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Micrometer-scale imprinting process for ceramic sheet from powder compound material

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Abstract

A micro patterning process for thin ceramic sheets is proposed and developed in this paper. Thin sheets with a micro pattern have been expected to improve performance of solid oxide fuel cell. The authors focused on imprinting and powder metallurgy processes, and have developed the combined process, which has been named micro powder imprinting process. In this process, ceramic powder and polymer binder materials are mixed with pure water by milling machine. After drying out the water from the slurry, a thin compound sheet was obtained. Subsequently, the sheet was pressed using a fine patterned mold with heating to transcribe a micro pattern on the sheet. Finally, the imprinted sheet was heated for removing the polymer binder and for sintering. As further improvement of the process, a compound sheet was stacked on a pure polymer sheet during the imprint process to transcribe a micro pattern on the both sides of the sintered sample. The technique is useful for improved solid oxide fuel cell.

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Keywords: Micro patterning; Imprinting; Ceramics; Electrolyte; Solid oxide fuel cell

1. Introduction

A micro patterning process for thin ceramic sheets is proposed and developed in this paper. Thin sheets with a micro pattern have been expected to improve performance of solid oxide fuel cell. The solid oxide fuel cell consists

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of three layered materials: anode, cathode, and electrolyte. The performance of solid oxide fuel cell can be improved by increasing the interface area between the electrodes and electrolyte layers. It is known that the electrochemical reaction is limited to the region close to the interface between the electrode and the electrolyte by less than 10 μm depth. Therefore, the mesostructure of approximately 100 μm scale is optimal for the high efficiency. Konno et al. (2011a) have reported that a wavy interface can increase the performance of the solid oxide fuel cell. Furthermore, Iwai et al. (2011) have performed shape optimization design of the interface by a computational method, and have found a wavy interface structure as an optimized structure. The above reports have proposed to give a micro pattern only on one side of the electrolyte. Konno et al. (2011b) have demonstrated higher performance to apply micro patterns on both sides of the electrolyte on the computational calculation.

Fig. 1 shows a schematic image of a cell with the wavy interfaces. This is an objective structure of this study. Konno et al (2011a) have tried to apply a micro grooving pattern on one surface of the electrolyte by a sand-blasting process. However, the scale of the groove was 200 μm, which was larger than optimal scale, 100 μm. And, the zirconia ceramic sheet is so fragile that it is not easy to apply a micro pattern by a removal machining process if the target sheet were thinner. Therefore, the authors have focused on other processes; nano-imprinting lithography (Chou et al., 1995) and powder metallurgy processes. We have proposed the combined process, which is named micro powder imprinting (μPI) process (Xu et al. 2011a).

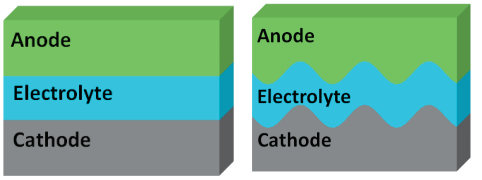

Fig. 1. Schematic structures of solid oxide fuel cell: (left) with flat interfaces, and (right) with wavy interfaces.

The nano-imprinting lithography has been used for fabrication of a nano-scaled structure although the process is only a simple hot-embossing process. Chou et al. (1997) have already shown example of a sub-10 nm imprint structure; it was far higher resolution than needed for this work. In the nano-imprinting lithography, a pure polymer material is used, while in the micro powder imprinting process, a compound material which is mixture of powder and polymer materials is employed for a starting material. A fine-patterned mold is put on the thin sheet of the compound with heat and pressure to transcribe the pattern on the thin sheet of the compound. Xu et al. (2011a) have employed a compound material with yttria-stabilized-zirconia powder, and have imprinted line-and-space patterns from 10 to 100 μm scale. The patterned compound sample has been successfully debound and sintered into a dense sheet with fine pattern. Xu et al. (2013) have shown improved cell performance by the patterning on the interface between the electrolyte and the anode.

