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Criteria of assessment of powders provided to spray by the APS method for new and conventional layers type TBC

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ABSTRACT

Purpose: Verification of up-to-now use of conventional powders, provided to spray by the APS method for layers type TBC and its possible adaptation to layers of new types, which are based on new ceramic compounds, sprayed on conventional high temperature creep resisting alloys. New types of used ceramic powders are so called pyrochlores of the $RE_2Zr_2O_7$ general formula.

Design/methodology/approach: A scope of investigations comprised review of up-to-now used criteria of assessment and verification of them on powders of new types. Investigations of chemical composition were realized, in consideration of carbon and sulphur contents and gas oxygen and nitrogen contents. Investigations on sizes of powders by a sieve method and investigations on surface morphology were carried out. Assessment of microstructure, considering homogeneity in chemical composition and porosity, was carried out. Assessment of phase contents of exemplary powders was carried out.

Findings: The carried out analysis enabled to compare criteria of assessment for two types of powders, provided to be sprayed by the APS method. It was stated that up-to-now used criteria of assessment of powders were correct also for materials of new types.

Research limitations/implications: The carried out investigations suggest a necessity to verify results also on an example of another type of new powders.

Practical implications: The got results reveal a possibility to use up-to-now procedures in assessment of powders for materials of a new type, completed with characteristics of physical and mechanical properties.

Originality/value: Information concerning basic principles in assessment of properties microstructure of powders of a new type is an original value, presented in the article.

Keywords: Metallic alloys, Thin&thick coatings; TBC; Powder characterization

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MATERIALS

1. Introduction

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. Generally, the TBC applied in gas turbines is made up of two components: a bond coat created by the vacuum or low pressure plasma-sprayed MCrAlY (M = Ni, Co) and a top coat of yttria and partially stabilized zirconia produced by the atmospheric plasma spraying or electron beam-physical vapour deposition (EB-PVD) [1-4]. A typical superalloy/TBC system consists of plasma-sprayed zirconia-yttria ceramic layer with a nickel-chromium-aluminium-yttrium bond coat on a substrate made of nickel-based superalloy. These superalloy/TBC systems can be applied in both aerospace and land-based gas turbine engines. In automotive use, the piston head for diesel engine is coated to enhance lifetime and performance as far as fuel demand reduction and power improvement are concerned. These coatings, nevertheless, exhibit relatively short lifetime, which is the result of the applied material and thermal contrast between the coating and the base metal [5-8].

The TBC coatings are produced the most often by a thermal spraying method with powders in the APS air atmosphere (Air Plasma Spray), at reduced pressure LPPS (Low Pressure Plasma Spray) or by the EB-PVD method (Electron Beam Physical Vapour Deposition). Barrier coatings on elements of combustion chambers and turbine guide vanes are made by thermal spraying methods by means of plasma guns, while moving blades are covered by application of the EB-PVD technology [9].

Zirconium oxide, modified with yttrium oxide (YSZ) is a main material of a ceramic layer. This material reveals a lot of required properties [10]:

- high melting point approx. 2700ºC;
- one of the lowest, among ceramics, coefficients of thermal conduction approx. 2.3 Wm^{-1}K^{-1}, decrease in temperature of substrate surface, increase in operation temperature and reduction in thickness of a ceramic layer;
- high coefficient of thermal expansion 11×10^{-6} ºC^{-1}, what reduces stresses resulting from differences in thermal expansion between metallic substrate and ceramic covering;
- low density – 6.4 g/cm^3, what enables to reduce mass of a turbine;
- low modulus of elasticity E=50GPa, what enables to reduce thermal stresses;
- high hardness approx. 14GPa, what makes the YSZ be a material resistant to erosion and impacts.

Although, the TBC barrier layers, which are based on ceramics type YSZ, have been used for 30 years, their life is a basic problem, because it limits wider application of them. There are many mechanisms, which destruct covering of such a type; nevertheless the following factors can be included to the most important:

- differences in thermal expansion between component elements i. e. between interlayer ceramics and metallic substrate;
- oxidation of substrate material (usually of nickel superalloys);
- changes in microstructure and chemical composition in individual elements of the TBC covering;
- degradation and phase changes in a ceramic layer;
- low resistance to the „*hot corrosion*" of the YSZ layer.

