Arch. Metall. Mater., Vol. 61 (2016), No 2B, p. 1121–1128

DOI: 10.1515/amm-2016-0188

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SYNTHESIS AND CHARACTERIZATION OF THERMAL PROPERTIES OF TYPE Eu_2O_3-ZrO_2 SINTERS

The oxides with pyrochlore or defected fluorite structure are a potential alternative ceramic materials for now widely used yttria-stabilized zirconia 8YSZ in the application for the insulation layer of thermal barrier coatings systems. This paper presents a procedure of synthesis of europium zirconate of $Eu_2Zr_2O_7$ type, by the method of high temperature sintering under pressure. The analysis of the effect of the powders` homogenization methods on homogeneity of final sintered material showed that the highest homogeneity can be obtained after mechanical mixing in alcohol. Moreover, the DSC investigation carried out on a mixture of powders before the sintering process and on the material after high temperature sintering under pressure, suggest the synthesis of a new phase an europium zirconate $Eu_2Zr_2O_7$ with the pyrochlore structure. Obtained phase was characterized by stability over the entire range of tested temperature, i.e. to 1450°C. The resulting material based on europium zirconate has a lower coefficient of thermal diffusivity than the now widely used 8YSZ.

Keywords: pyrochlores, europium zirconates, thermal diffusivity, TBC

1. Introduction

Gas turbines installed in airplane engines work in one of the most aggressive environments. These elements are exposed to high mechanical stresses and high temperature of exploitation, and are exposed to the influence erosion and corrosive media. Those forces the continuing need to modernize and improve the material and technological solutions [1-5]. In recent years widely promoted is the development of new thermal barrier coatings (*TBC*) systems, based on ceramic materials having the structure of pyrochlore type. Pyrochlore unit cell can be perceived as eight elementary cells of fluorite, each of which comprises, on average, a single oxygen vacancy. The stoichiometric general formula of pyrochlore structure is $A_2^{3+}B_2^{4+}O_7$, where A – are usually rare earth metals, and B – transition metals. The most promising materials in this group proved to be zirconates of La, Gd, Nd, Sm and Eu [6-7]. Compounds of the pyrochlore structure $RE_2Zr_2O_7$ are characterized by a lot of desirable properties, among others: very low coefficient of thermal conductivity, below 2,0 W/mK; high coefficient of thermal expansion above 10^{-5} °C^{-1} and working temperature up to 1600°C [8-10].

2. Research methodology

The studies were used nanocrystalline powders of zirconium oxide ZrO_2 provided by (Hefei EvNano Technology Co., Ltd.), and europium oxide Eu_2O_3 (Inframat Advanced Materials, LLC). The powders were weighed in the weight ratio of 1:1, which gives the mole ratio of ZrO_2 to Eu_2O_3 as 74% to 26%, with an excess of zirconium oxide as to the stoichiometric pyrochlore structure, which mole ratio is 67% to 33% (Fig. 1). The aim of such selection the composition was to get acquainted with the mechanism of synthesis and identification of intermediate phases.

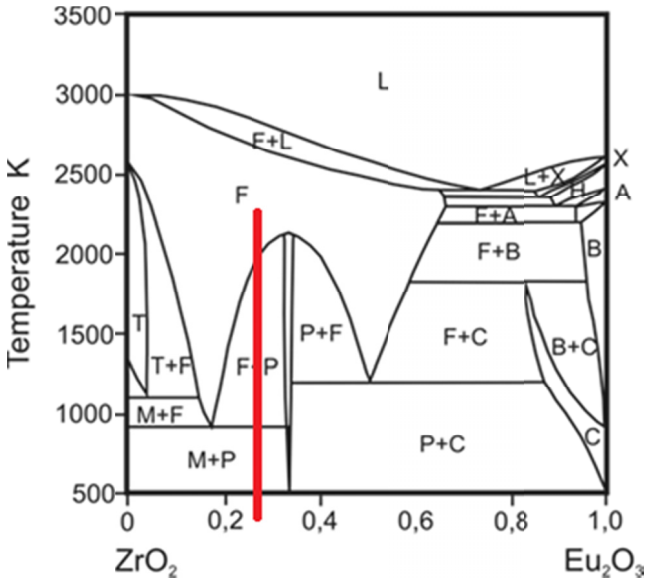

Fig. 1. Binary system of ZrO_2-Eu_2O_3 (mol. %) [5]

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In the next step, powders were homogenized by four methods, identified in the order DM, MA, USA, MUA:

- DM – dry mechanical mixing;
- MA – mechanical mixing in alcohol;
- USA – ultrasound-assisted mixing in alcohol;
- MUA – mechanical mixing in alcohol with additional ultrasound-assisted mixing in alcohol.

The investigation was carried out also on materials obtained using high temperature sintering under pressure (HTSP). HTSP process was realized in high temperature vacuum press by Degussa. The sintering temperature was 1350°C with the time of process – 2h. The compaction pressure was 15 MPa and whole sintering process was carried out in vacuum (10^{-2}Tr). Furthermore, X-ray phase analysis by XRD method (X-ray diffraction, Jeol JDX-7S) was also carried out both on starting oxides and in all final sintered materials. On this basis, the analysis of homogeneity of obtained compound $Eu_2Zr_2O_7$ was made. Moreover, microstructure observation, by scanning electron microscope (*SEM*), was made. This investigation were made on the Hitachi 3400N scanning microscopy. The observation by light optical microscopy (*LOM*) method was carried out using Olympus SZX9 microscopy. Calorimetry studies were performed on the DSC 404 F1 Netzsch apparatus. The study of thermal diffusivity was performed on the device type LFA 427/4/G by Netzsch.

