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ScienceDirect

Ceramics International 42 (2016) 1197–1209

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of the precursor nature and preparation mode on the coarsening of $La_2Zr_2O_7$ compounds

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Received 8 June 2015; received in revised form 1 September 2015; accepted 9 September 2015
Available online 16 September 2015

Abstract

This study addresses the thermal behavior of $La_2Zr_2O_7$ powders prepared via two different synthetic routes and the effect of the zirconium counter-cation on their properties, as carried out by dilatometric experiments.

Citrate-based compounds exhibit shrinkage, regardless of the precursors used. Preliminary thermal treatment permits the reduction in shrinkage. Nitrate based compounds calcinated at 600 °C show a higher shrinkage (-9.4%) than at 1200 °C (-5.2%) because of the decomposition of the trapped precursors, as revealed by DTA–TGA–MS. Coprecipitated samples present different behaviors as a function of the counter-cation nature. Chloride based compounds leads to shrinkage and phase mixtures, whereas expansion is observed for pure pyrochlore compounds that are synthesized with nitrate. The thermal expansion coefficients of the different compounds are similar to the literature values (9.5–$10.10^{-6}\ K^{-1}$).

This study allowed for a better understanding of the densification of the $La_2Zr_2O_7$ material and its adjusted properties, as a function of the precursor nature and the preparation mode, for application in thermal barrier coatings.

Keywords: $La_2Zr_2O_7$; Coarsening; TBC; Preparation mode; Precursor

1. Introduction

Improving the properties of thermal barriers, which are essential elements in the thermal protection of aircraft and rockets engine parts, is the subject of intensive research. This is intended to improve the efficiency of the engine cycle, which can result in reduction fuel consumption and greenhouse gas emissions, by increasing the operating temperature. The development of new alloys, particularly monocrystalline nickel-based superalloys [1,2], initially resulted in an increase in the operating temperature. The use of a ceramic layer ("topcoat"), which was elaborated by plasma spraying or electron-beam physical vapor deposition (EB-PVD), allowed the working temperatures to be above the melting point of the superalloys because of the low thermal conductivity [3,4].

Currently, partially stabilized zirconia (Y_2O_3–ZrO_2; YSZ) is widely used because of its low thermal conductivity ($2.1\ W\ m^{-1}\ K^{-1}$) and high thermal expansion coefficient ($10.7.10^{-6}\ K^{-1}$) to accommodate any stresses in the metal substrate ($16.10^{-6}\ K^{-1}$) [4] during thermal cycling. However, its structural instability above 1200 °C (transformation from tetragonal phase to the monoclinic and tetragonal phases) induces a volume expansion and generates compressive stresses in the deposit. Compressive stresses cause cracks to appear, which results in severe damage to the thermal barrier coating [5–7]. Moreover, the sintering resistance of the material is relatively low, which causes a significant densification that is responsible for the increase in thermomechanical stresses, which in turn are detrimental to the coating properties.

Research was conducted on the development of new materials to replace YSZ beyond 1200 °C. Doping zirconia

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http://dx.doi.org/10.1016/j.ceramint.2015.09.051
0272-8842/

by rare earth metals, such as lanthanum, was the subject of significant research because it enables the synthesis of crystallizing compounds in the pyrochlore structure ($La_2Zr_2O_7$). This structure is characterized by a structural stability up to its melting point (>2200 °C), an improved sintering resistance and a lower thermal conductivity than YSZ [8–11].

The degradation of the thermal barriers coatings (TBCs) during thermal cycling is complex because of different constituent materials are used (substrate/bond coat/topcoat). The first mode of degradation that is widely studied is the delamination of the topcoat by the growth of an oxide layer of aluminum, also called the thermally grown oxide (TGO), at the interface between the metallic bond coat (generally MC$_r$AlY, M=Ni, Co) and the ceramic topcoat. The native Al_2O_3 layer protects the substrate against corrosion at high temperatures from oxygen diffusion through the ceramic layer. However, its growth induces compressive stresses in the coating that are responsible for the formation and propagation of cracks [12–14].

The second mode of degradation is due to the high temperature densification of the ceramic coating. This results in volume shrinkage and an increase in Young modulus of the material. The rise in these phenomena increase the stresses that occur in the topcoat, where the formation and propagation of the cracks responsible for the component damage occur [15–18].