Considering very limited possibilities to increase operation temperature of gas turbines, what results from achieving similar operation parameters of turbines to a melting point of superalloys, one can state that development is necessary, from the one hand on high temperature creep resisting materials, on a base of high-melting metals, [11], and on the other hand materials, provided for a new type of thermal barriers, which are used to high temperature creep resisting alloys on a base of nickel and high-melting metals. Dependence, presenting influence of used materials at operation temperature of gas turbines and limitations resulting from material characteristics, are shown on Fig. 1.

The basic problem depends on production of a ceramic material, provided for an outer layer of thermal barriers (provided to be used in high temperature creep resisting alloys on a base of nickel and niobium as well), and this material is characterized by reduced thermal conduction, comparing to the YSZ, especially in high temperature, what enables to: [12]

- decrease temperature of metallic substratum surface, what increases life of turbine;
- increase operation temperature, what increases efficiency of a turbine.

A new type of a ceramic material should also reveal chemical stability in a contact with oxides, especially Al_2O_3 .

Intensive investigations are especially concentrated in this scope, on oxides type $RE_2Zr_2O_7$, which are characterized by the following specification of required properties [13]:

- thermal conduction less than 2.0 Wm^{-1}K^{-1};
- linear coefficient of thermal extension more than 10×10^{-6}C$^{\circ-1}$;
- max operation temperature higher than 1600°C;
- Young's modulus below 250GPa;
- hardness more than 6GPa;
- density below 7g/cm^{-3}.

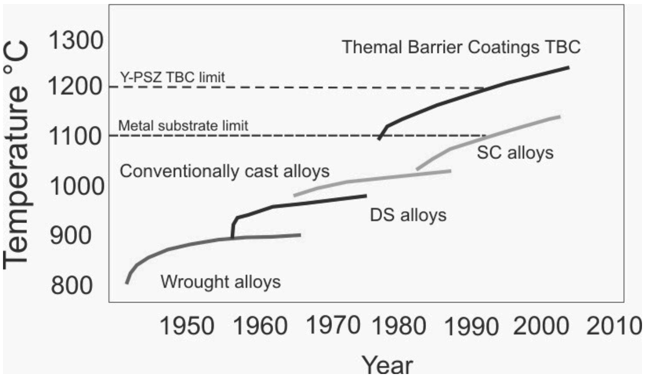

Fig. 1. Development of high temperature creep resisting materials and protective coverings [14]

Independent investigations led to a common conclusion that zirconates of rare-earths of a general formula $RE_2Zr_2O_7$, which crystallize in an ordered structure of pyrochlores, are the most promising group of materials to be used as the TBC ceramic layer. The carried out investigations proved that the $La_2Zr_2O_7$ compound (porosity 3%) demonstrated thermal conduction on the 1.6 Wm^{-1}K^{-1} level at a value 2.5 for the YSZ of porosity 8.8%. Usage of compounds type $M_2D_2O_7$, where M – Gd, La, Y, and D- Hf, Ti, Zr are proposed as well; a concept to use the same type of a compound, but where elements from lanthanoids' group from La to YB are the M components. Investigations on the Gd2Zr2O7 compound proved that in temperature 700°C, it had thermal conduction on the 1.3 $Wm^{-1}K^{-1}$ level at no porosity, while the same compound in a form of the EBPVD TBC barrier demonstrated thermal conduction on the approx. 1 $Wm^{-1}K^{-1}$ level. Now, in literature, there are data on thermal conduction of compounds on a base of pyrochlores. There is no information on systematic investigations in this scope. Nevertheless, accessible information shows that this group of materials demonstrates thermal conduction on the 1.5-1.6 $Wm^{-1}K^{-1}$ level, at porosity approx. 9-13%. Dependence between strength properties, related to density and analytical coefficient of thermal conduction and influence of a diameter of atoms A and B in compounds of the $A_2B_2O_7$ pyrochlore structure on thermal conduction, are shown in Figs. 2 and 3.

