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Characterization of powders used for LPPS Thin Film plasma spraying of thermal barrier coatings

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Properties

ABSTRACT

Purpose: The authors described in this article the basic properties of materials used for spray process of thermal barrier coatings under low pressure The characteristic of selected powders applied for bond-coats and outer ceramic layer was introduced. The authors presented the analysis of powders based on zirconium oxide stabilized by yttrium oxide, magnesium and calcium.
Design/methodology/approach: The described powders was analyzed by scanning electron microscopy and particle distribution by IPS U analyzer.
Findings: The ceramic powders were characterized by irregular particle shape caused by grinding process. The only exception was Metco 204 powder, with spheroid-shaped particles.
Research limitations/implications: The ceramic powders were made of zirconium oxide, which was stabilized by different types of oxides: yttrium (Metco 204), calcium (Metco 201) and magnesium (Metco 210). It is necessary to assess influence of the oxide, stabilizing the yttrium oxide, on stability of obtained ceramic layer of TBC coating.
Practical implications: Powders analysed in the article will be submitted to plasma spraying process with different methods.
Originality/value: The ceramic powder used for LPPS-Thin Film process were first time described.
Keywords: Metallic alloys; Ceramics and glasses; Corrosion; Electron; Microscopy; Thin & thick coatings; Surface treatment

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1. Introduction

Dynamic development of passenger aviation determines the development of aircraft engines. It is directed toward obtaining lower fuel consumption and reduction of pollutants emission. To achieve those goals, it is necessary to employ higher combustion temperature, which requires application of new materials characterized by higher heat resistance. The elevation of aircraft engines service temperature is possible through the use of turbine blades made of nickel superalloy with equiaxed microstructure (EQ), directional particle position (DS - directionally solidified) or with monocrystalline microstructure (DC - single crystal). The third SC alloys generation used in turbine engines is currently used. At present, there is also a development work on the fourth generation of those materials containing platinum metal alloy additions being done. High temperature resistant coatings are being deposited on blades surface. They have a function of corrosion protective, oxidation resistant and thermal isolating layer.

At present, the thermal barrier coatings are used for this purpose.Thermal barrier coatings are used for protection of element's surface of hot section of an aircraft engine. Those coating consist of, at least, two layers. Zirconium oxide stabilized by yttrium oxide is the outer layer. The inner metallic layer can consist of platinum-modified NiAl phase or multicomponent MeCrAlY alloy.

The outer ceramic layer is applied using the plasma spray method under atmospheric pressure (APS) or physical vapour deposition involving ingot evaporation with electron beam (EB-PVD). The bond-coats - according to their type - are obtained using two kinds of methods. Platinum-modified aluminide coatings are obtained during the platinum overlaying process followed by soaking and diffusion aluminizing. The aluminizing process can be realized by powder method, vapour deposition or CVD. The bond-coats based on multicomponent MeCrAlY alloy are deposited using PVD method (e.g. Arc-PVD or EB-PVD) or thermal spraying. Thermal spraying is realized most often by application of supersonic method or plasma method. Plasma spraying is used most frequently in industrial practice. The criteria of selection of the type of MeCrAlY powder depends on the type of base material and working conditions of the element and type of ceramic outer layer. There is a large amount of available powders used for plasma spraying under atmospheric pressure. Thermal spraying under low pressure (LPPS) as well as methods expanding this process - Thin-Film and PS-PVD are more modern methods of creating bond-coats based on MeCrAlY alloy. A low quantity of powders made for low pressure plasma spraying are available, hence it is necessary to characterize them (Fig. 1).

In the Research and Development Laboratory for Aerospace Materials one uses the plasma spraying technology under low pressure (LPPS-Thin Film). In this method, the metallic powder is partially melted and sprayed on blade surface with a use of plasma gun. For the first time in Poland it is possible to perform such a process in vacuum conditions. It ensures perfect properties of coating containing no oxides, which are created in processes of plasma spraying under atmospheric pressure (APS). Moreover, the obtained coatings are characterized by smaller thickness in comparison to those obtained during APS, as a result of using Thin Film technology.

Technology of plasma spraying under low pressure is also used to create outer, ceramic TBC coating. The unique function of LPPs-Thin Film device is ability to obtain low service pressure in a chamber (below 1 mbar), what allows to create high energy plasma jet, which enables evaporation of ceramic material (Plasma Spray- Physical Vapour Deposition). Formed ceramic layer can have complex columnar crystal microstructure - close to those obtained with EB-PVD method. This technology is unique not only in scale of the country but also in scale of the Europe and is a subject of interest of leading aircraft engine manufacturers and companies connected with other domains.

