

FREEFORM FABRICATION OF CERAMICS DENDRITES FOR FLUCTUATION MODULATIONS IN ENERGY AND MATERIAL FLOWS

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Abstract: Ceramics dendrite structures with geometrically ordered lattices had been created successfully by using a laser scanning and micro patterning stereolithography of spatial joining techniques. Micro rods of alumina, zirconia, titania and hydroxiapatite were connected to realize four, six, eight and twelve coordination numbers for fluctuation modulations of electromagnetic wave, electronic current propagation, heat diffusion, stress distribution, liquid flow and gas dispersion. Intensity profiles of these energy fields and material densities were visualized theoretically through finite element methods to compare with measured results. Technological concepts of these ceramics dendrites will be applied to novel sensor devices, composite materials, solid electrodes and biological implants in near future industrial and medical fields. In this paper, fabrication processes of ceramic dendrites and numerical simulations of spatial gas flows or electromagnetic wave propagations will be discussed for novel energy harvesting devices.

Key words: Ceramics dendrite, Solid Electrolyte, Dielectric Material, Stereolithography, Finite Element Method.

1. INTRODUCTION

For sustainable development and emission reduction of carbon oxides, solid oxide fuel cells (SOFCs) are investigated as novel generation systems of electric powers with high efficiencies in energy conversion circulations. Yttria stabilized zirconia (YSZ) with high ion conductivities for incident oxygen is widely adopted material for solid electrolyte anodes as the SOFC components, (Minh, N, 1993). Recently, porous network structures were introduced into YSZ electrodes in micrometer or nanometer sizes to increase surface areas of reaction interfaces and gap volumes of stream paths. In this investigation, solid electrolyte dendrites composed of YSZ spatial lattice structures with various coordination numbers were fabricated successfully by using micro patterning stereolithography and nanoparticles sintering techniques. In these dendrite structures, stress distributions and fluid flows were simulated and visualized by using a finite element methods. These new computer aided design, manufacture and evaluation (CAD/CAM/CAE) have been investigated to create micro components of various ceramic materials in our investigation group, (Kirihara, S., et al, 2011), (Kirihara, S., et al., 2011).

Subsequently, novel electromagnetic devices were created. Photonic crystals with periodic arrangements of dielectric media can reflect the electromagnetic wave perfectly and can exhibit forbidden gaps in transmission spectra through Bragg diffraction, (Kirihara, S., 2009), (Kirihara, S., 2011). Through introductions of air cavities into the periodic lattices, the electromagnetic waves having specific wavelengths can resonate with structural defects, and localized modes of transmission peaks appear in the photonic band gap. Such localization function of electromagnetic waves can be applied to various devices, for example resonators, waveguides, and antennas. The photonic crystals with a diamond structure composed of alumina lattices were fabricated by using the micro patterning stereolithography. The artificial crystals can reflect the electromagnetic waves perfectly and prohibit the propagations for all directions in terahertz frequency range. Moreover, the twinned diamond lattice structures including the plane defect were created to resonate with the terahertz waves and localize the electromagnetic energies for directional emissions. The terahertz waves are expected to detect micro cracks in material surfaces and structural defects in electric circuits by fine wave interferences, and to analyze cancer cells in human skins and toxic bacteria in natural foods through the higher frequency excitations. The electromagnetic wave transmissions were measured by using a terahertz wave spectroscopy. The resonance and diffraction behaviors were visualized and analyzed by a transmission line modeling method of a finite difference time domain simulations.

2. EXPERIMENTAL PROCEDURE

The solid electrolyte dendrites with spatial lattice structures were designed by using a computer graphic application. These surface areas of reaction interfaces and the gap volume of stream paths were calculated geometrically for the dendrite lattice with four coordination numbers as shown in figure 1. The dendrite lattices of 1.16 in aspect ratio can be considered to exhibit the higher reaction efficiencies and gas trans-

