Paper

Wavy Micro Channels in Micropatterned Ceramic Sheet Formed by Combined Process of Laser Beam Machining and Imprinting

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ABSTRACT

Micro channels made of polymers are commonly used for MEMS and μ TAS (micro-total analysis system) devices. In this research, we developed a process for fabricating a ceramic sheet with micro channels. The developed process is based on powder metallurgy process. A compound material, a mixture of ceramic powder and polymer, was prepared as sheet material. We employed laser machining to machine the sacrificial layer to form micro channels inside the sheet. We also employed imprinting, which is a process of pressing with a mould while heating, to form a structure with surface patterns and micro channels curving along with it. After the imprinted sheet was debound and sintered by heating, a ceramic sheet with micro-surface patterns and micro channels was obtained. As ceramics have high heat durability and low chemical reactivity, ceramic micro channels can be used for flow sensors or chemical reaction testers operated in harsh environments, such as high temperature or mechanical parts operated with reactive chemicals. In addition, by imprinting wavy patterns, the surface area can be increased. Therefore high efficiency heat exchangers can be built. Moreover, this method can be applied on SOFCs (solid oxide fuel cell) by fabricating YSZ (yttria stabilized zirconia) micro channels.

KEY WORDS

micro channels, imprinting, laser beam machining, ceramic

1 Introduction

Micro channels formed of polymer materials are commonly used for chemical reaction testers or MEMS (Micro Electro Mechanical Systems). The use of micro channels helps downsizing these devices as well as increasing the operating efficiency. Several fabrication processes for polymer micro channels have been reported¹⁻⁵⁾.

In this paper, we propose a fabrication method for ceramic micro channels. Since ceramic materials have low chemical reactivity and high heat durability, ceramic micro channels can be applied for chemical reaction testers or MEMS used in harsh environments. In addition, as our microchannel fabrication method enables surface patterning, micro channels with large surface area can be obtained. Therefore high efficiency heat exchangers can be built. Moreover, by using YSZ (yttria stabilized zirconia) as structure material, this microchannel forming method can be applied on SOFCs (Solid Oxide Fuel Cells).

In the process of forming ceramic micro channels, micro powder imprinting method, which has been developed by our group⁶⁻¹³⁾, was employed in order to fabricate alumina compound sheets

with surface patterns. The micro powder imprinting method has been proposed to enable micro patterning on the surface of ceramic sheets. Micro patterned ceramic sheets can effectively improve the performance of solid oxide fuel cells¹⁴⁻¹⁷⁾. This method combines powder metallurgy (P/M) process and nanoimprinting lithography¹⁸⁻²²⁾, which is an approach to transfer fine patterns to plastic polymer materials by using patterned moulds. The authors focused on powder processing. A compound material which is a mixture of powder material and polymer can be thermally imprinted. After removing the polymer by heat and sintering, the powder material consolidates, and a dense inorganic structure is obtained. This process can be applied on any material suitable for the powder metallurgy process.

We also employed laser beam machining in order to form micro channels. Laser beam machining removes material by melting or by direct vaporization and ablation. It is non-contact machining and inflicts almost negligible force to the machined object, which enables machining of delicate objects. In addition, it can remove material at atomic level. This allows micro machining.

Our micro channel forming process combines laser beam machining, a technique of interposing laser beam machined sacrificial layers,

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and imprinting. In our previous work²³⁾ we were successful at forming micro channels with micro patterns. In this work we have carried out thermal analysis on alumina compound sheets in order to find the optimum imprinting temperature. In addition, we attempted on forming micro channels curving along surface patterns by using a deep mould during the imprinting process.

2 Materials

In order to fabricate alumina compound sheets, poly(vinyl alcohol) (Wako Pure Chemical Industries. Ltd., polymerization degree: 500, T_m : 194 °C), glycerin (Wako Pure Chemical Industries.Ltd.) and alumina powder (TM-DAR, Taimei Chemicals Co. Ltd., particle diameter: 0.10 μm) were prepared. We also prepared polyimide (Upilex-25RN, Ube Industries, Ltd.) as middle layer material.

We carried out thermal analysis of alumina compound sheets, as fluidity of alumina compound sheets at different imprinting temperatures and decomposition temperatures of polymers included in the alumina compound sheet are important elements in our work.

The DSC (Differential Scanning Calorimetry) curve of alumina compound sheet [50 vol% alumina, 35 vol% poly(vinyl alcohol) and 15 vol% glycerin], which was conducted in N_2 atmosphere at a heating rate of 10 °C/min, is shown in Fig. 1. From this curve, we can see that the T_m (melting temperature) of PVA included in the alumina compound sheet decreased to 119 °C due to the influence of glycerin working as plasticizer. TGA (Thermogravimetric analysis) was also carried out in air flow at a heating rate of 10 °C/min. As shown in Fig. 2, there were three reduction peaks. The first peak is the decomposition of glycerin, which is decomposed entirely at 200 °C. The following two peaks indicate PVA decomposing in two stages at 270 °C and at 450 °C.

