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ScienceDirect
Journal of the European Ceramic Society 31 (2011) 1269–1276
www.elsevier.com/locate/jeurceramsoc

Directionally solidified CeO_2 (or GDC)/CoO eutectic ceramics as cermet precursors for SOFCs anodes: Microstructure cross-over

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Received 15 December 2009; received in revised form 2 June 2010; accepted 30 June 2010
Available online 25 July 2010

Abstract

Rods of CeO_2 and gadolinium-doped CeO_2 (GDC)–CoO eutectics were prepared by directional solidification using a laser heated floating zone (LFZ) technique. The microstructure has been studied as a function of the growth rate from $V = 10$ to 750 mm/h. Regular eutectic microstructures are obtained except for the highest growth rate. The interspacing follows the $\lambda^2 V = C$ law with $C = 4.1(3) \times 10^{-17}$ and $2.6(3) \times 10^{-17}$ m^3/s for CeO_2–CoO and GDC–CoO eutectics, respectively. A cross-over between fibrous and lamellar eutectic microstructures was observed depending on the growth rate. The crystallography of the eutectics was studied by Electron Backscatter Diffraction (EBSD). The growth directions $[1\,1\,0]_{GDC} \sim //[110]_{CoO}$, and the interfacial planes $(200)_{GDC}//(111)_{CoO}$, were identified. Solubility of Co in the ceria matrix was determined by Energy Dispersive X-ray (EDX) Spectroscopy after Co was leached out from the matrix. Co solubility in ceria at 1650 °C was found to be less than 1 mol%.

Keywords: B. Composites; B. Microstructure-final; D. CeO_2; E. Fuel cells; Eutectics

1. Introduction

Composites obtained by solidification of a melted binary eutectic mixture have been the subject of great interest since the middle of last century for their superior mechanical properties that may be used in the field of structural materials.[1] Initial studies were mostly confined to metal–metal eutectics but the extraordinary mechanical response and excellent thermal stability promoted thorough studies of the microstructure and crystallography of several Directionally Solidified Eutectic (DSE) oxides turned later the attention to oxide ceramic composites.[2,3]

The interest in this DSE oxides has not decreased with time, and eutectics have been proposed to be good candidates for use in several applications, namely optical, electronic, magnetic and in the energy production.[4,5] The unique microstructure of regular eutectics, made up of ordered arrays of alternating lamellae or fibres with sharp and clean interfaces, induces new functional properties, such as directional transport of light and improved ionic and electronic conductivity.[6]

The possibility of using eutectic ceramic oxides as precursor materials to obtain new composites, such as porous metal–ceramic mixtures has been successfully demonstrated by Revcolevschi and Dhalenne.[7,8] Metal–ceramic composites (cermets) containing an ionic conductor such as stabilised zirconia (or ceria) and a transition metal, such as Ni, Co or Cu, that are good catalysers of several chemical reactions, find applications in the fields of heterogeneous catalysis and in solid oxide fuel cell (SOFC) technology.[9] The continuous ionic conducting phase allows oxygen diffusion in and out the eutectic bulk; in this way reduction of the transition metal oxide phases inside the eutectic matrix is possible, making DSE oxides useful as precursor materials to obtain porous cermets.

SOFCs are foreseen as one of the cleanest and most efficient alternative energy sources to fossil fuel combustion in the near future.[10,11] The state of the art anode in SOFCs is a cermet of yttria stabilised zirconia (YSZ) with Ni particles. These cermets are usually synthesised via conventional solid state routes (raw oxides are mixed, fired and, after sintering, reduced under H_2), which result in very fine ceramics but have the disadvantage of grain coalescence at Fuel Cell working temperatures (600–1000 °C).[12]

This deficiency of conventional cermets can be considerably minimised in cermets produced from DSE oxide precursors.

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doi:10.1016/j.jeurceramsoc.2010.06.012

Table 1
compositions and growth rates applied to all the rods prepared.

