In the nanoimprint process, the transfer failure due to the air involved from pressing the mold against the transfer material and the gas generated from the transfer material has been reported as a serious problem. We have investigated the relationship between the thickness of the mold and the gas permeation flow rate in a single-layer gas permeable mold with only a low density structure and a two-layer gas permeable mold with a low density structure and a lattice structure manufactured by a 3D printer. Furthermore, we imprinted the transfer material containing volatile solvents using two gas permeable molds, and investigated the presence of transfer defects due to gas. As a result, the gas permeation flow rate increased as the thickness of any gas permeable mold became thinner. In addition, when the gas permeable mold having a two-layer structure and the gas permeable mold having a single-layer structure are compared, the gas permeation flow rate of the two-layer structure is about 20 times as large as that of the single-layer structure. Furthermore, as a result of investigating the presence or absence of transfer failure due to gas in imprint molding, transfer failure due to gas occurred in the non-gas permeable mold, but transfer failure due to gas did not occur in the gas permeable mold having the two-layer structure. Therefore, the lattice structure designed for the gas passage can greatly improve the gas permeation flow rate, and it can be expected to reduce the transfer failure due to the gas at the time of imprint.

Keywords: Photo imprint lithography, Gas permeable mold, Gas permeation flow rate, 3D printer

1. Introduction

Nanoimprint has attracted attention as a micro-fabrication technology. Since nanoimprinting can process patterns on the order of 10 nm, it is expected to be active in various fields. For example, optical devices, electronic devices, cell culture sheets. As the nanoimprint technology, there are thermal nanoimprint lithography using a thermosetting resin and photo nanoimprint lithography using a photopolymerizable resin.

In the case of curing the transfer material, thermal nanoimprint lithography has a limitation in pattern accuracy because shrinkage due to heat occurs. Therefore, photo nanoimprint lithography has been proposed in which light is used to cure a transfer material [1-3]. Photoimprint lithography has the following excellent features:

1) The pressure for filling the resin into the mold is low
2) It is relatively easy to cope with the large area
3) Because the influence of thermal expansion is small, the pattern accuracy is good etc.

However, problems such as transfer failure due to gas and template breakage have also been reported. The causes of gas generation in the template are air that is trapped between the template and the transfer material when the template is pressed against the transfer material, or volatile gas generated from an additive of the transfer material, reaction gas generated by thermal reaction or photoreaction [4-6]. Then, gas permeation templates using plant-derived materials have been reported as means for
discharging gas out of the mold [7-12]. Furthermore, the gas permeation template also evaluates the gas permeability to various volatile solvents such as acetone and cyclopentane, and at the same time, the durability of the printing number is also evaluated [13].

However, while the effect of gas discharge has been recognized, there is a problem in that the mechanical strength of the gas permeation template is insufficient in order to increase the area of the transfer surface. The following two can be considered as a method of solving the problem. The first method is to improve the mechanical strength of the template itself, and the second method is to reinforce the template with other members. The first method is a method of adding reinforcing fibers such as glass fibers and carbon fibers to a template. Further, in recent years, researches have also been reported in which cellulose nanofibers are added to improve mechanical strength [14].

As shown in Fig. 1, the second method uses a gas permeable mold produced by the 3D printer proposed by the author.

![Fig. 1. Comparison of a) conventional method and b) our proposal method.](image1)

This method improves the mechanical strength at the time of imprinting without impairing the gas permeation amount by imparting gas permeability to the mold for installing the gas permeation template. However, in the previously reported gas permeable mold, the positions of the gas permeable pores were not designed, and the places where the gas permeated were limited. In addition, all the pores present in the mold were not connected, and the gas permeation amount was limited.

In this study, test pieces controlled gas permeation structure and pore position were manufactured, and the gas permeability of the test pieces was evaluated. Moreover, in order to confirm the transfer failure of a transfer material, imprint was carried out on the transfer material containing a volatile solvent using the test piece which evaluated gas permeability.

