Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 28 (2008) 2673–2680
www.elsevier.com/locate/jeurceramsoc

Laser drilling of Ni–YSZ cermets

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Received 25 February 2008; accepted 17 April 2008
Available online 4 June 2008

Abstract

Pulsed Nd:YAG laser was used for efficient drilling of cylindrical hole patterns in porous Ni–YSZ cermet plates. Green NiO–YSZ oxide ceramic substrates obtained via tape casting technique were machined using 8–80 ns pulses at the fixed wavelength of 1064 nm. The etched volume, drill diameter, shape and depth were evaluated as a function of the processing parameters such as pulse irradiance and pulse number. The laser machining mechanism was discussed by means of laser–material interaction parameters such as beam absorptivity and plasma formation and the impact to the overall process discussed. Holes with uniform diameter from 30 to 110 μm and up to 1 mm depth were drilled with a high efficiency of up to 0.1 mm^3 per pulse. Green state machining showed significant efficiency whereas the properties of the cermet substrate were kept unchanged.

Keywords: Tape casting; Laser drilling; Transition metal oxides; ZrO_2; Fuel cells

1. Introduction

Ceramics machining with laser is a mature technology that comes from microelectronics industry for scribing an aperture drilling.[1,2] Recent developments and progresses of laser technology have lowered their price and increased their versatility, thus making them an attractive option for a wider range of materials to be processed and machined with.[3,4] Their application to ceramic industry is of particular interest because of the nature of conventional methods used, which are extremely laborious and time-consuming. Furthermore, laser-based machining techniques present unique advantages due to their ability to produce high precision machining with excellent surface quality while yielding small heat affected zones.

Nevertheless the laser machining of ceramics in the sintered state may present some shortcomings due to the presence of spatter and resolidified matter around the hole entrance or microcrack formation resulting from thermal shock.[2,3,5] Heat input can be kept low by using nano-, pico- or femtosecond lasers.[3] However a more efficient approach to ceramic machining is the laser machining of the ceramics in their green state.[1,2,4–7] Green state machining showed to be successful in part by the fact that green ceramics presents lower heat conduction than sintered ceramics. In addition presence of organic matter, as binder or gelling agent, produces a material etching mechanism quite different from that of fired ceramics. In short, the ceramic particles in the green body absorb the laser radiation and heat up significantly, the surrounding organic matter pyrolizes producing a gas jet. The expanding gas jet drags the surrounding matter outside of the processing site. Depending on the laser wavelength used and because of the different threshold fluence between the organic matter and the ceramic particles a "cold" ablation can be achieved. The material being removed with no significant heating of the ceramic.[6] Critical issue on cold ablation processing is the absorption of the laser radiation by the organic compounds.

Previous works with laser drilling of the ceramics in the green state deals mainly with alumina or alumina composite sheets machined with Nd:YAG- or CO_2-pulsed lasers. The wavelength at 1064 nm of Nd:YAG laser for alumina resulted in a better spatial resolution but with relative low removal rate because of the weak absorption.[5] In order to improve the absorption properties of green alumina substrates Slocombe et al.[7] suggested the addition of pigments. A different strategy to increase cold ablation efficiency was used by Nowak et al.[6] They used the CO_2 laser for ablation tests of LTCC composite (20–40 wt.% of Al_2O_3). The presence of such a high amounts of organic matter (26–46 wt.%) permitted to activate the ablation mechanism without presence of any thermal effects within oxide matter.

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0955-2219/$ – see front matter
doi:10.1016/j.jeurceramsoc.2008.04.012

Table 1
Some characteristics of the solid oxide powders used in the study

Powder (manufacturer)	d_{V50} (μm)	ρ_{TD} (g/cm^3)	Absorption coefficient at 1.064 μm
NiO (nickel(II) oxide, Alfa Aesar GMBH, Germany)			
As received	44	6.67	1.520
Milled	1.7	6.67	0.370
ZrO_2 (8 mol% Y_2O_3) (TZ-8YS, TOSOH, Japan)			
As received	0.1	5.9	0.002

The purpose of this work is to produce micron size channels in Ni–YSZ cermets to improve gas permeation. We used a three-step procedure. First, holes were machined in NiO–YSZ green ceramic substrates with an industrial Nd:YAG laser working at the wavelength of 1064 nm. Nd:YAG laser was chosen due to its excellent beam focus ability, precision in machining large areas and accuracy in the iteration of the process. The high absorption of laser radiation by the NiO particles and fast heat transfer to organic binders only present in amounts of 5 wt.% of solids resulted in fast material removal rates. In a second stage the machined NiO–YSZ plates were fired. Porous Ni–YSZ cermets with the desired drilled pattern were produced by reduction of the sintered NiO–YSZ ceramic plates.