mittances according to Nernst equation. In the optimized dendrite structure, the diameter and length of YSZ rods were decided 92 and 107 μm , respectively. The lattice constant was 250 μm . The graphic data was converted into a stereolithographic format through polyhedral approximations. The solid model was sliced into the cross sectional numerical data sets to input the stereolithographic equipment (D-MEC: SI-C1000, Japan.). Photo sensitive acrylic resin dispersed with YSZ particles of 60 and 100nm in first and second diameters at 30 volume % were fed over a substrate from a dispenser nozzle. The highly viscous resin paste was fed with controlled air pressure, and spread uniformly by a mechanical knife edge. The thickness of each layer was controlled to 10 μm . The cross sectional pattern was formed through illuminating visible laser of 405 nm in wavelength on the resin surface. The high resolution image could be achieved by applying a digital micro mirror device (DMD) and an objective optical lens. Figure 2 shows a schematic illustration of the micro patterning stereolithography system. The DMD is an optical element assembled by micro mirrors of 14 μm in edge length. The tilting of each tiny mirror can be controlled according to the cross sectional data transferred from a computer. The solid micro structures were built by stacking these patterns layer by layer. In order to avoid deformation and cracking during dewaxing, careful investigations for the heat treatment processes were required. The formed precursors with dendrite structures were heated at various temperatures from 100 to 600 $^{\circ}\text{C}$ while the heating rate was 1.0 $^{\circ}\text{C}/\text{min}$. The dewaxing process was observed in respect to the weight and color changes. The YSZ particles could be sintered at 1500 $^{\circ}\text{C}$ for 2 hs. The heating rate was 8.0 $^{\circ}\text{C}/\text{min}$. The density of the sintered sample was measured by using Archimedes method. The ceramic microstructures were observed by a digital optical microscope and scanning electron microscopy. In the lattice dendrites, fluid flow velocities and pressure stress distributions were simulated and visualized by a finite volume method (FVM) application. Subsequently, the photonic crystals with diamond lattices composed of the alumina were fabricated by using the same methods. The whole structure was 6 \times 6 \times 2 mm in size consisting of 6 \times 6 \times 2 unit cells. The aspect ratio of the dielectric lattices was designed to be 1.5. The crystal structure was designed to open the perfect band gap as shown in figure 3. Acryl precursors including alumina particles of 170nm at 40 volume % were heated at various temperatures from 100 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$ while the heating rate was 1.0 $^{\circ}\text{C}/\text{min}$. Nanometer sized alumina particles could be sintered at 1500 $^{\circ}\text{C}$. The heating rate was 8.0 $^{\circ}\text{C}/\text{min}$. The transmittance and the phase shift of incident terahertz waves were measured by using terahertz time domain spectroscopy (J-Spec2001: Advanced Infrared Spectroscopy, Japan). Electric field intensities were simulated by transmission line modeling (TLM) method program.

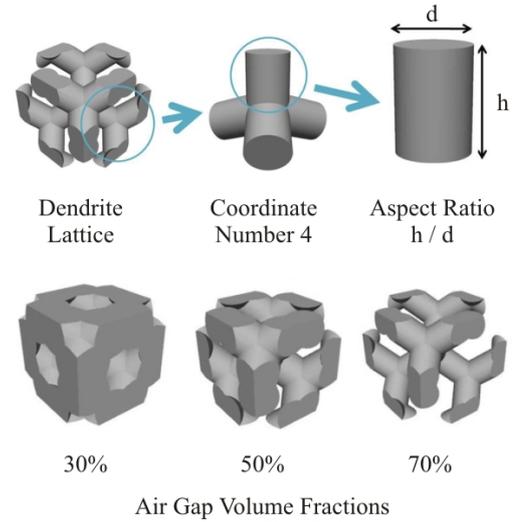


Fig. 1. Computer graphics of lattice distributions of dendrite structures with coordination number 4. Air gap volume fractions are changed with aspect ratios

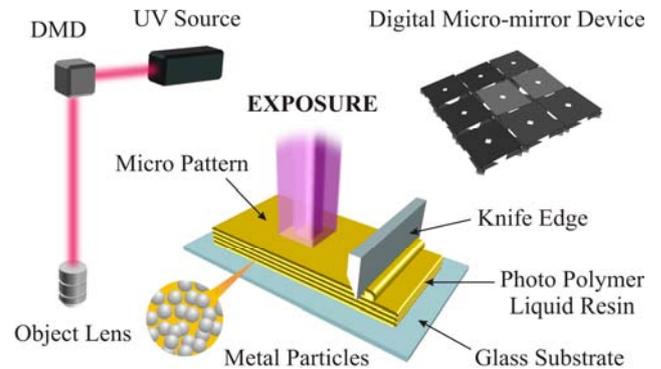


Fig. 2. Schematic illustrations of micro patterning stereolithography system. Two dimensional cross sectional layers are stacked up to create three dimensional structures automatically

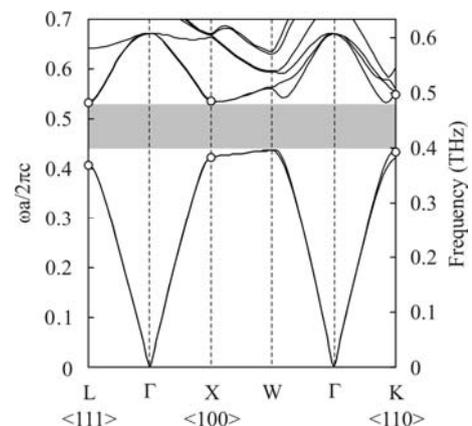


Fig. 3. A photonic band diagram calculated by the plane wave expansion method. Opened circles are measured edge frequencies of photonic band gaps. The dielectric constant of the lattice was 10. The frequency range with gray color indicates the perfect band gap in common for all directions