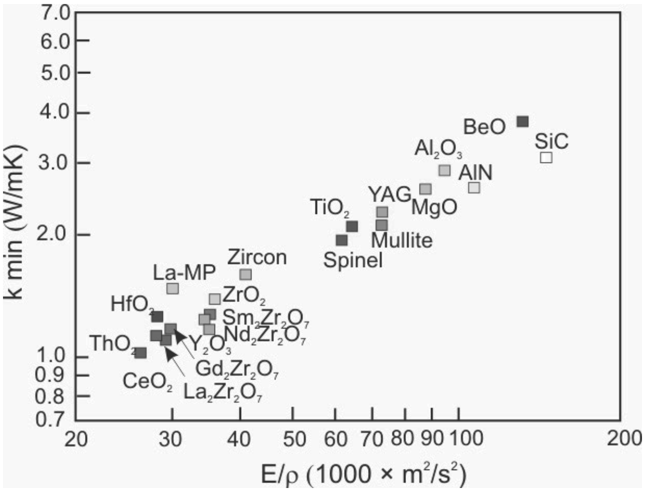

Fig. 2. Coefficient of thermal conduction in a function of the specific Young's modulus [15]

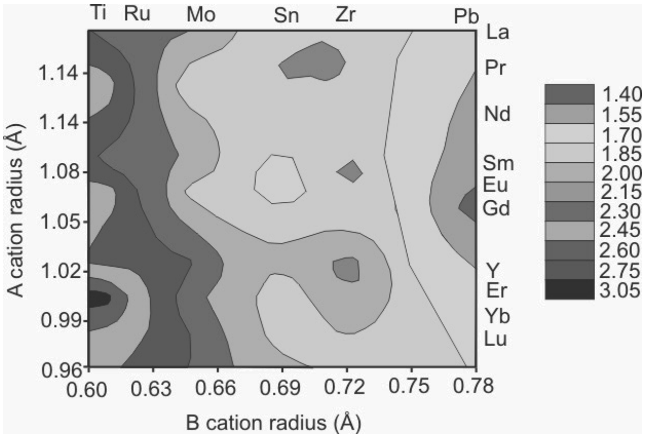

Fig. 3. Coefficient of thermal conduction in a function of the atomic radiuses of the elements A and B

In the last decade, investigations concentrated on:

- **zirconia modified with elements of rare-earths type $RE_2Zr_2O_7$ of pyrochlore structure,** - these materials demonstrate considerably low thermal conduction than the YSZ and high structural stability up-to temperature 1,500°C. Here, zirconia La, Gd, Nd, Sm, Eu are the most promising [16-18].
- **zirconates modified with elements of rare-earths type $RE_2Zr_2O_7$ of pyrochlore structure, modified with oxides of rare-earths, -** comparing to a basic material of pyrochlore structure, usage of doping enables to reduce more thermal conduction with preservation of stable properties and structure. Pyrochlores type $La_2Zr_2O_7$ doping 30% at. oxides Gd, Sm and Nd are the most effective [16-18].
- **oxides of fluorite structure e.g. CeO_2, HfO_2 and ThO_2,** - natural successor of the YSZ, also of structure of fluorite. However, compounds type $RE_2Ce_2O_7$, also of fluorite structure e. g. $La_2Ce_2O_7$ or $Nd_2Ce_2O_7$ seem to be more promising. They also demonstrate considerably less thermal conduction than the YSZ [12].
- **zirconium oxides stabilized with oxides other than yttrium oxide e. g. MgO, CaO, RE-O, HfO_2, CeO_2** – use of modification of zirconium oxide, in a form of metal oxides on the +2, +3 and +4 oxidation state, enabled to increase structural stability of a cubic and tetragonal phase to ambient temperature. It prevents to transform from a tetragonal phase into monoclinic phase, what could lead to appear micro-cracks in a result of change in volume of a unit cell. Mechanism of stabilization is related with introduction, to structure of zirconium oxide, of some additional oxygen vacancies, what together with density of point defects, while this density is generated by a dopant e. g. yttrium oxides (and reduction in mean distance between defects is a result of it), improves required thermal properties. Systems of zirconium oxides with oxides: Pr, Nd, Sm, Er and Sc were tested [12, 19].
- **zirconium oxides modified with two different additives e. g. CaO-CeO_2-ZrO_2,** - in this investigative area it was expected that use of more than one modifier considerably will improve thermal properties. Satisfying results were got, when calcium oxides and cerium oxides were used. Systems with yttrium oxide, cerium oxide, scandium oxide and multi-component systems were investigated as well type YSZ-Nd, -Yb, -Nd,Yb, - Gd,Yb,- Sm, Yb. It was stated that lowered thermal conduction had been observed only at contents of dopants approx. 6-15% for methods of plasma spraying [20].
- **other materials on a base of zirconium oxides –** from a point of view of improvement in corrosion resistance in environment of sulphur and vanadium, some materials were proposed on the $20YTaO_4Z$ base – tetragonal zirconium oxide, modified with tantalum oxide and yttrium oxide and orthorhombic zirconium oxide with addition of tantalum oxide 14TZ [21].
- **materials not comprising zirconium oxides** – among this group of materials so called garnets ($Y_3Al_xFe_{5-x}O_{12}$), LHA of structure of magnetoplumbit $LaMgAl_{11}O_{19}$, $LaPO_4$ were tested. All other materials demonstrate relatively low thermal conduction but they are not competitive for pyrochlores [21].
- **nanocrystalline and amorphous materials** – low structural stability, related to tendency of grain coarsening and crystallization is a basic problem within this group of materials, what in an effect leads to lose its input advantages [15].
- **gradient layers, including DCL (double ceramic layer)** - concept of multi-layer barriers (gradient layers) is especially useful from a point of view of resistance of thermal shocks. It

