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CHARACTERIZATION OF MICROSTRUCTURE AND PROPERTIES OF TBC SYSTEMS WITH GRADIENT OF CHEMICAL COMPOSITION AND POROSITY

CHARAKTERYSTYKA MIKROSTRUKTURY ORAZ WŁASNOŚCI POWŁOKOWYCH BARIER CIEPLNYCH TBC Z GRADIENTEM POROWATOŚCI I SKŁADU CHEMICZNEGO

The article presents results of microstructural investigation and properties characterization of gradient TBC. The study has been done on AMS 5599 type alloy with 4 different type of thermal coatings with gradients of porosity and chemical composition. In all specimens, NiCoCrAlY VPS-sprayed powder was employed as the bond coat. In addition, $ZrO_2 \times 8\%Y_2O_3$ powder (applied on its own or together with NiCoCrAlY powder, to form graded coatings of varied porosity and/or chemical composition) was used for the outer layer spraying. Four variants of coatings were prepared for further investigation: variant included the spraying of bondcoat and of 5 successive YSZ and NiCoCrAlY (APS) powder layers of a given thickness, so as to obtain the composition gradient; second variant included the spraying of bondcoat type powder and of a layer consisting of YSZ and NiCoCrAlY powders mixture of a particular capacity proportion of both of them. Next two variants included the spraying of NiCoCrAlY bondcoat and YSZ ceramic layers with a different thickness. The porosity gradient was created by a suitable modification of APS spraying parameters, whereas the step and smooth chemical composition transition resulted from the consecutive spraying of zirconium oxide and NiCoCrAlY powder (step gradient), and, in the second case, the smooth proportion change of the sprayed powder from the pure 100% NiCoCrAlY to the pure 100% zirconium oxide (smooth gradient), which led to the smooth proportion change of the two powders in the transition area. First of investigated area is related to quantitative and qualitative description of TBC's ceramic top surface such as application of confocal microscopy for characterization of top coat by topographic surface maps and their 3D reconstruction. The numerical treatment of the qualitative results provided the means for quantitative characterization of the surface roughness, employing parameters such as Ra, Rz etc., and using surface and linear methods of confocal image analysis. Second area of investigations is connected to XRD characterization of TBC's systems. The purpose of this research was identification of the residual stress in the top coat of different type of thermal barrier coating with gradient of chemical composition and gradient of porosity. The research allowed the identification of qualitative and quantitative phase constitution of top coat and residual stress measurement by $\sin^2\Psi$ method form surface of coatings. It was found that the dominant phase in all the top coats was tetragonal zirconia with minor addition of monoclinic type of ZrO_2 and in the case of residual stress the tensile stress conditions was observed in the case of gradient porosity and compressive stresses in the case of chemical gradient. Another subject is related to microstructural characterization of TBC gradient systems from their quality point of view. The parameters which identify the quality of the bond coat and the ceramic coating consist: the thickness of the layers; the quality of the connection between the metal base and the bond coat; the presence of cracks and oxides; porosity; globular grains; bond coat integrity; the roughness of the bond-coat surface; the microstructure of the ceramic layer – the analysis involves the porosity assessment, randomly oriented cracking and their shape, metallic impurities and globular grains.The last area of presented investigations is related to degradations of gradient thermal barrier coatings during oxidation test. Obtained results showed that TBC with gradient of chemical compositions are not the best solutions for improvement of life-time of TBC. More effective is application of thermal insinuations with gradient of porosity.

W artykule przedstawiono wyniki badań dotyczące mikrostruktury i właściwości gradientowych warstw typu TBC. Stopem podłoża był nadstop na bazie niklu typu AMS 5599 z 4 typami pokryć gradientowych o zmiennym składzie chemicznym i porowatości. We wszystkich analizowanych przypadkach jako warstwę podkładową zastosowaną proszek NiCoCrAlY natryskiwany metodą VPS. Jako zewnętrzną warstwę ceramiczną zastosowano standardowy proszek typu $ZrO_2 \times 8\%Y_2O_3$ natryskiwany samodzielnie lub w połączeniu z proszkiem NiCoCrAlY w celu uzyskania gradientu składu chemicznego. Do badań wykonano cztery warianty warstw barierowych. Pierwszy z nich to pokrycie z gradientem składu chemicznego złożone z pięciu naprzemianległych warstw ceramiki YSZ i proszku NiCoCrAlY o założonej grubości natryskane metodą APS. Drugi rodzaj pokrycia z gradientem składu chemicznego charakteryzował się płynną zmianą zawartości proszku ceramicznego i NiCoCrAlY