3. Results

First step of investigation was related with the analysis of phases composition of initial materials as well as a final sinters. Fig. 2a shows the XRD pattern of ZrO_2 oxide where only zirconia with monoclinic (M) crystal system was detected. Fig. 2b shows the XRD pattern of Eu_2O_3 oxide with dominated cubic crystal system (C) and the residue of monoclinic phase (M) with the same chemical composition. Morphological characterization of materials used was showed in the next figures, where in Fig. 3a the morphology of ZrO_2 powder was showed. Zirconia powder is generally built from conglomerates of nanosized nearly spherical particles. In the case of Eu_2O_3 (Fig. 3b), it can be observed the particles with form of polyhedron. Their structure is built from conglomerates of nanosized nearly spherical particles such as in the case of ZrO_2.

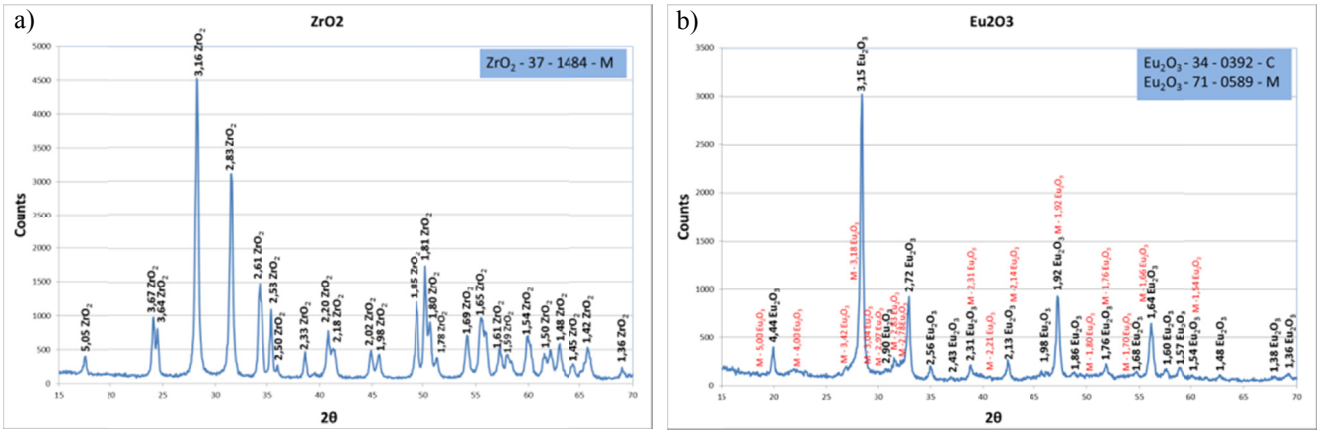


Fig. 2. XRD pattern of based ZrO_2 and Eu_2O_3 oxides

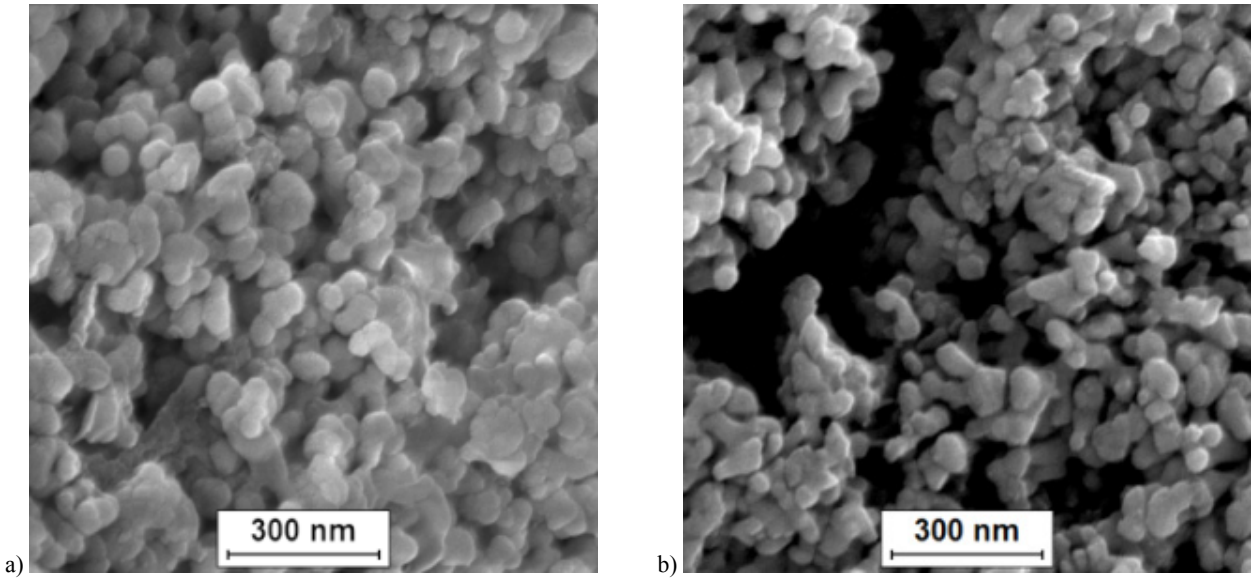


Fig. 3. Morphology of based ZrO_2 and Eu_2O_3 oxides (SEM)

The next step of investigation was related to the characterization of sintered materials. The first criteria of evaluation was the LOM analysis of the microstructure sintered materials. This investigation revealed that the method of homogenization of the starting powders significantly influenced the homogeneity of investigated sintered materials (Fig. 4). The lowest phase homogeneity was detected in the case of material obtained by DM mixing method of based powders. From the other site the best homogenization proceeded in the case of material obtained by MA method of powders mixing. Other methods preparation mixture of powders such as USA and MUA, also showed a high level of heterogeneity of the structure. The reason of this situation can be inaccurate homogenized the volume of sintered powder. At the time of sintering occurs to exhaustion one of the reagents which resulted in impossibility of synthesis progress in entire volume.

