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DUPLEX STRUCTURES, CERAMIC, MICROSTUCTURATED, ON THE BASIS OF PARTIALLY STABILIZED ZIRCONIA WITH CERIUM OXIDE

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Abstract*: Protection systems type thermal barrier (TBC) is widely accepted solution for increasing performance and endurance of the "hot parts"(combustion chambers, ducts, vanes, adjustable nozzles, diffuser, etc.). Thermal Barrier Coatings (TBC) are known to play a critical role in the working behavior of high temperature components of turbo engines, co generative systems, metallurgy, etc. In this sense the development of new TBC coatings resistant at high temperature, thermal shock, erosion, corrosion, etc. is proposed in this papers.*

There are known many theoretical studies and experiments that aim the phase transformations of ceramic materials based on zirconia, during the processes of heating and cooling, especially occurring routinely during the flight of aircraft and in particular the special conditions - take-off, in-flight engine stop, landing failure, etc. The cooling processes of ceramic layers are associated with phase changes from tetragonal to mono-clinic zirconia in relation to the intensity of the processes (time, gradient) and consequent exfoliation of TBC. For stabilization of tetragonal and cubic structures at room temperature, to zirconia are added metallic oxides such as CaO, MgO, ScO_3, Y_2O_3, *or other dopant type* Yb_2O_3, Er_2O_3, Gd_2O_3 *or* Nd_2O_3.

In the paper we present experimental results and investigations related to the formation of a duplex structures made of refractory Nimonic alloy type of TBC, duplex structures with bonding layer of type MeCrAlY and a ceramic coating on the basis of stabilized zirconia with CeO_2 *and co-doped with* Y_2O_3.

In this paper are presented techniques and associated parameters to obtain the duplex structure as well as the scanning electron microscope (HRSEM) investigations achieved.

Key words: *TBC, duplex, ceramic, zirconia, APS, HRSEM*

1. INTRODUCTION

During the last decades one of the main research topics related to the turbo engine efficiency was the increase of the temperature in the gas turbine inlet. In order to achieve this goal, a high performance and long life time hot parts components are needed since the supper alloys has reached their upper thermal limit. In this respect one could increasing the specific core power (SCP)parameter of the gas turbine by arising the turbine entry temperature (TET) (Fig.1). The limit for the TET in an engine is related to the materials used in its hottest parts [1].

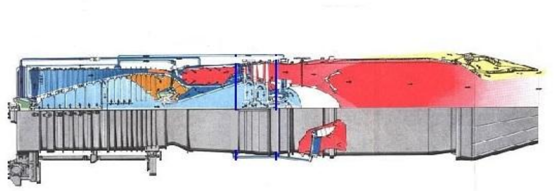


Fig.1 Thermal fields in a turbo engine. Blue-cold section; red-hot section

Usually the exhaust gas temperature (EGT) for commercial aircraft exceeds 1200 °C. In this respect, modern gas turbines blades and vanes are air cooled since the surrounding gas temperatures are close to the melting point of the super alloy used. So, higher TET need more component cooling but this fact will involve the reduction of engine efficiency so there is a limit beyond which efficiency increases cannot be achieved by cooling. Additionally, extreme functional conditions of turbo engines such as take-off thrust, in-flight engine stop, landing failure, etc. could occur leading to sudden changes of temperature. Furthermore, wear factors such as pyrolyze particle erosion caused by sulfur compounds contained by hot gas, at velocities above 3 Mach, chemical corrosion and adhesion in the adjusted nozzles will act simultaneously along with the extreme functional conditions challenging the life time of the turbo engine mechanical components. The most disturbing wear factor is the thermal shock [2], so the durability of components exposed to high temperature and high cooling-heating rates can be extended by protecting their surfaces with different types of coatings.

The use of thermal barrier coatings (TBC) for the „hot parts” of a turbo engine is the generally accepted procedure because it acts as a thermal barrier, lowering the temperature of the substrate and thus making it possible to raise the TET of an engine and hence achieving the objective of increasing the engine efficiency. TBCs can also be used to extend component life by improving the creep behavior and service life of the substrate.

The configuration of a multilayer TBC (fig. 2) consists of a ceramic top coat which lowers the temperature of the substrate by 150÷200°C, a thermal grown oxide (TGO) layer mainly composed of alumina whose thickness extends as the temperature is raising and an MCrAlY (where M=Ni, Co) bond coat deposited directly on the substrate alloy whose main characteristic is to provide a better chemical bond between the top coat and the substrate.