A previous study [19] was carried out on the synthesis of $La_2Zr_2O_7$ compounds using different preparation techniques and zirconium precursors. The results showed that the nature of the zirconium counter-cation impacts whether a single phase structure or a mixture of phases of pyrochlore is formed. Larger particles were observed for the phase mixtures compared with the single phase compounds at the same calcination temperature. As such, it would be interesting to study the thermal behavior of the different compounds by dilatometry because few studies have been conducted on the densification process. Indeed, only the final volume shrinkage and relative densities have been determined by the Archimedes method for $La_2Zr_2O_7$ synthesized by hydrothermal [20,21], and coprecipitation methods [9,22] have been reported.

This study focuses on the influence of the nature of the zirconium counter-cation on the $La_2Zr_2O_7$ densification synthesized via the citrate route and by coprecipitation. The results of dilatometry experiments are correlated with the structural and microstructural analysis of the elaborated compounds.

2. Experimental procedure

2.1. Compounds synthesis

The lanthanum zirconate compounds were synthesized using lanthanum nitrate ($La(NO_3)_3$, $6H_2O$) and three zirconium precursors characterized by different counter-cations: nitrate ($ZrO(NO_3)_2$, $6H_2O$), chloride ($ZrOCl_2$, $8H_2O$) and acetate ($Zr(OH)_3CO_2CH_3$). Lanthanum and zirconium precursors were dissolved in stoichiometric amounts in water. The two synthetic modes used were the citrate route and the coprecipitation, as described previously [19].

The resulting powders were ground in a mortar and calcinated at different temperatures (600, 800, 1000 or 1200 °C) in air for 2 h. For simplification, the following nomenclature was adopted for the calcinated compounds: *Zr precursor_Synthesis method_Calcination temperature,* and for dilatometric samples: *Zr precursor_Synthesis method_TMA Calcination temperature* . For example, a powder synthesized using the citrate method (VC) from zirconyl nitrate (ZrN) and lanthanum nitrate (LaN), and calcinated at 600 °C was denoted *ZrN_VC_600*, and a compound prepared by coprecipitation (CP) from zirconium oxychloride (ZrCl), calcinated at 600 °C, and analyzed by dilatometry was denoted *ZrCl_CP_TMA 600* (Table 1).

2.2. Characterization techniques

Dilatometric analysis was performed on a vertical Setsys Evolution TMA dilatometer from Setaram. The samples were analyzed with a thermal cycle characterized by a maximum temperature of 1400 °C with heating and cooling rates of 10 °C/min under air. The dimension variation of the samples was measured using a mechanical displacement transducer in alumina, and the applied force was 50 N. Calcinated powders were prepared under cylindrical shapes ($\varnothing=6$ mm et $L\approx5$ mm) by powder pressing. Platinum sheets were placed at each side of the samples to avoid any chemical reaction at high temperature between the lanthanum zirconate sample and the alumina components of the apparatus. Experiments were carried out on compounds that had been synthesized using the citrate route, ZrN_VC, calcinated at 600, 800, 1000 and

Table 1
Precursors and solvent nomenclature.

Name	Formula	Code
Zirconium oxynitrate	$ZrO(NO_3)_2$, $6H_2O$	ZrN
Zirconium oxychloride	$ZrOCl_2$, $8H_2O$	ZrCl
Zirconium acetate hydroxide	$Zr(OH)_3CH_3CO_2$	ZrAc
Lanthanum nitrate	$La(NO_3)_3$, $6H_2O$	LaN
Water	H_2O	H

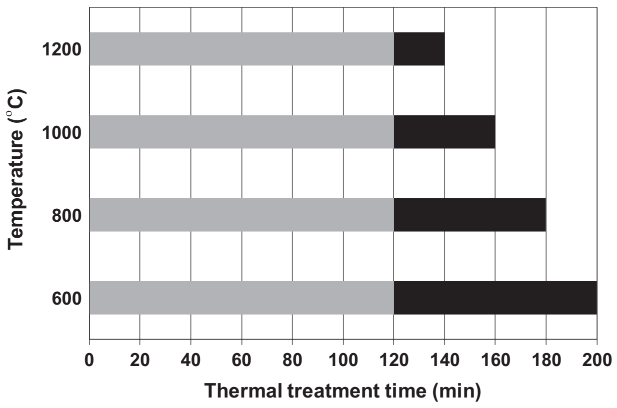

Fig. 1. Thermal treatment time (□: calcination dwell time and ■: TMA time from calcination temperature to 1400 °C) for ZrN_VC calcinated at different temperatures.