3. RESULTS AND DISCUSSION

The sintered solid electrolyte dendrite with the YSZ micro lattice structure was shown in Fig. 4. The deformation and cracking were not observed. The volume fraction of the air gaps was 50 % by the open paths. In the other previous investigations, the porous electrodes were formed by sintering the YSZ surly with polystyrene particles dispersion. Therefore, it is difficult to realize the prefect opened pores structures with the higher porosity over 40 % in volume fraction. In the dense microstructure of the YSZ lattice, the average grain size was approximately 4 μm . The relative density reached at 95 %. Micrometer sized cracks or pores were not observed. The obtained dense YSZ lattice structure will be exhibit the higher performances in mechanical properties as the porous electrodes of the solid electrolyte dendrites. The fluid flow velocities were visualized by using the FVM method as shown in Fig. 5. All air paths were opened for outsides and connected with each others in the YSZ dendrite lattice structures. The fluid flows can transmit the one direction smoothly. The pressure stress distributions in the dendrite were visualized as shown in Fig. 6. The fluid pressures were gradually distributed for flow direction, and the localization of the stress was not observed. The fabricated solid electrolyte dendrites with YSZ lattices can be considered to have higher performances as novel ceramic electrodes in near future SOFCs. Subsequently, the diamond structure formed by the micro stereolithography and sintered and the sintered alumina lattice were shown in Fig. 7-(a) and (b), respectively. The micrometer order dielectric pattern was created successfully according the geometrical design. The micro clacks or pores were not observed in the microstructure observations. The part accuracy of sintered sample was reacted at $\pm 10\mu\text{m}$ comparing with the designed structure. Through the computer aided design and manufacture processes, the twinned diamond lattice was fabricated as shown in Fig. 8. These mirror symmetric diamond lattices were formed with high part accuracies. The lattice constant of the diamond structure is 375 μm . The relative density reached 97.5 %. The measured band gap frequencies were compared with calculation results by the TLM method. The measured frequency ranges of opaque regions corresponded to the calculation. The complete photonic band gap opened between 0.40 and 0.47 THz. Two and three period lattice structures were arranged on the right and left side of the plane defect, respectively. The terahertz wave was transmitted from the left side to the right direction. In the measured transmission spectrum, one localized mode peak was observed in the band gap at the frequencies of 0.42 THz. The measured band gap region and the peak frequency of the localized mode were compared with calculations by the TLM method. They were in

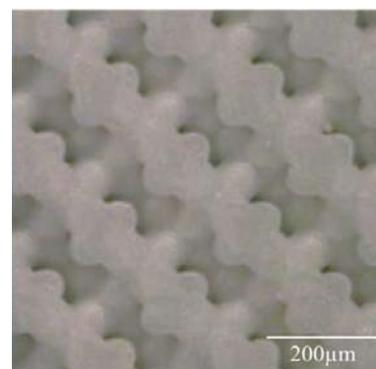


Fig. 4. Dendrite lattices of YSZ solid electrolyte processed by using the micro stereolithography and the nanoparticles sintering techniques successfully

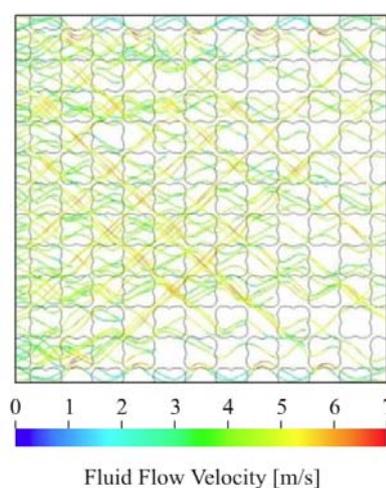


Fig. 5. A distribution of fluid flow velocities in the dendrite lattice structure simulated and visualized by using a FVM method. The curved lines show the fluid flow paths according to the velocity vectors

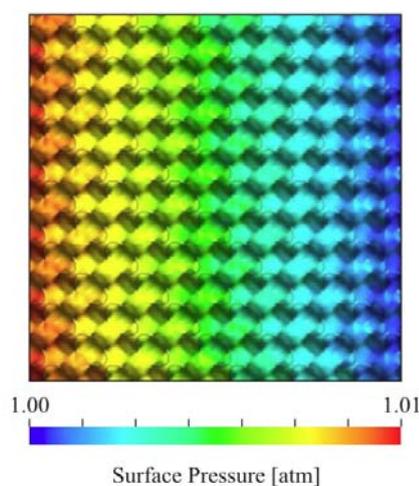


Fig. 6 The distribution of the surface pressure on the ceramics lattice of dendrite structure. The red and blue areas show the higher and lower gas pressures on the reaction interfaces, respectively