enables to produce a system consisting of a layer, which is resistant to erosion, as an outer covering, barrier layer, layer resistant to oxidation and diffusive zone. Coverings type YSZ-$La_2Zr_2O_7$ are tested in this group [15].

2. Criteria in assessment of performance properties of powders provided for layers type TBC

Application of new ceramic powders, of different physical properties, requires verification of adequacy and usability of up-to-now criteria of assessment, which were used up-to-now for conventional powders on a base of oxides type YSZ, and especially ones, which are related to technological parameters of a process of thermal spraying.

Detailed characteristics of powders, provided to thermal spraying, should comprise the following:

- characteristics of chemical and phase composition:
  - analysis of contents of gas oxygen and nitrogen;
  - analysis of contents of carbon and sulphur;
  - micro-analysis of chemical composition;
  - quality analysis and quantity analysis of phase composition;
- characteristics of sizes of powders:
  - results of analysis of sizes of powders, including e. g. sieve analysis;
  - statical characteristics, which describes distribution of sizes of powders;
- characteristics of morphology of powders:
  - investigations on powders by use of scanning microscopies, which characterize surface of them;
  - investigations on powders on metallographic micro-sections;
- characteristics of technological properties:
  - results of measurements of density: true, bulk, tapped and untapped density;
  - results in assessment of flow rate of powders;
  - assessment of preservation of powders in spraying conditions;
  - efficiency during spraying procedure;
- characteristics of physical and mechanical properties:
  - results of tests of thermal properties:
    - diffusiveness and thermal conduction,
    - coefficient of thermal expansion,
  - modulus of elasticity E;
  - hardness.

3. Exemplary results of criterion assessment of quality of conventional and new powders, provided to spray the TBC layers

In this section, there are presented some exemplary results, got during quality and microstructural assessment of powders on a base of zirconium oxide (YSZ) and powders of a new type on a base of zirconia of rare-earths.

Table 1.
Results of analysis of chemical composition of analysed powders

Weight %	$ZrO_2x8Y_2O_3$	$Gd_2Zr_2O_7$
Gd	-	59,7
Zr	63.9	28.5
Y	6.10	0.068
Al	0.17	0.088
Si	<0.10	<0.10
Cu	<0.01	<0.01
Ti	0.067	<0.005
S	0.004	0.002
C	0.018	0.006

Table 2.
Results of analysis of contents of gas nitrogen and oxygen in analysed powders

	$ZrO_2x8Y_2O_3$	$Gd_2Zr_2O_7$
N	101 ppm	311 ppm
O	12.9 %	8.8 %

The first stage of investigations comprised an analysis of chemical composition and phase composition of powders in a delivery state. Powders of types $ZrO_2xY_2O_3$ and $RE_2Zr_2O_7$ underwent tests. Results of analysis of chemical composition of these powders are shown in Table 1. Results of comparative analysis of contents of gas components in powders are shown in Table 2.

As a mean value of chemical composition says nothing on inhomogeneity in distribution of components in powders, so it is necessary to recognize distribution of alloy components in individual particles (Figs. 4 and 5, Table 3 and 4).

Got results demonstrate the high homogeneity of chemical composition of tested powders in an input state. Structures of high porosity and „granularity" are visible. In a case of standard powder, individual particles in powder have a similar colour and morphology. Presence of areas of very fine structure of particles and very low density were stated. Observed inhomogeneity was local and related mainly to different yttrium contents.

