INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–11

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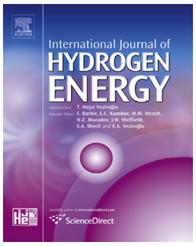

Femtosecond laser micromachining of metallic/ceramic composite material for solid oxide fuel cell devices

Aroa Morán-Ruiz [a], Karmele Vidal [a], Aitor Larrañaga [b], Raúl Montero [b], María Isabel Arriortua [a,*]

[a] Departamento de Mineralogía y Petrología, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Barrio Sarriena S/N, 48940 Leioa, Vizcaya, Spain

[b] Servicios Generales de Investigación (SGIker), Universidad del País Vasco (UPV/EHU), Barrio Sarriena S/N, 48940 Leioa, Vizcaya, Spain

ARTICLE INFO

Article history:
Received 14 December 2015
Received in revised form
6 July 2016
Accepted 18 July 2016
Available online xxx

Keywords:
Femtosecond laser
Micromachining
Metallic/ceramic composite
Microstructure
Solid oxide fuel cells

ABSTRACT

In a solid oxide fuel cell (SOFC), the high power output of interconnect/cathode interphase results from using a contact layer between both materials, which has adequate oxygen diffusion and high electron conduction. Ultrashort pulse laser drilling holes have been performed in a Fe–22Cr mesh dipped into $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ (LNC), $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ (LNF) and $(La_{0.8}Sr_{0.2})_{0.95}Fe_{0.6}Mn_{0.3}Co_{0.1}O_3$ (LSFMC) slurries to form alternative contact composites for SOFC. The optimal conditions to induce micro-pores with minimal damage in the suggested contact materials were 4000 laser pulses of 20 μJ and 40 fs width each one. The efficiency of laser micromachining in the studied specimens was independent of the ceramic composition. According to X-ray spectroscopy (EDX) chemical analysis, the laser effect on the initial elemental composition was very located without influencing the system performance.

Introduction

High electrical conductivity with an appropriate microstructure and gas permeability of electro-ceramic materials are critical issues in many electrochemical devices [1]. In particular, in the oxidizing side of solid oxide fuel cells (SOFCs) the cathode contact materials are required to reduce cell power losses, improving electrical contact between the interconnect ribs and the electrode [2]. Another critical issue, which limits the commercialization of SOFCs, is the evaporation of volatile Cr-rich species from chromia-forming ferritic stainless steel interconnect materials, i.e. CrO_3 (g) or $CrO_2(OH)_2$ (g), leading to rapid cathode degradation known as Cr-poisoning. Upon combination with oxygen ions, the volatile Cr-rich species are reduced back to Cr_2O_3 and decrease the cathode active area [3]. A cathode contact material has to be formulated to fulfill the requirements of a high electrical conductivity, low chromium cation and oxygen anion diffusivity, chemical compatibility with the chromia-forming interconnects and the perovskite cathodes, and an adequate gas permeability, maintaining the mechanical integrity of the formed layer [4]. The perovskite

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* *Corresponding author.*
E-mail address: maribel.arriortua@ehu.es (M.I. Arriortua).

http://dx.doi.org/10.1016/j.ijhydene.2016.07.122

Please cite this article in press as: Morán-Ruiz A, et al., Femtosecond laser micromachining of metallic/ceramic composite material for solid oxide fuel cell devices, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.07.122

structured oxides, $A^{3+}B^{3+}O^{2-}{}_3$, where A is a rare-earth element and B is a first row transition metal, have been used by several authors as highly protective/conductive "Cr getter" interconnect coatings [5–8]. An improvement in electrons mobility through the interconnect/contact material interface could be achieved using a dense and continuous contact oxide layer on the metallic interconnect. According to previous studies [9], the incorporation of conducting wires and the design of porous channels in SOFC electrodes could increase cell performance via enhancing the transport of electrons as well as of the gases. In this context, we have recently demonstrated the viability of a new system configuration [10] consisting in the combination of a dense electron conduction ceramic material with Fe–22Cr composed mesh, that could give to a contact layer the required good mechanical properties to provide the continuity of the coating on the channeled interconnect. The obtained area specific resistance (ASR) values were reproducible and stable indicating good adherence between the composite material and interconnect. However, one of the main drawbacks of the mentioned alternative configuration is the lack of O_2 permeability. In order to overcome this problem, here we propose the dense microstructure adaptation at the requirement of the contact materials by means of high aspect ratio laser drilled micropores [11].

