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Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc



Short communication

Fabrication of dense and defect-free diffusion barrier layer via constrained sintering for solid oxide fuel cells

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ARTICLE INFO

Article history:

Received 13 February 2017
Received in revised form 20 March 2017
Accepted 21 March 2017
Available online xxx

Keywords:

Gadolinia-doped ceria
Diffusion barrier layer
Constrained sintering
Sintering aid
Solid oxide fuel cell

ABSTRACT

To enable the development of next-generation solid oxide fuel cells (SOFCs), the fabrication of dense and defect-free diffusion barrier layers via constrained sintering has been a significant challenge. Here, we present a double layer technique that enables complete densification of a defect-free gadolinia-doped ceria diffusion barrier layer. In this approach, top and bottom layers were individually designed to perform unique functions based on systematic analysis of constrained sintering. The top layer, which contains 1 wt% CuO as a sintering aid, provides sufficient sintering driving force via liquid-phase sintering to allow complete densification of the film, while the bottom layer without a sintering aid prevents detrimental chemical reactions and regulates the global sintering rate to eliminate macro-defects. Such fabrication of dense diffusion barrier layers via a standard ceramic processing route would allow the use of novel cathode materials in practical SOFC manufacturing. Furthermore, the strategy presented in this study could be exploited in various multi-layer ceramic applications involving constrained sintering.

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1. Introduction

Solid oxide fuel cells (SOFCs) represent one of the most efficient and cleanest technologies for direct conversion of chemical fuels into electric power and heat [1,2]. Among the various types of fuel cells, SOFCs operate at the highest temperature, which provides unique advantages as well as technical limitations for their commercial development. The key issues associated with high-temperature operation are high system costs and rapid performance degradation, and hence, extensive research efforts have been devoted to lowering the operating temperature to an intermediate temperature range of 650–800 °C [3]. To obtain satisfactory performance and stability at reduced operating temperatures, ceria-based diffusion barrier layer is acknowledged as one of the most critical components because it allows stable use of highly active mixed ionic- and electronic-conducting (MIEC) cathode materials [4,5]. In particular, cobalt-containing MIEC cathode materials, such as $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSC), are not chemically compatible with the yttria-stabilized zirconia

(YSZ) electrolyte, and a diffusion barrier layer must be deposited between these two components to suppress the formation of detrimental secondary phases such as SrZrO_3 and $\text{La}_2\text{Zr}_2\text{O}_7$ [6].

While open porosity in the diffusion barrier layer should be minimized to completely block detrimental chemical interactions, it is extremely difficult to form a dense film using common ceramic processing routes. Generally, a doped ceria diffusion barrier layer is applied on top of the pre-sintered YSZ electrolyte and sintered below ~ 1250 °C to avoid the high-temperature chemical reaction between YSZ and doped ceria and the subsequent formation of high resistivity reaction products [7]. Because of the refractory nature of ceria [8,9], it is challenging to densify the diffusion barrier layer at such low sintering temperatures. Furthermore, the diffusion barrier layer is fabricated on a pre-sintered YSZ electrolyte via constrained sintering, and the restricted film shrinkage in the lateral direction due to the rigid substrate hinders the densification of the film [10]. Due to these inherent limitations in the standard cell fabrication process, various alternative deposition techniques, including pulsed laser deposition [11], magnetron sputtering [12], atomic layer deposition [13], and chemical solution deposition [14], have been explored, and considerable achievements have been reported in enhancing the density of the diffusion barrier layer. However, considering the manufacturing costs and scale-up capability, the practical application of such methods to mass production beyond lab-scale experiments remains questionable; a standard powder

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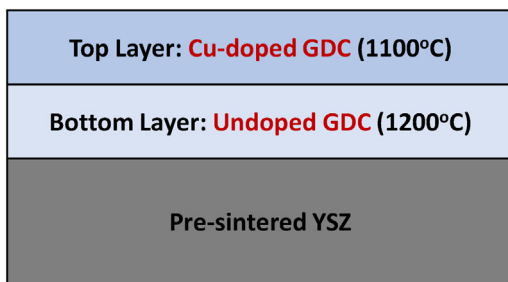


Fig. 1. A schematic showing the basic concept of double layer approach.

processing technique for the fabrication of the dense diffusion barrier layer is greatly needed.

In this study, we developed a double layer process that allows densification of a gadolinia-doped ceria (GDC) diffusion barrier layer at temperatures below 1200 °C via standard screen printing and constrained sintering. The sinterability of GDC was enhanced by introducing CuO as a sintering aid, and the top and bottom layers were individually optimized to overcome the technical challenges associated with constrained sintering. A general strategy for achieving dense and defect-free films via constrained sintering is proposed.

2. Experimental

To prepare a typical diffusion barrier layer paste, a polymeric dispersant (Hypermer™ KD-6) was added to a solvent (α -terpineol (Sigma Aldrich, USA)) and mixed in a planetary mill (Pulverisette 7, Fritsch, Germany) at 250 rpm for 30 min, followed by the addition of GDC powder (ultra large surface area (ULSA) grade, $Gd_{0.1}Ce_{0.9}O_{1.95}$, Rhodia, France), binder (BH-3, Sekisui Chemical, Japan), and plasticizer (dibutyl phthalate (DBP), Junsei Chemical, Japan) and planetary milling at 250 rpm for a further 24 h. For preparation of Cu-doped GDC paste, 1 wt% copper (II) oxide (99.99%, Sigma Aldrich, USA) was added with the GDC powder using the same mixing procedure.