Here, we proposed micro powder imprinting process for layered material for fabrication of micro patterns on both sides of a thin ceramic sheet. Fig. 2 shows the schematic of the process. The imprinting process for layered material has been proposed by Xu et al. (2011b). Tsumori et al. (2013a) have simulated the process by a computational method. We employed the layered material's imprint process with the micro powder imprint process; it means that the powder compound material was used as an upper layer and pure polymer material as a lower layer. By this technique, a thin and wavy ceramic structure can be easily obtained. The detailed process is described in the next section.

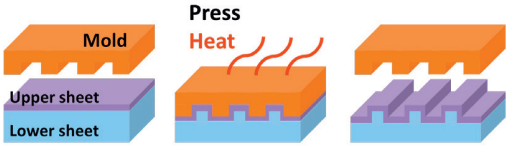

Fig. 2. Schematic of the imprint process for layered material. Two stacked sheets are pressed under heating. Micro patterns are made on both surface and interface between sheets.

2. Micro powder imprinting for layered material

Fig. 3 shows the flow of the micro powder imprinting process for layered material. At first, slurry of ceramic powder and polymer binder materials are mixed in solvent by a milling machine. After drying out the solvent from the slurry, thin compound sheet was obtained. Subsequently, the sheet was pressed using a fine patterned mold with heating to transcribe a micro pattern on the sheet. Finally, the imprinted sheet was heated for removing the polymer binder and for sintering. As described in the previous section, a compound sheet was stacked on a pure polymer sheet during the imprint process as shown in Fig. 3(III) to transcribe micro patterns on the both sides of the sintered sample. The lower layer was removed after the imprinting process.

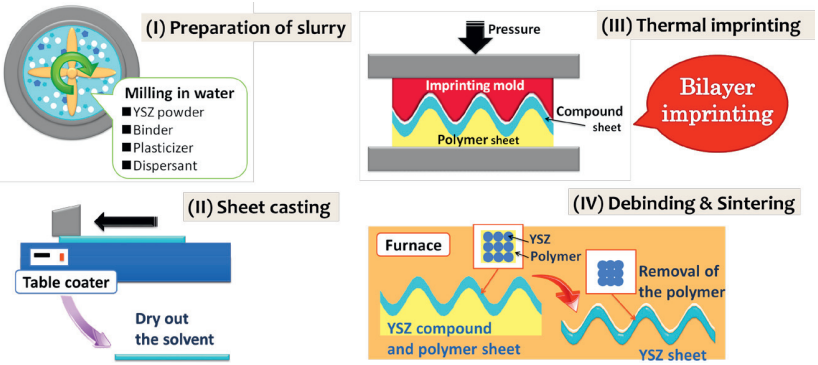

Fig. 3. Flow of the proposed fabrication process: (I) preparation of slurry, (II) sheet casting, (III) thermal imprinting, and (IV) debinding and sintering.

2.1. Slurry preparation

In this work, yttria stabilized zirconia was prepared as a ceramic powder material, polyvinyl alcohol as a binder material, and glycerine as plasticizer. This compound system is same with that of micro powder imprinting experiment for single layer material by Tsumori et al. (2013b). Mean diameter of the yttria-stabilized-zirconia powder (TOSOH, TZ-8Y) was 600 nm. And polyvinyl alcohol's property was as follows; degree of polymerization: 500; and degree of saponification: 86-90 %. Polyacrylic dispersant (Toagosei, AS-1800) was also prepared for good dispersion of the powder. The mixture was stirred by 10 min using a milling equipment (Ashizawa Finetech, Lab star mini) with yttria-stabilized-zirconia beads of 50 μm diameter. In this work, we prepared 2 types of sheet materials: compound sheets of yttria stabilized zirconia and binder, and polymer sheets without yttria-stabilized-zirconia powder for the process with a layered sheet, which will be described later. For the powder compound sheets, three types of slurry were prepared, changing the yttria-stabilized-zirconia powder loading by 35, 45, and 55 %. A material without yttria-stabilized-zirconia powder was prepared for the lower part of the layered imprinting. In all materials, volume fraction of polyvinyl alcohol and glycerin was kept constant, 7:3.

2.2. Sheet casting

Homogeneous slurry was obtained after the milling process, which was thinly applied on a polyethylene telephthalate sheet using a table coater (Mitsui Seiki Electric, PI-1210). Then the applied slurry was kept at 60 ^{o}C for 30 min in an oven to dry out the water to be formed into a compound sheet. The thickness of the sheet was controlled to be about 30 μm. A polymer sheet without yttria-stabilized-zirconia powder was also prepared by the same procedure. The controlled thickness of the polymer sheet was about 120 μm.