In this work we take advantage of the capability of ultrashort pulses to efficiently drill holes, without sample degradation caused by thermal decomposition [12–21], in a Fe–22Cr mesh/ceramic contact composite with different ceramic compositions: $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ (LNC), $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ (LNF) and $(La_{0.8}Sr_{0.2})_{0.95}Fe_{0.6}Mn_{0.3}Co_{0.1}O_3$ (LSFMC). The optimal conditions to induce micro-pores with minimal damage in the composite materials have been determined. The morphology and chemical composition changes due to the laser processing have been analyzed by a scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX) system.

Experimental equipment and materials

Laser system

The laser set-up is described elsewhere (Fig. 1) [20]. Femtosecond laser pulses were generated by a Ti: Saphire oscillator-regenerative amplifier system (1 kHz, 4.0 mJ, 40 fs pulses at 800 nm). The pulse energy is controlled by means of a variable neutral density filter in the 1-40 μJ range.

The light is focused onto the sample, which is mounted in a 3D translation stage (1 μm precision) at atmospheric pressure, using a fused silica lens (f = 100 mm). Fig. 2 shows an image of the beam obtained by placing a CMOS camera at the focal plane. The diameter of the spot $D(1/e^2)$ is 40 μm. Polarization is linear and parallel to the sample surface.

In some of the experiments a Si photodiode is placed under the "sample" with the aim of determine the number of pulses needed to through it.

Materials

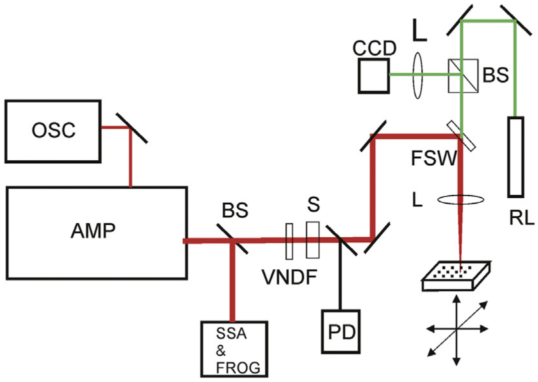

Fig. 1 – Schematic diagram of the experimental set-up: OSC: Ti: Shapphire oscillator. AMP: Ti: Shapphire regenerative amplifier. BS: Beam splitter. SSA & FROG: Single shot autocorrelator and FROG. VNDF: Variable neutral density filter. S: Shutter. L: f = 100 mm lens. RL: reference laser. CCD: camera.

The compositions of ceramic powders used in this study were $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ (LNC), $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ (LNF) and $(La_{0.8}Sr_{0.2})_{0.95}Fe_{0.6}Mn_{0.3}Co_{0.1}O_3$ (LSFMC), all of them from NexTech, Fuel Cell Materials. In order to obtain metallic/ceramic composite, a Fe–22Cr stainless steel mesh (Fiaxell SOFC Technologies), with mesh opening of about 175 μm and a thickness of ~250 μm, was cut into 10 × 10 mm squares, cleaned with acetone in an ultrasonic bath and dried. The quantitative EDX analysis revealed that Fe–22Cr mesh contains as additives: tungsten (W) (2.3(2) % wt.), niobium (Nb) (0.4(1) % wt.), manganese (Mn) (0.6(1) % wt.) and titanium (Ti) (<0.1% wt.). The squared-meshes were preoxidized at 600 °C for 10 h to reduce Cr and Fe transport into the ceramic coating, after heat treatment [22]. Then, they dip coated [23] with corresponding ceramic paste (dip coating rate = 4.5 mm s^{-1}). The ceramic slurry was composed of ceramic powder (12.5% in volume), dispersant (Dolapix, 1% relative to ceramic powder, Zschimmer & Schwarz, Chemische Fabriken) to avoid the accumulation of ceramic particles and a binder (PVB, polyvinyl butyral, 5% relative to the ceramic powder, Solutia Solutions) to increase the viscosity

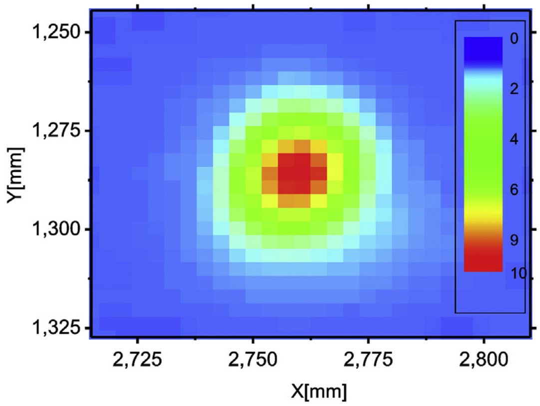

Fig. 2 – Image of the intensity profile of the laser beam obtained by placing a CMOS camera at the focal plane (color scale in arbitrary units). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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