Microhardness and fracture toughness of $Ce_{0.9}Gd_{0.1}O_{1.95}$ for manufacturing solid oxide electrolytes

R.V. Mangalaraja [a,*], S. Ananthakumar [b], Kasimayan Uma [c], Romel M. Jiménez [d], Marta López [a], Carlos P. Camurri [a]

[a] Department of Materials Engineering, Faculty of Engineering, University of Concepción, 270, Edmundo Larenas, Concepción, Chile
[b] Institut Charles Gerhardt Montpellier, PMOF, Université Montpellier 2, France
[c] Department of Environmental Technology and Urban Planning, Nagoya Institute of Technology, Nagoya, Japan
[d] Department of Chemical Engineering, University of Concepción, Concepción, Chile

ARTICLE INFO

ABSTRACT

Synthesis of nanocrystalline gadolinium doped ceria ($Ce_{0.9}Gd_{0.1}O_{1.95}$) was attempted by nitrate-fuel combustion technique involving different organic fuels namely urea, citric acid, glycine and poly ethylene glycol. As-combusted ceria precursors were calcined at 700 °C for 2 h for obtaining fully dense, nanocrystalline ceria powders. Cylindrical ceria discs were fabricated by uni-axial pressing and sintered intentionally at low temperature of 1200 °C for 2 h for assessing the sintering characteristics of the nano powders as well as the mechanical performance of the sintered ceria body. The study confirms that the nano powders could be sintered to 98% theoretical sintered density at 1200 °C with a grain size of 400 nm to 1 μm. The sintered samples exhibited the Vickers microhardness of 8.82 ± 0.2 GPa and the fracture toughness of 1.75 ± 0.3 MPa m$^{1/2}$ at a load 20 N for glycine and citric acid fuels derived ceria, respectively. A comparison between the fuels was made with respect to the sintering and mechanical properties of doped ceria. Citric acid and glycine fuels resulted in sintered ceria with high hardness where as the urea and polyethylene fuels derived nano ceria resulted in high fracture toughness.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Rare earths (RE) doped cerium oxide have been regarded as a promising candidate material in designing electrolytes for intermediate temperature solid oxide fuel cells (IT-SOFC). A high oxygen ionic conductivity compared to yttria stabilized zirconia was the motivation for developing the rare earth doped CeO_2 [1–3]. $CeO_{2-\delta}$, is a fluorite structured ceramic and contains oxygen vacancies ($V_o^{\bullet\bullet}$) as the predominant ionic defect. Pure CeO_2 is a poor oxide ion conductor. However, the substitution of rare earth ions improved the ionic conductivity. Gadolinia doped ceria is particularly given more attention and 10 mol% of gadolinia doped ceria ($Ce_{0.9}Gd_{0.1}O_{1.95}$) is being extensively attempted for electrolyte applications in IT-SOFC [4,5]. The issues that are still to be solved are the narrow down of a chemical or physical synthesis for producing bulk nano scale Gd^{3+} doped ceria powders, complete densification at low sintering temperatures, fabrication of economically viable SOFC for domestic applications and recycling of the electrolyte materials. Combustion synthesis of ceria is advantageous compared to many chemical routes because of its easiness in scaling up as well as its efficiency for obtaining reactive ceria powders that can give low temperature densification.

The ceramic materials used in SOFC's may have to undergo frequent heating and cooling and therefore experiencing aggressive thermo-mechanical stresses. In fact ceria has a linear thermal expansion behavior with respect to operating temperatures and therefore the development of thermal stress is exceptionally high. Also it has inherent low mechanical strength and hardness and that is the reason it is used in CMP's. Studies also confirmed that Gd^{3+} doped ceria showed large thermal expansion coefficient ($\sim 8.125 \times 10^{-6}$ K^{-1}) due to linear increase in the unit cell parameters and unit volume at elevated temperatures [6]. Since CeO_2 is a recognized thermal barrier coating material many research works have been devoted to study the structural stability and thermal properties of CeO_2 coatings. The mechanical properties of CeO_2 coatings were also extensively attempted. However, in the case of ceria electrolytes, only a very few reports dealt with the mechanical properties of [7–12]. Recently Zhang et al., have reported the mechanical hardness and fracture toughness values for $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ ceramics sintered at 1250 °C. However, the powder was prepared by precipitation of ceria precursors using hexamethylenetetramine as precipitant agent [7,8].