2. Experimental

2.1. Preparation of ceramic substrates

The ceramic substrate was prepared using commercial ceramic powders (Table 1) via colloidal processing route based on the tape casting technique. The composition of 71 wt.% NiO and 29 wt.% of 8 mol% yttria-stabilized zirconia (named NiO–YSZ) was used in this study. Prior to the slurry preparation, the nickel oxide powder was attrition milled in organic media during 4 h using zirconium bath (d = 1 mm). The resulted powder showed the mean particle size of 1.7 μm as determined by scanning electron microscope (SEM) measurements. The deionised water was used as a solvent and polyacrylic acid-based polyelectrolyte (PAA, Duramax D-3005, Rohm and Haas, USA) was used as dispersing agent. The ceramic powders were dispersed in solvent using 50 vol.% solids loading with the dispersant concentration of 0.5 wt.%, referred to solids. Obtained suspension was ball milled with a planetary mill during 2 h. Two acrylic polymers were used as binders, a low glass transition temperature binder (Duramax B-1000, Rohm and Haas, USA, $T_g = -26$) and a high glass transition temperature one (Duramax B-1235, Rohm and Haas, USA, $T_g = 14$). The final proportion of binders was 10 wt.% referred to ceramic powder. The suspension was stabilized for 24 h using a low-speed rotating roller. Tape casting was performed on fixed Mylar carrier film using Doctor Blade equipment with the blades gap of 600 μm. After the drying in air for 24 h tapes obtained the final thickness of ≈500 μm and green density of 54% ($\rho_{green} = 3.5 \pm 0.1$ g/cm^3). Some tapes were stacked and cold rolled to obtain the substrates with the desired thickness.

For comparison purposes some substrates were sintered prior to laser machining using single binder burnt out and sintering cycle. Binder burn out was carried out with a heating rate of 1 °C/min up to 600 °C, followed by a dwell time of 30 min. Subsequent sintering was carried out by increasing the temperature with a heating rate of 5 °C/min up to the sintering temperature (1400 °C) with a dwell time of 2 h. Obtained substrates reached 95% of theoretical density ($\rho_{sintered} = 6.2 \pm 0.1$ g/cm^3). Some relevant thermo-physical properties of both green state and sintered NiO–YSZ ceramics are compiled in Table 2.

A reduction cycle of 2 h in a 5 vol.% N_2/H_2 gas mix at 800 °C completely transforms the sintered NiO–YSZ bodies into Ni/YSZ porous cermets of volume composition, 43.5% YSZ, 33.1% metallic Ni and 23.4% pores. According to previous studies on the reduction process in compounds of similar composition, reduction proceeds without a significant microstructure coarsening or sample contraction.[8,9]

2.2. Laser processing of the ceramic substrate

A commercial diode-pumped Nd:YAG laser has been used in this work (Rofin-Sinar E-Line 20). The laser system operates at its fundamental wavelength of 1064 nm with a maximum mean power of 11 W, in a Gaussian beam mode TEM_{00} with a beam quality factor $M^2 < 1.3$. The opto-acoustical Q-Switch commutator controls the cavity output in continuous and in pulsed mode, being generated pulses as short as 8 ns in a frequency rank of 1–40 kHz.

Since we search for a high speed drilling procedure of relatively small holes (less than 100 μm diameter) we used the fixed-beam percussion method instead of trepanning optics method more appropriated for larger diameter holes. The beam

Table 2
Some thermo-physical properties of NiO–YSZ ceramics[10–13]

	Green[a]	Sintered	Cermet
Density, ρ (g/cm^3)	3.5 ± 0.1	6.2 ± 0.1	5.48 ± 0.1
Specific heat, c_p (J/(g K))	0.503	0.503	≈0.5
Thermal conductivity, κ (W/(cm K)) (1000 °C)	0.018	0.033	0.24
Thermal diffusivity, D (cm^2/s) (1000 °C)	7.2×10^{-3}	7.2×10^{-3}	8.7×10^{-2}
Thermal diffusion length, L_{th} (μm) (8 ns pulse)	0.15	0.15	0.53
Vaporization enthalpy, H_v (kJ/cm^3)[b]	18.36	32.3	
Melting temperature, T_M (°C)	1851.58	1851.58	1453.85 Ni, 2676.85 YSZ

[a] 10 wt.% of binder has been discounted. ρ and c_p are taken as mass averages.
[b] From solid phase at 26.85 °C. Mass averages.