

"HENRI COANDA" AIR FORCE ACADEMY ROMANIA



"GENERAL M.R. STEFANIK" ARMED FORCES ACADEMY SLOVAK REPUBLIC

INTERNATIONAL CONFERENCE of SCIENTIFIC PAPER AFASES 2013 Brasov, 23-25 May 2013

## A STUDY ON FLUE GAS CORROSION AND WATER VAPORS SORPTION ON A ZrO<sub>2</sub>/20%Y<sub>2</sub>O<sub>3</sub> PLASMA SPRAYED COATING FOR TURBINE BLADES APPLICATION

## CRÎŞMARU Ionuț Vasile\*, PINTILEI Geanina Laura\*, PAPATOIU BINIUC Carmen\*, IVANCU Ionel\*, BĂSESCU Gică Narcis\*, MUNTEANU Corneliu\*

\*"Gheorghe Asachi" Technical University of Iasi, Faculty of Mechanical Engineering, 61-63 Prof. dr. doc. D. Mangeron Blvd, 700050, Iasi, Romania

**Abstract:** This paper presents a concept of thermal barrier coating which consists of a  $ZrO_2/20\%Y_2O_3$  ceramic top layer and a NiCrAlY bond layer, both deposited by atmospheric plasma spraying (APS) on a Ni based super alloy. Atmospheric plasma spraying (APS) is a widely used deposition method for obtaining variable thickness coatings on surfaces with different degrees of complexity. The analyzed samples were obtained by thermal deposition with the METCO 7 MB plasma jet installations. The corrosion test followed the chemical influence of the flue gas on the deposited coating. This test is important because the turbine blades are corroded by the flue gas during operation, so the chemical behavior of the ceramic coating is an important aspect for a safe service. Due to the significant amount of water vapors in the flue gases the sorption capacity of the coating is assessed. The highlighting and interpretation of the structural and chemical changes caused by the high temperature flue gas were made by using modern methods of structural analysis.

*Keywords:* ZrO<sub>2</sub>/20%Y<sub>2</sub>O<sub>3</sub>, flue gas, corrosion

#### **1. INTRODUCTION**

This paper analyzes coatings deposited by atmospheric plasma spraying on a Ni based super alloy material used in the manufacturing of turbine blades. 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 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. [1] TBC layers permit lowering the temperature of the "hot parts" targeted in the energy industry and aeronautics with 100-200°C. [2] The high temperature flue gas also causes corrosion to the base material of the blades. For this reason the deposited ceramic coating also has the role to protect de base material from corrosion. [3]

The obtained quality for thermal spray coatings can be assessed by: roughness, thickness, strength and porosity. [4] These aspects can be influenced by the technological parameters used for the adopted spraying methods. Another parameter is the chemical stability of the ceramic material so it can withstand high working temperature without the appearance of oxidation and corrosion. [4]

Because there is a significant amount of water in the flue gases (water vapors from intake air and water vapors resulted from the combustion process) it is important to assess the sorption capacity of the deposited ceramic coating. [5]

## 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.

Table 1:	Parameters	of deposition
----------	------------	---------------

Technological	NiCrAlY	ZrO <sub>2</sub> /
parameters		$20\%Y_{2}O_{3}$
Spray distance, (mm)	120	120
Injector	1,8	1,8
Plasma gas intensity, (A)	600	600
Arc voltage (U)	62	65
Speed of rotation	55	55
(rot/min)		
Argon flow $(m^3/h)$	50	40

The samples used for the test were made from a Ni base super alloy of rectangular cross section with the dimensions 30x8x2 mm. The ceramic coating deposited on the samples has different thicknesses. The coating thickness for the three samples is:  $100\mu$ m,  $200\mu$ m şi  $400\mu$ m. The samples were placed in the exhaust pipe of a boiler. The AV00 boiler uses diesel fuel and the gas circulation is forced (the flue gases are discharged by a fan) (Fig.1). The excess air coefficient has the value of 1,5.



Fig.1. The placing of the samples in the exhaust pipe of the AV00 boiler

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.



Fig.2: Quanta 200 3D electron microscope

The water vapors sorption capacity of the analyzed samples was measured at 25°C in the relative humidity domain of RH=0-90%. The test was done using the IGAsorp equipment. This equipment is fitted with a ultrasensitive microbalance which measures the mass changes of the studied material along with the change of humidity in the sample chamber. The temperature in the chamber is kept constant with the help of a thermostat.

