Fabrication of Micro Patterned Ceramic Structure by Imprinting Process

Yang Xu*,1, Fujio Tsumori*,2, Hyung-Goo Kang*2 and Hideshi Miura*2

*1Dept. Intelligent Machinery and Systems, Graduate School of Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.
*2Dept. Mechanical Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.

Received July 19, 2011

SYNOPSIS
In this report, an improved fabrication method of micro powder imprinting (μPI), which has the industrial value in reducing the cost and procedures, is introduced to fabricate the thin yttria-stabilized zirconia (YSZ) sheet with the micrometer scale patterns. The Kapton film mold was designed and employed in thermal imprinting in order to prevent the breakage of sheet as mold removing. After imprinting, debinding and sintering procedures, the well pattern consistence line and space patterns in scale of 8μm were obtained on 300μm thick ceramic sheets. The morphology of sintered ceramic patterns was observed and the behaviors of debinding and sintering were investigated in this report. Meanwhile, the imprinting on bilayer ceramic sheet was carried out and the results showed the well wave interface of each layer, which have the potential utilization for solid oxide fuel cell directly.

KEY WORDS
ceramic thin sheet, YSZ, Micro Powder Imprinting, μPI, SOFC

1 Introduction
The application of the solid oxide fuel cells (SOFC) is moving towards miniaturization and this component miniaturization displays a huge potential in the fields of communication and information technology, biotechnology. By now the scale of SOFC has come to sub-micrometer, even nanometer thickness9. In order to improve the electrical capability of micro SOFC, the recent researches are focused on three directions: the improvement and innovation of material component for electrode2-3) or electrolyte4-5); the porosity of micro structure for the electrode6); and the reduction of electrolyte thickness and increasing of reactive interface between electrolyte and electrode7). In this report, the fabrication process of micro patterned thin electrolyte sheet by micro powder imprinting method is discussed in detail.

For the electrolyte material, yttria-stabilized zirconia (YSZ) has been considered as the best ceramic component by now because of its attractive ionic conductivity, low electronic transference number, stability in dual environments (oxidizing and reducing) and stability against the electrode materials. Besides the electrolyte of SOFC, the YSZ ceramic thin sheets has been utilized as the functional ceramics in the field Micro Electro Mechanical Systems (MEMS)8-11), such as electro circuit substrate and monolithic ceramic capacitor, etc. Therefore the manufacturing of thin YSZ sheet has been paid more and more attention by the researchers. For the conventional fabricating methods, such as micro Powder Injection Molding (μPIM)12,13) and inkjet printing14,15), the high requirement of tools and procedure controlling limit their usage in the potential industrial production. On the other hand, owing to the requirements of application, a variant of fabricating process has been developed in order to manufacture patterns or structures which have micro/nanometer dimensions. The nanoinprint lithography (NIL) technique16,17) is one of them. By the NIL method, the complex three dimension patterns in micro/nanometer scale can be imprint on a substrate layer, whose components always belong to polymer material such as poly methyl methacrylate (PMMA) and so on.

In this paper, we proposed a improved method of Micro Powder Imprinting (μPI) to fabricate the ceramic thin sheets with micro patterns, based on the conventional powder warm compaction procedure18) and nanoinprint lithography techniques. Micro Powder Imprinting combines plastic imprinting process and powder metallurgy. This process is appropriate to small and complex-shaped components manufacturing at a low cost in comparison to other traditional powder technologies. By the μPI method, it comes to
possible that the ceramic sheet with three dimension patterns on single or multilayer ceramic layer can be gained by a few processes comparing with the conventional method.

2 Experimental Procedure

2.1 Ceramic Material

The feedstock powder (PXA500, TOSOH Corp.) for Powder Injection Molding process was employed as the ceramic material, in which the nanometer scale (average size of particle is about 600 nm) YSZ powder was kneaded with organic binders. In order that the cavity of the imprinting mold could be filled, the ingredients were heated to its glass transition temperature \( T_g \) of 130~140°C, and at this temperature the resistance of deformation reduces dramatically. The states of ingredients can be considered as continuous materials that have the mechanical properties of a viscoelastic or hyperelastic solid.\(^{(9, 20)}\)

2.2 Thermal imprinting and imprinting mold

For imprinting, the heating ratio, holding time and cooling ratio were 30°C/min, 5 minutes, and 10°C/min; the pressure was no less than 0.5 MPa to ensure the mold cavities could be full-filled. Meanwhile, the imprinting in vacuum prevented the existence of bubbles in the ingredients and the space in the cavity of mold. Figure 1 depicts the schematic process of imprinting.