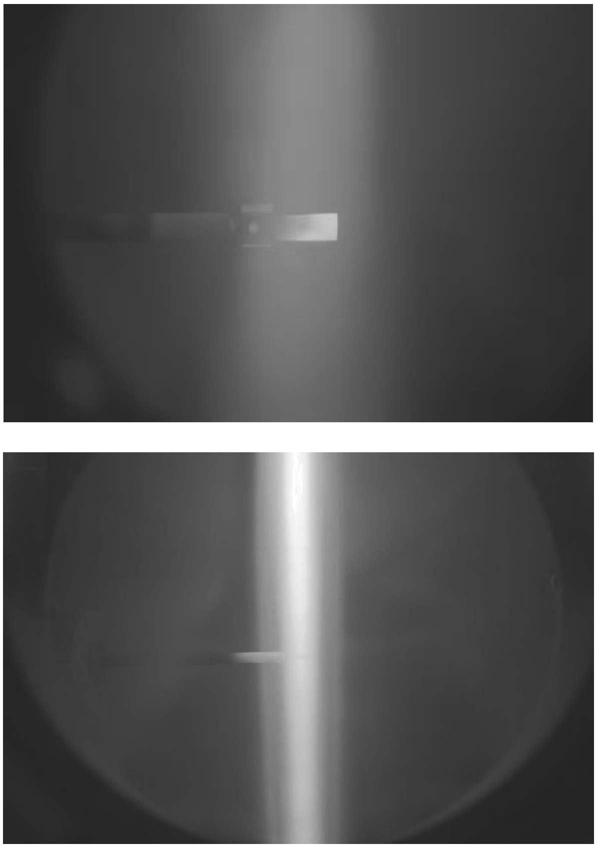

Fig. 1. Plasma spraying of aeroengine turbine blade in PS-PVD process

The conventional materials used for turbine blades reached their limit of capabilities and the further development was directed toward elaboration and creating the ceramic thermal barrier coatings (TBC). The TBC coatings are deposited on the rotating blades and other elements of turbines working under conditions of high temperature. They are used in order to increase the service temperature in the first stages of aircraft engine.

The oldest ceramic coatings used in aviation were frit enamel coatings (made of fusible glaze) developed by National Advisory Committee for Aeronautics (NACA). Layer made of calcium oxide stabilized by zirconium dioxide, created on the exhaust nozzle of X-15 manned rocket aircraft, in the 60-ies of 20th century is considered to be a first application of thermal barrier in manned flight. The working elements of aircraft jet engine are submitted to mechanical, chemical and thermal stresses. Few types of coatings such as: Al_2O_3, TiO_2, mullite, CaO/ MgO+ZrO_2, YSZ, CeO_2+YSZ, zirconium $La_2Zr_2O_7$, etc. were assessed as TBC materials [1,2,8-10].

The basic requirements for TBC coatings are [1]:

- high fusion temperature,
- lack of phase transition between room temperature and service temperature,
- low thermal conductivity,
- chemical inertness,
- thermal expansion close to the value for base material - nickel superalloy,
- good adhesion to bond-coat- and base material.

The amount of materials, which can be used as thermal barrier coatings is significantly limited. So far only few materials were qualified as satisfying above requirements.

1.1. Materials used as ceramic layers for TBC coatings

Zirconium oxide

Zirconium oxide stabilized by yttrium oxide is the most commonly used material for TBC coatings. It ensures the best properties of coatings under condition of high temperature, which is present in diesel engines and gas turbines. It has been proved, that YSZ coatings are more resistant to sulfur corrosion than CaO- or MgO-stabilized ZrO_2 coating. The maximum temperature in long-lasting application is the basic limitation. In the higher temperature, the phase transition from tetragonal to regular and monocline structure begin to appear, causing increase of fracture amount in TBC coating [1,11].

Mullite

Mullite is the substantial ceramic material due to its low density, high thermal stability, stability in difficult chemical conditions, low thermal conductivity as well as favourable mechanical strength and creeping properties. Mullite is a mixture of SiO_2 and Al_2O_3 with a composition of: $3Al_2O_3$ for $2SiO_2$. In comparison with YSZ, mullite has lower thermal coefficient of expansion and higher thermal conductivity, and higher oxidation resistance [1,3].

Al_2O_3

α-Al_2O_3 is the only stable phase among the aluminium oxides. It is characterized by high hardness and chemical inertness. The erosion properties of aluminium oxide coatings obtained during plasma spraying process under condition of vacuum or atmospheric pressure, were investigated and compared with propierties of slack material. The addition of certain amount of aluminium to YSZ coatings may improve their hardness and strength. High hardness of a coating can be obtained also through spraying of the outer coating made of aluminium oxide on the YSZ coatings. However, the coating made of aluminium oxide during plasma spraying process consist of many unstable phases γ and δ-Al_2O_3. Those unstable areas transform into α-Al_2O_3 during cyclic annealing, which involves a significant volume change [1,4].

CeO_2+YSZ

CeO_2 has higher thermal coefficient of expansion and lower thermal conductivity than YSZ, and the addition of CeO_2 to the YSZ coating is considered to be an effective way of improving its durability under cyclic oxidation conditions . Significant improvement of tolerance to thermal shock was obtained by addition of CeO_2 to YSZ.

The coating with the addition of ceria oxide has better tolerance to thermal shock, mainly with regard to [1,9]:

- low phase transition between monocline phase and tetragonal phase in CeO_2+YSZ coating;
- the stress created by oxidized bond-coat is lower in CeO_2+YSZ coating due to better thermal isolation;
- thermal coefficient of expansion is higher for the CeO_2+YSZ coating.