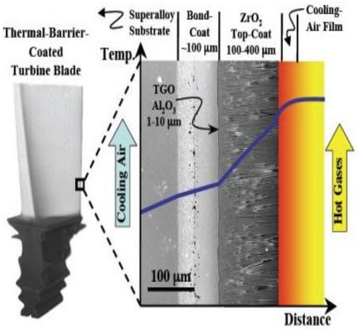


Fig. 2 Basic configuration of a TBC multilayer system from a turbine blade [3]

The main goal of this paper is to present the significant structural characteristics of the ZrO_2-CeO_2 ceramic. These data are part of an thermal shock experiment preparation which was performed in order to characterize the thermal properties of this type of coating.

2. PHASES IN CERIA-ZIRCONIA BINARY SYSTEM

Zirconia based oxides have influenced the direction of many research investigations and technology solutions due to its high temperature resistance. It is well known that for pure zirconia (ZrO_2) the tetragonal-monoclinic transformation is a problematic issue since it occurs at a temperature in the range of the service temperature in gas turbines. The tetragonal→mono-clinic transformation is martensitic in nature and involves a 5÷7 % volume increase that induces internal stresses which compromise the the structural integrity of the ceramic. One method to solve this issue is by adding to zirconia a stabilizing oxide such as CeO_2. It already has been reported that the cerium doped Ce-TZP (tetragonal zirconia polycrystal) shows an improvement of the thermal stability and a high toughness [4]. The thermal stability is due to a non-transformable tetragonal phase t'

formed by rapid cooling during coating deposition and ranges from the room temperature to approximately 1200°C (fig.3). At temperatures higher than 1200°C the monoclinic phase is unstable and will change to the tetragonal phase *t*.

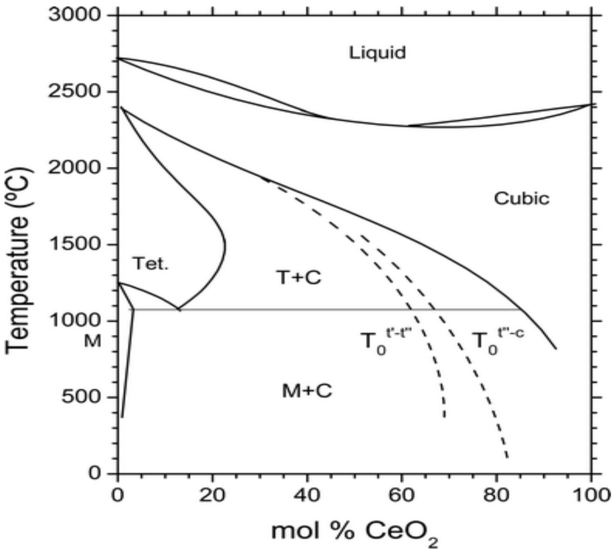


Fig.3 Phase diagram of ZrO_2-CeO_2 binary system [5]

3. MICROSCOPIC INVESTIGATIONS

The samples which have been investigated were made of a sandwich-type structure consisting of:

-substrate, Ni-Cr-Co alloy, NIMONIC super alloy

-bond coat layer NiAl, deposited by high-velocity oxy-fuel method (HVOF)

-ceramic zirconia based layers doped with cerium for thermo-resistant structures deposited by air plasma spray technique (APS).

Micro-structural investigations were performed by a high resolution scanning electron microscope (HRSEM) equipped with a field emission gun (FEG) and an energy-dispersive detector (EDS) EDAX type (fig4.a). Results for three investigated points in the sample are given below (Tables 1-3).

For the Ni base alloy substrate the composition field is given in table 1 (% weight):

Table1

Field	AlK	TiK	CrK	FeK	CoK	NiK
Sb 1	2.72	3.02	19.2	1.36	16.45	57.25
Sb 2	2.68	3.01	19.65	1.38	16.14	57.15
Sb 3	2.71	2.95	19.12	1.28	16.94	57.00
Avr.	2.70	2.99	19.32	1.34	16.51	57.13

For the Ni-Al bond coat the composition field (% weight) is given in table 2:

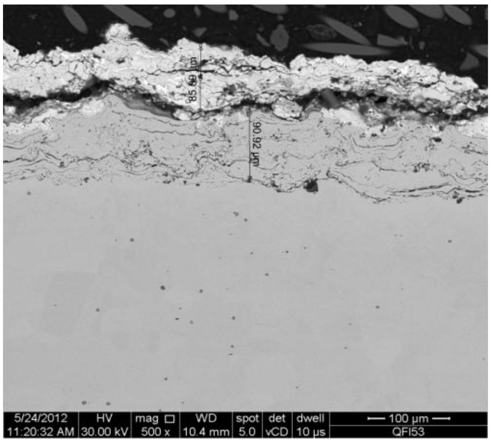
Table 2

Field	AlK	NiK
Bc 1	1.84	98.16
Bc 2	3.3	96.7
Bc 3	2.34	97.66
Average	2.49	97.51

For the O-Zr-Y-Ce top coat, the micro structural composition data (% weight) revealed two types of regions: poor (zone 1) and rich (zone 2) Ce region respectively (fig 4.b).