The silicon oxide mold on which the line and space patterns were curved by Nano Imprint Lithography (NIL) method, were employed for thermal imprinting on the thick ceramic sheet. But it is difficult to separate the mold from the thin ceramic sheets without breakage, especially, when the thickness comes to the micrometer scale. In this report, a polymer of polymide (Kapton, Dupont) was used as the mold material and the micrometer line and space patterns were carved by laser on the 75 μm thick Kapton polymer film.\(^{(21)}\) (Fig. 2). The micrometer scale line & space patterns from 5 μm to 1 mm were employed in order to investigate the effects of pattern size on the morphology of imprinted ceramic sheets.

2.3 Debinding and sintering

The ceramic sheets with imprinted pattern were debound and sintered in the air atmosphere under the various temperature-time conditions. The debinding temperatures mainly were among 200~500°C, in which the heating rate was 30°C/h. The low heating rate could lead to the full evaporation of binders and avoid the large gaps caused by the ceramic powder movement. According to the pre-experimental results, the crack caused by thermal stress appeared on the samples which were cooled after being debound. Therefore, we adopted the continuous debinding & sintering procedure in our work. The sintering temperature was settled at 1500°C for YSZ material, and holding time was 2 hours. The heating rate was about 200°C/h from 500°C to 1500°C, while the cooling one was 100°C/h from 1500°C to 900°C and 50°C/h from 900°C to room temperature.

In addition, owing to the anisotropic shrinkage in ceramic sheet caused by the micrometer scale thickness and 3D patterns on it, the bending of ceramic sheet appears in the sintering procedure. Sintering parts are burred into the fine Al₂O₃ powder to avoid bending caused by the thermal shrink stress of the sheets. In practice, we have to keep the thickness of Al₂O₃ powders more than 25 mm in our experiment.

![Fig.1 Schematic process of micro thermal imprinting on ceramic sheet.](image)

![Fig.2 (a) The surface of SiO₂ mold was coated by surface agency; (b) micro patterns on SiO₂ mold; (c) micro patterns on Kapton mold; (d) the profile of cross section of Kapton mold.](image)
3 Results and Discussion

3.1 The morphology of micro pattern

Kaptone polymer has good thermal stability and stiffness even when the temperature reaches 300 °C. Therefore, the micrometer scale patterns can be imprinted on both surfaces of the 300 μm thick YSZ ceramic sheets. The imprinted results showed the well pattern consistency with the mold even when it comes to the 5 μm scale. Based on the controlling of parameter of debinding and sintering, a serial of sintered YSZ ceramic patterns were obtained. The sintered YSZ sheets show 20% linear shrinkage and the sintered patterns of line and space from 20 μm to 8 μm have a good consistence with the initial ones as shown in Fig. 3 (a), (b) and (c). The aspect ratio can reach two in Fig. 3 (b) and the minimum size of well pattern can reach 8 μm to 8 μm in Fig. 3 (c). The result in Fig. 3 (d) also illustrated that the patterns have distortion and linked to each other in 4 μm line and space size. The reason could be stated that the high debinding temperature and quick heating speed may cause the high internal vapor pressure and dramatic evaporation. And this internal pressure from binder vaporization during rapid heating results in the blisters or craters where the vapor pockets may erupt. This kind of inhomogeneous structure causes the distortion in thin section finally.

3.2 Debinding and sintering behavior

The porosity or relative density of sintered ceramic sheet is one of the most important parameter in this experiment. The utilization of YSZ sheet in SOFC asks for the full density for the electrolyte. Otherwise the transmission of oxygen will cause the reduction of oxygen partial pressure and the electron conductivity. The sintering temperature and keeping time are considered as the decisive factors and the effect of sintered temperature on the relative density of YSZ is illustrated in Fig. 4, in which the holding time maintain two hours. It is obviously that the max value appears at the temperature of 1400 °C. For the reducing of relative density when the temperature reach 1500 °C, the reasons can be laid on the following two points: The first is that pore coarsening will cause the mean pore size to increase while the number of pores will decrease at high temperature. Differences in the pore curvature lead to growth of the larger pores at the expense of the smaller, less table pores, known as Ostwald ripening. If the pore has a trapped gas, then solubility of the gas in the matrix will influence the rate of pore elimination. In surface, it causes the evacuated pores in the final stage. And within samples, pore growth can cause the decrease in density. Based on the research of Mr. Rao on sintering behavior of YSZ, stable cubic crystal will exist under the temperature of 1400 °C and monoclinic crystal will appear when ZrO₂ is cooled from the temperature above 1400 °C. Namely, 1400 °C is the critical temperature of phase transformation, and this transformation will cause the real density decreased.