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od czystego proszku podkładowego do czystej warstwy ceramicznej YSZ. Kolejne dwa typy pokryć gradientowych wykazywały różna porowatość i różną grubość warstwy ceramicznej na bazie fazy YSZ. Zmianę porowatości uzyskano poprzez modyfikację parametrów natryskiwania APS w trakcie procesu osadzania warstwy TBC. Zakres badań obejmował ilościową i jakościową charakterystykę powierzchni ceramicznej poprzez zastosowanie konfokalnej mikroskopii laserowej i stworzenie map topograficznych powierzchni oraz jej odwzorowanie 3D. Numeryczna analiza uzyskanych wyników pozwoliła na określenie ilościowych parametrów charakteryzujących chropowatość powierzchni takich jak Ra, Rz itd. Do badań zastosowano metodę liniową oraz powierzchniową. Drugi typ badań związany był z charakterystyką warstw TBC metodami jakościowej i ilościowej rentgenowskiej analizy strukturalnej. Celem tych badań było również określenie stanu naprężeń w różnego typu warstwach barierowych metodą $\sin^2\Psi$. Stwierdzono, że dominującą fazą jest faza tetragonalna z niewielką ilością fazy jednoskośnej ZrO_2. Badania stanu naprężeń wykazały naprężenia dodatnie w przypadku warstw z gradientem porowatości i ujemne w przypadku gradientu składu chemicznego. Kolejny obszar przedstawionych badań dotyczy charakterystyki jakościowej i ilościowej mikrostruktury warstw barierowych. Ocenie podlegały następujące parametry jakościowe warstw gradientowych: grubość poszczególnych warstw, jakość połączenia pomiędzy podłożem a podkładem, obecność pęknięć i tlenków, porowatość; obecność ziaren o globularnej morfologii, ogólna jakość międzywarstwy podkładowej, chropowatość podkładu oraz mikrostruktura warstwy ceramicznej – ocena porowatości, losowo zorientowanych pęknięć i ich kształtu, a także obecność zanieczyszczeń metalicznych i ziaren globularnych. Ostatni obszar przedstawionych badań dotyczy trwałości i degradacji warstw barierowych z gradientem składy chemicznego i porowatości. W tym celu przeprowadzono testy odporności na utlenianie cykliczne. Uzyskane wyniki wskazują, że zastosowanie pokryć z gradientem składu chemicznego nie jest najlepszym rozwiązaniem. Natomiast warstwy ze zmienną porowatością zachowywały się poprawnie prze cały czas trwania testu.

1. Introduction

During the last decade, research efforts have been devoted to the development and manufacturing of ceramic TBCs on turbine parts because the traditional turbine materials have reached the limits of their temperature capabilities. Thermal barrier coatings (TBCs) are used to sustain the highest temperature on the surface of high temperature superalloy substrates. TBCs have been widely used in hot-section metal components in gas turbines either to increase the inlet temperature with a consequent improvement to the efficiency or to reduce the requirements for the cooling air. Ni-based superalloys have usually been used with thermal barrier coating (TBC) for vanes and blades in gas turbines and jet engines. Recently TBC system has been applied to the hollow high pressure turbine blades in advanced gas-turbine engines to decrease the average metal temperature. Typically, this kind of protective coating is a two-layered system, consisting of a ceramic top coat and an underlying metallic bond coat. Ceramic top surface should be characterized by lower thermal conductivity and relatively higher thermal expansion coefficients. In the case of bond coat material, good oxidation resistance, adherent thermally grown oxide (TGO), thermal expansion coefficient and stability adequate to the substrate are required. Today's standard layered coating system consists typically of a 200 μm thick partially stabilized zirconia ceramic layer (PSZ for example yttria stabilized zirconia YSZ) on top of a nickel superalloy substrate and a bond coat of about 100 μm thickness, MCrAlY type. Two different processing routes have been established for the manufacturing of TBCs – EBPVD and APS coatings. TBCs prepared by electron beam physical vapour deposition (EBPVD) show superior thermal cycling lifetime, when compared to plasma-sprayed systems (APS) at the expense of higher manufacture cost and lower processing flexibility. The bond coat is either vacuum-plasma-sprayed MCrAlY or an Al diffusion coating such as beta-(Ni,Pt)Al [1-4]. It has been reported that the failure of TBC systems is mainly caused by the thermal expansion mismatch between the ceramic and metal coating layers of the systems [5-7]. One way to overcome this problem is to introduce the concept of functionally gradient material (FGM) into TBCs, which are referred to as 'FGM TBCs'. FGM TBCs are sprayed in the form of multi-layered coatings, the composition of which varies from 100% metal, applied directly to the substrate, to 100% ceramic for the topcoat. While the concept of FGM TBC itself is rather intuitive and simple, while the fabrication of a fine mixture of ceramics and metals with a compositional gradient is quite difficult. Several processing techniques have been explored, e.g. plasma spraying, powder metallurgy, in situ synthesis, etc. but the optimum process for the fabrication of FGM TBCs still remains a challenging task [6-9].

2. Materials and methodology

The study has been done on an AMS 5599 type alloy with 4 different type of thermal coatings with gradient of porosity and gradient of chemical composition. In all specimens, (NiCoCrAlY) VPS-sprayed powder was employed as the interlayer. In addition $ZrO_2 \times 8\%Y_2O_3$ powder (applied on its own or together with NiCoCrAlY powder, to form graded coatings of varied porosity and/or chemical composition) was used for the outer layer spraying. Four variants of coatings were prepared for further investigation:

– TBC-2 variant (Fig.1) including the sprayed of NiCoCrAlY interlayer and of 5 successive YSZ and NiCoCrAlY powder layers of a given thickness, so as to obtain the composition gradient;