2. Experimental

2.1. Production of gas permeable mold

Figure 2 shows the processing process. First, in the method of preparing the gas permeable mold, metal powder which is a main raw material is spread on a base plate. Then, the metal powder is irradiated with a laser to melt and solidify the metal powder. Repeat the work of laser irradiation and laying of metal powder, and when 5 μm is laminated, shift to cutting. The mold material having a low density structure or a lattice structure was shaped by changing shaping conditions such as laser output and laser path.

As a processing machine, a metallic light shaping combined processing machine Avance 25 manufactured by Matsuura Machinery Co., Ltd. was used. And the metal powder used as a main raw material used Matsuura maraging II supplied by Matsuura Machinery Co., Ltd. The particle size of the metal powder is 20 μm to 30 μm.

![Fig. 2. Metal laser sintering process.](image2)

2.2. Types and structures of gas permeable molds

Figure 3 shows the schematic view of the structures of two types of gas permeable molds produced by the 3D printer used in this experiment. Figure 3 (a) shows a single-layer gas permeable mold having a porous structure, and Fig. 3 (b) shows a two-layer gas permeable mold having both a porous structure and a lattice structure. The porous structure suppresses the laser output of the 3D printer, and by irradiating the metal powder with a laser arbitrarily, an unmelted area and a melted area...
are created. The feature of porous structure is that since the unmelted portion becomes pores through which the gas passes, the amount of gas permeation is small, but the unevenness of the gas permeable pores is not noticeable on the surface. The lattice structure is produced by scanning a laser in the form of a lattice, and the gaps between the lattices become pores through which gas passes. The feature of the lattice structure is that the shape is transferred to the transfer material because lattice holes appear on the surface, but the gas permeation amount is significantly larger than that of the porous structure.

Fig. 3. Schematic of the structure of two gas permeable molds made by 3D printer.

2.3. Gas permeation flow rate
2.3.1. Preparation of gas permeation flow rate test pieces

Figure 4 is a schematic view of a test piece prepared to measure the gas permeability of a gas permeable mold. The shape of the test piece is a circular and has an outer diameter of 40 mm and a thickness of 7 mm. The portion of 20 mm to 40 mm in diameter of the test piece has a structure without gas permeability. The portion of 20 mm in diameter of the test piece has a structure with gas permeability. The gas permeation part of the test piece has two types of structure, the first type has a single-layer structure and the second type has a two-layer structure. The single-layer structure (Single-layer test piece) is formed of a porous structure, and the two-layer structure (Two-layer test piece) is formed of a porous structure and a lattice structure. The gas permeation rates are measured by changing the type and thickness of these structures. The gas permeation flow rate is measured by changing the type and thickness of these structures.

Table 1 shows the relationship between the type of structure at the center of the test piece and the thickness, Table 2 shows the conditions for forming the porous structure and the lattice structure.

Then, Fig. 5 shows confocal micrographs of the porous structure and the lattice structure of the surface of the gas permeation flow rate test piece prepared.

![Fig. 4. Schematic of test piece for gas permeation flow rate.](image)

![Fig. 5. Confocal micrographs of the (a) porous structure and (b) lattice structure of the surface of the test piece.](image)

2.3.2. Gas permeation flow rate measuring device

Figure 6 shows a schematic of the gas permeation flow rate measuring device used in this experiment. In this gas permeation flow rate measuring device, the gas permeation flow rate test piece is sandwiched and fixed by two jigs located on the upper and lower sides. Air is supplied from the lower jig with a pressure pump, and the amount of aeration discharged from the upper jig is measured. Here, the pressure difference between the upper and lower jigs is pressure loss $\Delta P(P_1 - P_2)$ [MPa].
and the amount of air flow discharged from the upper jig is Q2 [L/min]. The pressure sensor is model number AP-C33, and the flow sensor model number FD-A100 is both made by Keyence Corporation.