3 Fabrication procedure

The fabrication of alumina micro channels is carried out through 4 processes. The outline of the whole procedure is described in Fig. 3. At first, an alumina compound sheet with a resin layer on top is prepared (Fig. 3a). Next, the resin layer is laser beam machined into the shape of micro channels (Fig. 3b). After this, an alumina compound sheet is added on top of the laser beam machined resin layer. A mould is placed on top of this stack, and the imprinting process is carried out (Fig. 3c). During the imprinting process, the upper and lower layer alumina compound sheets push through gaps, which were formed by laser beam machining prior to this process, and the stack is fabricated into a single sheet with surface patterns and a resin layer in the middle (Fig. 3d). Finally, the imprinted sheet is put into a furnace for debinding, which is a process for decomposing, which is a process for eliminating polymer within the alumina compound sheet, and sintering. After the whole process, a wavy patterned alumina sheet with micro channels are obtained.

The details of each process are indicated in the following sections;

Fig. 1 Differential Scanning Calorimetry of 50 vol% alumina compound sheet.

Fig. 2 Thermogravimetric Analysis of 50 vol% alumina compound sheet.

sect. 3.1 for the preparation of alumina compound sheets, sect. 3.2 for laser beam machining, sect. 3.3 for imprinting and sect. 3.4 for debinding and sintering.

3.1 Preparation of alumina compound sheets

The alumina compound sheets are prepared by sheet casting a mixture of alumina powder, binder [poly(vinyl alcohol)], plasticizer (glycerin) and water. The composition was homogenously dispersed by ultrasonic treatment, and then sheet casted to form thin uniform sheets using a table coater (Mitsui Electric, TC-1). The sheets were then placed into an oven and heated at a temperature of 80 °C for 15 minutes to dry out. The thickness of alumina compound sheets were set at 70 μm , since on attempts of forming thicker sheets, uniformity was compromised.

Three kinds of alumina compound sheets with compounding ratios as indicated in Table 1 were prepared for our experiment. The compounding ratio of alumina was 55 vol%, 50 vol% and 45 vol%. This is an important factor for the following imprinting process and debinding process. Less alumina powder allows better formability during the imprinting process, however, it causes larger shrinkage, which could lead to cracks or deformation during the debinding process.

3.2 Laser beam machining

Laser beam machining was employed in order to process middle layer resin into the shape of micro channels. A diagram of the laser beam machining apparatus is shown in Fig. 4. The laser beam is discharged from the laser oscillator (Q-switch DPSS laser, LVE-G0300,

Fig. 3 Outline of micro channel forming process.

Spectronix Co.), and is guided through the beam expander and the attenuator, which controls the output power. Next, the laser beam enters the Galvano mirror, which controls the path of the laser

beam according to the machining program prepared on a computer. Finally, the laser beam is converged by the F-theta-lens and the object on the substrate is laser beam machined. The speculation of the laser oscillator is shown in Table 2. Wave length of the laser beam is 532 nm, and the spot diameter is 9.6 μm .

Polyimide with a thickness of 25 μm was prepared as middle layer resin, as its optical and mechanical properties are suitable for laser beam machining and imprinting. A simple line-and-space pattern with a width of 50 μm and a pitch of 150 μm as shown in Fig. 3b was machined in this research. The laser power was set at 650 mW, the pulse frequency was 200 kHz and the pattern was machined 8 times in order to achieve fine machined samples.

3.3 Imprinting

Alumina compound sheets and laser beam machined polyimide were stacked up as shown in Fig. 5 before imprinting. As our sheet casting method only allows fabrication of alumina compound sheets with a thickness of up to 70 μm , we piled up several alumina compound sheets in order to achieve sufficient thickness. Six alumina compound sheets were piled up as lower layer, a laser beam machined polyimide layer was placed above and two more alumina compound sheets were added on top of the polyimide layer. This stack was first laminated by heating at 40 $^{\circ}\text{C}$ and compressed to form a 450 μm sheet. Next, a steel mould was placed on top for the imprinting process. The mould, which has a depth of 300 μm and a pitch of 600 μm is shown in Fig. 6. It was prepared by wire electric discharge machining. Imprinting depth was set at 350 μm and the imprinting temperature was altered.

Heating is a key factor of the imprinting process. Imprinting temperature is commonly set at temperatures where the fluidity of the polymer being imprinted is sufficient to form surface patterns without cracks. The imprinting conditions were set, taking the DSC curves obtained earlier into account. The imprinting temperatures were selected at 40 $^{\circ}\text{C}$ which is before the melting starts, 70 $^{\circ}\text{C}$ where the melting starts, 100 $^{\circ}\text{C}$ which is in the middle of the melting process and 130 $^{\circ}\text{C}$ which is passed the peak of the melting process for alumina compound sheets with alumina compounding ratios of 45 vol%, 50 vol% and 55 vol%.

