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Synthesis and thermal properties of zirconate, hafnate and cerate of samarium

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ABSTRACT

The basic direction of the development of thermal barrier coatings (TBC) systems is connected with new materials solutions dedicated for bond-coats and ceramic insulating layers. The present article shows the synthesis and thermal properties of different types of insulating ceramic materials based on zirconia, hafnia and ceria. The analyzed materials were synthesized via solid state reaction (SSR) of the mixtures of nanocrystalline feedstock powders of zirconia, hafnia, ceria and samaria. The synthesized materials were analyzed in view of chemical and phase composition. The morphological characterization of the utilized feedstock powders was showed as well. The basic range of the investigation was related to the analysis of thermal parameters such as a thermal diffusivity and coefficient of thermal expansion in temperature range 25 ÷ 1100 °C. The P-type samarium zirconate and hafnate were synthesized as well as F-type non-stoichiometric samarium cerate. The chemical homogeneity of obtained solid materials was satisfactory. The dilatometric measurements showed that $Sm_2Zr_2O_7$ and $Sm_2Hf_2O_7$ may be beneficial materials for TBC insulating layer due to the thermal expansion coefficient close to metallic substrate. These materials were also beneficial taking into account the results of thermal diffusivity measurements. In the temperature range 25–1100 °C, samarium hafnate and zirconate were characterized by substantially lower thermal diffusivity compared to that of 8YSZ. In the case of cerate of samarium with fluorite type of structure, the more beneficial thermal properties compared to that of YSZ were observed, however, were considerably less promising related to pyrochlore ceramic materials based on zirconia and hafnia.

1. Introduction

Thermal barrier coatings (TBC) are multi-layer coating systems, which are widely used in aircraft and power industries. TBC are usually deposited on combustion lines, first-stage blades and vanes, as well as on the other hot-path components in order to provide thermal insulation and protection of the metallic substrate against hot and corrosive gas streams [1–4]. The turbine components coated with TBC systems are exposed to extremely detrimental conditions, i.e. high mechanical load at elevated temperature, thermal fatigue and considerable environmental degradation due to molten deposits arising from the low quality fuels and air-ingested foreign particles [4–6]. The melts of environmental contaminants (dust, sand, volcanic ashes and runway debris) are known as CMAS (calcium–magnesium–alumina–silicate); these impurities cause deterioration of the durability and thermo-mechanical characteristics of coatings due to erosive wear and blockage of cooling holes [7–10]. The another factor being crucial to the lifetime of TBC systems is hot corrosion, caused by a molten sodium sulfate and oxides of vanadium, which are other fuel impurities [11–13].

Therefore, the number of materials dedicated for this application is very limited due to numerous requirements, such as high melting point, lack of phase transitions between the operating temperature and room temperature, very low thermal conductivity, chemical innerness, thermal expansion coefficient (TEC) close to that of metallic substrate, good adherence to the substrate and low sintering rate of the porous microstructure [14–16]. The 70s was the time of an introduction of thermal barrier coatings to the gas turbine industry, whereupon the most commonly used material for top-coat has been 7–8 wt% yttria-doped stabilized zirconia owing to the best performance in the high-temperature applications at this time [17]. Although these materials are still commonly used as the insulating layer in TBC, their phase stability and low sintering resistance are substantial limitations, regarding to the increasing turbine inlet temperature [15,18].

For this reason, a lot of effort has been made in order to find new top-coat materials, which may be an effective replacement for yttria-stabilized zirconia. From few last years, rare earth zirconates with overall formula $RE_2Zr_2O_7$ and two types of structure (pyrochlore and fluorite) have gained a substantial interest as the promising materials