2.3. Thermal imprinting for layered material

We propose an imprinting process for a layered material to create patterns on both sides of the sheet material in this paper. By conventional imprinting methods, the micropatterns can be transcribed on only one side of the sheet material. By introducing bilayer imprinting, it is possible to form the patterns on both sides of the material. The flow of the process has been already shown in Fig. 2. In this work, we prepared 2 types of lower sheet materials. One was polyvinyl alcohol as described before, and the other was poly-dimethylsiloxane, which is a soft silicone rubber material.

The polyvinyl alcohol is the same material with the binder in the compound sheet for the upper layer. The polyvinyl alcohol layer disappeared during the subsequent debinding process by heating. Instead, the poly-dimethylsiloxane lower layer was removed before the debinding. poly-dimethylsiloxane has low surface energy so that removal from the upper layer is easy. Two types of poly-dimethylsiloxane, silicone rubber and silicone gel (Toray Dow, Sylgard 184 and 527, respectively), were prepared for the lower layer. These poly-dimethylsiloxane were mixed to obtain sufficient soft silicone material. The mixture rate of Sylgard 184 to Sylgard 527 was 1:4 by volume. The schematic flow after heating for each lower layer material is shown in Fig. 4. The lower polyvinyl alcohol layer was removed by heating in an oven during the debinding process, and the lower poly-dimethylsiloxane was peeled off just after imprinting.

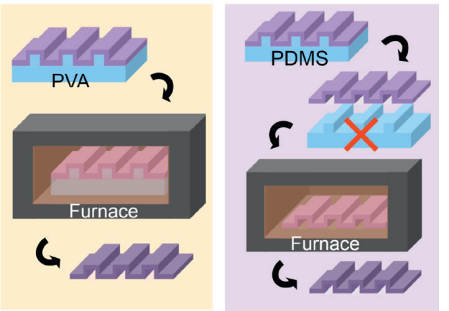

Fig. 4. Flow of processes after imprinting with polyvinyl alcohol (a) and poly-dimethylsiloxane (b) as lower sheets.

The imprinting pressure and temperature was the same with those of the previous work (Tsumori et al., 2013b). The imprinting temperature was 100 ^{o}C, and the pressure 3.5 MPa. As a mold material, a polyimide sheet with a line-and-space pattern which was formed by laser was prepared. The width of the line was 100 μm, and the pitch 200 μm.

2.4. Debinding and sintering

The formed compound sheet was heated to remove organic binder components. This process is called debinding. Also the lower polyvinyl alcohol sheet was removed during this process. The debound sample was sintered subsequent heating. The sintering temperature is much higher than that of debinding process, so that the organic composition was completely removed.

To obtain sound samples without bending or breakage, process conditions for debinding and sintering are important. For example, the heating rate during the debinding process is directly related to cracking. It is also necessary to set a proper sintering condition, such as temperature and keeping duration at the sintering temperature, to control crystal grain size of sintered yttria stabilized zirconia. We set the debinding and sintering temperature on the basis of the thermal analysis and the literature (Han et al., 2007) to fabricate sheets without defects. Holding temperatures (200, 350, and 600 ^{o}C) were determined by considering TGA experiment, where 2 hours were taken for each temperature as keeping duration. After debinding, the samples were sintered. For sintering, the temperature was raised to 1400 ^{o}C, and was slowly decreased from 1400 to 1300 ^{o}C taking 10 hours. The decreasing the sintering temperature resulted reduction of the crystal grain size.