The basic flaw of CeO_2 addition is decrease of hardness and change of coating stoichiometry as a result of CeO_2 evaporation, reduction of CeO_2 to Ce_2O_3 and higher velocity of coating sintering.

$La_2Zr_2O_7$

$La_2Zr_2O_7$ (LZ) was introduced lately as promising material for TBC coating. It has a cubic pyrochlore structure. This material is one of few oxides with pyrochlore structure (such as $La_2Zr_2O_7$, $La_2Hf_2O_7$, $Pr_2Hf_2O_7$, $Ce_2Zr_2O_7$ and $Sm_2Ti_2O_7$), that preserve phase stability up to melting point, which is the main argument in favour of its usability as a material for TBC coatings. On the other hand $La_2Zr_2O_7$ has lower thermal conductivity than YSZ [1,5,7,11].

Silicate

Form the whole wide group of silicides, only the spraying of zirconium ($ZrSiO_4$) or natural zirkonium sand were characterized. Zirconium has very low thermal coefficient of expansion (4.99×10^{-6} K^{-1}, 300-1700 K) and high thermal conductivity (3.46 W m^{-1} K^{-1}, 365-1810 K). Zirconium doesn't have real melting point, because it decays before melting. Thermal destruction of zirconium occurs in the temperature of 1949 K, even for temperature not exceeding 1558 K, which depends on its purity. During the plasma spraying process zirconium decays and the obtained coatings consist of the mixture of crystalline ZrO_2 and amorphous SiO_2. In case of using zirconium as TBC coating in diesel engine, decayed SiO_2 can cause problems related to evaporation SiO and $Si(OH)_2$. It is believed that the protective effect is created in connection with ZrO_2 phase of the coating [1].

Rare earth oxide

The mixture of rare-earth oxides is easily available and very cheap. The coatings of the rare earth oxides (La_2O_3, CeO_2, Pr_2O_3 and Nb_2O_5 as main phases) have lower thermal diffusivity, higher thermal coefficient of expansion than ZrO_2 and are potential material for thermal barrier coatings (TBC). There is a lack of further available research concerning this material. The majority of rare earth oxides is polymorphic in above temperatures, and their phase instability will surely influence on resistance to thermal shock of coatings made from them [1,6,10].

Metallic- glass composite

It is a completely new TBC system. Powdered metal mixture and ordinary glass may be plasma sprayed under condition of vacuum. With proper composition, this TBC material has thermal coefficient of expansion close to the value for metal base material. Its thermal conductivity is about 2 times higher than for YSZ. There are three basic reasons of high durability of metallic-glass TBC coating under the conditions of cyclic oxidation:

- high thermal coefficient of expansion ($12.3x10^{-6} K^{-1}$),
- good adhesion to bond-coat,
- lack of open porosity.

This type of coating doesn't have open pores, which prevents oxidation of bond-coat by corrosive gases [1].

$SrZrO_3$ and $BaZrO_3$

Till now, only 2 materials with perovskite structure, i.e. $SrZrO_3$ and $BaZrO_3$, were investigated. They have very high melting point (correspondingly: 3073 and 2963 K), however their thermal coefficient of expansion (correspondingly: $10.9x10^{-6} K^{-1}$ and $7.9x10^{-6} K^{-1}$, 303-1273 K) are lower than for YSZ. The earlier work concerning the TBC coating made of $BaZrO_3$ proved that the coating wasn't characterized by better resistance to sudden temperature change than YSZ [1].

Lanthanum aluminate

Newly developed ceramic coating on the base of aluminum oxide, consisting of La_2O_3, Al_2O_3 and MgO ($MMeAl_{11}O_{19}$, M=La, Nd; Me=rare earth metals with magnetoplumbit structure) have long-lasting structural- and thermochemical stability up to 1673 K. This coating has significantly lower sintering rate than TBC coatings on the base of zirconium dioxide [1].

$LaPO_4$

Lanthanum phosphate has monocline structure with four identical particle units $LaPO_4$ in $P_{21/n}$ molecule. It is considered to be a potential material for coating used for thermal isolation of superalloy substrate made on a base of nickel, due to its stability in high temperature (2345±20 K), high thermal expansion and low thermal conductivity (comparable to conductivity of zirconium dioxide). It is also expected, that lanthanum phosphate will be characterized by good corrosion resistance in environment which contains sulphur and vanadium salt [1].

2. Experimental

One of leading manufacturers of powders used for plasma spraying is Sulzer-Metco company. There are about 30 types of powders used for plasma spraying under low pressure and recommended by manufacturer. Two types of powders used for MeCrAlY bond-coats as well as three types of powders used for obtaining ceramic layers manufactured by Sulzer-Metco company were selected for analysis.

Properties of some types of powders are restricted by recipients - aircraft engine manufacturers. Chemical composition- and morphology analysis were conducted with a use of Hitachi S-3400 scanning electron microscope equipped with the attachment for chemical composition microanalysis manufactured by Thermo company.

Nominal chemical composition for metallic powders given by manufacturer is presented in Table 1 and for ceramic powders - in Table 2. The nominal granularity of the powder is presented in Table 3.

