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Cold laser machining of nickel-yttrium stabilised zirconia cermets: Composition dependence

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ABSTRACT

Cold laser micromachining efficiency in nickel-yttrium stabilised zirconia cermets was studied as a function of cermet composition. Nickel oxide-yttrium stabilised zirconia ceramic plates obtained via tape casting technique were machined using 8–25 ns pulses of a Nd: YAG laser at the fixed wavelength of 1.064 μm and a frequency of 1 kHz. The morphology of the holes, etched volume, drill diameter, shape and depth were evaluated as a function of the processing parameters such as pulse irradiance and of the initial composition. The laser drilling mechanism was evaluated in terms of laser-material interaction parameters such as beam absorptivity, material spallation and the impact on the overall process discussed. By varying the nickel oxide content of the composite the optical absorption (-value is greatly modified and significantly affected the drilling efficiency of the green state ceramic substrates and the morphology of the holes. Higher depth values and improved drilled volume upto 0.2 mm^3 per pulse were obtained for substrates with higher optical transparency (lower optical absorption value). In addition, a laser beam self-focussing effect is observed for the compositions with less nickel oxide content. Holes with average diameter from 60 μm to 110 μm and upto 1 mm in depth were drilled with a high rate of 40 ms per hole while the final microstructure of the cermet obtained by reduction of the nickel oxide-yttrium stabilised zirconia composites remained unchanged.

1. Introduction

Optimisation of strength, electrical connectivity and gas permeability of electro-ceramic materials is a critical issue in many electrochemical devices. In particular, in the anode supported conventional solid oxide fuel cells (SOFC) the structural material is a nickel-yttrium stabilised zirconia (Ni-YSZ) cermet, which has to be formulated to fulfil the requirements of good thermo-mechanical strength, electrical conductivity and gas permeation [1-5]. Low long term durability of SOFC's is the main obstacle for the commercial application of SOFC's [6]. In anode supported SOFC's cracking of the electrolyte caused by volume expansion of the anode under redox cycling conditions is the main motive for cell failure [7,8]. Anode cermets are fabricated by reduction of Nickel oxide-yttrium stabilised zirconia (NiO-YSZ) precursors and percolation of pores and metal is provided by increasing the NiO/YSZ ratio of the composite upto values of about 70 wt.% of NiO. Increasing NiO charge has two main drawbacks. First the ceramic weakens and its performance as supporting component deteriorates; second it becomes less resistant to redox cycling induced by accidental incorporation of oxygen into the anodic chamber under operation conditions. One of the possible solutions to the aforementioned drawbacks would be the functional structuring of YSZ rich cermets by generating channels for gas transport.

The present work is dedicated to explore the possibility of using laser machining technology to efficiently drill holes in cermets with different YSZ content in order to increase the permeability for gasses beyond the constraints imposed by the metal oxide content and/or pore former addition. Laser-based machining techniques present unique advantages due to their ability to produce high precision machining with excellent surface quality while only yielding small heat affected zones. Due to these particular features and as a consequence of recent developments in laser technology, these techniques are a very attractive option for the advanced ceramics industry. The shortcomings observed in dense ceramics in the form of spatter and micro-crack formation can be totally eliminated if machining step is performed while the ceramics are still in the green state, "cold machining" [9–14]. Furthermore, laser machining of green ceramic substrates showed significantly higher material removal rates if compared to the results for the same composition ceramics in the sintered state [14].

NiO-YSZ ceramic substrates with varying NiO/YSZ ratios were machined to generate cylindrical hole patterns in green, sintered

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and reduced states with an industrial Nd:YAG laser working at the wavelength of 1.064 μm. Green state machining efficiency showed to be significantly higher than in the sintered and reduced states. Final cermet microstructures with drilled pattern were prepared by a second stage process consisting of reducing machined and fired substrates, the final microstructure of the Ni-YSZ cermet substrate being kept essentially unchanged. The interesting feature to note is that NiO amount variation significantly affected both the material removal efficiency and the hole shape.

2. Experimental

2.1. Preparation of ceramic substrates

Three compositions of ceramic substrates were prepared via colloidal processing route based on the tape casting technique using different proportions of YSZ and NiO commercial ceramic powders. The ratios in vol.% of YSZ/NiO chosen were: 30/70 which is the conventional one, 50/50 and 70/30 (Table 1). Relevant thermo-physical properties of green state ceramic substrates for the compositions used in this study are compiled in Table 2. The starting powders were NiO (Alfa Aesar GMBH, Germany) and YSZ stabilised with 8 mol.% Y_2O_3 (TZ-8YS, TOSOH, Japan). The deionised water was used as a solvent. Polyacrylic acid based polyelectrolyte (PAA, Duramax D-3005, Rohm and Haas, USA) was used as dispersing agent and about 17.23 vol.% acrylic polymers (Duramax B-1000 and B-1235, Rohm and Haas, USA) were used as binders. Details of the suspension preparation procedure can be found in Ref. [14]. Tape casting was performed using Doctor Blade equipment. Tapes were around 500 μm thick and green densities of ≈65% of theoretical density (including organic phase). For comparison of the laser machining efficiencies between the green, sintered and cermet states some substrates were sintered prior to laser treatment, at 1400 °C with a dwell time of 2 h (sintered state). Sintered substrates reached ≈95% of theoretical density. Cermets were produced by reduction of the sintered ceramics (2 h in a 5 vol.% N_2/H_2 gas mix at 800 °C). Electrical conductivity of cermets was measured using equipment and procedure depicted in Ref. [15]. The volume fractions of YSZ, Ni and porosity as well as the resistance of the cermets of different compositions are given in table [3].