Table 3.
Results of micro-analysis of chemical composition of powder $ZrO_2x20Y_2O_3$ (Fig. 4)

Weight %	Y	Zr
pt1	5.80	94.20
pt2	13.75	86.25
pt3	19.01	80.99
pt4	27.64	72.36

Table 4.
Results of micro-analysis of chemical composition of powder $Gd_2Zr_2O_7$ (Fig.5)

Weight %	Zr	Gd
pt1	13.42	86.58
pt2	80.88	19.12

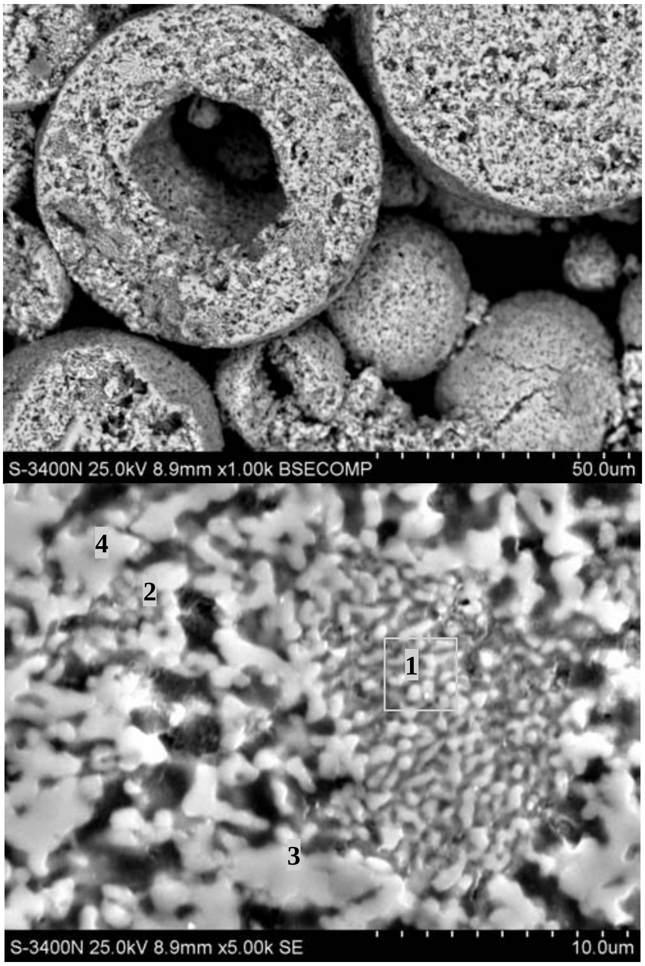

Fig. 4. Microstructure of powder type $ZrO_2x20Y_2O_3$

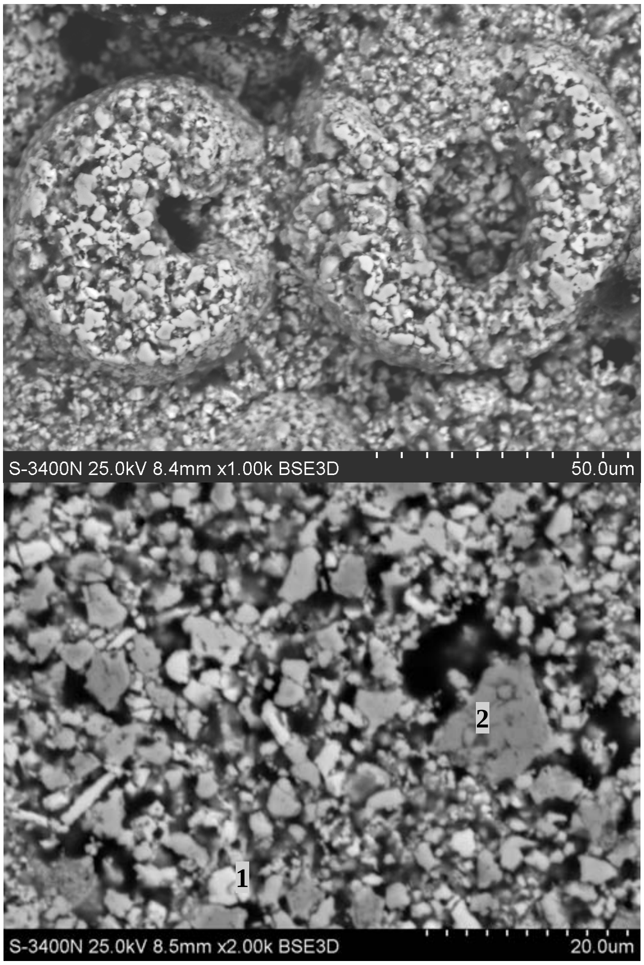

Fig. 5. Microstructure of powder type $Gd_2Zr_2O_7$

Areas of structure of very fine particles demonstrated relatively very low contents of yttrium, which is approx. 6% pursuant to (Pt.1). Area 2, similar in construction, but of considerably less area, demonstrated contents of yttrium approx. 14%. In other points, contents of this element were considerably higher.