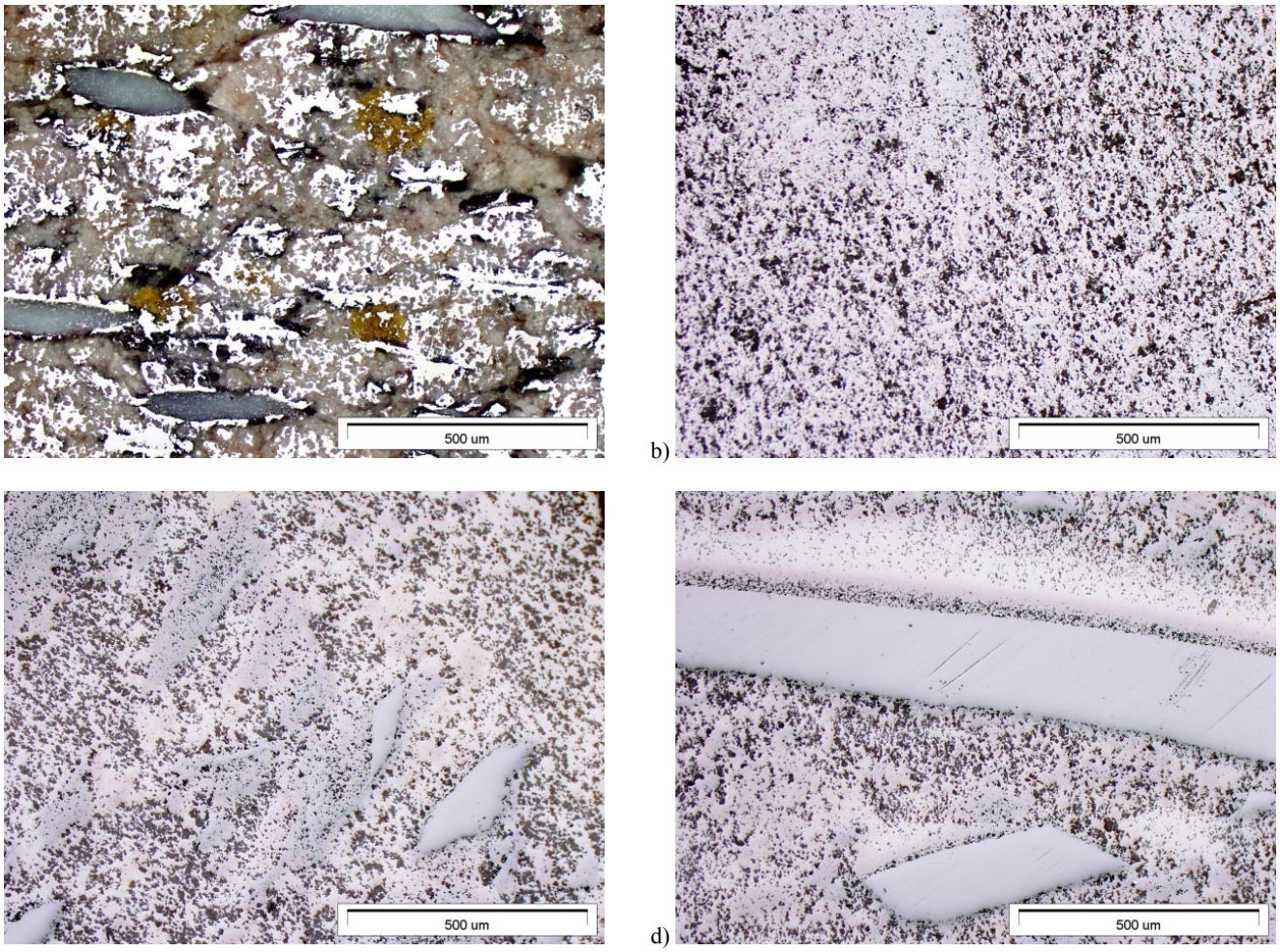
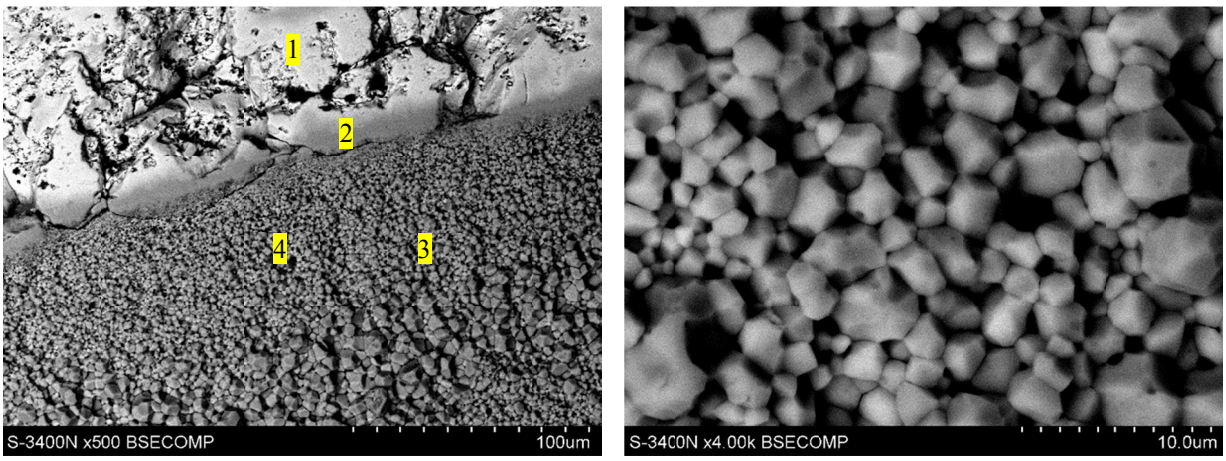


