Novel Fabrication Method of Minute Cylindrical Structures Such as Stents using Lithography, Etching, and Chemical Polishing

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Abstract: Applicability of characteristic subtractive processes of stainless-steel pipes to fabrication of minute structures such as stents was demonstrated. Pipes with an outer diameter of 2 mm, a thickness of 50 µm, and a length of 50 mm were coated with a resist PMER N-CA3000 PM in approximately 10 µm thick in 20 mm area at the tip parts of pipes. Next, stent-like mesh patterns composed of 30 rhombuses on an ordinary flat film reticle were replicated on a pipe using a rotary scan-projection exposure system, in which patterns were precisely and homogeneously replicated by synchronously scanning the reticle linearly in perpendicular to the pipe axis and rotating the pipe at a constant speed. All the patterns on the reticle were continuously replicated during the pipe was rotated 360º. After printing the stent-like mesh patterns, the pipes were processed in two steps. In the first step, they were wetly etched in $FeCl_3$ aqueous solution, and in the second step, they were chemically polished in a chemical compound on the market. As a result, a stent-like meshed pipe with mesh widths of 83±6 µm was precisely fabricated.

1 INTRODUCTION

Diseases of blood vessels are one of the typical illnesses in the present age. Choked, damaged, or adhered vessels prevent the supply of fresh blood to organs and tissues, and cause the necrosis and degradation of organs. For this reason, effective medical treatments have to be given in the early stages of diseases.

Insertions of stents are considered as prospective treatments (Varghese, 2015) (Rahal, 2014) (Caiazzo, 2015). Stents are cylindrical components with net-like structures, and have appropriate elasticity and rigidity. When the stents are inserted in blood vessels, they should be folded or shrunk in diameter. On the other hand, once they are inserted, they have to support the blood vessels from inside and secure the blood paths (Tammareddi, 2016).

For this reason, various methods have been researched and developed for fabricating stents superior in usability, functionality, and mechanical properties. Knitting of wires or fibres (Rebelo, 2015) and cutting of metal pipes using laser beams (Kesavan, 2013) (Ando, 2017) (Nishi, 2013) are typical methods.

On the other hand, the authors have researched on lithography systems for patterning on fine cylindrical specimens such as pipes, wires, shafts, and others. For this reason, as a typical application of the system and related lithography and etching technologies, fabrication of stent-like structures is investigated here.

Generally speaking, patterning accuracies of lithography and etching are higher than laser beam cutting. In addition, it is expected that roughness of part-edges obtained by lithography and etching is improved by serially adding chemical polishing after the etching. Based on these considerations, this research has been performed.

As a lithography tool, a handmade rotary scan-projection exposure system (Horiuchi, 2015) (Horiuchi, 2016) is used. In this system, patterns on a flat reticle in an oblong slit area is projected on a cylindrical ridge of specimen pipe. When the reticle is linearly scanned across the slit and the pipe is rotated around its axis synchronously, patterns on the reticle are continuously replicated on the cylindrical surface of the pipe.

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Lithography tools for printing on cylindrical pipes have not been commercially available. Although various ideas have been reported (Lee, 2011) (Haoa, 2011) (Lim, 2014), performances comparable with or superior to those of our system have never been shown for printing aimed complicated patterns.

After the pipes with stent-like patterns of resist are etched in an aqueous solution of ferric chloride ($FeCl_3$), original shapes of stent-like meshed pipes were fabricated. Fabrication methods up to this stage have been already developed in the past researches of authors (Ito, 2017) (Horiuchi, 2019).

However, in the past researches, the minimum mean mesh width was 109 µm, and it was difficult to reduce the widths without making locally broken parts. For this reason, as a new idea, chemical polishing process is added here. By polishing the meshed pipes slowly and carefully, the mesh widths are reduced down to 83 µm. The roughness of the meshes is also improved.

2 FABRICATION PROCESS OF STENT-LIKE MESHED PIPES

Meshed patterns were designed by connecting rhombuses at their corners sequentially. The rhombuses were arrayed 5 in the axial direction and 6 in the circumferential direction. Figure 1 shows the reticle patterns designed by extending the aimed meshed pipe shape. After 5×6=30 rhombuses were regularly arrayed, connections at 12 corners were intentionally separated for giving flexibility or deformability to the meshed pipe. The rhombus pattern width was 130 µm.

