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Original Article

Simulation of nanosecond IR laser annealing of cerium gadolinium oxide

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ABSTRACT

Laser induced densification of ceramic oxide has shown great promises. However to control this process in regards of the final properties of the material, it is necessary to understand phenomena occurring during laser matter interaction, especially heat diffusion through the material. A thermal simulation of cerium gadolinium oxide (CGO) submitted to infrared laser pulses is presented. In order to determine the temperature profile during laser treatment, optical properties of CGO must be known; for this purpose, ellipsometry measurements were performed in order to obtain absorption coefficient and reflectivity. Finally, a thermal model based on heat equation was developed. Experimental observations of irradiated CGO surfaces were in agreement with the simulation results, in particular at maximum temperature when the material reaches fusion.

1. Introduction

In Single Chamber Solid Oxide Fuel Cell (SC-SOFC), as the generation of the open circuit voltage (OCV) depends mainly on the electrocatalytic activity and selectivity of the electrodes, and not only on a dense electrolyte as in conventional SOFC, it is possible to operate without a gastight electrolyte [1,2]. It allows to use simple and conventional processing methods to prepare the electrolyte. For example, screen-printing, a simple and low-cost deposition technique can be used to prepare a thin and porous layer, because in such a case a dense electrolyte is not required [2–4]. However, some authors [2,3,5] have indicated that the porosity related to the electrolyte may allow the transport of the hydrogen produced locally at the anode to the cathode, which can generate an OCV drop and a decrease of cell performances. To prevent hydrogen transportation, it is thus recommended to have a dense electrolyte or at least a diffusion barrier layer, while at the same time preserving the porosity of the electrodes [2,3,5].

Solid oxide electrolytes based on cerium gadolinium oxide (CGO) materials are considered to be the most promising candidate materials for use in single-chamber solid oxide fuel cells, because they offer considerably high ionic conductivity at intermediate operating temperatures (450–700∘C) [6,7]. Nevertheless, the achievement of dense materials requires sintering temperatures above 1400∘C [8–10]. Densification of the electrolyte by conventional heat treatment is obviously possible, but this also leads to an undesired densification of the support material (most often anode). To solve this difficulty, Mariño et al [5] proposed to selectively densify the electrolyte in anode supported SC-SOFC by a laser treatment, using either a pulsed nanosecond ultraviolet (UV) laser or an infrared (IR) laser.

Laser annealing is a technique that allows localized modifications to the materials without affecting the entire structure [10,11]. This technique has been employed successfully to treat ceramic materials with an increasing interest in their densification [12–18] and it has been demonstrated that pulsed laser irradiation offers an attractive alternative to conventional thermal annealing for oxides densification [11,12].

The changes induced on the surface of a material treated by a laser strongly depend on the amount of energy absorbed by the material. To obtain the desired results, it is important to figure out the surface temperature and its distribution within the material. However, the *in situ* measure of the temperature remains still difficult during a laser treatment with a pulsed laser [13,14]. For a better understanding and control of the laser annealing process, this work proposes a numerical simulation of laser-mater interaction based on previous experiments made by Mariño et al concerning local densification of CGO electrolyte in SOFC [5]. Here, we will only focus on results obtained with a pulsed IR laser. Furthermore, a measurement of the optical properties of CGO material as a function of temperature is presented, necessary to implement realistic simulation of material properties.

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Table 1
Physical properties of CGO used for simulations

Properties	Values [Reference]
Cp_s [J.kg^{-1}.K^{-1}]	350 [19]
κ [W.m^{-1}.K^{-1}]	2.52 [19]
D [m^2.s^{-1}]	1.0×10^{-6} [19]
ρ [kg.m^{-3}]	7220 (provider)

2. Thermal modelling

The temperature distribution in a material, induced by the absorption of a laser irradiation can be described by the heat equation which depends on the optical and thermal parameters of the medium[15]. If the thermal diffusivity length (defined hereafter) is negligible with respect to the laser beam diameter [14,16], a one dimensional model can be used and the heat equation can be expressed by the Eq. (1). The heat radial diffusion is then neglected. In this case, the differential Eq. (1) is a model of the temperature.

$$\rho(T)C_p(T)\frac{\partial T(x,t)}{\partial t} - \frac{\partial}{\partial x}\left(\kappa(T)\frac{\partial T(x,t)}{\partial x}\right) = Q(x,t) \quad (1)$$

The left part of the equation represents the temporal and spatial distribution of the temperature. The temporal distribution of the temperature is determined by the density of the material ρ(T) and the heat capacity C_p(T), while the spatial evolution depends on the thermal conductivity κ(T) and also determines the heat diffusion in the material [15–17]. Values used in this work for cerium gadolinium oxide (CGO) are presented in Table 1.