Fig. 4. The microstructure of final sintered materials, homogenized by different methods

The second method of materials criterial analysis and description of theirs homogeneity or inhomogeneity was structure investigation using scanning electron microscopy (SEM) equipped with EDS. SEM observation and EDS analysis showed a strong effect of chemical elements segregation, in the entire volume of investigated materials, in the case of sintered materials which was homogenized by DM method (Fig. 5) and much lower range of segregation in the case of material which was homogenized by MA method (Fig. 6).

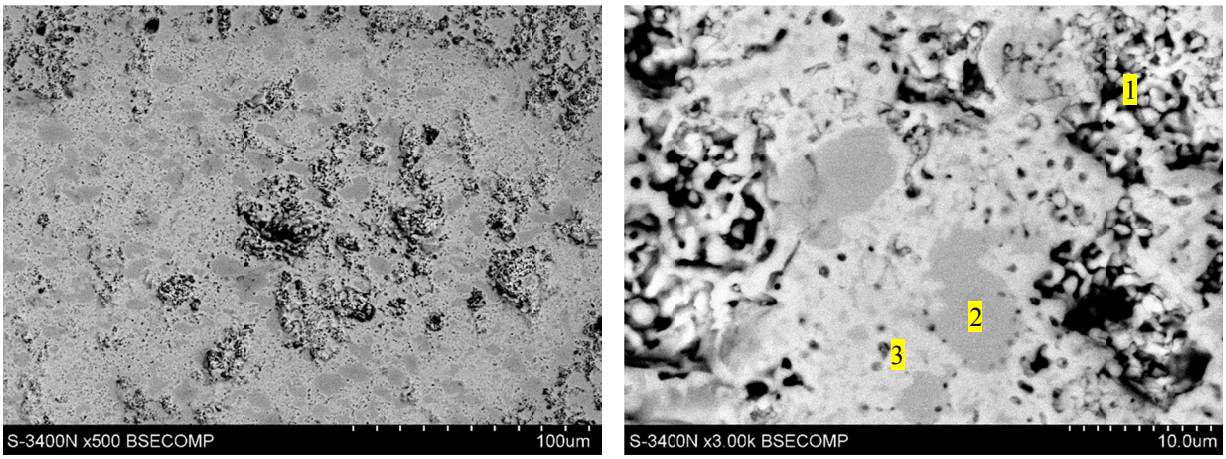
The detailed analysis of sintered material obtained by initial DM method of mixing revealed the different morphological elements can be observed in the microstructure. Generally the microstructure was porous in the highest level in areas where "pure" zirconia were detected (visible as a cubic or polyhedron structure). These areas, forming regular blocks are the weakest places in europium oxide. From the other site the microstructure of the sintered material homogenized by MA method is the most homogenous. However, there are also the ZrO_2 – rich areas, identify by the EDS analysis. The sintered materials, which were homogenized by USA and MUA methods, are also characterized by high segregation of the basic elements and in those cases different morphological areas can be observed (Figs. 7 and 8). But in comparison to DM materials the areas similar to initial zirconia, observed at Fig. 5, were no detected.

The next investigation was calorimetry characterization of initial powders mixed by four different methods as well as the materials after HTSP process. Analysis of calorimetric curves of powders prepared by various method of homogenization were showed at Fig. 9. This analysis doesn't allow clearly stated the fact of occurring synthesis a new compound $Eu_2Zr_2O_7$. However, it has



Area	% at.	
	Zr-L	Eu-L
pt1	57.0	43.0
pt2	91.0	9.0
pt3	93.6	6.4
pt4	94.3	5.7

Fig. 5. Internal morphology of sintered material homogenized by DM method (SEM)