3.4 Debinding and sintering

After Imprinting, the stack was placed into an oven for debinding and sintering. Taking the TGA result into account, the debinding and sintering process was executed according to the timetable of Fig. 7. First, the oven is heated up to 200 $^{\circ}\text{C}$ and kept for 7.2 ks (2 h) for the glycerin to decompose. Next, the temperature is increased to 270 $^{\circ}\text{C}$ and held for 2 h. After this, the temperature is raised and held at 450 $^{\circ}\text{C}$ for 2 h. At this point, the polymers included in the alumina compound sheet are expected to be fully decomposed. Next, the oven is heated up to, and kept at 1350 $^{\circ}\text{C}$ for 2 h for the sintering process. During this, the polyimide strips decompose, the alumina powder consolidates, and a dense alumina structure with micro channels is formed.

Table 1 Composition of alumina compound sheets.

Alumina (vol%)	Poly(vinyl alcohol) (vol%)	Glycerin (vol%)
55	31.5	13.5
50	35	15
45	38.5	16.5

Fig. 4 Schematic of laser beam machining apparatus.

Fig. 5 Experimental setup for laminating and imprinting.

Table 2 Speculation of laser oscillator.

Wave length	532 nm
Output	3 W at 50 kHz
Repetitive frequency	Max 200 kHz
Pulse energy	70 μJ at 50 kHz
Pulse width	15 ns at 50 kHz
Spot diameter	9.6 μm

Fig. 6 Mould with a depth of 300 μm and a pitch of 600 μm.

Fig. 7 Time table of debinding and sintering process.

4 Results and discussion

4.1 Laser beam machining

Laser beam machining of the middle layer polyimide was carried out at a relatively low output power of 650 mW for 8 scans. The laser beam machined polyimide is shown in Fig. 8. By carrying out the laser beam machining process at low output power for several scans, the machined surface was smoother than that obtained with higher output power for fewer scans.

Since the width of the machined polyimide determines the width of the micro channels, the reduction of pitch will enable fabrication of smaller micro channels. With the present laser beam machining apparatus, we have succeeded in forming 50 μm channels. By reducing the spot diameter of the laser beam, smaller micro channels can be formed.

Fig. 8 Laser beam machined middle layer polyimide.

4.2 Imprinting

Optical images of the imprinted samples with alumina compounding ratios of 55 vol%, 50 vol% and 45 vol% are shown in Fig. 9, Fig. 10 and Fig. 11 respectively.

The imprinted samples of 55 vol% alumina compound sheet had cracks on the upper layer at any temperature. This shows that the fluidity was too low.

As for 50 vol% alumina compound sheet, surface cracks were detected in samples imprinted at 70 °C or lower. At an imprinting temperature of 100 °C, surface patterns had no defects and the middle layer curved along the surface patterns. However at imprinting temperature of 130 °C, the middle layer was exposed in some areas at the valley of the surface patterns. This is due to too high fluidity. Comparing this result to the DSC results of 50 vol% alumina compound sheet indicated earlier, it can be said that the suitable imprinting condition is at the middle of $T_{m \text{ onset}}$, which is the temperature that melting begins, and T_m .

As for 45 vol% alumina compound sheet, no cracks occurred even at a low temperature of 40 °C. At 130 °C the fluidity of 45 vol% alumina compound sheets were too high, that the middle layer exposed at the valley of surface patterns alike the 50 vol% alumina compound sheets, which was imprinted at the same temperature.

From these results, it can be said that high compounding ratios of alumina powder lowers the fluidity of alumina compound sheets. Compounding ratios of 55 vol% or higher are not suitable for imprinting. 100 °C for 50 vol% alumina compound sheets and 40 °C for 45 vol% alumina compound sheets are the best imprinting

Fig. 9 Optical images of imprinted 55 vol% alumina compound sheet samples.

Fig. 10 Optical images of imprinted 50 vol% alumina compound sheet samples.

conditions. In these conditions, surface cracks were not found and the middle layer polyimide curved along the surface patterns.

4.3 Debinding and sintering

The CT (Computed Tomography) scanned image of sintered sample of 50 vol% alumina micro channels is shown in Fig. 12. Micro channels without defects were successfully formed. During the debinding process, the polymers in the alumina compound sheet decompose as gasses. These gases can cause inner pressure and lead to cracks in the structure. In our work, the heating program was controlled to allow polymers to decompose slowly. No fractures or cracks occur during the sintering process. The shrinkage rate of 50 vol% and 45 vol% alumina compound sheets were 19 % and 21 %, respectively. This indicates that shrinkage is reduced by including less polymers in the alumina compound sheets.

Micro channels formed by this method become a single ceramic structure. Due to this, the micro channels are strong against inner

pressure. In addition, as these micro channels are not formed by laminating different materials, separation between upper and lower layer caused by difference in thermal expansion coefficient will not occur.

5 Conclusion

We propose a process to form alumina sheets with micro channels curving along surface patterns. By combining laser beam machining, imprinting with a deep mould, and a process of interposing sacrificial layers inside alumina compound sheets, we were successful in fabricating sound micro channels. These alumina micro channels can be applied as high-efficiency heat exchangers or Micro Electro Mechanical Systems used in harsh environments. By altering the laser beam machining program, shape of mould and stacking order of alumina compound sheets and laser beam machined layer, our microchannel forming process allows fabrication of complex out-of-plane micro channels.

Fig. 11 Optical images of imprinted 45 vol% alumina compound sheet samples.

Fig. 12 CT scanned image of the alumina micro channels.

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