Similar structure, considering morphology, was observed also in the second case of new powder type $Gd_2Zr_2O_7$. Equally as conventional powder, a new material was constructed of agglomerates of different particles of a size approx. some microns and particles of sizes approx. 10μm. However, contrary to the YSZ, the observed particles have got entirely different colour, what demonstrates less homogeneity of chemical composition.

The carried out micro-analysis of chemical composition showed that bright particles comprised mainly gadolinium and darker particles comprised zirconium.

Higher „coarse-granularity" is distinctly visible and it occurs in zirconia powder of a new type. Individual particles are considerably bigger than in a case of standard powders. Strong porosity and presence of voids inside powders are visible, what demonstrates its original agglomeration and sintering.

Table 5.
Results of quality and quantity Roentgen analysis of phase composition of tested conventional powders and of a new type

Weight %	$ZrO_2x20Y_2O_3$	$Gd_2Zr_2O_7$
ZrO_2 – T	67	3
ZrO_2 – M	30	
ZrO_2 – C	3	
$Gd_2Zr_2O_7$		72
Gd_2O_3		25

In order to get a precise assessment of phase composition, the Roentgen analysis of phase composition was carried out. In order to determine quantity participations of individual components, the Ritveld method was used. This method proved presence, in a case of YSZ powders, of three crystallographic forms of the ZrO_2 phase, what could prove high homogeneity of chemical composition. Investigations on new powder proved three kinds of phases. Besides a dominating phase type $Gd_2Zr_2O_7$, some oxide phases ZrO_2 and Gd_2O_3 were also stated, what occurred as reflection in construction of powders in a form of mixture of different phases.

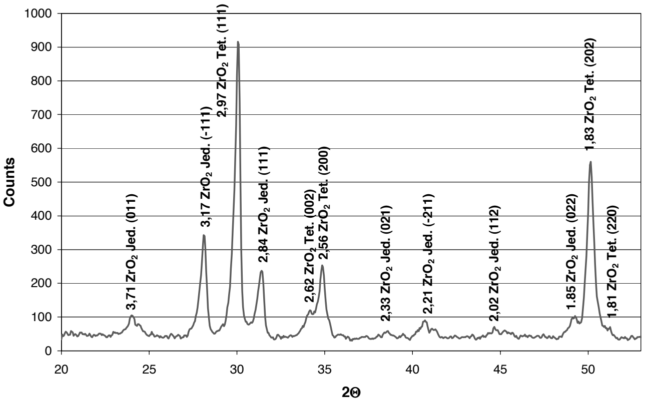

Fig. 6. Roentgen diffraction of powder type $ZrO_2x20Y_2O_3$

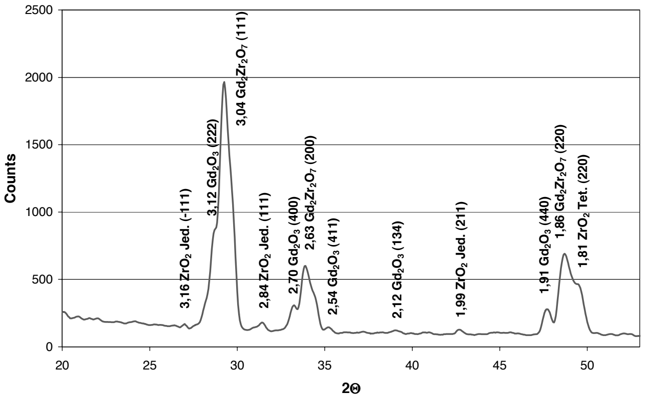

Fig. 7. Roentgen diffraction of powder type $Gd_2Zr_2O_7$

The got results are shown in Table 5. They demonstrate dominating participation of main components of powders i. e. respectively of the ZrO_2 phase of tetragonal structure and $Gd_2Zr_2O_7$ phase.