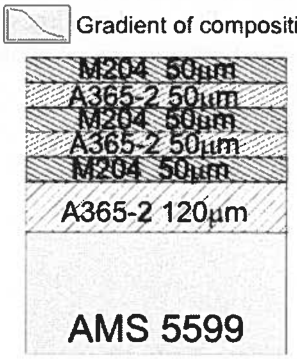

Fig. 1. The conception of TBC system with the gradient of chemical composition

– TBC-3 variant (Fig.2) included the spraying of NiCoCrAlY type interlayer and YSZ powder layers of a given thickness, modifying the APS process so as to obtain the porosity gradient;

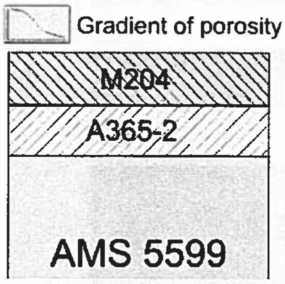

Fig. 2. The conception of TBC system with a gradient of porosity

– TBC-4 variant (Fig. 3) including the sprayed of NiCoCrAlY type interlayer and of a layer consisting of YSZ and NiCoCrAlY powders mixture of a particular capacity proportion of both of them, modifying the APS spraying process so as to get the composition gradient;

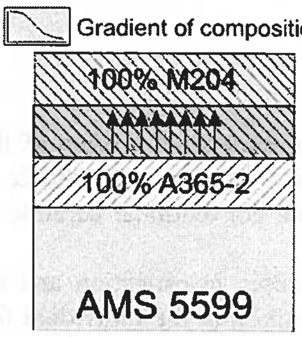

Fig. 3. . The conception of TBC system with a gradient of chemical composition

– TBC-5 variant (Fig.4) was parallel to the TBC-3 variant, except for the fact that the ceramic layer was substantially thicker and the process was directed so as to obtain the porosity gradient;

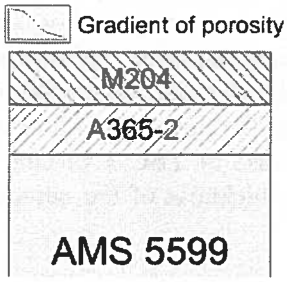

Fig. 4. The conception of TBC system with a gradient of porosity

Microstructural studies were carried out by light and scanning electron microscopy. The chemical composition microanalysis has been done by EDS method using Six Sigma system attached to Hitachi 3400N microscope. The qualitative and quantitative phase analysis has been conducted by X-ray diffraction method. X-ray measurements in the mode Θ-2Θ angles in the range of 20-90° using Cu Kα (40 kV, 20 mA) radiation in steps of 0.02 were performed in order to access the structural characterization of the coatings. Residual stresses were determined by X-ray diffraction using the $\sin^2\Psi$ technique. Measurements on [620] lattice plane of ZrO_2 were performed to obtain the coatings surface strain values. The diffraction angle for this plane occurred at about 2Θ = 144.58. The Ψ angle was scanned from -25° to 25° by steps of 5° in order to get the interplanar distance d_{hkl}. The biaxial stresses in the plane parallel to the interface were calculated considering an isotropic biaxial stress distribution with σ33=0. The XRD spectra were acquired for the as-sprayed coatings at initial conditions. The tests were done at JDX-7S JEOL diffractometer.

The TBC coatings top surface were investigated with the use of Olympus LEXT confocal system, whose main function are three-dimensional high-resolution surface analysis performed with UV laser beam of 408 nm wave length. The resolving power of the microscope in x-y surface amounts for 0,12 μm, while in z axis it equals 0,01 μm. While working with LEXT microscope, no sample preparation is required prior to fitting onto the microscope stage. The observations and measurements in three dimensions are performed in actual time.

3. Results

3.1. Microstructural investigations

The microstructure of the studied coatings is visible in the general view shown in Fig. 5. The obtained graded coatings differ in thickness and structure. In case of the TBC-2 variant, the total thickness of the coating amounts for circa 550 μm, out of which about 165 μm is constituted by the interlayer, while the 385μm thick graded coating, exhibiting step chemical composition and phase transition, is composed of (counting from the interlayer): the ceramic layer (165*muu*pm), NiCoCrAlY zone (60μm), the ceramic layer (80μm), NiCoCrAlY zone (50μm) and the outer zirconium oxide layer, circa 30μm thick. In case of TBC-3 variant with the porosity gradient, the thickness of the ceramic layer and the interlayer equal respectively 510μm and 220μm. The graded TBC-4 coating analysis proved the presence of 160μm-thick interlayer, the transition gradient layer with a smooth chemical and phase composition change, which is circa 380μm thick, and the outer ceramic layer, which was circa 65 m thick. The total thickness of the TBC-5 coating amounts for 1350μm, out of which 1150 μm is constituted by the ceramic layer.