Table 1.
The nominal chemical composition of metallic powders used for bond-coats

Chemical composition (nominal wt. %)	Metco 4451	AMDRY 997
Co	bal.	20-26
Ni	29.0-35.05	bal.
Cr	18.0-24.0	18-23
Al	5.0-11.0	6-11
Y	0.1-0.8	0,3-0,9
Other (max.)	1	2-6 (Ta)

Table 2.
The nominal powder composition

Phase composition (nominal wt. %)	Powder type		
	Metco 201 B NS	Metco 204 NS	Metco 210
ZrO	91.5	bal.	bal.
Y_2O_3	-	8-9	-
CaO	4.5-5.5	-	-
MgO		-	15-30
other	bal.	approx. 1%	Up to 7%

Table 3.
The nominal size of powder particle

Powder	Grain size (μm)
Metco 4451	- 90+45
AMDRY 997	- 38 + 5
Metco 201 B_NS	- 53+11
Metco 204 NS	- 125+11
Metco 210	- 90+11

The research, made with a use of IPS U analyzer produced by Kamilka company, was conducted in order to verify graining, introduced by the manufacturer. The measurement method of IPS analyzer is complex. It consist in measurement of the smallest (0.5 to 1000 μm), humid and balling-up particles, with consideration to influence of the laser diffraction, and then goes continuously through, for larger particles, to variation measurement of flux of the radiation, which is dispersed by moving particles. The flux of infrared radiation enables the identification of particles size and allows to count particles precisely in the whole measuring range. For each particle there is a electrical impulse proportional to its size. The original measurement of a particle set involves partitioning it into 4096 size classes and transforming it (calibration) into 256 size classes available for the user. The results of quantitative distribution measurement is presented on Figs. 2-3 and average values of graining were put together in Table 4.

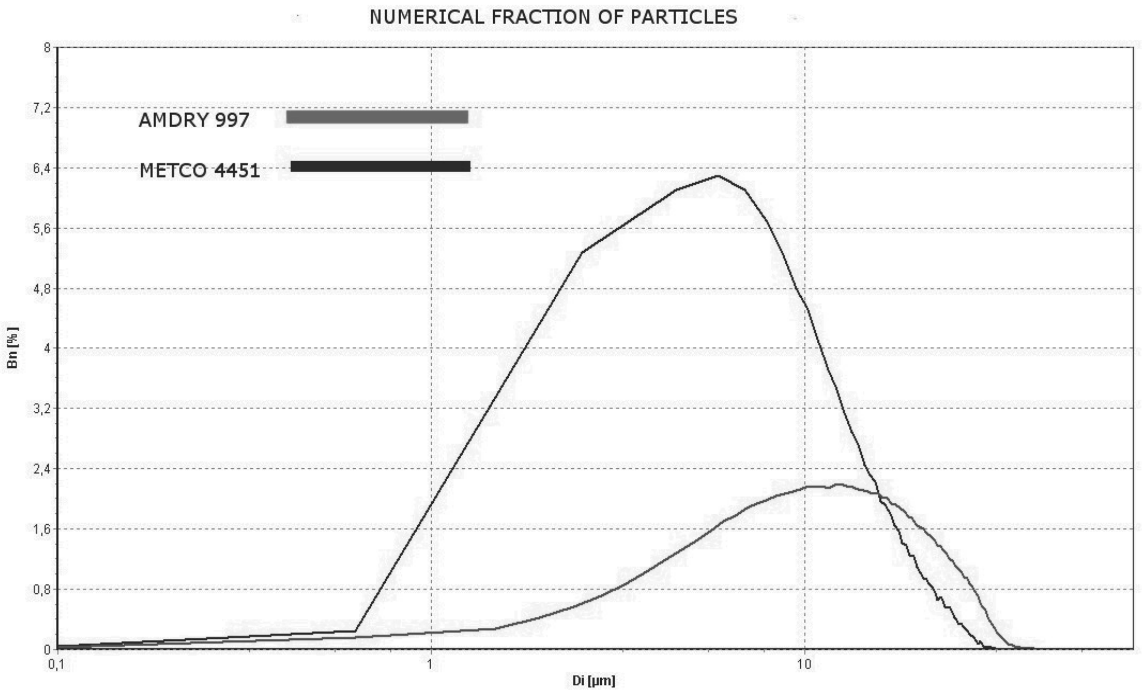

Fig. 2. Graining distribution for powders, which are used for bond-coats.