Table 3

Field	OK	AlK	CeL	NiK	YK	ZrK
Zone1	12.57	1.47	21.99	2.1	6.55	55.32
Zone2	11.94	1.69	44.58	1.9	5.42	34.46



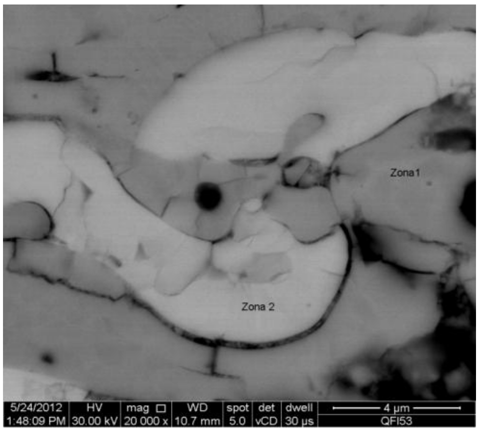


Fig 4. Back scattering elections image of N71 sample: (a) general view-magnification x500; (b) top coat image revealing by contrast in brightness the different Ce content-magnification x20000

From the frame of assembly of composition investigation (tab. 1, 2, 3), back scattering electrons images (fig. 4), the EDS specter in the substrate, bond coat and top coat (fig. 5) and especially the distribution images in surface of relative intensity of X radiation (fig. 6), we present the following observations:

-substrate, nickel based alloy presents a compositional uniform repartition

-the bonding has a non homogeneity structure of Ni-Al, shows frequent films of aluminum oxides at base material

-ceramic layer shows the separation in the adherence zone, micro fissures, the relative inhomogeneity of, zirconia and punctual concentrations of cerium

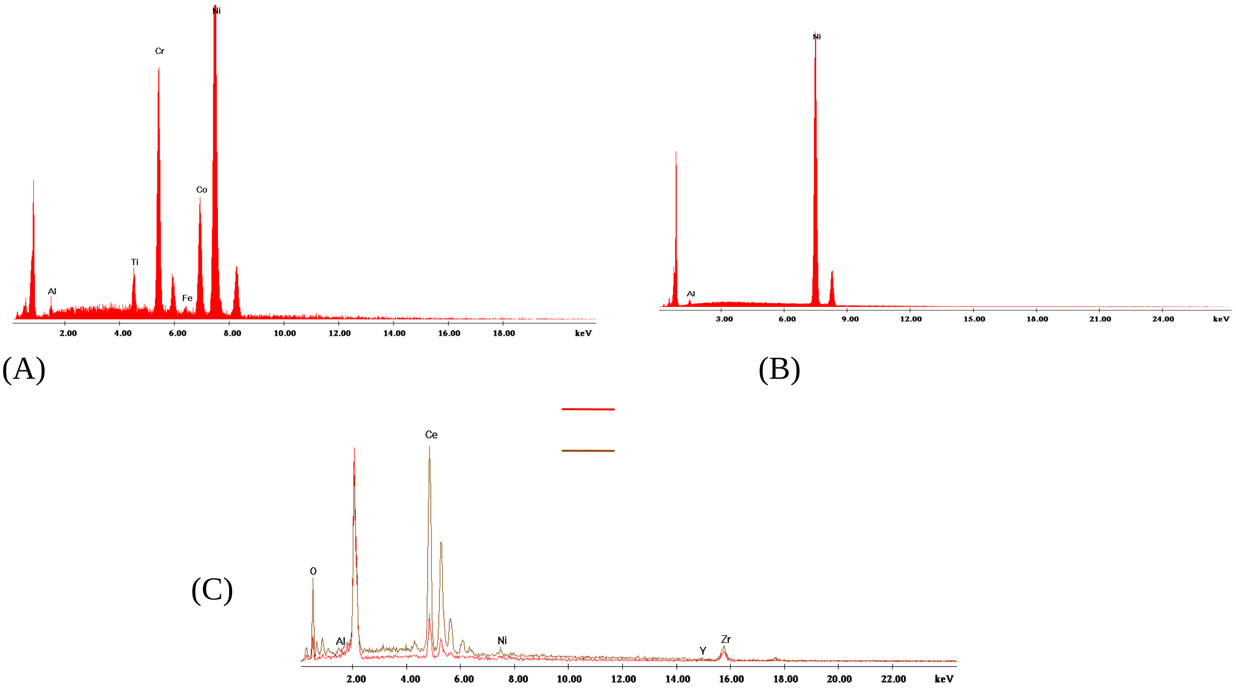


Fig. 5 EDS spectra of the substrate (A), bond coat (B) and top coat (C)