## 3. STRUCTURAL ANALYSES OF THE LAYERS SUBJECTED TO CORROSION IN FLUE GASES

The samples were placed in the exhaust pipe of the boiler. The clamping of the samples in the exhaust pipe is presented in Fig.1.

The corrosion test followed the chemical influence of the high temperatures flue gases on the ceramic layer deposited on the samples. The coating was subjected to gravimetric analyze and elementary chemical analyze (EDAX).

Following the gravimetric analyses for the three samples subjected to corrosion a loss of mass was measured. For the samples with the layer thickness of 100  $\mu$ m the loss of mass is greater than in the case of the other two samples. This happens due to the exfoliation of the layer. The 100  $\mu$ m coating has a weaker adherence to the base material then the other two coatings. On the other two samples no exfoliations marks are present and the lost of



"HENRI COANDA" AIR FORCE ACADEMY ROMANIA



"GENERAL M.R. STEFANIK" ARMED FORCES ACADEMY SLOVAK REPUBLIC

#### INTERNATIONAL CONFERENCE of SCIENTIFIC PAPER AFASES 2013 Brasov, 23-25 May 2013

mass is due only to the evaporation of volatile matter.

In Table. 2. are presented the results of the gravimetric analyses.

T 11 A 7	C1 1.	0.1	• . •	1	
lahle 7	I he reculte	of the	orguimetric	analy	ICAC
1 auto 2.1	inc icsuits	or the	gravinnente	anar	y 303

The layer	The mass	The mass	The mass	The
thickness	of the	of the	los [g]	mass los
sample		sample		from the
	before the	after the		initial
	test [g]	test [g]		mass [g]
100 µm	3,49	3,48	0,01	0,28
200 µm	3,143	5,14	0,003	0,06
400 µm	5,108	5,10	0,008	0,16

After the corrosion test the sample with the layer thickness of 100  $\mu$ m shows macroscopic marks of exfoliation. This fact is presented in Fig.3.



Fig.3. The sample with the coating thickness of 100  $\mu$ m after the corrosion test.

In the SEM imagine from Fig. 4-a it can be observed that the layer structure is made of elongated grains, separation surfaces and pores of different dimensions. In Fig. 4-b a crack in the coating is visible. The crack is produced by the exfoliated tendency of the layer due to the velocity the flue gas and the high working temperature. The elongated grains preserve their shape and no corrosion is present.





Fig. 4. Cross section SEM images of the  $ZrO_2/20\%Y_2O_3$  coating with the thickness of 100 µm: a) before the corrosion test and b) after the corrosion test.



Fig. 5. EDAX of the  $ZrO_2/20\%Y_2O_3$  ceramic layer after the corrosion test

From the elementary chemical analyses results that some chemical changes occurred due to the fact that traces of carbon are present on the coating. The carbon comes from the chemical composition of the flue gases (Fig.5).

In Fig. 6 are presented cross section SEM imagines of the sample with the layer thickness of 200 µm, before and after the corrosion test. The bond layer shows a structure composed of elongated grains. [7] These grains are elongated due to the high kinetic energy of the sprayed plasma which converts to energy of variation of the shape. In the coating pores of different dimensions are also present (fig. 6-a). After the corrosion test it can be observed in Fig. 6-b that no significant changes appear in the coating. The grains have the same elongated shape, the pores tend to combine (coagulation) to the surface areas of the layer. Also some micro cracks are present in the layer.



Fig. 6. Cross section of the  $ZrO_2/20\% Y_2O_3$  layer with the thickness of 200  $\mu$ m: a) before corrosion test and b) after corrosion test

From the EDAX analyses carbon traces are present on the sample surface from the composition of the flue gas (fig. 7). [8]



Fig. 7. EDAX chemical analyses of the 200  $\mu$ m ZrO<sub>2</sub>/20%Y<sub>2</sub>O<sub>3</sub> ceramic layer

In Fig. 8 are presented SEM cross section images, before and after the corrosion test, of the sample with the layer thickness of 400  $\mu$ m. The ceramic layer before corrosion test is presented in Fig. 8-a. The structure of the layer is uniform with pores of different dimensions with different orientations. After the corrosion test different dimension pores are also present, the bond layer is made of elongated grains and no corrosion zones are present at the interface between layers (fig. 8-b). [7]



Fig. 8. SEM imagines of the 400  $\mu$ m layer in cross section: a) before corrosion test and b) after corrosion test





"GENERAL M.R. STEFANIK" ARMED FORCES ACADEMY SLOVAK REPUBLIC

INTERNATIONAL CONFERENCE of SCIENTIFIC PAPER AFASES 2013 Brasov, 23-25 May 2013

Also in this case the EDAX analyses shows traces of carbon on the coating due to the flue gas composition (fig. 9).