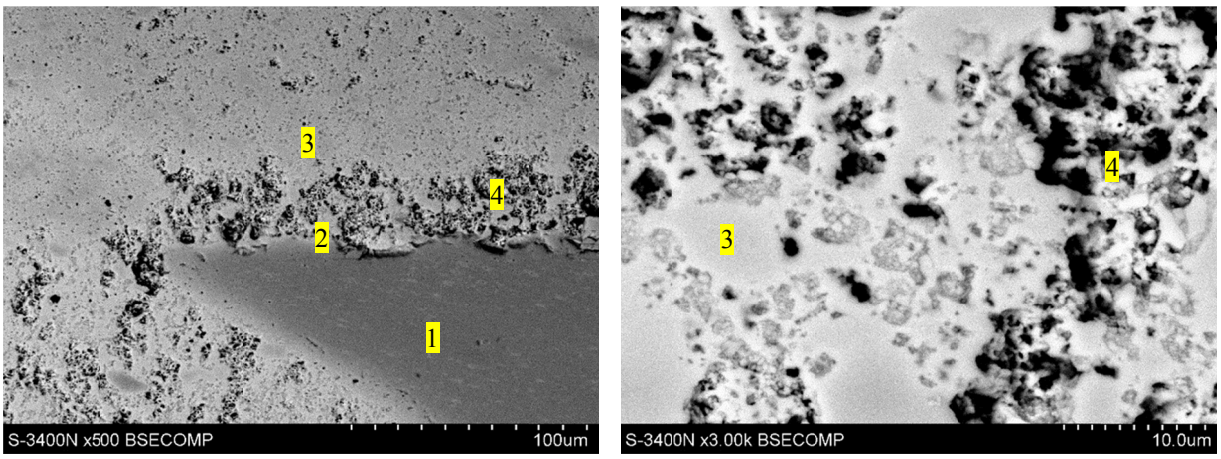


Area	% at.	
	Zr-L	Eu-L
pt1	57.1	42.9
pt2	67.9	32.1
pt3	57.8	42.2

Fig. 6. Internal morphology of sintered material homogenized by MA method (SEM)

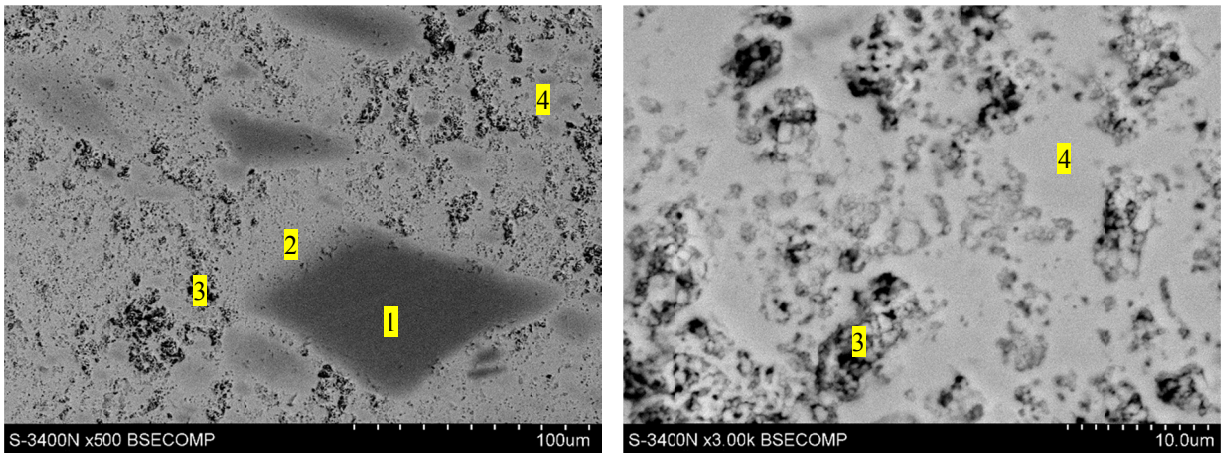
already been observed the lack of peak from a reverse phase transformation of tetragonal ZrO_2 to the monoclinic form during cooling, for powders homogenized by MA, USA, MUA methods, and very low intensity peak for the powder obtained by DM method (2,64 J/g). The second important information is related with the presents of a sharp decline of calorimetric curve probably due to so called "parasitic heat capacity". From the other site this phenomenon could be related with the reduction of thermal conductivity in tested materials due to the formation of a new phase with lower thermal conductivity – for examle some types of europium zirconates.

Calorimetric curves of sintered materials obtained during HTSP process (Fig. 10) confirm the possibility of new phases formation. The character of obtained heat flux curves revealed that this phase is stable in the entire temperature range of investigation. In sintered materials, which were prepared by MA, USA and MUA methods, the DSC curves showed that probable



Area	% at.	
	Zr-L	Eu-L
pt1	91.3	8.7
pt2	66.0	34.0
pt3	58.7	41.3
Pt4	46.3	53.7

Fig. 7. Internal morphology of sintered material homogenized by USA method (SEM)



Area	% at.	
	Zr-L	Eu-L
pt1	88.1	11.9
pt2	62.1	37.9
pt3	48.7	51.3
Pt4	52.2	47.8

Fig. 8. Internal morphology of sintered material homogenized by MUA method (SEM)

there was no "new" phase transformation. Only in the material prepared by DM method has the endothermic peak (–11,85 J/g) at temperature 961°C during heating and the exothermic peak (31,93 J/g) at temperature 1273°C during cooling were visible. Those peaks may be derived from monoclinic to tetragonal phase transformation of ZrO_2 which in this case has not fully reacted.

The last part of analysis was dedicated to characterization of phase constituents of final sintered materials. These investigations should got information about phenomena observed during calorimetric investigations of mixed powders and sintered materials. The XRD patterns from sintered materials showed strong differences in phase constituents depended on mixture preparation method (Fig. 11). The most homogenous material,