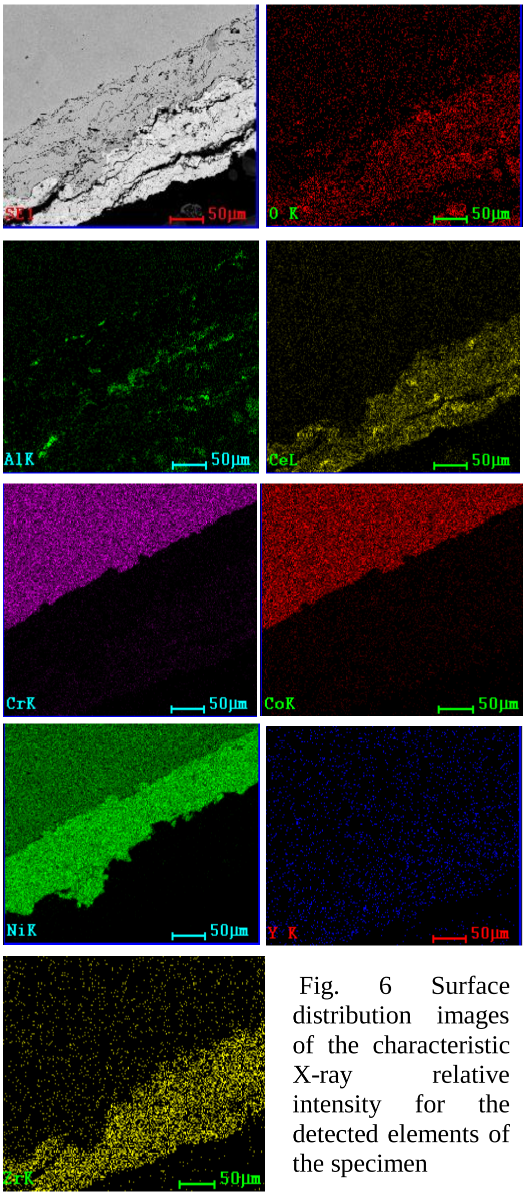


Fig. 6 Surface distribution images of the characteristic X-ray relative intensity for the detected elements of the specimen

4. CONCLUSIONS

The „hot parts" of turbo engines as well as of co-generative systems from power industry are severely subjected to wear factors occurring due to the extreme functional conditions and the surrounding thermo-chemical factors.The thermal fatigue associated to the thermal shock acts the most disturbing on the TBC protective coatings. Better compositional TBC solutions are expected to increase the life time of hot parts. Investigations of electronic microscopy (HRSEM) on TBC based on zirconia doped with cerium oxide reveal, thanks to evidence of some inhomogeneity in duplex structures the need to improve in technology APS assigned to this complex type composite ceramic powder. Micro structural characteristics of the partially stabilized zirconia with cerium oxide duplex system are revealed through a scanning electron microscopy method. Between the bond coat and the top coat one can notice the thermally grown oxide layer (TGO) which was formed due to oxidation of the bonding layer. The specimen is intended to be tested at thermal shock in order to be compared to other ceramic coatings in terms of thermal endurance [6]. During this thermal testing the TGO is getting thicker leading to ceramic delamination after a certain number of heating-cooling cycles. This kind of experiments are worth for the coating selection and developing of delamination mode models.

5. REFERENCES

[1]F. O. Soechting, *A design perspective on thermal barrier coatings.* Thermal barrier coating workshop, NASA Conference Publication 3312, p. 1-15, 1995

[2]V. Manoliu, Gh. Ionescu, S. Ilina, C. Valcu, *"Wear factors acting on aviation turbo engines"*, The 13th international conference of scientific papers "Scientific research and education in the air force", 26-28 May 2011, Brasov, Romania, page 882, ISSN 2247-3173

[3]Padture, N. P., Gell, M., & Jordan, E. H. (2002). *Thermal barrier coatings for gas-turbine engine applications.* Science (New

York, N.Y.), 296 (5566), 280-4

[4]Tsukuma, K. and Shimada, M., *Strength, fracture toughness, and Vickers hardness of Ce-stabilized tetragonal zirconia poly crystals (Ce-TZP)*. J. Mater. Sci., 1985, **20**, 1178–1184

[5]M. Yashima, H. Arashi, M. Kakihama, M. Yoshimura, *„Raman-Scattering study of Cubic-Tetragonal Phase-Transition in* $Zr_{1-x}Ce_xO_2$ *solid solution"*, Journal of the American Ceramic Society 77[4], p.1067, 1994

[6]V. Manoliu, Gh. Ionescu, A. Stefan, C. Serghie, S. Ilina, C. Valcu, "*Quick Thermal Test Shock Installation – QTS1*", page 116-121, INCAS Bulletin, Vol.1, Number 2/2009, ISSN 2066-8201