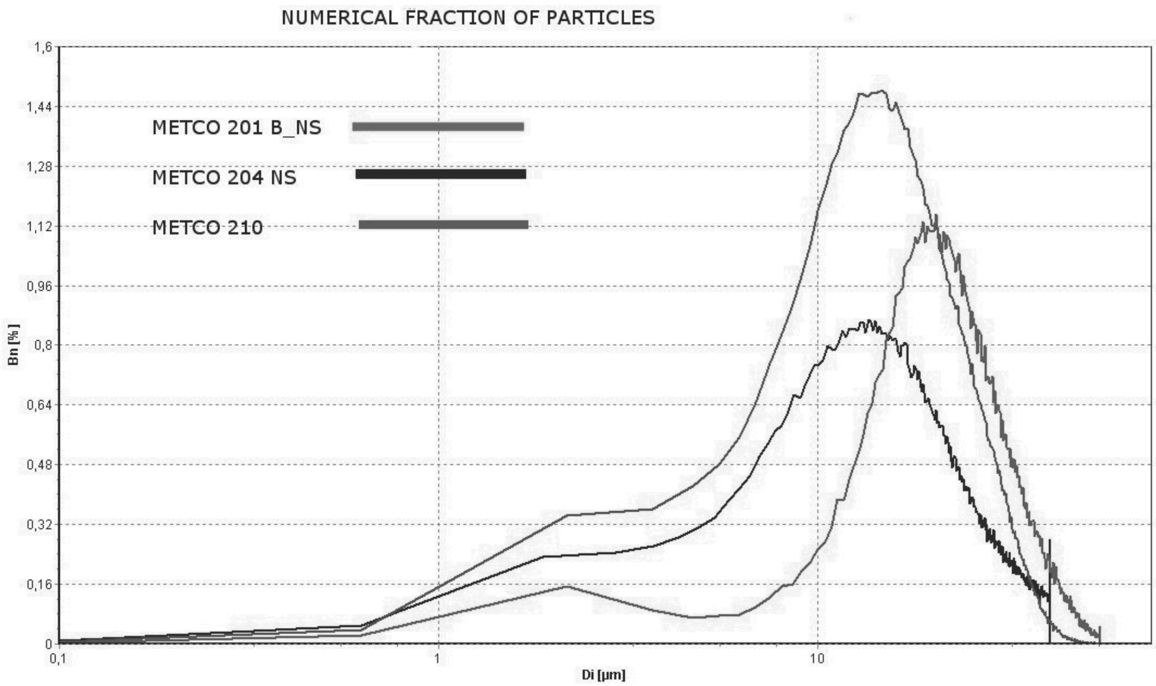

Fig. 3. Graining distribution for ceramic powders, which are used for LPPS-TF plasma spraying

Table 4.
Average grain distribution

Powder type	Average grain size(µm)
Metco 4451	10.3
AMDRY 997	11.0
Metco 201 B_NS	17.4
Metco 204 NS	16.8
Metco 210	23.0

2.1. Analysis of AMDRY 997 powder

This powder consists of multicomponent NiCoCrAlY alloy. Introduction of Co and Cr ensures lesser brittleness of the coating and introduction of tantalum increases oxidation resistance. According to information given by manufacturer, this kind of powder should ensure high oxidation and hot corrosion resistance. It is also used for plasma spraying under low pressure as well as using ultrasonic HVOF method. The powder is used, above all, as a bond-coat for thermal barrier coatings (TBC coating). Conducted morphology research proved, that the powder has, according to the manufacturer data, spherical shape (Fig. 4).

2.2. Analysis of Metco 4451

Metco 4451 is a CoNiCrAlY-type powder. According to the data given by manufacturer, size of the particle should be of -38 – +5.5 micrometers. This powder has spheroidal shape and is gas atomized. It was confirmed by observation made with a use of electron microscopy (Fig. 5). The powder can be applied during the plasma spraying process under low pressure. There are also available modifications of this powder, which are used for ultrasonic HVOF spraying and for plasma spraying under atmospheric pressure. The powder is used as a bond-coat for thermal barrier coatings (TBC).

2.3. Analysis of Metco 201

Metco 201 consists of zirconium oxide stabilized by calcium oxide (ZrO_2*5CaO) (Fig. 6). This powder was designed in order to increase the resistance to thermal shock and sulfur corrosion. Particles have irregular shape and were obtained during the grinding process. The purpose of calcium application is stabilization of zirconium oxide and minimization of possibility of formation of the phase transition in zirconium oxide. This powder is used for creating TBC coatings, which are applied in combustion chambers of the rocket- and turbine engines as well as other hot elements. It is also applied in metallurgy as protective layer for the crucibles. Metco 201 should provide, according to the manufacturer's data, resistance to erosion for the temperature above 845°C. It can be also used to increase the wear resistance for cylinders of the diesel engines and for the cylinder heads. Wetting resistance and corrosive effects of molten metal are features, which determine its application in metallurgy. This powder can be sprayed during APS as well as LPPS method. NiAl-, NiCr- or MCrAlY alloys should be used as bond-coats. The typical porosity should be of 5-10% and thermal conductivity of: 0.9-1.4 [W/mK]. The thermal expansion coefficient should be of 10 [Jm/m °C].