2.4. Transfer to solvent-containing photocurable resin transfer material using gas permeable mold

2.4.1. Components of photocurable resin transfer material

Figure 7 shows the components of the photocurable resin transfer material used in this experiment. The photocurable resin transfer material consists of 66 wt% isobornyl acrylate, 33 wt% n-butyl acrylate, 4.0 wt% 2-hydroxy-2-methylpropiophenone, 3.0 wt%. This photocurable resin contained 50 wt% of acetone.

2.4.2. Photoimprint process

Figure 8 shows the transfer process. First, a transfer material which is a photocurable resin is applied to a glass substrate. Next, the mold subjected to release treatment was pressed against the transfer material, and UV was irradiated from the back surface of the glass substrate with a UV lamp for 600 seconds to cure the transfer material. Finally, mold was separated from the transfer material, and the surface of the transfer material was observed with a confocal microscope.

Two types of molds are used, one is a mold having no gas permeability, and the other is a gas permeable mold having a porous structure and a lattice structure.

3. Results and discussions

3.1. Gas permeation flow measurement in gas permeable mold test pieces

Figure 9 shows the result of gas permeation flow rate measurement in the single-layer test piece.

According to the Fig. 8, it was confirmed that the single-layer test piece with a thickness of 1.0 and 2.0 mm permeates the gas, but it is confirmed that the single-layer test piece with a thickness of more than that does not transmit the gas. It is considered that as the thickness increases, the pores are clogged as the gas permeation pores inside the single-layer test piece are not all connected. Furthermore, it is inferred that the reason why the pores are not...
connected is due to the forming method of the porous structure. In the porous structure forming method, the laser output is suppressed, and the laser path is arbitrarily scanned to form the unmelted portion to be the pores, so the clear pores are not designed. Therefore, it is considered that the design of pores is indispensable for the improvement of the gas permeation amount.

Figure 10 shows the result of gas permeation flow rate measurement in the two-layer test piece. According to Fig. 10, it can be confirmed that the gas permeation flow rate hardly changes when the thickness of the two-layer test piece is 0, 0.5 mm. In addition, when the thickness of the two-layer structure is 1.5 mm or more, it can be confirmed that the gas permeation amount decreases.

![Figure 10](image1)

**Fig. 10.** Measurement results of gas permeation flow rate in the two-layer test piece.

Figure 11 shows the result of gas permeation flow rate measurement of single-layer test piece and the two-layer test piece in the case of the same thickness of 1.0 mm. According to Fig. 11, it can be confirmed that the two-layer test piece has a gas permeation flow rate much more than that of the single-layer test piece. It is considered that since the lattice structure constituting two-layer test piece has a hole penetrating to the surface of the mold, it can pass gas without pressure loss.

![Figure 11](image2)

**Fig. 11.** Measurement results of gas permeation flow rate in the single-layer test piece and the two-layer test piece in the case of the same thickness of 1.0 mm.

3.2. Observation of solvent-containing transfer material using gas permeable mold

Figure 12 shows a confocal microscopic image a material containing 50 wt% acetone imprinted using (A) non-gas permeable mold and (B) gas permeable mold having two-layer structure. According to Fig. 12, a white bubble is observed in Fig. 12 (A), but it cannot be confirmed in Fig. 12 (B). In Fig. 12 (A), it is considered that acetone gas is trapped in the mold and the transfer material because the mold does not have gas permeability. In Fig. 12 (B), it is inferred that acetone gas is discharged to the outside through the pores because the mold has gas permeability. However, it can be confirmed pores of the gas permeable mold having a size of about 20 μm to 30 μm in Fig. 12 (B). The pore pitch of the gas permeable mold cannot be made smaller than this size under the current shaping conditions. Therefore, it is necessary to develop metal powder pulverization, granulation and 3D printers.