The electron conductivity of electrolyte material can be separated into transmitting capability by the grain and grain boundary. It is considered that the electron conductivity

![Fig. 3 SEM images of sintered line and space pattern on ceramic sheet; the size of single pattern across section on imprinting mold: (a) 50×10 μm; (b) 40×80 μm; (c) 10×10 μm; (d) 5×5 μm.](image-url)
of grain is better than that of grain boundary. The reason can be stated that there is more oxide space in grain than in boundary. Therefore the larger grain size is expected in order to improve the electron transmitting and it can be gained by operating the high sintering temperature and long holding time. For our work, the average grain size of sintered YSZ ceramic is about 5 μm.

### 3.3 Bilayer imprinting

The milli/micrometer patterns can be introduced on the bilayer ceramic sheet which consists of two kinds of ceramic sheets. In order that the ingredients could fullfill the cave of the imprinting mold, the volume rate of binder in each layer is different from each other, which result in the different viscosity at the deforming temperature. Usually it is considered that the lower stiffness in lower layer make it easier to fullfill the cave of mold\(^{[37]}\). Figure 5 shows the result of bilayer imprinting. Furthermore, owing to the differernt linear shrinkage of each layer, separating always was observed in the interface when the multilayer ceramics are sintered. But non-planar interface caused by co-imprinting process can avoid this phenomenon when the multilayer materials are co-sintered.

### 3.4 Application in micro SOFC

Up to now the thickness of solid oxide fuel cell has come to micrometer scale in order to fit the requirement of industrial utilization\(^{[34]}\). The reduction of SOFC size asks for the larger reaction areas ratio in the interface of electrode material and electrolyte than the conventional flat interface in order to improve the real electron conductivity. The YSZ electrolyte sheet with line and space patterns can play an important role for this purpose and the cell samples have been obtained in our lab by screen printing the anode and cathode material on the patterned YSZ electrolyte sheet. For the future work, the bilayer imprinting and co-sintering skill will be used on the fuel cell to reduce the procedure steps.

### 4 Summary

Micro powder imprinting (μPI) method proposed in this
Fabrication of Micro Patterned Ceramic Structure by Imprinting Process

References


2) B. Huang, S.R. Wang, R.Z. Liu, X.F. Ye, H.W. Nie, X.F. Sun, and T.L. Wen: "Performance of La0.25Sr0.75
Ce0.5Sr0.5O3-δ Perovskite-structure Anode Material at Lanthanum Gallate Electrolyte for IT-SOFC Running on Ethanol Fuel", J. Power Sources, 167(2007) 39-46.

3) X.G. Zhang, M. Robertson, S. Yick, C. Dečespitet, E. Styles, W. Qu, Y.S. Xie, R. Hui, J. Roller, O. Kesler, R. Maric, and D. Ghosh: "Sm0.5Sr0.5CoO3+ Sm0.5Ce0.8O1.9 Composite Cathode for Cermet Supported Thin Sm0.5Ce0.5O1.9 Electrolyte SOFC Operating below 600 'C", J. Power Sources, 160(2006) 1211-1216.


5150.
21) H.G. Kang, Y. Xu, F. Tsumori, and H. Miura: 
"Fabrication of Micro Patterned Ceramic Mold by 
Laser Patterning. Proceeding of International 
Conference on Sintering 2011", Jeju, Korea, 2011, 
accepted.
22) R.M. German: "Sintering theory and Practice", John 
23) P.G. Rao, J.D. Ye, M. Iwasa, and K. Kondou: 
"Mechanical and Wear Properties of Low-Temperature-
Sintered 3Y-TZP Ceramics", Journal of South China 
University of Technology (Nature Science Editon), 29 
and K.B. Kim: "High-performance Micro-solid Oxide 
Fuel Cells Fabricated on Nanoporous Anodic 
Aluminum Oxide Templates", Adv. Funct. Mater., 21 
(2011)1154-1159.