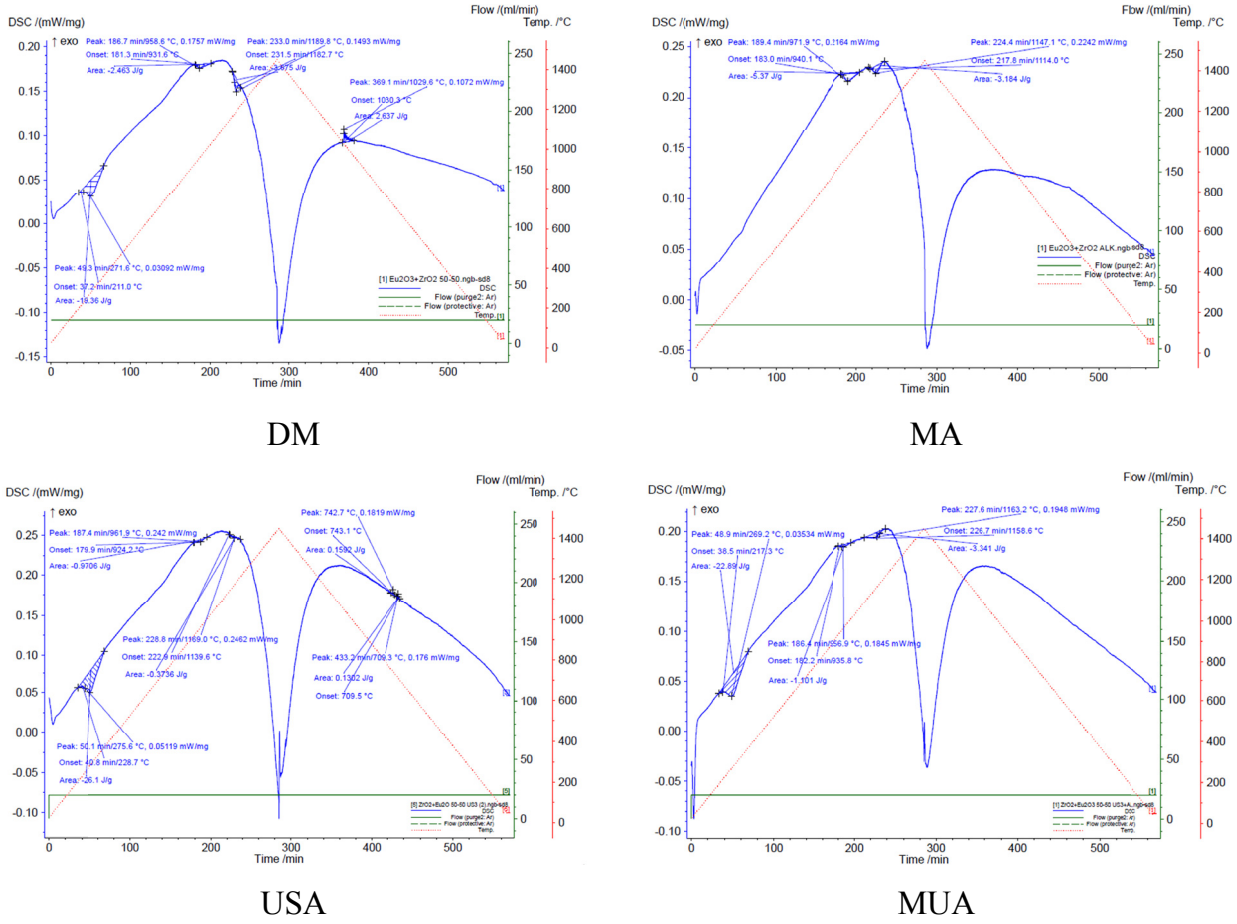


Fig. 9. The DSC curves of based powders mixed by different methods

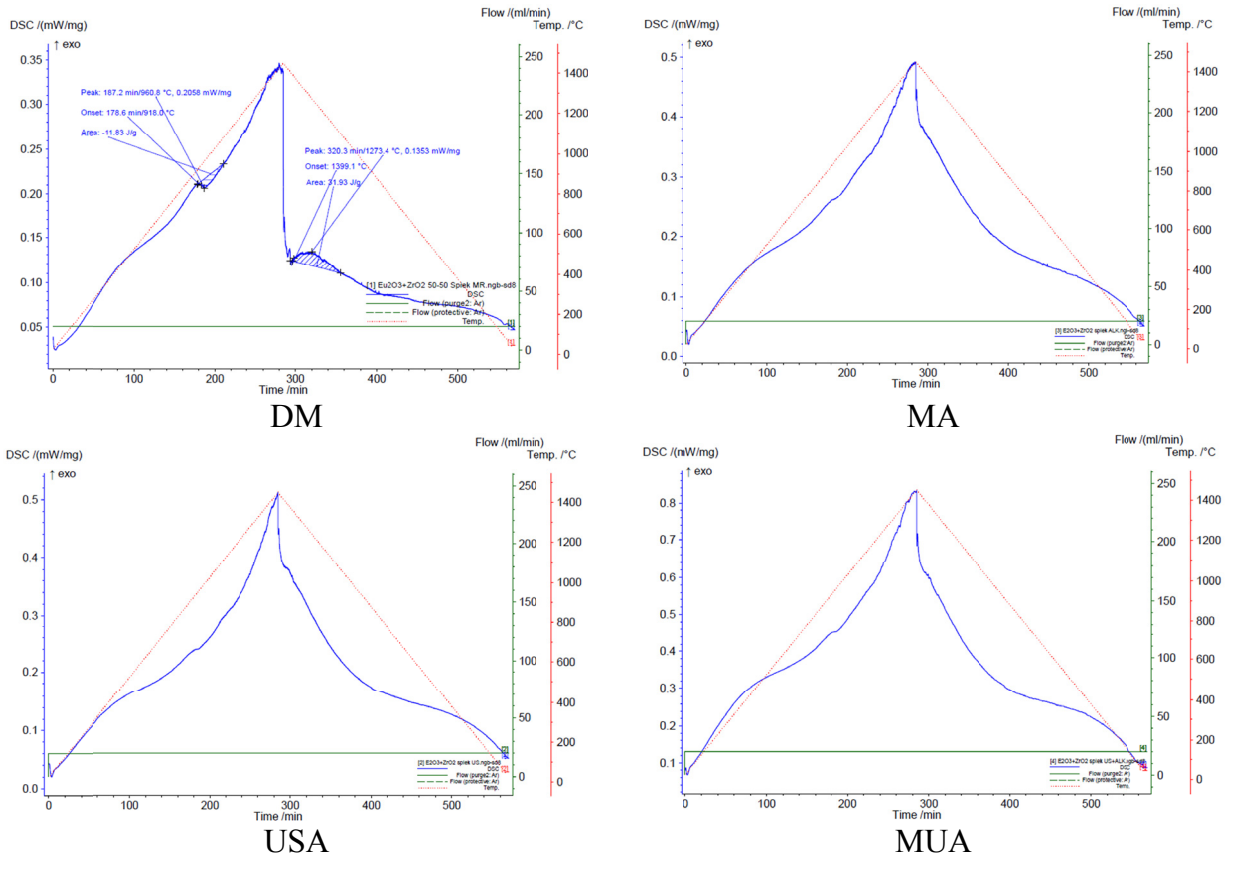


Fig. 10. The DSC curves of sintered material obtained from powders mixed by different methods

from phase constituents point of view, was obtained in the case of MA method. In this case generally only stoichiometric europium zirconate with formula $Eu_2Zr_2O_7$ and pyrochlore type of lattice was detected by XRD method. The most complicated phases composition was detected for material obtained by DM method, where $Eu_2Zr_2O_7$ phase with pyrochlore type of lattice and other nonstoichiometric europium zirconates were detected. In this case the XRD pattern showed also diffraction peaks derived from:

- probably (Eu, $Zr)_2O_3$ oxide with cubic structure (C) (detected as (Eu, $Lu_{0,5}$, $Ta_{0,5}$)O_3 complex oxide with isomorphic type of lattice to suggested (Eu, $Zr)_2O_3$);
- the ZrO_2 base oxide with monoclinic type of lattice;
- non-stoichiometric europium zirconates of $Eu_{0,2}Zr_{0,8}O_{1,9}$ type with fluorite structure (F);
- The europium zirconates with formula $Eu_{0,5}Zr_{0,5}O_{1,75}$ similar to $Eu_2Zr_2O_7$ phase but with fluorite structure.

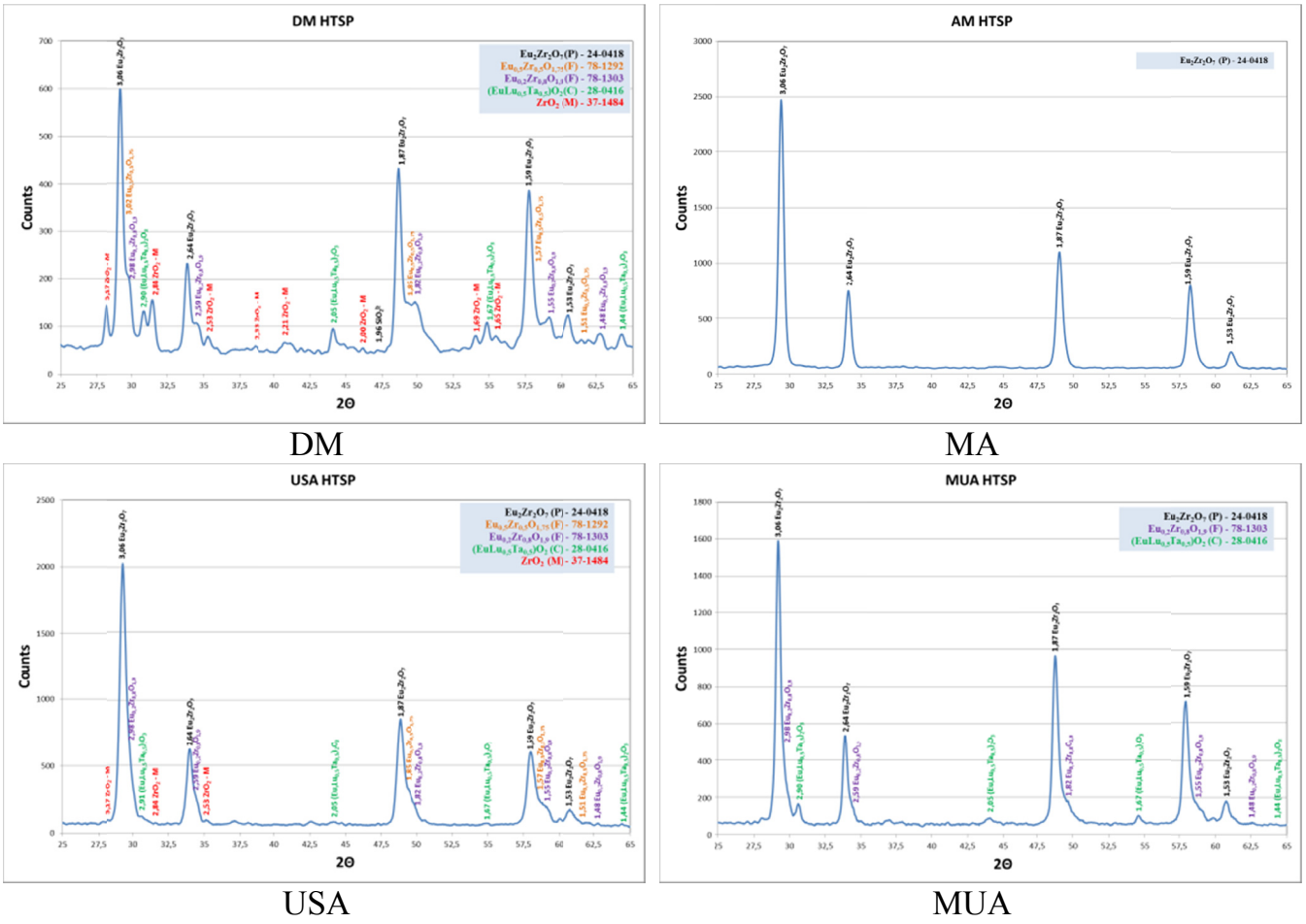


Fig. 11. The XRD patterns of sintered materials obtained from powders mixed by different methods