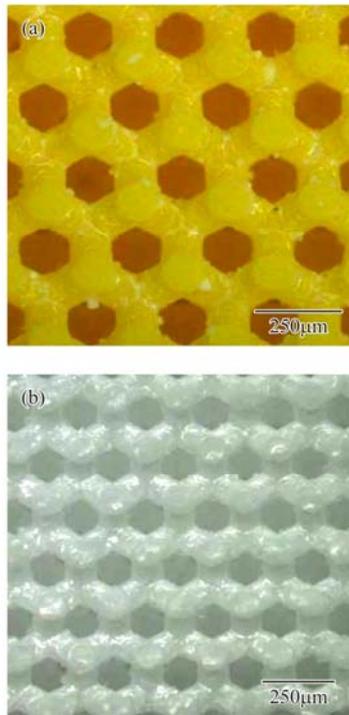


Fig. 7. Photonic crystals with diamond structures formed by the sterelithography and sintering. the acryl composite (a) and sintered alumina lattices (b)

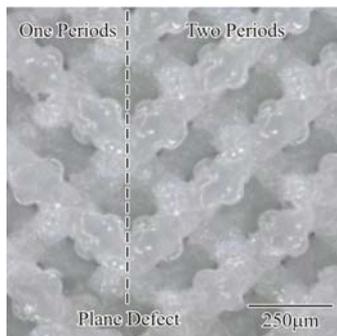


Fig. 8. A modified diamond photonic crystal with a plane defect between twinned lattice structures

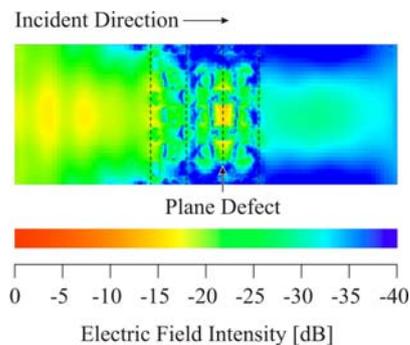


Fig. 9. A cross sectional images of electric field intensity in the twinned diamond photonic crystal

good agreement. The electric field distribution in the twinned diamond lattices was simulated as shown in figure 9. Incident terahertz wave was resonate and lo-

calized in the plane defect region between the twinned diamond lattices. The amplified electromagnetic wave by multiple reflections can transmit through the photonic crystal. Therefore, the transmission peak will be formed in the band gap. On the right side of the sample, the radiation pattern showed the plane wave expansion. The micro photonic crystal with the twinned ceramic lattice of the diamond structure can be applied to a terahertz beam emitters.

4. CONCLUSIONS

We have fabricated solid electrolyte dendrites with yttria stabilized zirconia lattices for anode electrodes of solid oxide fuel cells. Acryl precursors including ceramic particles were formed successfully by using micro patterning stereolithography. Thorough careful optimization of process parameters in dewaxing and sintering, we have succeeded in fabricating dense ceramic micro components. These solid electrolyte dendrites with opened air path networks exhibited effective transmission properties of fluid flows. These novel ceramic electrodes have potentials to contribute for developments of compact fuel cells. Moreover, alumina photonic crystals with a diamond structure were created with high part accuracies. Twinned dielectric lattices including plane defect can realize directional emission of electromagnetic waves in terahertz frequency ranges. These formed micro devices will be applied for sensor heads to detect harmful materials in the air or water of environmental fields.

6. REFERENCES

1. Minh, N., (1993). *Ceramic fuel cells*, Journal of the American Ceramic Society, Vol. 76, pp. 563-588.
2. Kirihara, S., Noritake, K., Tasaki, S., Abe, H., (2011). *Smart Processing of Solid Electrolyte Dendrites with Ordered Porous Structures for Fuel Cell Miniaturization*, Ceramic Interconnect and Ceramic Microsystems Technology, Vol. 7, pp. 17-22.
3. Kirihara, S., Noritake, K., Tasaki, S., Abe, H., (2011). *Smart Materials Tectonics: Development of Solid Electrolyte Dendrites*, Proceeding of the 19th Annual International Conference on Composites / Nano Engineering, Vol. 19, pp. 579-580, Shanghai.
4. Kirihara, S., (2009). *Terahertz wave control using ceramic photonic crystals with diamond structure including plane defects fabricated by micro stereolithography*, International Journal of Applied Ceramic Technology, Vol. 6, pp. 41-44.
5. Kirihara, S., (2011). *Development of Photonic and Thermodynamic Crystals Conforming to Sustainability Conscious Materials Tectonics*, WIT Transactions on Ecology and Environment, Vol. 154, pp. 103-114.