The right part of Eq. (1), Q(x,t), corresponds to the laser energy absorbed by the material. It depends on the optical properties of the material like the absorption coefficient (α) and the reflectivity (R), the laser fluence (F) and the time dependence of the laser pulse q(t) [15,18]. If the absorption coefficient α is constant (and then not dependent on the temperature), the integrated form of the Beer-Lambert law may be used as in equation (2).

(2) $Q(x,t) = F(1-R)q(t)\alpha\exp(-\alpha x)$ [w m^{-3}]

Thermal simulations based on previous equations were carried out using an IR pulsed laser on a CGO surface. The induced temperature profile after laser pulse irradiation was calculated using COMSOL Multiphysics software, which uses a finite element method. This software has a database of equations to model different phenomena. In this case, the heat transfer in solids module was used.

We remind here that the thermal diffusivity length l_τ is defined qualitatively by Eq. (3).

$$l_\tau = 2\sqrt{D\tau} \quad (3)$$

τ is the laser pulse duration. D is the thermal diffusivity of the material which depends on the thermal conductivity κ, the heat capacity C_p and the density of the material ρ, reported in Eq. (4).

$$D = \frac{\kappa}{\rho C_p} \quad (4)$$

The program solves the macroscopic thermal Eq. (1) at each node of the grid and generates the temperature profile inside the volume of the structure.

Several steps and conditions were determined to carry out this simulation:

a The geometry of the 1D model is simple (Fig. 1) as we consider only 1D diffusion in CGO electrolyte. The thickness of the CGO layer is around 20 µm in depth and it is assumed that the heat diffusion is limited in the electrolyte layer and no thermal effect reach the anode.

b The time profile of the laser pulse q(t) (5) is described by a normalized Gaussian function [15] depending on laser characteristics.

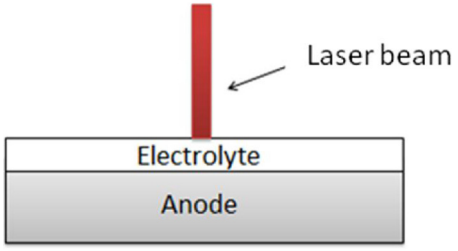

Fig. 1. Schematic representation of laser annealing procedure.

$$q(t) = \frac{1}{\sqrt{2\pi}\,{}^*t_s}\exp\left(-\frac{(t-t_o)^2}{2{t_s}^2}\right) \quad (5)$$

where $t_s = \frac{\tau}{2\sqrt{2\ln 2}}$ and $t_o = 3\,{}^*t_s$. τ is the laser pulse duration, this parameter being specific to the used laser.

c Meshing: This procedure is a very important step for the reliability of the simulation results. The meshing functionality allows the geometric model to be discretized into small units of simple shapes, called mesh elements. After several simulation tests with different meshing sizes, we have checked that the maximum meshing size that we can use has to be lower than the optical adsorption depth, which is defined as the reverse of the adsorption coefficient α. In such conditions, meshing size has minor effects on simulation results.

d Heat source is defined by Eq. (2), thereby it is necessary to determine optical properties of CGO (α and R).

e Limit conditions have to be defined. The initial temperature of the sample is the ambient temperature, set at 20 °C. The lower edge (bulk of material) is considered as adiabatic according to Eq. (6) where n is the normal vector at the surface.

$$-n.(-\kappa\nabla T) = 0 \quad (6)$$

On the upper surface (in contact with air), heat is lost by the combined action of natural convection and thermal radiation according to Eq. (7).

$$-n.(-\kappa\nabla T) = h(T-T_\infty) + \varepsilon\sigma(T^4-T_\infty^4) \quad (7)$$

where T∞ is the ambient temperature (20 °C), h is the convective exchange coefficient (10 W.m^{-2}.K^{-1}), σ the Stefan-Boltzman constant (5.67×10^{-8} W m^{-2} K^{-4}) and ε the emissivity of the material (0.8). These values have been extracted from the literature for cerium dioxide [20] because no values were found for CGO. We observed from various calculations that convection and thermal radiation do not have a significant influence on the results.

f Concerning the solver: the time step (dt) of calculation must be imperatively less than the laser pulse duration (τ) for the calculation convergence.

The simulation was first developed for a single laser pulse. Then, simulations presented at the end of this paper consider consecutive laser pulses on CGO surface.

3. Experimental procedure

3.1. Laser annealing of CGO samples

3.1.1. CGO Samples Preparation

Half cells “electrolyte/anode” were prepared to perform laser annealing tests on CGO layers. All the materials used for cells preparation are commercial powders purchased from Fuel Cell Materials. The experimental procedure used to prepare half cells is described in detail elsewhere [3,5]. Anode support was prepared by uniaxial pressing at 250 MPa to obtain a 22 mm diameter disc. The powder mixture was composed of NiO (60 wt%) and CGO (40 wt%), where CGO refers to