For the fabrication of the conventional diffusion barrier layers used as controls in this study, the prepared pastes were screen printed on pre-sintered YSZ electrolyte substrates (Fuel Cell Materials, U.S.A.) and then sintered at 1200 and 1100 °C in air for the undoped and Cu-doped GDC, respectively. The double layer was fabricated by screen printing the standard GDC paste and sintering at 1200 °C in air, followed by screen printing the Cu-doped GDC and sintering again at 1100 °C in air (Fig. 1). The prepared samples were impregnated with epoxy under vacuum and polished down to 1 μ m. Microstructural and compositional analyses were performed on these polished samples using scanning electron microscopy (SEM) (Ispect F50, FEI) and electron probe micro-analysis (EPMA) (JXA-8500F, JEOL). The image analysis was performed using Image J software.

Cu-doped GDC powder samples were collected by heat-treating the paste at 500 °C. The crystal structure and sintering behavior of the undoped and Cu-doped GDC powders were examined using X-ray diffraction (XRD) (DMAX-2500, Rigaku) and dilatometry (DIL420C, Netzsch), respectively. XRD scan was performed between 20 and 80° with the scan rate of 2° min⁻¹. For dilatometry measurements, disc-shaped compacts with a diameter of 1 cm and a thickness of 3.5 mm were prepared by uniaxially pressing the powders at 60 MPa for 10 min. Dilatometry measurements were performed in air. To investigate the chemical reactions between YSZ and Cu-doped GDC, the two powders were mixed in a 1:1 weight ratio by ball milling for 24 h and their phase evolution was ana-

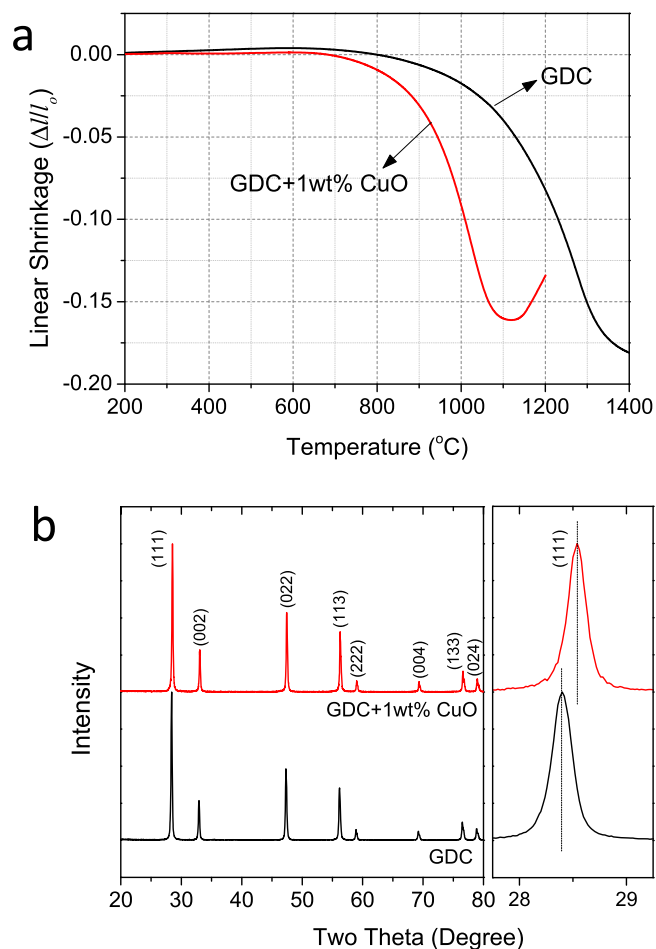


Fig. 2. (a) Linear sintering shrinkages as a function of temperature and (b) XRD patterns of normal and Cu-doped GDC.

lyzed using high-temperature XRD between room temperature and 1200 °C.

3. Results and discussion

To fabricate a dense diffusion barrier layer at a temperature not exceeding \sim 1200 °C, the sinterability of GDC should be substantially improved; typically, a high sintering temperature above 1400 °C is required for full densification of ceria-based materials due to their refractory nature [8,9]. A wide variety of additives have been studied to improve the sintering behavior of GDC, and Cu is known to be one of the most effective without adversely affecting the electrical properties [15–17]. Fig. 2(a) shows the effect of the addition of 1 wt% CuO on the sintering shrinkage behavior of GDC. The GDC without a sintering aid exhibited gradual shrinkage over a wide temperature range of 800–1400 °C. The addition of 1 wt% CuO resulted in a reduction of the onset and termination temperatures of shrinkage by 200–300 °C. The effective sintering aid behavior of Cu for GDC is explained by the Vegard's slope and the size and charge of the dopants. The Vegard's slope for ceria is expressed as [18]:

$$X = (0.0220r_i + 0.00015z_i) \quad (1)$$

where r_i is the difference between the ionic radii of the dopant and Ce^{4+} in 8-fold coordination in Å, and z_i is the difference in charge of the dopant and Ce^{4+} . The dopants with moderate absolute values of Vegard's slope show effective liquid phase sintering behavior [19], while undersized acceptor dopants enhance solid state atomic

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