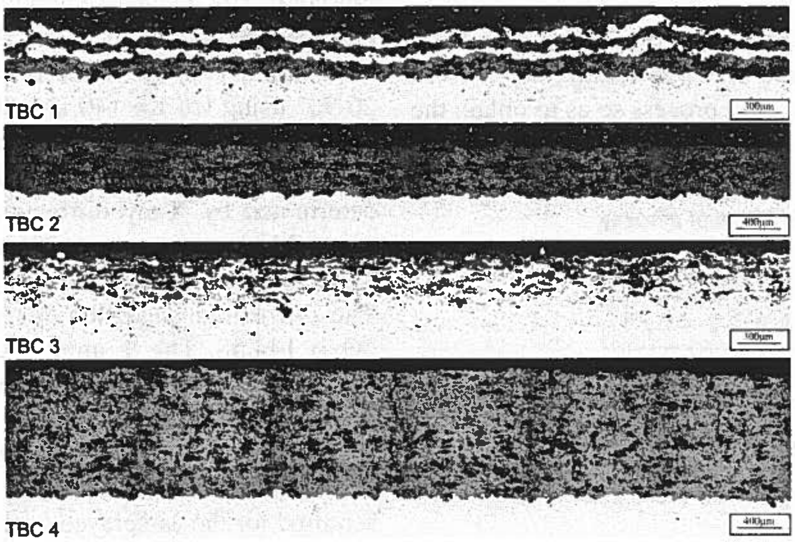

Fig. 5. The general view of gradient TBC systems

The parameters which identify the quality of the bond coat and the ceramic coating are as follows: the thickness of the layer; the quality of the interface between the metal base and the bond coat; the presence of cracks; the presence of oxides; porosity; globular grains; bond coat integrity; the roughness of the bond-coat surface; the microstructure of the ceramic layer – the analysis involves the porosity assessment, randomly oriented cracks and their shape, metallic impurities and globular grains. The detailed analysis of the microstructure with the help of optical and scanning microscopy provided the means for the positive identification of the investigated coatings in terms of the assumed criteria, applied for the assessment of the conventional ceramic layers and the interlayer.

The microscopic investigation and the analysis of chemical composition in the individual fields of TBC-2 and TBC-4 graded coatings explicitly proved the effect of the chemical content gradient, which is sufficiently confirmed by the microscopic SEM examination with BSE technique application (Fig.6).

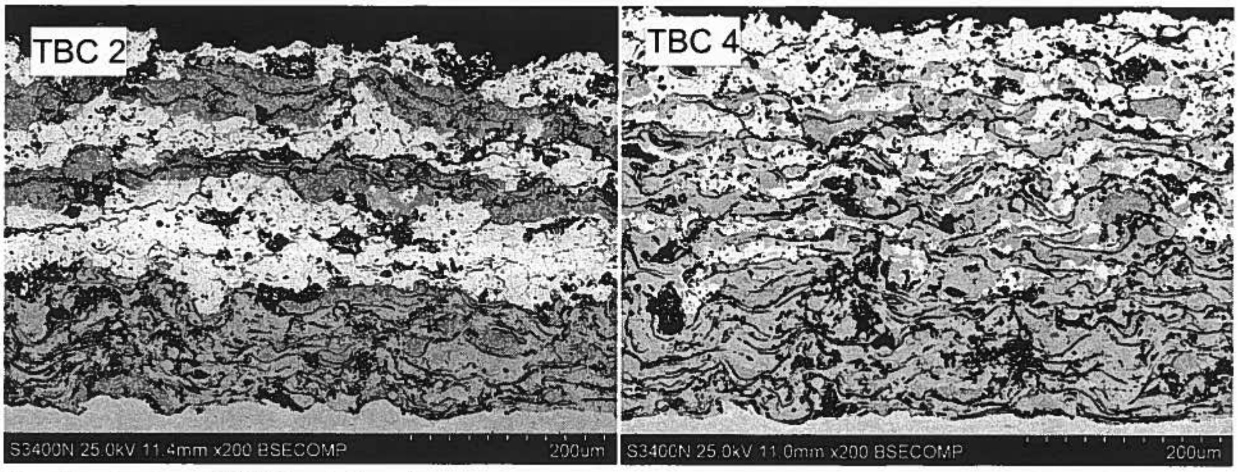

Fig. 6. The microstructure of TBC-2 and -4 specimens

Consequently, the article is focused on the porosity gradient assessment of the sprayed coatings, both in the coatings with the intended porosity gradient and in those with the intended composition gradient (Fig 7).

