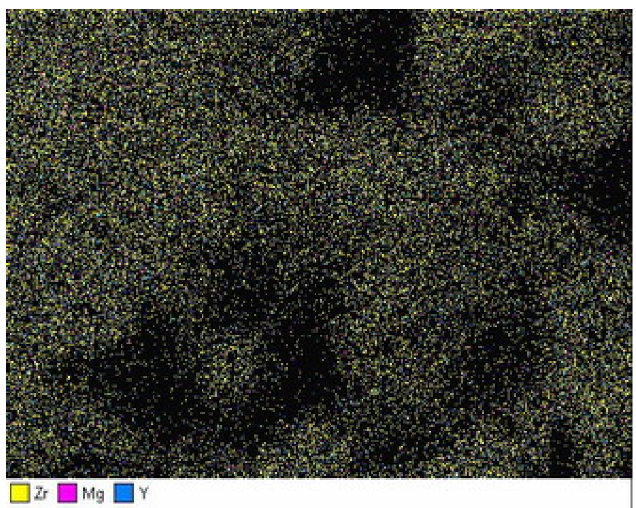

Fig. 9. Elements distribution image obtained by calitative analyse of zirconium layers stabilesed with yttrium and MgO_2.

Figure 10 emphasizes the specific drops for the tetragonal and cubic phases of zirconium layers, for 2θ angles, when using k-alfa radiation of copper and nickel filter, by using some program sequences with specialized soft. We noticed that the reaction products that result as a consequence of preparing the surface of the aluminum alloy, through the treatment of this surface with $Al(OH)_3$-(85%)H_3PO_4 in a diluted solution with 20% distilled water cannot be identified through the applied diffraction on the surface of the deposited layer as thermal barrier.

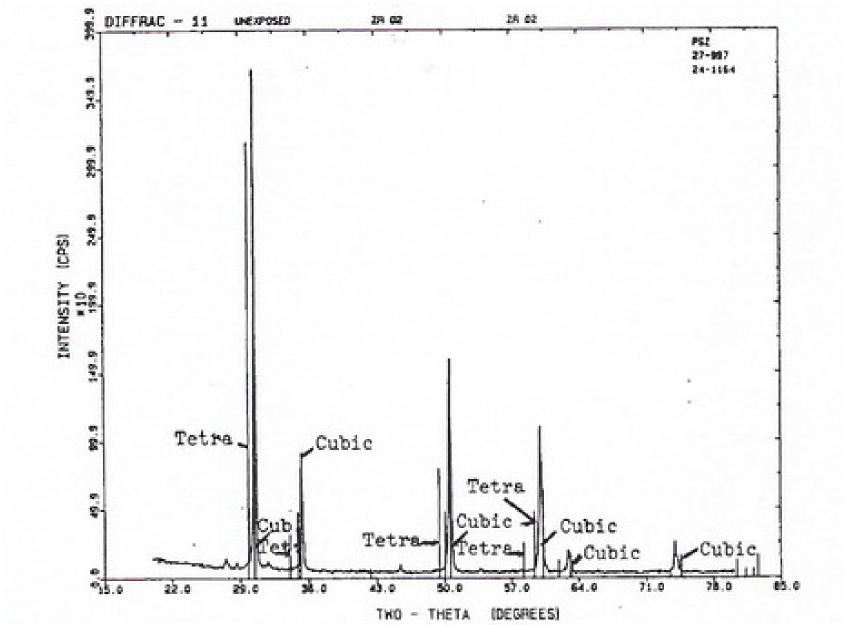

Fig. 10. X- ray diffraction for the deposited layers. The characteristics of phases are emphasized (cubic- tetragonal for the zirconium layers)

REFERENCES

1. Andritschky M., Teixeira V., Adherence of combined physically vapor-deposited and plasma-sprayed ceramic coatings Surface and Coatings Technology 76-77, 1995, p.101-105;

2. Steffens H.D., Babiak Z., Gramlich M., Some Aspects of Thick Thermal Barrier Coating Lifetime Prolongation, Journal of Thermal Spray Technology, 8(4), 1999, p. 517-522;

3. Yonushonis T.M., ThichThermal Barrier Coatings for Diesel Components National Aeronautics and Space Administration Lewis Research Center Nasa Cr-187111 NASA.

4. Freitas D., Kuranaga C., Machado A.J.S., Sintese de pos de zirconia cubica policristalina, Ceramica v.45 n.291 Sao Paulo, 1999. ISSN 0366-6913.

5. Gualco C., Cordano E., Fignino F., Gambaro C., Ahmaniemi S., Tuurna S., Mäntylä T., Vuoristo P.,An improved deposition process for very thick porous Thick Thermal Barrier, Proceedings of the International Thermal Spray Conference, 2002, p. 195-201.

6. Rejda E.F., Socie D.F., Deformation behavior of plasmasprayed thick thermal barrier coatings Surface and Coatings Technology 113, 1999,p.218-226.

7. Stover D., Funke C., Directions of the development of thermal barrier coatings in energy applications, Journal of Materials Processing Technology, 92-93, 1999, p.195-202.

8. Yonushonis T.M., ThichThermal Barrier Coatings for Diesel Components National Aeronautics and Space Administration Lewis Research Center Nasa Cr-187111 NASA.

9. Zhu, Dongming and Miller R.A.: Development of Advanced Thermal and Environmental Barrier Coatings Using a High-Heat-Flux Testing Approach. Presented at the 27th Annual International Conference on Advanced Ceramics and Composites, Cocoa Beach, FL, 2003.

Rusu Ion – Doctor of Engineering Sciences, Associate professor, Faculty of material science and engineering, tel. 0232-27-86-88, e-mail: vrusu 2003@yahoo.com

Georgescu Silvia – Engineer, Faculty of material science and engineering, tel. 0232-27-86-80

Baciu Constantin – Doctor of Engineering Sciences, Professor, Faculty of material science and engineering, tel. 0232-27-86-80, e-mail: constantinbaciu_2004@yahoo.com.

Technical University "Gheorghe Asachi" from Iasi, Romania.

Aurelian Buzăianu – Collaborator of scientific centre SC. METAV-R&D SA Bucureşti, tel. 0232-27-86-80.