The presence of complex oxides, has also been identified in the case of materials which powders were homogenized by USA and MUA method. ZrO_2 has also been identified in USA sintered material. The presents of this phases is related with fact that investigated materials were prepared with about 7% molar excess of ZrO_2, which in the case of AM method has been dissolved, what suggests a lack of reflections coming from this oxide.

The final data and basic goal of presented investigation was related to characterization of thermal insulation properties of synthesized materials, and comparison them with data for usually used in TBC systems yttria stabilized zirconia with addition of 8 % wt. of yttria (8YSZ – $ZrO_2 \times 8\ Y_2O_3$) sintered by the same method. For this analysis the laser flash method was used and thermal diffusivity of sintered materials at temperature range from 25 to 700°C was analyzed (Fig. 12). This investigation was carried out only in the case of material obtained by MA method as a material with the most desirable phase constituents. Laser flash analysis revealed that sintered material based on europium zirconate has a lower thermal diffusivity coefficient in comparison with standard 8YSZ ceramic material in the whole temperature range of investigation. This results suggests that it may be a good material for the application of the TBC.

4. Summary and conclusions

The investigation presented in this paper showed that method of preparation of powders mixture has a strong effect on degree of homogenisation of the final material. The most beneficial effect on morphology of sintered material has a method of mechanical mixing in alcohol of based powders. In this case sintered material was characterized by the most homogenous

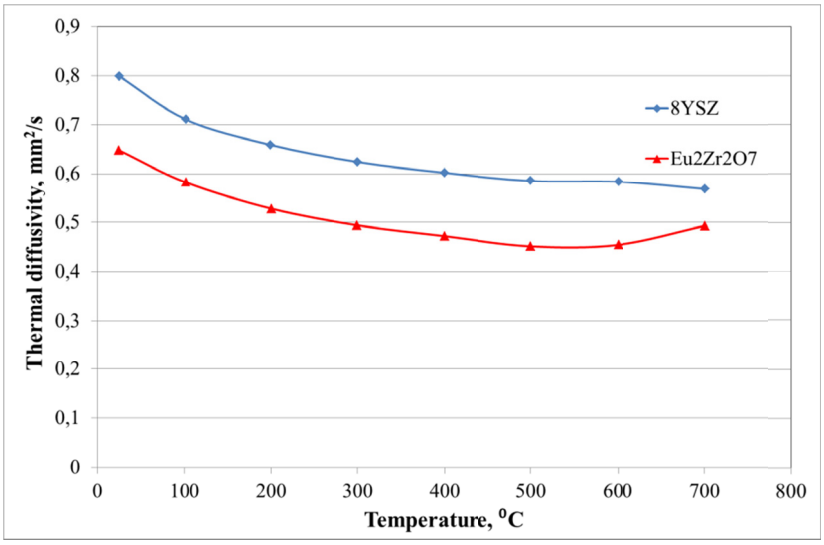


Fig. 12. The thermal diffusivity of $Eu_2Zr_2O_7$ based material obtained by initial MA mixing of based powders in comparison to referential 8YSZ sinter obtained by the same technique

microstructure and phases constituent. Ultra-sound assisted method of preparation of powder mixture don't get satisfactory results in both variants of mixing procedure, although the phase constituents of material prepared by these two method are very similar to those obtained by mechanical mixing in alcohol.

Very good and sensitive method of powder mixture characterization is calorimetric analysis by DSC method. This analysis get the possibility of final sintered material homogeneity prediction, what was conformed in the case of MA and DM prepared powders.

In analyzed application of mechanical mixing based powders in alcohol with next solid state synthesis in high-temperature vacuum press and continuous pressing in vacuum made the possibility of relatively uniform final material on the base of europium zirconate.

For the other site the other method of initial powder mixture preparation made the possibility of transition stages of sintering process observation and characterization of different complex oxides formation from based ZrO_2 and Eu_2O_3powders to final stoichiometric $Eu_2Zr_2O_7$ with pyrochlore type of lattice. The great convenience was in this case the applications of powders with an excess of one of the components – zirconia.

On the base of obtained results, the final conclusion can be formulated:

- DSC investigations of mixed oxides in all variant of mixing process suggest the synthesis of a new phase took places. Diffraction studies of phase constituents indicate the presence of a stoichiometric phase of $Eu_2Zr_2O_7$ type with pyrochlore lattice crystal structure as well as fluorite nonstoichiometric phase of similar chemical composition.
- Application of mechanical mixing of based powders in alcohol, get the possibility of good quality final sintered material on the base of europium zirconate, which was characterized by lower thermal diffusivity, approx. 20% lower than the usually used 8YSZ oxide. This result suggests that it may be a good material for the application of the TBC.

Acknowledgments

This work was supported by Institute of Materials Science of Silesian University of Technology, as a part of Statutory Research no BK220/RM3/2015 (11/030/BK-15/0025).

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