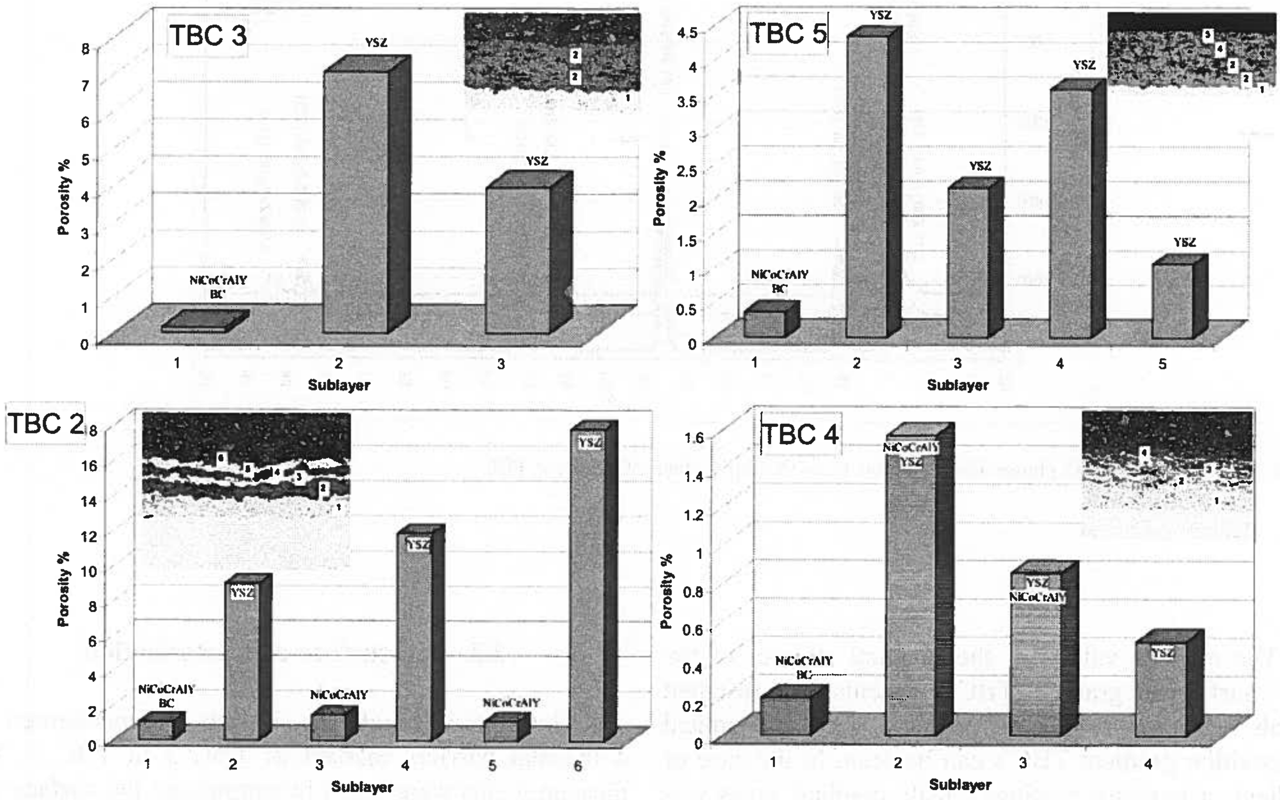

Fig. 7. The results of porosity measurement (%)

3.2. Qualitative and quantitative characterization

Fig. 8 shows XRD patterns for all plasma sprayed coatings in as-sprayed condition. The X-ray phase content analysis enabled both the qualitative and quantitative evaluation of the outer zone of the investigated graded coatings. The tetragonal phase including monoclinic phase was dominant in all of the studied specimens where the main diffraction peak corresponds to the < 011 > planes. No presence of phases generated by the second element of the graded coatings, i.e. NiCoCrAlY powder, was detected. Results of quantitative characterization are showed in Tab.1.

TABLE 1

The quantitative results of XRD analysis (fraction of monoclinic phase)

	TBC-2	TBC-3	TBC-4	TBC-5
Value of monoclinic phase % wt.	12.50	5.90	7.90	8.15

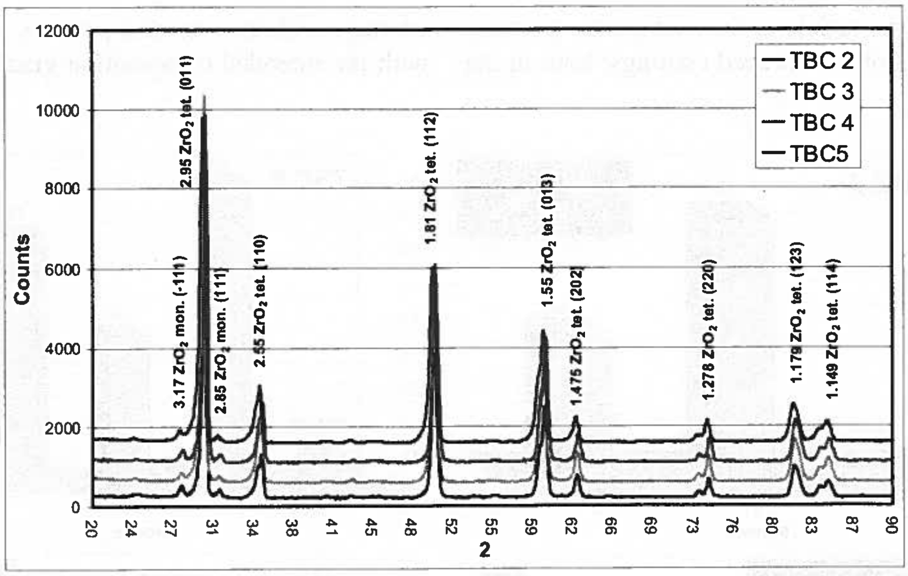

Fig. 8. The results of XRD phases identification from the top surface of gradient TBC

The average values of the residual stresses at the top – surface of gradient TBC's systems are presented in Tab. 2. A compressive residual stresses in a chemical composition gradient TBC's can be seen. In the case of gradient of porosity coatings tensile residual stress was observed.