3. Imprinting and sintering results

3.1. Bilayer sheet with lower polyvinyl alcohol layer

The imprinted samples were cut at the center for observation. Cross-sectional views of imprinted samples are shown in Fig. 5. The white part corresponds to the upper compound layer, and the dark layer below the upper layer corresponds to the lower polymer layer. It was found that the formability due to the change in the composition is related to the shape change of the wavy pattern. Fig. 5(a) shows that the upper layer was the sheet with the least powder loading in this work (35 %). The upper layer of this sheet was so soft (low viscosity) that it easily flowed into the mold cavity, whereas the lower layer of the polymer could not flow into the cavity. This behavior resulted in a less wavy pattern on the interface between layers. In Fig. 5(b), the powder loading ratio is 45 %. In this case, the peak height of the wavy interface pattern was larger, which means that the lower layer flowed more into the mold cavity. The thickness of the wavy upper layer was more uniform than that of the previous sample, and was about 30 μm. Figure 5(c) shows the sample with 55 % powder loading. This yttria-stabilized-zirconia compound sheet became harder so that the interface deformed slightly.

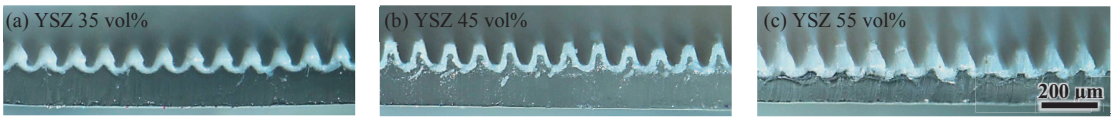

Fig. 5. Micro photos of cross sections of wavy interface structures with lower polyvinyl alcohol layer.

The surface area was evaluated by image analysis. The upper surface areas of 35, 45 and 55 vol% samples were 1.92, 2.06 and 2.06 times as much as the flat surface, respectively. And the lower surface areas were 1.21, 1.87 and 1.23 times. This result can indicate that the sample with yttria-stabilized-zirconia 45 vol% might improve the solid oxide fuel cell performance best among these three samples. Note that the interface pattern can be controlled by changing the material composition, as in the experimental results shown here. For a more precise design of the interface shape, computational simulation could be a powerful tool, as reported by Tsumori et al. (2013a).

The imprinted layered sheet was debound and sintered subsequently. However, it was difficult to obtain sound samples without breakage. This may be related to the volumetric change of the lower polyvinyl alcohol layer during the debinding process. Some debinding heat patterns were tried, and some samples were broken into several pieces, and others into many pieces.

3.2. Bilayer imprinting with lower poly-dimethylsiloxane layer

As described above, debinding of the layered sheet with the lower polyvinyl alcohol layer was difficult because of volumetric change in the lower layer by heating. If the poly-dimethylsiloxane sheet were used as lower layer, there would be no problem since the poly-dimethylsiloxane layer is removed before heating as shown in Fig. 4(b).

Fig. 6 shows cross-sectional images of as-imprinted and as-sintered samples with the lower poly-dimethylsiloxane layer. The upper layer was the compound with yttria-stabilized-zirconia 45 vol%. The soft poly-dimethylsiloxane layer deformed well to form the wavy interface during the imprinting process. And the lower layer was easily removed after imprinting. Fig. 6(a) shows the sample after removing the lower poly-dimethylsiloxane layer. The imprinted sample was successfully sintered without any crack as shown in Fig. 6(b). Similar structure was obtained after sintering. In this paper, only one example was shown for the lower poly-dimethylsiloxane layer. Of course, the interface shape can be controlled by changing mechanical properties of the upper compound layer and the lower poly-dimethylsiloxane layer as same with the previous examples of the lower polyvinyl alcohol layers.

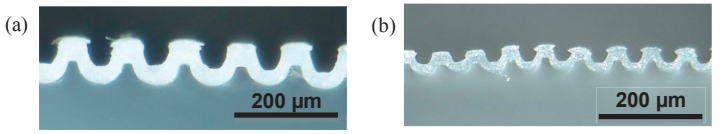

Fig. 6. Cross-sectional views of as-imprinted sample with lower poly-dimethylsiloxane layer (a), and as-sintered sample (b).

4. Conclusions

We proposed a new imprinting process using bilayer sheets. As a result, thin sintered ceramic sheets with patterns on both sides were successfully obtained. The wavy shape can be controlled by adjusting the formability of the sheets. In addition, the poly-dimethylsiloxane lower layer was effective to avoid breakage during the debinding step. The obtained microstructure is effective for improving the solid oxide fuel cell performance. A performance test for the solid oxide fuel cell by the present process is our future work.

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