Quantity characteristics, of sizes of powders, is the next basic criterion in assessment of usability of the powders to a process of thermal spraying. In order to define distribution of sizes of particles, e. g. a sieve analysis is used. Sieves are stacked ("nested") with the largest apertures at the top and the smallest at the bottom. A sample of powder is placed on the top sieve and shaken for a fixed period of time at a given amplitude and pulse frequency. The weight of powder on each sieve can then be calculated and the particle size distribution obtained. Particles must have two dimensional profile smaller than the sieve aperture in order to pass through a particular sieve. A mean sieved diameter is calculated. Since the weight of particles on each sieve is determined the mean sieved diameter represents a mass distribution. The sizes of the apertures in each sieve are denoted by a mesh number. The mesh number is the number of wire strands (of constant diameter) per inch used to weave the square mesh pattern. The side length of the aperture in microns is inversely related to the mesh number. An exemplary distribution of sizes of the $Gd_2Zr_2O_7$ powder, got by a sieve method, is shown in Fig. 8. Percentile distribution of sizes of particles in shown in Fig. 9.

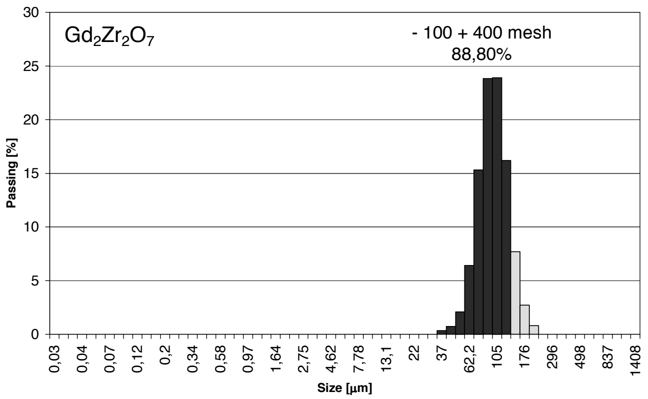

Fig. 8. Statical distribution of graining of powder type $Gd_2Zr_2O_7$

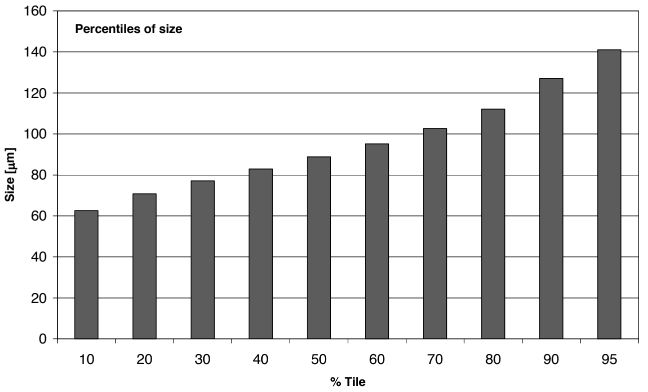

Fig. 9. Percentile distribution of powder type $Gd_2Zr_2O_7$

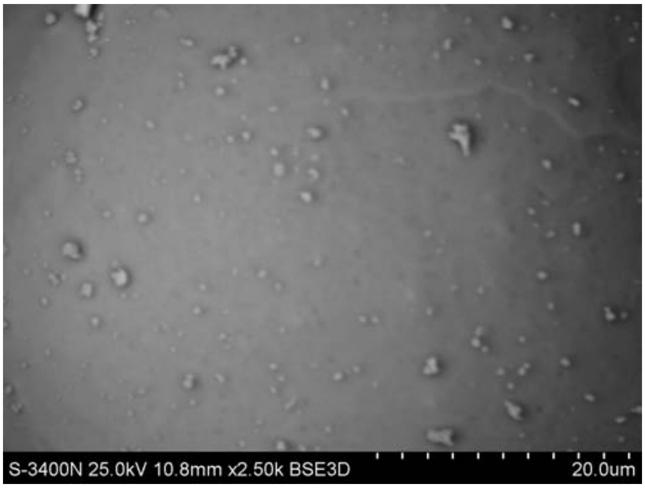

Fig. 10. Morphology of surface of powder type $ZrO_2x20Y_2O_3$

A characteristic of surface morphology is the next stage in criterion assessment of powders. Powders shape is unerringly controlled by the production process and determines the material transport from the powder hopper to the spray torch. The powders surface textures have quite different characteristics, depending on the production method as well. Thus, determination of this characteristic is essential. The ideal particle morphology is spherical, although needle-like and platelet forms are of interest since they may confer special properties to the coating. From flow capability point of view the most perfectly flowing material would be monosized and have smooth surface. Exemplary microphotographs of powder surface id shown in Figs. 10 and 11.