TABLE 2

Residual stresses measured at the top-surface determined with different types of gradient in TBC's system

	TBC-2	TBC-3	TBC-4	TBC-5
Residual Stress [MPa]	-65	62	-15	45

3.3. Top surface characterization

The surface roughness analysis was performed for 4 thermal barriers marked as TBC 2 to TBC 5. The measurements were taken by employing the surface and the linear methods on 6 various profiles. The results of surface method analysis are displayed in Tab. 3, while the linear method measurements are shown in Tab. 4. On the basis of the presented results, TBC 2 sample was confirmed to be characterized by the highest roughness (SRa – 14,25); its topographical map is shown in Fig. 9. The TBC 3 sample is marked by the lowest roughness (SRa – 7,25). The linear and surface analyses are in a complete accord. Fig. 10 present the 3-D surface visualization of TBC samples.

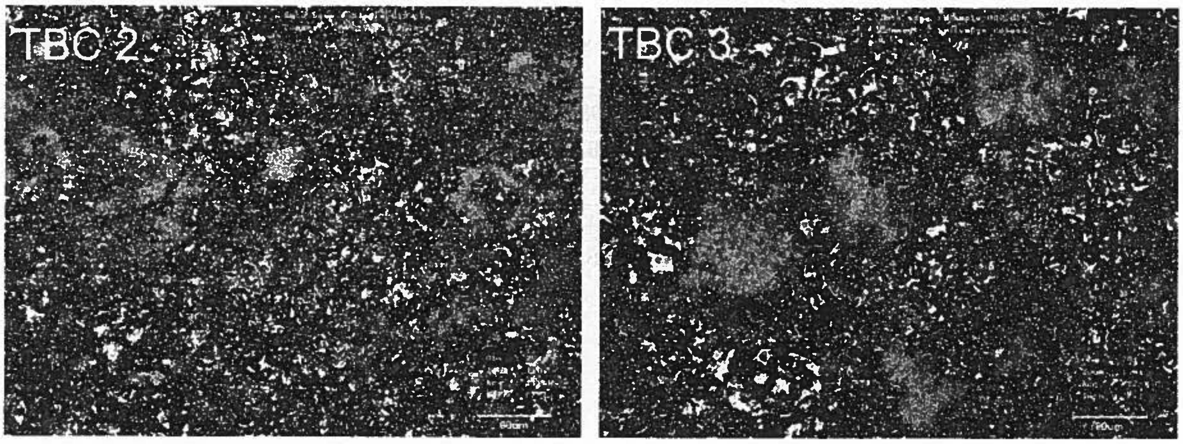

Fig. 9. The topographical maps of TBC samples

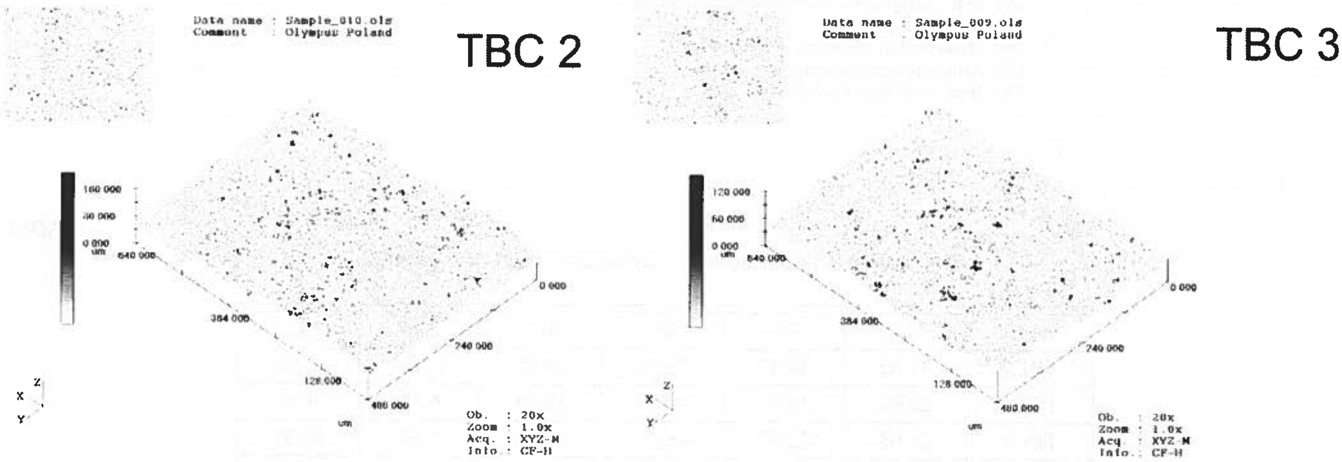

Fig. 10. The 3-D maps of TBC samples

TABLE 3

The results of surface analysis

Items	SRp	SRv	SRz	SRc	SRa	Rq
TBC2	47.02	51.20	98.22	29.94	14.25	17.23
TBC3	41.37	36.60	67.97	15.66	7.25	9.10
TBC4	36.60	38.01	74.62	17.13	9.04	11.29
TBC5	35.11	31.45	66.56	13.66	6.61	8.51

Definition of Roughness Analysis Items - Surface Roughness Analysis:
SRp: Max. peak of roughness curved surface
SRv: Max. valley depth of roughness curved surface
SRz: Max. roughness
SRc: Mean peak of roughness curved surface
SRa: Arithmetic mean roughness
SRq: Root mean square roughness