Table 1
Chemical reactions during combustion synthesis for various fuels.

Types of fuel	Chemical reactions
Urea	$0.9Ce(NO_3)_3 \cdot 6H_2O + 0.1[2Gd(NO_3)_3 \cdot 6H_2O] + 2.35NH_2CONH_2 \rightarrow Ce_{0.9}Gd_{0.1}O_{1.95} + 2.35CO_2 + 10.7H_2O + 3.85N_2$
Citric acid	$0.9Ce(NO_3)_3 \cdot 6H_2O + 0.1[2\ Gd(NO_3)_3 \cdot 6H_2O] + 0.783CH_2COOHCOHCOOHCH_2COOH \rightarrow Ce_{0.9}Gd_{0.1}O_{1.95} + 4.698CO_2 + 9.132H_2O + 1.5N_2$
Glycine	$0.9Ce(NO_3)_3 \cdot 6H_2O + 0.1[2Gd(NO_3)_3 \cdot 6H_2O] + 1.567NH_2CH_2COOH \rightarrow Ce_{0.9}Gd_{0.1}O_{1.95} + 3.134CO_2 + 9.92H_2O + 2.284\ N_2$
Polyethylene glycol	$0.9Ce(NO_3)_3 \cdot 6H_2O + 0.1[2Gd(NO_3)_3 \cdot 6H_2O] + 1.41CH_2CH_2O \rightarrow Ce_{0.9}Gd_{0.1}O_{1.95} + 2.82CO_2 + 8.82H_2O + 1.5N_2$

In this study, gadolinia doped ceria ($Ce_{0.9}Gd_{0.1}O_{1.95}$) was prepared by nitrate-fuel combustion involving urea, citric acid, glycine and poly ethylene glycol as fuels. The low temperature sintering of combustion derived doped ceria was attempted and the mechanical hardness and fracture toughness were assessed at room temperatures. The dependence of the organic fuels on the ceria powder characteristics, reactivity at low sintering temperatures, evolution of microstructure and grain size, Vickers microhardness and fracture toughness were studied.

2. Experimental

The nitrate-fuel combustion method for the preparation of $Ce_{0.9}Gd_{0.1}O_{1.95}$ powders was carried out as follows. Urea, citric acid, glycine and poly ethylene glycol were used as organic fuels. High purity (>99.9%) cerium nitrate [$Ce(NO_3)_3 \cdot 6H_2O$] and gadolinium nitrate [$Gd(NO_3)_3 \cdot 6H_2O$] were used as precursor reagents. The general steps involved in the combustion synthesis are the dissolution of metal nitrates and organic fuels in distilled water followed by heating at temperatures above 500 °C for the combustion.

In this study the required amounts of organic fuels for the complete combustion was calculated from the basic principle of propellant chemistry [13]. In a typical experiment, for synthesizing 1 mol of $Ce_{0.9}Gd_{0.1}O_{1.95}$ powders 2.35, 0.783, 1.567 and 1.41 mol of urea, citric acid, glycine and polyethylene glycol were taken, respectively. After making the clear homogeneous precursor solution, the reaction mixture was transferred into platinum crucible (100 ml). It was inserted inside a preheated furnace at a temperature of 500 °C. Once the reaction mixture reached the point of spontaneous combustion, it started burning vigorously. Porous solid foam was finally obtained within few minutes. The as-combusted foams were collected and converted to powders by simple grinding. During the combustion reactions gaseous N_2, CO_2, and H_2O were produced as by products. The outgoing brown fumes indicated the release of these gaseous products. The combustion reactions involved with various fuels were given in Table 1.