2.4. Analysis of Metco 204

Metco 204 is a typical powder made of zirconium oxide stabilized by yttrium oxide used for obtaining of thermal barrier coatings. This powder is characterized by spheroidal shape of particles (Fig. 7). Basically, its used for protection of element's surface of aircraft engines, such as transition piece (sealings, exhaust reheaters, thermal shields, turbine blades). It is also used in automotive industry ensuring the thermal protection in the temperature of 900°C in metallic elements of petrol - and diesel engines i.e. cylinder heads, piston heads, intake- and outlet valves, turbo-chargers. The powder should have an application ensuring erosion protection up to temperature of 1250°C, like other conventional YSZ powders, up to temperature of approx. 1350°C. The typical coating obtained during the plasma spraying process should be characterized by porosity of 8-20% and thermal conductivity between 0.8-1.3 [W/mK]. The value of thermal expansion coefficient shoulf be of 10 [Jm/m °C].

a)

b)

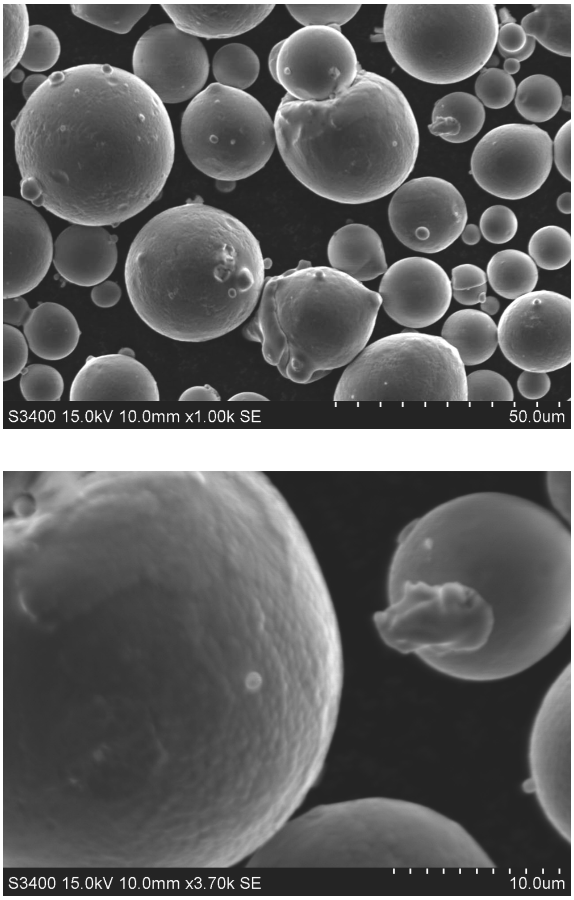

Fig. 4. Morphology of the AMDRY 777 powder

a) b)

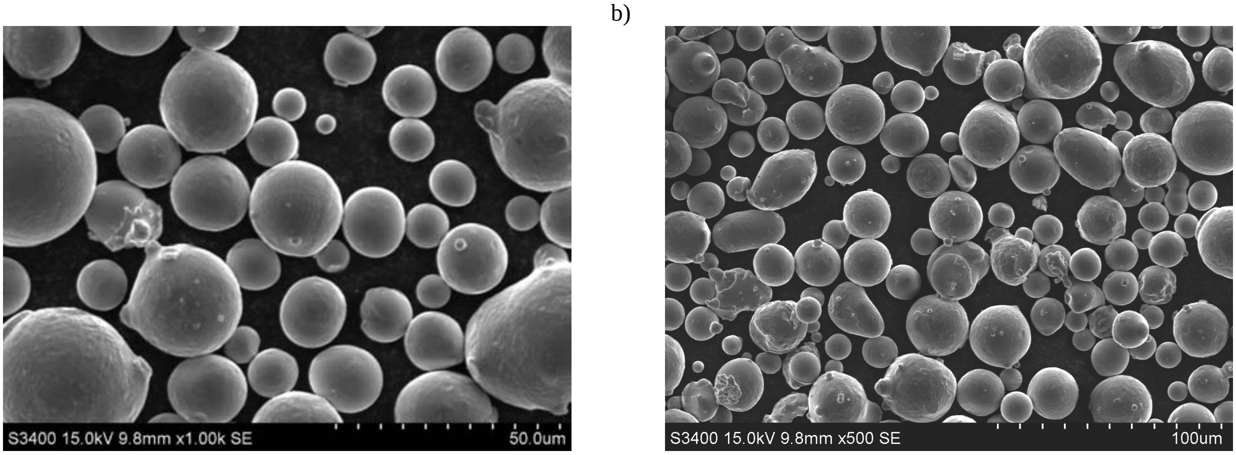

Fig. 5. Morphology of the Metco 4451 powder

a) b)