TABLE 4

The results of linear analysis – arithmetic mean of 6 profiles

Items	SRp	SRv	SRz	SRc	SRa	Rq
TBC2	33.62	38.47	72.09	29.46	13.83	16.80
TBC3	20.98	19.97	40.94	16.23	6.81	8.31
TBC4	23.68	22.97	46.65	17.84	9.13	10.91
TBC5	16.17	18.14	34.31	12.64	5.69	6.96

Definition of Roughness Analysis Items - Line Roughness Analysis
Rp: Max. peak of roughness curve
Rv: Max. valley depth of roughness curve
Rz: Max. of roughness
Rc: Mean of roughness curve elements
Ra: Arithmetic mean roughness
Rq: Root-mean-square of roughness

3.4. Degradation of gradient TBC

In order to define durability of gradient TBC systems cyclic oxidation test was carried out. Parameters of test were chosen as follow: temperature – 1100°C and 23 h cycles with 1h of cooling. After each one of cycles the macroscopic inspection of samples was made (Fig.11). Those inspections showed that TBC systems with gradient of chemical compositions for once cycle exhibit the loss of basic property such as good adhesion of ceramic top surface to the bondcoat. This effect was showed by delamination of ceramic layer and their partial spallation (Fig.12). In the case of TBS systems with gradient of porosity their macroscopic condition was satisfactory to the last 40-thy cycles (rys.13).

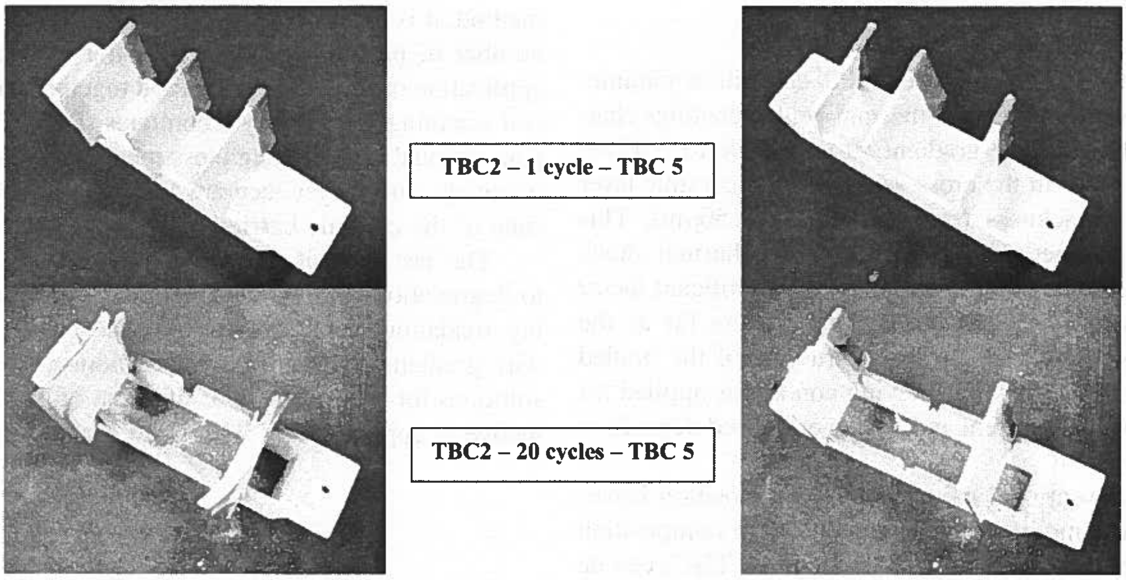

Fig. 11. Macroscopic view of gradient TBC systems (TBC 2 and 5) after 1 and 20 cycles of cyclic oxidation test at 1100°C

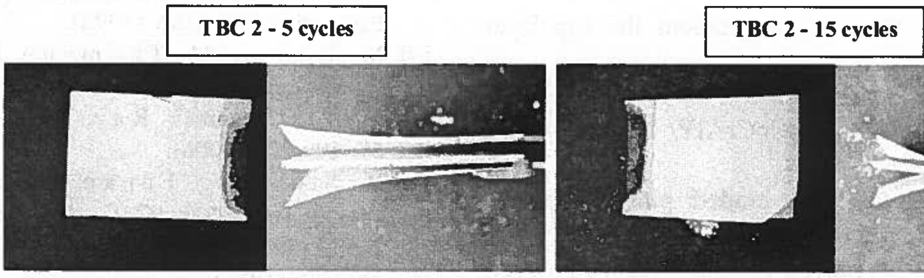

Fig. 12. Macroscopic view of gradient TBC 2 systems after 5 and 15 cycles of cyclic oxidation test at 1100°C