The $Ce_{0.9}Gd_{0.1}O_{1.95}$ powders derived from urea, citric acid, glycine and polyethylene glycol fuels were denoted as U-$Ce_{0.9}Gd_{0.1}O_{1.95}$, C-$Ce_{0.9}Gd_{0.1}O_{1.95}$, G-$Ce_{0.9}Gd_{0.1}O_{1.95}$, and P-$Ce_{0.9}Gd_{0.1}O_{1.95}$. The as-combusted $Ce_{0.9}Gd_{0.1}O_{1.95}$ powders were calcined at 700 °C for 2 h for obtaining fully crystalline ceria phase [3,7].

Crystalline nature and phase purity were examined using powder X-ray diffraction technique (X'Pert Pro, Philips X-ray diffractometer). The X-ray diffraction was recorded using Cu K_α radiation. The crystallite sizes were determined using Scherrer̆s equation [14]. Morphology, particle size and distribution of the powders were analysed by both scanning electron microscope (SEM-JEOL 6460 LV) and transmission electron microscope (TEM-JEOL JEM 2000 EX). TEM samples were prepared by dispersing the powder in dilute ethanol medium under ultrasonic agitation. A drop of suspension was placed on a carbon coated fine mesh copper grid. Once ethanol was evaporated, images were seen under TEM.

The powders calcined at 700 °C for 2 h were uni-axially pressed into cylindrical pellets (thickness, t = 3 mm and diameter, D = 10 mm) and sintered at 1200 °C for 2 h. The sintered densities of the specimens were measured by water immersion technique.

The sintered samples were carefully diamond polished to produce optical finish. The Vickers hardness of the polished samples was measured at room temperature by Struers hardness tester. The hardness was determined by the ratio of the applied load via a geometrically defined indenter to the contact (projected) area of the resultant impression using the relation:

$$H_v = 1854.4P/d^2 \ (\text{GPa})$$

where H_v is the Vickers hardness (GPa), P is the applied load (kg) and d is the indentation diagonal length (mm). In a typical indentation test, load was varied from 1 N to 20 N. The indentation time was 10 s. Six to eight indentations were made for each load on all the samples. The fracture toughness was determined by the indentation technique using the same instrument. The fracture toughness is a measure of the resistance of a material to crack propagation or to damage. A fixed load of 20 N was applied to measure the fracture toughness of the sintered $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics. Both diagonal lengths of the indentation images and crack lengths were first found and the fracture toughness (K_{IC}) values were calculated using the formula [15]:

$$K_{IC} = 0.16H_v a^2 c^{-3/2} \ (\text{MPa m}^{1/2})$$

where H_v is the Vickers hardness, a and c are diagonal and crack length generated by the indentation.

3. Results and discussion

Thermal decomposition analysis of all the GDC powders is shown in Fig. 1. The weight loss curves are nearly identical for all the fuels. Since the reactants mixture is already exposed to combustion the weight loss is significantly low below 200 °C in all the cases. Above this temperature range, a gradual weight decrease is seen. Obviously, the weight loss below 400 °C is caused by the evolution of N_2, NO_2, NH_3, CO_2 and H_2O gaseous products from cerium
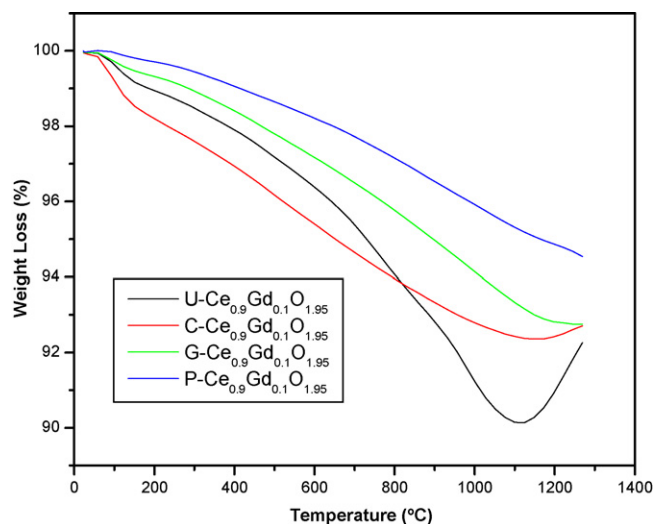

Fig. 1. TGA of as-prepared $Ce_{0.9}Gd_{0.1}O_{1.95}$ powders prepared using different organic fuels.