![Figure 12](image3)

**Fig. 12.** Confocal microscopic image of transfer material imprinted by using (A) non-gas permeable mold and (B) gas permeable mold having two-layer structure.

4. Conclusion

As a result of measuring the gas permeation flow rate, it has been confirmed that the gas permeation flow rate of the two-layer test piece is significantly large. In other word, it was confirmed that the lattice structure was effective for the increase of the gas permeation amount. As a result of transferring to a transfer material containing 50 wt% of acetone using a gas permeable mold having two-layer structure, no bubbles could be confirmed on the surface of the transfer material.

While gas permeable molds are expected to reduce gas transfer failure in photoimprinting, there are still problems to solve for the transfer of pore trace to the transfer material.
Acknowledgments

This project was supported by JSPS KAKENHI No. 16K04920, JSPS Bilateral Joint Research Projects 2017 in Belgium, JST program No. VP29117936791, Toyama Nanotech Cluster of Ministry of Education, Culture, Sports, Science and Technology, Japan, The Canon Foundation, The Amada Foundation, The Die and Mould Technology Promotion Foundation, The Murata Science Foundation, The Osawa Scientific Studies Grants Foundation, Advanced Machining Technology & Development Association, and The Ogasawara Foundation.

References

1. J. Haisma, M. Verheijen, K. van den Heuvel, and J. van den Berg, J. Vac. Sci. Technol. B, 14 (1996) 4124.
2. M. Colburn, S. C. Johnson, M. D. Stewart, S. Damle, T. C. Bailey, B. Choi, M. Wedlake, T. B. Michaelson, S. V. Sreenivasan, J. G. Ekerdt, and C. G. Willson, Proc. SPIE, 3676 (1999) 379.
3. T. Bailey, B. J. Choi, M. Colburn, M. Meissl, S. Shaya, J. G. Ekerdt, S. V. Sreenivasan, and C. G. Willson, J. Vac. Sci. Technol. B, 18 (2000) 3572.
4. S. H. Ahn and J. S. Guo, ACS Nano, 3 (2009) 2304.
5. S. Y. Chou, P. R. Krauss and P. J. Renstrom, J. Vac. Sci. Technol. B, 14 (1996) 4159.
6. J. G. Kim, Y. Sim, Y. Cho, J.W. Seo, S. Kwon, J. W. Park, H. G. Choi, H. Kim, and S. Lee, Microelectron. Eng., 86 (2009) 2427.
7. S. Takei, S. Nakajima, K. Sugahara, M. Hanabata, Y. Matsumoto, and A. Sekiguchi, Macromol. Mater. Eng., 301 (2016) 902.
8. M. Hanabata, S. Takei, K. Sugahara, S. Nakajima, N. Sugino, T. Kameda, J. Fukushima, Y. Matsumoto, and A. Sekiguchi, Proc. SPIE, 9777 (2016) 97771G.
9. S. Nakajima, S. Takei, Z. Zhou, H. Maki, K. Sugahara, M. Hanabata, Y. Matsumoto, and A. Sekiguchi, J. Photopolym. Sci. Technol., 29 (2016) 189.
10. S. Takei and A. Sekiguchi, Appl. Sci., 2 (2012) 24.
11. S. Takei, N. Sugino, T. Kameda, S. Nakajima, and M. Hanabata, Proc. SPIE, 9985 (2016) 99852C.
12. S. Nakajima, S. Takei, M. Hanabata, N. Sugino, T. Kameda, Y. Matsumoto, and A. Sekiguchi, Proc. SPIE, 10354 (2017) 103541B.
13. K. Mizui, K. Kurematsu, S. Nakajima, M. Hanabata, and S. Takei, J. Photopolym. Sci. Technol., 31 (2018) 289.
14. S. Murayama, I. Motono, K. Mizui, K. Kondoh, M. Hanabata, and S. Takei, J. Nanomater., 2019 (2019) 5180460.