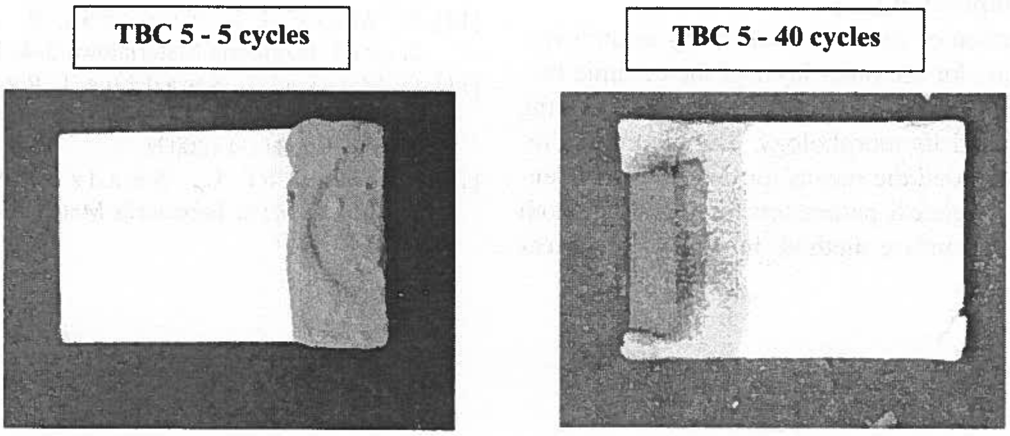

Fig. 13. Macroscopic view of gradient TBC 5 systems after 5 and 40 cycles of cyclic oxidation test at 1100°C

4. SUMMARY

With the modification of APS deposition parameters, it is possible to obtain thermal graded coatings characterized by porosity gradient (from 0,16% to 3,97%), which is visible in the cross-section of the ceramic layer with varied thickness (from 165μm to 1150μm). This is one of the methods of enhancing the thermal shock resistance, which additionally can be a significant factor for decreasing the thermal conductivity. As far as the porosity is concerned, the microstructure of the graded coating is typical for the spraying conditions applied for this type of TBC system and for the employed deposition technique.

The conventional method of APS deposition leaves room for the modification of the chemical composition of zirconia top coat as well. This modified TBCs can be graded in step or smooth form. The obtained chemical graded TBCs consist of the top layer, which, in the case of the step gradient, is composed of the following:

- Bond coat – NiCoCrAlY
- Graded top coat – YSZ/ NiCoCrAlY/ YSZ / NiCoCrAlY/ YSZ

and in the case of the smooth gradient the top layer consists of:

- Bond coat – NiCoCrAlY

Graded top coat – YSZ + NiCoCrAlY/ NiCoCrAlY + YSZ / YSZ [10].

The residual stresses of graded plasma sprayed ZrO_2-8wt.%Y_2O_3 coatings have been measured at room temperature in the as-sprayed coatings for two different type of chemical composition and porosity gradient. The top-surface of TBC presents a dominated tetragonal phase with minor addition of monoclinic phase. The thermal barrier coatings (YSZ as top coat/ MCrAlY as bond coat) with gradient of porosity presents a tensile stress state at the free surface which increase with decreasing of coating thickness. The residual stresses show an compression type in the case of coating with gradient of chemical composition [11].

The application of confocal microscopy as an investigation technique for the outer layer of the ceramic barrier coatings enabled precise topographical images of the coating surface and its morphology. The qualitative results analysis provided the means for determining quantitative surface roughness parameters by employing both the linear and the surface method. In case of the linear method, it is possible to verify the results of an arbitrary number of profiles, located in arbitrary directions. The application of the confocal method together with the special scanning microscopy techniques (BSE, TOPO) and conventional surface roughness measurements enables a relatively simple, yet accurate analysis of the outer layer state of the ceramic barriers [12].

The last area of presented investigations is related to degradations of gradient thermal barrier coatings during oxidation test. Obtained results showed that TBC with gradient of chemical compositions are not the best solutions for improvement of life-time of TBC. More effective is application of TBC with gradient of porosity.

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REFERENCES

[1] J. Wigren, L. Pejryd, in: C. Coddet (Ed.), Proceedings of the 15th International, Thermal Spray Conference on Thermal Spray Meeting the Challenges of the 21st Century, France, ASM International, Materials Park, 1531 OH, USA (1998).

[2] M. Konter, M. Thumann, Journal of Materials Processing Technology 92-117, 386-390 (2001).

[3] Ashok Kumar Ray, Materials Characterization **57**, 199-209 (2006).

[4] D. Stover, C. Funke, Journal of Materials Processing Technology 92-93, 195-202 (1999).

[5] A. Miller, C. E. Lowell, Thin Solid Films 95, 265-273 (1982).

[6] A. Kawasaki, R. Watanabe, M. Yuki, Y. Nakanishi, H. Onabe, Materials Transaction JIM 37, 788-795 (1996).

[7] J. Musil, J. Fiala, Surface and Coating Technoogy 52, 211-220 (1992).

[8] Y. Shinohara, Y. Imai, S. Ikeno, I. Shiota, T. Fukushima, ISIJ Int. **32**, 893-901 (1992).

[9] A. S. Demirkiran, E. Avci, Surface and Coating Technoogy **116/119**, 292-295 (1999).

[10] G. Moskal, L. Swadźba, B. Mendala, M. Góral, Inżynieria Materiałowa **3-4**, 192-199 (2007).

[11] G. Moskal, L. Swadźba, T. Rzychoń, Journal of Achievements in Materials and Manufacturing Engineering **23**, 31-34 (2007).

[12] G. Moskal, L. Swadźba, S. Roskosz, B. Mendala, Inżynieria Materiałowa **3-4**, 443-448 (2007).