Fig. 9. EDAX chemical analyses of the ceramic layer with the thickness of 400  $\mu$ m after the corrosion test

#### 4. THE DINAMIC SORPTION CAPACITY OF WATER VAPORES

The vapore pressure in the sample chamber was made in steps of 10% humidity, each step having an equilibrium setting of 20-30 minutes. At each step the absorbed or lossed mass is recorded when equilibrium is reached.

Before the sorption - desorption isotherm mesurament, the drying of the samples is done using nitrogen flow (250 mL/min) at a temperature of 25°C untile the sample mass reaches a constant value at a relative humidity smaller then 1%. In Table 2 is presented the sorption capacity of the three samples.

Table 2. The sorption capacity of the samples depending on the coating thickness

Sample (µm)	Sorption capacity (%)
100	0.2996
200	0.1252
400	0.3398

The thin coating  $(100 \ \mu m)$  has a sorption capacity of around 0.3% and to drops in the case of the sample with the coating of 200  $\mu$ m to the value of 0,125%, which implies a greater compactness of the layer. The layer with 400 µm thickness, due to a successive disposition of the splats with micro cracks between them, shows a greater sorption 0.34%. capacity of around The sorption/desorption isotherms recorded in this conditions are shown in Fig. 10, Fig. 11 and Fig. 12.



Fig. 10. Comparative representations of the sorption/ desorption isotherms



Fig. 11. Comparative representation of the sorption isotherms



Fig. 12. Comparative representation of the desorption isotherms

# 5. CONCLUSIONS & ACKNOWLEDGMENT

The corrosion test is relevant because the turbine blades are corroded by the flue gases and the chemical behavior of the deposited ceramic coating is very important. The samples with the ceramic layer thickness of 200  $\mu$ m and 400  $\mu$ m behaved very well to the corrosion test and are recommended for deposition on turbine blades. The coating with the thickness of 100  $\mu$ m was strongly influenced by the flue gases and presents exfoliation marks.

The low values of the water vapors sorption capacity for the studied samples prove their hydrophobic nature. The shape of the sorption/desorption isotherms for all samples can be correlated with type V according to the IUPAC classification. The hysteresis happens due to the different speeds for which the two physical processes take place. Also it can be concluded that the desorption speed is lower than the sorption one.

The sample with the layer thickness of 200  $\mu$ m behaved better than the other two from the point of view of water vapors sorption. This is due to the greater compactness of the layer. It can be concluded that the layer with the thickness of 200  $\mu$ m is recommended for turbine blade deposition from the point of view of water vapors sorption.

Acknowledgment: We thank to SC Plasma Jet SA for the support in the plasma jet deposition of the analyzed 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.

#### REFERENCES

- Aghaie-Khafri M. and Farahany S., Creep Life Prediction of Thermally Exposed Rene 80 Superalloy, Submitted September 10, 2008; in revised form July 23, (2009)
- Bick, H. and Jürgens, W. (1983). Advanced high velocity thermal spraying of metallic and ceramic powders, in Proceedings of the 10th International Thermal Spray Conference, DVS, Düsseldorf, Germany, pp. 92–94.
- 3. Creța, G. *Turbine cu abur și cu gaze*, Ed. Tehnică, București, 1996.
- 4. Draganu Valeriu, *Tehnologii pentru motoare turboreactoare*, ISBN 978-973-0-11581-9, Bucuresti (2011).
- Dimitriu S., Manoliu V., Buzaianu A., Ionescu Gh., Stefan A., *"Behavior of some ceramic TBC structures in extreme thermal conditions"*, Fray International Symposium, CANCUN, Mexico 2011.
- Fauchais P., Vardelle M., Vardelle A., Bianchi L., Leger A.C. "Parameters Controlling the Generation and Properties of Plasmas Sprayed Zirconia Coatings, Plasma Chemistry and Plasma Processing, 1996, 16(1), pp. 99S-125S.
- Freslon, A. (2003) Dépôts résistants à la corrosion par la projection à froid, in 1st International Meeting on Thermal Spraying, L. Pawlowski (Ed.), ENSCL, Lille, France, 3–4 December, pp. 185–185 unpublished conference proceedings.
- 8. Ho, S-M., On the structural chemistry of zirconium oxide, Materials Science and Engineering, 1982, 54, p. 23-29.