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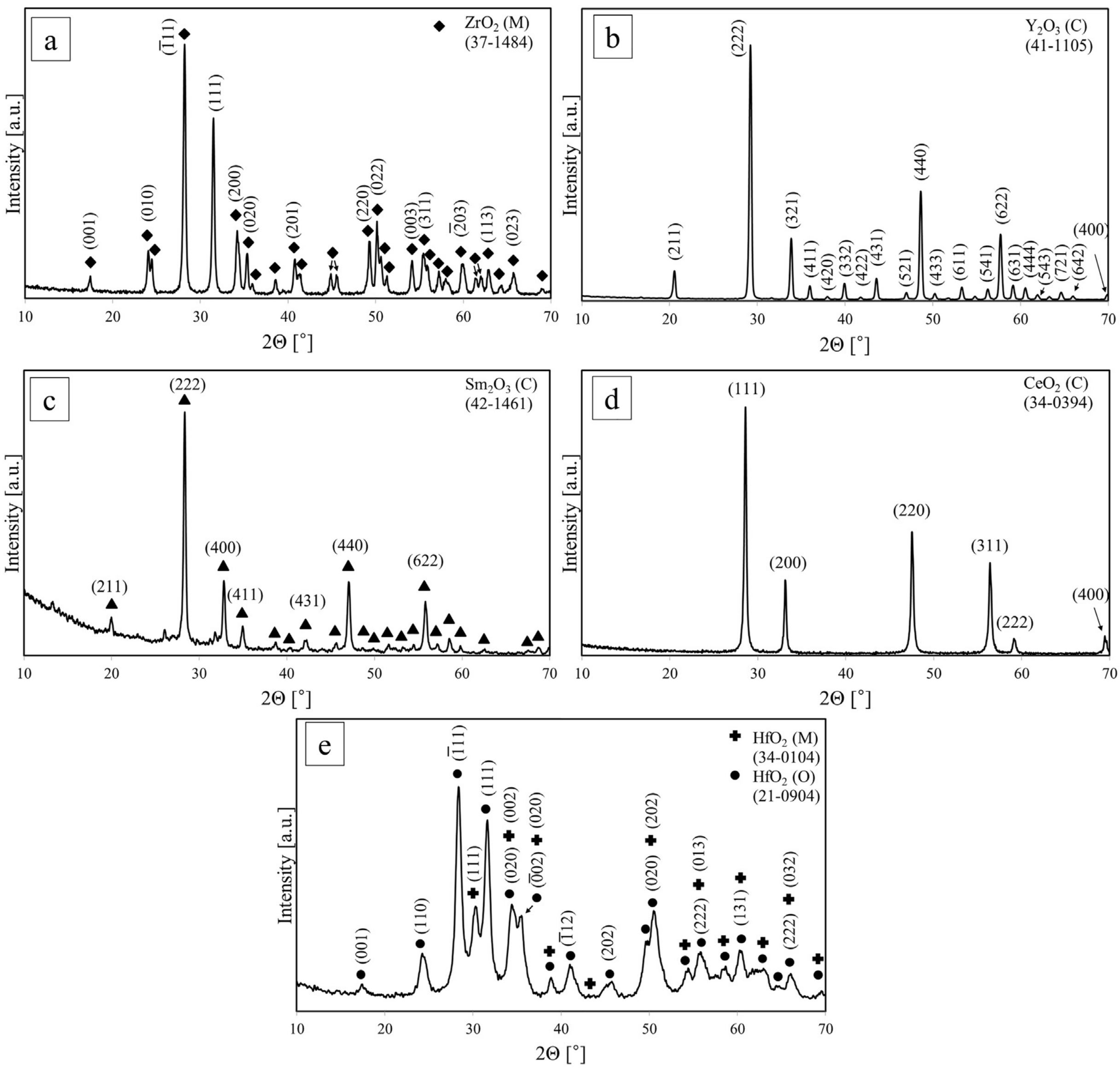

Fig. 1. XRD patterns showing phase composition of feedstock powders.

for TBCs application [19,20]. The stability of P-type structure is ruled mainly by the cation radius ratio (r_A/r_B). It is generally understood that the cation radius ratio lower than 1.48 promotes the fluorite structure, whereas the pyrochlore structure is stable while the value of r_A/r_B is in the range 1.48 ÷ 1.76. Furthermore, the ordering of crystal structure also depends on stoichiometry and thermal history of material [21,22]. Pyrochlore/fluorite-type ceramics with general formula $A_2B_2O_7$ (the A-site is occupied by larger $^{3+}$ cations and the B-site by the smaller $^{4+}$ cations) are materials with high scientific and technological importance.

The main areas of interest in the case of discussed materials and their applications are advanced technologies. These materials may be applied as solid oxides' electrolytes in high-temperature fuel cells [23]. The discussed materials may be also used in an immobilization of nuclear wastes [24] or utilized as proton solvents [25]. One of the most important potential applications of the pyrochlore and defective fluorite ceramics in view of the aircraft and power industries are insulating materials for the outer layer in the thermal barrier coatings [26]. The representatives of this group of materials, proposed as the top-coat candidates are zirconates, cerates and hafnates of rare earth metals [26–28]. Several authors investigated the thermal properties of La [29], Pr [30], Nd [31,32], Eu [33], Gd [29,34], Dy [35,36], Ho [30] zirconates. In many cases, the improvement of thermal properties of $A_2B_2O_7$ type ceramics compared to that of yttria-stabilized zirconia was reported. Furthermore, the papers regarding rare earth hafnates [30,37] and cerates [38–42] dedicated for top coat deposition are available, however, the literature data concerning these materials is less common, especially in the case of hafnia-based ceramics and their thermal properties. Therefore, these materials are of interest in view of the development of materials dedicated for top coat in TBC systems.

The authors synthesized three ceramics materials with formula of $A_2B_2O_7$, where A was samarium and B was Zr, Hf and Ce. The samarium zirconate, hafnate (both with P-type structure) and samarium cerate (fluorite structure) were obtained via solid state reaction (SSR) as well as the reference material, which was 8 mol% yttria-stabilized zirconia (8YSZ). The paper aims to characterize starting powders, synthesis and thermal properties of discussed ceramic materials. The data concerning new ceramic materials was compared to that of commercially used 8YSZ.