2.2. Laser processing of the ceramic substrate

A diode-pumped Nd:YAG laser (Rofin-Sinar E-Line 20) operating at wavelength of 1.064 μm with a Gaussian beam mode TEM_{00} with maximum mean power of 11 W and a beam quality factor $M^2 < 1.3$ has been used in this work. Incorporated opto-acoustical Q-Switch commutator generated pulses in rank 8–25 ns at 1 kHz frequency. Percussion method instead of trepanning technique is more appropriate for relatively small diameter holes. An optical magnifier 5× and a 100 mm optical lens enabled laser spots as small as ø = 15 μm in diameter. Laser beam was deflected by CAD software controlled galvanometer mirror allowing us to predefine the hole pattern and processing procedure. However, the optical system introduces some misalignment between the laser pulse and the subsequent ones which do not exactly coincide in position making the holes broader than the laser beam size. The sample can be properly processed because in our case the laser angular deviation is small, below 22 μrad.

The depth, diameter and eroded volume were determined as a function of the pulse number and the irradiance per pulse. Laser irradiation was calculated taking as laser beam diameter that of laser imprint on methacrylate after 10 pulse processing. Detailed laser output parameters are given elsewhere [14].

Table 1
Starting composition and corresponding porosity evolution at different processing steps of ceramic substrates used in the study.

Composition (solids vol.%)	NiOYSZ-1	NiOYSZ-2	NiOYSZ-3
NiO	58.84	41.38	24.83
YSZ	23.93	41.39	57.94
Organic binders	17.23	17.23	17.23
Green state density*			
ρ (g/cm^3)	3.6 ± 0.1	3.4 ± 0.1	3.3 ± 0.1
TD* (%)	65 ± 2	64 ± 2	63 ± 2
Sintered state density			
ρ (g/cm^3)	6.2 ± 0.1	5.9 ±0.1	5.8 ± 0.1
TD (%)	96 ± 2	94 ±2	96 ± 2
Reduced state density			
ρ (g/cm^3)	4.4 ± 0.1	4.8 ± 0.1	5.4 ± 0.2
TD (%)	59 ± 2	70 ± 2	83 ± 3

* Organic phase density ρ = 1.3 g/cm^2. Error corresponds to standard deviation value of three samples.

Table 2
Some thermo-physical properties corresponding to ceramic substrates in green state used in the study.

Composition	NiOYSZ-1	NiOYSZ-2	NiOYSZ-3
Specific Heat[a] c_p (J/g K)	0.503	0.530	0.555
Thermal Conductivity κ (W/cm K)	0.029	0.024	0.0195
Thermal Diffusivity D (cm^2/s)	8.9×10^{-3}	7.7×10^{-3}	6.6×10^{-3}
Vaporization enthalpy H_V (kJ/cm^3)[b]	23.45	21.49	19.46
Thermal diffusion length l_T (μm) (8 ns pulse)	0.17	0.16	0.145
Melting temperature T_M (K)[c]	2160	2245	2520
Melting enthalpy H_M (kJ/cm^3)[d]	4.96	4.84	5.08
Absorption coefficient at 1.064 μm (cm^{-1})	8500	4445	2980
Optical length (μm)	1.20	2.25	3.35

[a] c_p taken as mass average. Maxwell volumetric average used for thermal conductivity and diffusivity considering that influence of pores (≈1 μm diameter) is negligible.
[b] From solid phase at 300 K. Mass averages.
[c] Estimated from phase diagram.
[d] From 300 K to T_M.

2.3. Characterization techniques

The geometrical parameters of the drills including the drill volume were analysed with an optical confocal profilometer (OCP, Dual Sensofar PLμ 2300) with maximum lateral resolution of 0.3 μm. A minimum of 10 drills were measured for each processing variable. Scanning electron microscopy (SEM) was performed using a JEOL JSM6400 microscope. Energy dispersive X-ray analysis (EDAX) was carried out for phase identification. Absorption coefficients in the green ceramics were determined from optical absorption measurements of very thin samples produced by tape casting in a Cary 500 spectrophotometer.

3. Experimental results and discussion

In order to compare drilling efficiencies with the state of the ceramic we performed laser drill experiments in substrates in the three different, green NiO-YSZ, sintered NiO-YSZ and reduced Ni-YSZ (porous Ni cermet) states of the same NiO/YSZ initial composition using constant laser processing parameters (distance to laser focus, number of pulses and pulse irradiance). In Fig. 1 we give the results of machining the NiOYSZ-1 substrates using 25 laser pulses of 8 ns pulse length and 2.7 mJ corresponding to irradiances of about 51 GW/cm^2. Laser drilling of substrates in sintered (Fig. 1b) and cermet (Fig. 1c) states proved to be rather inefficient and poor quality process as compared with those in the