Sample group	CeO_2 (mol%)	GDC (mol%)	CoO (mol%)	Growth rates (mm/h)
1	18	–	82	10, 100, 200, 500 and 750
2	–	18	82	
3	16.5	–	83.5	10, 200 and 750
4	18.5	–	81.5	

In fact reduction of the eutectic ceramic leads to channelled Ni(Co)–YSZ(GDC) porous cermets with alternating porous metal and ionic conductor lamellae that provide good electrical conductivity, gas permeation and a thermal expansion coefficient similar to that of the YSZ(GDC) ceramic scaffold. As a result the thermo-mechanical integration with other components in the SOFC is favoured.[13] In these materials the catalyser particles, of submicron size, are confined between the YSZ narrow lamellae.[14] The good adhesion through low-energy interfaces that is obtained in DSE cermets between the metal and the ceramic scaffold induces a great stability of the metallic particles against coarsening.[15]

In the present case, the fabrication of Co/ceria (or Gd doped ceria) oxide composites by the laser floating zone (LFZ) technique is investigated in order to evaluate their suitability as cermet precursors for SOFC anodes. The idea of using ceria phases instead of YSZ is due in part to the higher ionic conductivity of ceria vs. YSZ when working at low operation temperatures.[16] In addition, ceria is an excellent catalyser. Lowering the working temperatures is for low cost and high efficient SOFC technology. The eutectic microstructure of the Co/ceria (or Gd doped ceria) oxides has been microscopically characterised. The influence of the composition and solidification parameters in the microstructure of the composites grown at different rates by the LFZ method has been also studied.

2. Experimental

Rods of CeO_2 (and GDC):CoO eutectic compositions were grown with a CO_2 laser ($\lambda = 10.6\,\mu m$; Blade600, Electronic Engineering, Firenze) using a LFZ system following the same procedures detailed in previous studies.[17] The precursors for the rods were prepared from CeO_2 (99.9%, Aldrich) or 10% Gd doped CeO_2 (GDC) obtained from inorganic salt precursors as described by Gil et al.[18] and CoO (98% + 2% Co_3O_4, prepared from Co_3O_4 99.7%, Alfa Aesar) powders. The starting oxides were mixed in the desired composition in an agate mortar and the obtained powder was isostatically pressed for 4 min at 200 MPa and sintered for 4 h at 1350 °C. Four different compositions, given in Table 1, were prepared in order to fully characterise the eutectic point of this system and the associated microstructure. The eutectic composition CeO_2(or GDC):CoO with a molar ratio of 18:82 used for samples 1 and 2 was originally proposed by Chen et al. for the CeO_2/CoO eutectic.[19]

Rods approximately 2.5 mm in diameter were grown in air in two steps, first a downward pulling (densification) and later an upward growth. Different growth rates from 10 to 750 mm/h (see Table 1) were applied. Identical seed and feed pulling rate without diameter reduction was used in all the cases except for growth rates of 750 mm/h for which the rod diameter was reduced to one half of the initial size. The rotation speed of the source rod and/or the grown eutectic rod in the initial step was fixed to 50 rpm in counter rotation but in the final step no rotation was used. The length of the molten zone was maintained at about 1.5 times the rod diameter. A polycrystalline seed rod was used to initiate the growth.

Microstructures were observed from polished transverse and longitudinal cross-sections of the grown rods using a scanning electron microscope (SEM, model 6400, Jeol, Tokyo, Japan) equipped with an INCA300 energy dispersive spectroscopy (EDS) system (Oxford Instruments). Computer analysis of SEM images was used to estimate the volume fraction of phases and interlamellar spacing.

The orientation relationships between the different phases of the resulting eutectic microstructures in the CeO_2:CoO system at different growth rates were studied by electron backscattered diffraction (EBSD) using an Oxford Instruments HKL EBSD system attached to the SEM described before.

3. Results

Electron micrographs taken on transversal cross-sections at the rod's centre showing the microstructures of the samples with eutectic composition (groups 1 and 2) are presented in Fig. 1. Most samples show a fully aligned regular eutectic microstructure, either fibrous or lamellar, arranged in eutectic grains that are composed of ceria (or GDC) as the second phase (light) in a cobalt oxide matrix (dark). At 750 mm/h there is some tendency to form a colony type structure, which is more evident in the gadolinium-doped ceria eutectic (Fig. 2). Tendency to form colonies at high growth rates, *i.e.* high under-cooling rates, is typical in eutectic growth and is consistent with the constitutional under-cooling effect associated with high solidification rates that provoke a non planar growth front.[1,20] Constitutional under-cooling is sometimes attributed to the presence of impurities, but none were observed in the present study. The addition of Gd may have slightly altered the CoO:CeO_2 eutectic point and this small deviation could be the origin of instabilities in the growth, particularly at high growth rates, which would explain the observed result. The same tendency to form colonies of similar morphology was observed by Sayir and Farmer when a third component, Y_2O_3, was added to the binary Al_2O_3/ZrO_2 eutectic, confirming that small changes in composition can produce some modifications in the microstructure.[21] In any case, the microstructure inside colonies is quite regular and is lamellar.