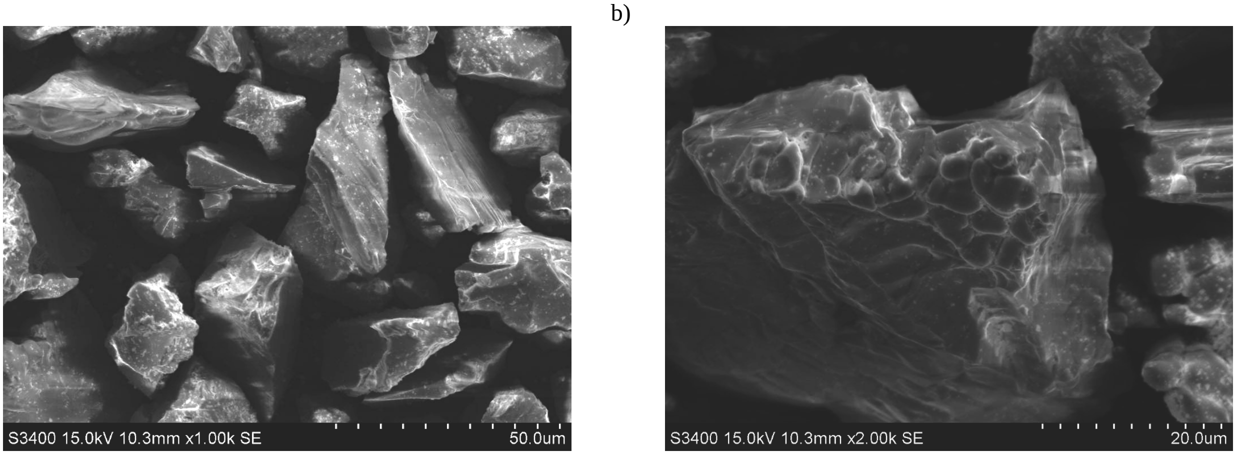

Fig. 6. Morphology of the Metco 201 powder

a) b)

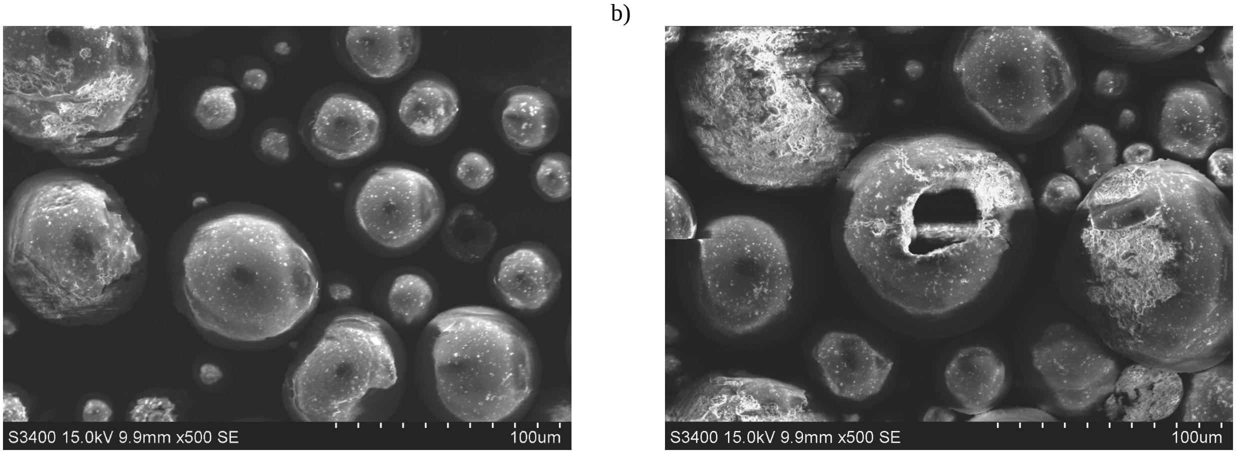

Fig. 7. Morphology of Metco 204 powder

a) b)