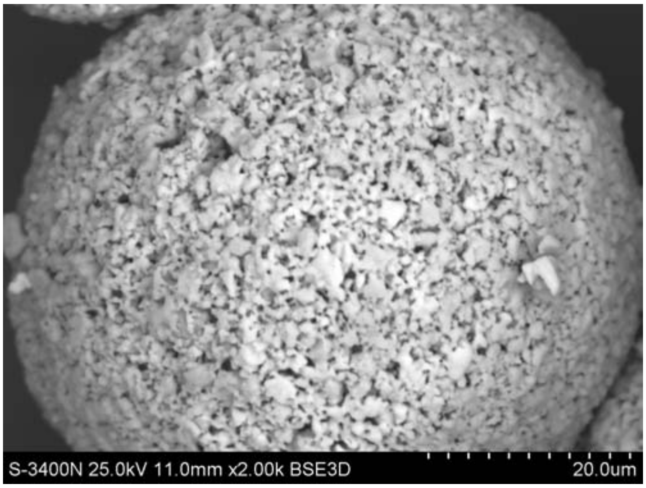

Fig. 11. Morphology of surface of powder type $Gd_2Zr_2O_7$

Table 6.
Results of measurements of density and angle of repose

	Angle of Repose [°]	Bulk Density [g/ml]	Tapped Density [g/ml]	Untapped Density [g/ml]
$Gd_2Zr_20_7$	31	1.78	2.07	1.78

Density of powders and their “flow rate” are the next parameters in assessment. In a case of density, several parameters can be used to describe the density. The true density (ρt) of a powder sample is the weight per unit volume of the material with no air spaces between particles. Therefore, if a material has a true density of 1 g cm^{-3}, 100 g of material will occupy 100 mL assuming individual particles fit together exactly. In practice most powders do not fit together very well. Therefore, if one fills a graduated cylinder to 100 mL with a powder, the weight of powder required may only be 70 g. This apparent density is known as the bulk or expanded density (ρb, 0.7 g cm^{-3}). If the100 mL cylinder is then tapped, the particles slide past each other and become consolidated. The 70 g of particles which once occupied 100 mL may now only occupy 80 mL. They have an apparent packed or tapped density (ρp) of 0.875 g cm^{-3}. Measurement of an angle of repose is the simplest in a case of measurement of flow rate of powder. The angle of repose (sometimes incorrectly confused with the 'Angle of Internal Friction') is an engineering property of granular materials. The angle of repose is the maximum angle of a stable slope determined by friction, cohesion and the shapes of the particles. When bulk granular materials are poured onto a horizontal surface, a conical pile will form. The internal angle between the surface of the pile and the horizontal surface is known as the angle of repose and is related to the density, surface area, and coefficient of friction of the material. Material with a low angle of repose forms flatter piles than material with a high angle of repose. In other words, the angle of repose is the angle a pile forms with the ground. Results of measurements of density and angle of repose are show in Table 6.

Selected results of investigations on thermal properties will be introduced in other articles, published on the AMME2009 Conference [22].

4. Summary

- The worked out analysis of results in investigations of mechanical, thermal, technological and microstructural properties, carried out on conventional and new powders, which are provided to get layers type TBC by the APS method, proved that used methods and criteria in assessment of powders and provided to assess conventional materials on a base of zirconium oxides, is actual for materials of a new type on a base of zirconates of rare earths.
- Equally, as in cases of standard materials, technological properties, which were defined during industrial tests, have essential importance.
- Besides the standard criteria concerning powders, this assessment should consider a final effect as well, i. e. the TBC coverings, which were got in a result of spraying of new powders [23, 24]. The architecture of pores and cracks, adhesiveness and integrity of got layers and their phase composition have got the essential importance
- In a case of application of powders of a new type, working out their material characteristics, essential from a point of view of expected requirements, has got essential importance, what concerns especially technological properties and thermal and mechanical properties themselves and TBC layers as well, after having been sprayed over.

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