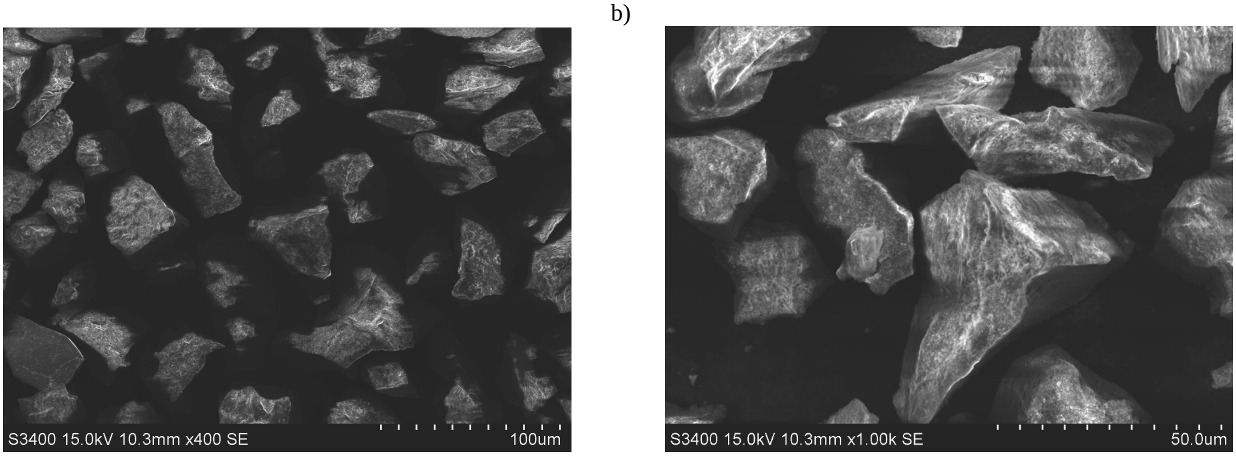

Fig. 8. Morphology of Metco 210 powder

2.5. Analysis of Metco 210

This powder is made of zirconium oxide stabilized by magnesium. It is characterized by low thermal conductivity and high melting point. It can be used as TBC coating under condition of high temperature. This powder, similarly to the Metco 201 powder, is characterized by irregular particles (submitted to crushing, Fig. 8). The coatings made of the Metco 210NS-1 powder are resistant to particle erosion in high temperature and to wetting using melted zinc, iron, steel, copper and aluminium. The basic applications of the powder are thermal barrier coatings for elements of aircraft engines and coatings used for coating of non-ferrous metals. TBC coatings are also used for rocket nose cone, in order to achieve erosion resistance in the temperature of over 845°C. They are also applied for equipment used in heat treatment and plastic working. The coating obtained form the described powder should be characterized by porosity between 5 - 8% and thermal conductivity between 1.0-1.5 [W/mK]. The coating hardness should be of 95 HRB - 31 HRC.

3. Summary

The authors analyzed materials used for plasma spraying under low pressure. By putting together the available data, the authors showed a possibility of using only approx. 30 types of standard powders recommended by manufacturer of LPPS-Thin Film device. Two types of powders used for MCrAlY bond-coats and three powders used to obtain the ceramic outer layer were chosen for morphology analysis. The metallic powders were characterized by spheroidal particle shape. The ceramic powders were characterized by irregular particle shape caused by grinding process. The only exception was Metco 204 powder, with spheroid-shaped particles. The ceramic powders were made of zirconium oxide, which was stabilized by different types of oxides: yttrium (Metco 204), calcium (Metco 201) and magnesium (Metco 210).

Powders analyzed in the article will be submitted to plasma spraying process with different methods. It will allow to assess influence of the oxide, stabilizing the yttrium oxide, on stability of obtained ceramic layer of TBC coating.

4. Conclusions

- The metallic powders were characterized by spheroidal particle shape. The ceramic powders were characterized by irregular particle shape caused by grinding process. The only exception was Metco 204 powder, with spheroid-shaped particles.
- The ceramic powders were made of zirconium oxide, which was stabilized by different types of oxides: yttrium (Metco 204), calcium (Metco 201) and magnesium (Metco 210).
- Powders analysed in the article will be submitted to plasma spraying process with different methods.
- It will allow to assess influence of the oxide, stabilizing the yttrium oxide, on stability of obtained ceramic layer of TBC.

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References

[1] X.Q. Cao, R. Vassen, D. Stoever, Ceramic materials for thermal barrier coatings, Journal of the European Ceramic Society 24 (2004) 1-10.

[2] R. Vaßen, M.O. Jarligo, T. Steinke, D. Emil Mack, D. Stöver, Overview on advanced thermal barrier coatings, Surface & Coatings Technology 205 (2010) 938- 942.

[3] C. Amaya, W. Aperador, J.C. Caicedo, P. Prieto, F.J. Espinoza-Beltrán, J. Muñoz-Saldaña, G. Zambrano, Corrosion study of Alumina/Yttria-Stabilized Zirconia (Al_2O_3/YSZ) nanostructured Thermal Barrier Coatings (TBC) exposed to high temperature treatment, Corrosion Science 51 (2009) 2994-2999.

[4] E. Garcia, J. Mesquita-Guimarães, P. Miranzo, M.I. Osendi, Crystallization studies in mullite and mullite-YSZ beads, Journal of the European Ceramic Society 30 (2010) 2003-2008.

[5] O. Fabrichnaya, M.J. Kriegel, J. Seidel, G. Savinykh, L.P. Ogorodova, I.A. Kiseleva, H.J. Seifert, Calorimetric investigation of the $La_2Zr_2O_7$, $Nd_2Zr_2O_7$, $Sm_2Zr_2O_7$ and $LaYO_3$ compounds and CALPHAD assessment of the La_2O_3-Y_2O_3 system, Thermochimica Acta, 2011 [in press].

[6] W. Ma, D. Mack, J. Malzbender, R. Vaßen, D. Stover, Yb_2O_3 and Gd_2O_3 doped strontium zirconate for thermal barrier coatings, Journal of the European Ceramic Society 28 (2008) 3071-3081.

[7] In situ small-angle neutron scattering study of $La_2Zr_2O_7$ and $SrZrO_3$ ceramics for thermal barrier coatings, Scripta Materialia 55 (2006) 545-548.

[8] C.G. Levi, Emerging materials and processes for thermal barrier systems, Current Opinion in Solid State and Materials Science 8 (2004) 77-91.

[9] S.A. Tsipas, Effect of dopants on the phase stability of zirconia-based plasma sprayed thermal barrier coatings, Journal of the European Ceramic Society 30 (2010) 61-72.

[10] A.N. Khan, S.H. Khan, F. Ali, M.A. Iqbal, Evaluation of ZrO_2-24MgO ceramic coating by eddy current method, Computational Materials Science 44 (2009) 1007-1012.

[11] P. Diaz, M.J. Edirisinghe, B. Ralph, Microstructural changes and phase transformations in a plasma-sprayed zirconia-yttria-titania thermal barrier coating, Surface and Coatings Technology 82 (1996) 284-290.