It was planned to fabricate this structure according to the following processes, as shown in Figure 2. At first, the meshed patterns of resist were printed on

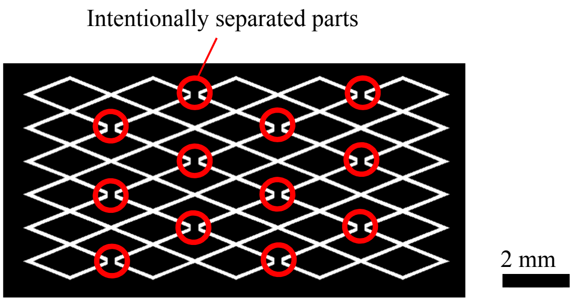


Figure 1: Reticle patterns designed for printing stent-like rhombus mesh.

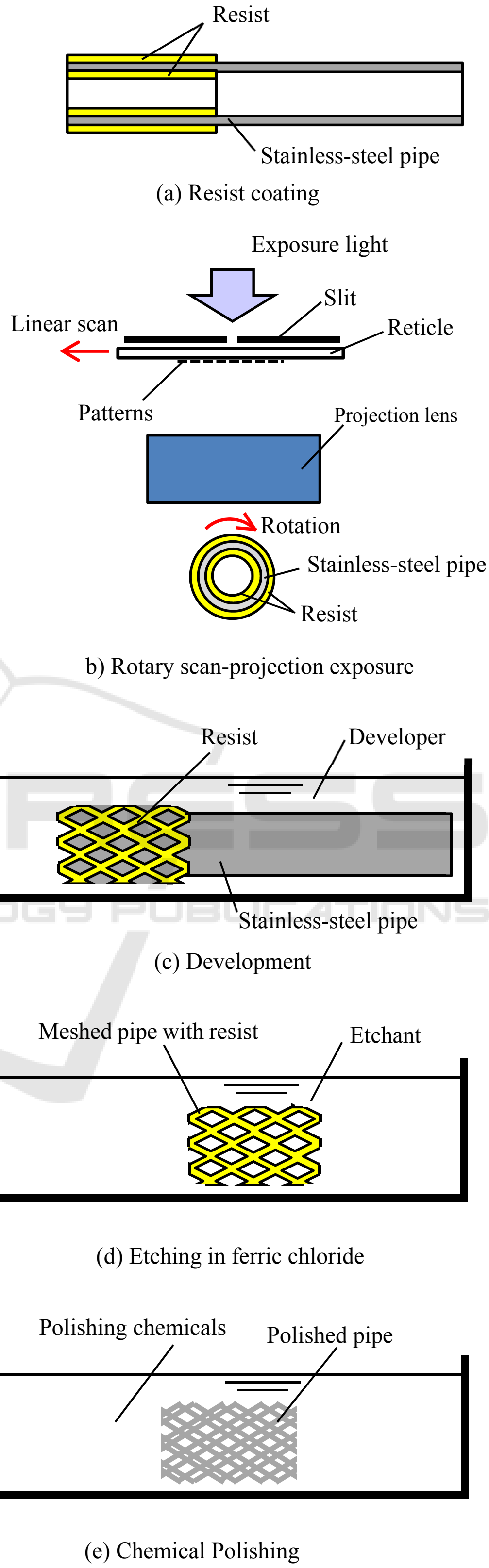


Figure 2: Processes for fabricating the aimed structure.

SUS304 stainless-steel pipes using the rotary scan-projection lithography. The contents of SUS304 are shown in Table 1. The other part of the alloy is iron (Fe). Main components are Fe, Cr, and Ni.

Table 1: Contents of SUS304 except iron.

Element	Content
Cr	18.00-20.00
Ni	8.00-10.50
Mn	≤ 2.00
Si	≤ 1.00
C	≤ 0.08
P	≤ 0.045
S	≤ 0.030

In this lithography system, patterns on the reticle were replicated on a pipe coated with a resist film during the flat reticle was linearly scanned in the horizontal direction, and rotating a pipe 360º synchronously around its axis.

Next, the pipe was etched in an aqueous solution of $FeCl_3$ using the mesh patterns of resist as etching masks. After the etching, meshed pipe with the still remained resist patterns on the outer surface was polished in a chemical liquid compound on the market.

Although the resist was almost removed during the polishing, it remained partially. For this reason, the polished pipe was cleaned finally by dipping in acetone and adding ultra-sound wave vibration.

By these processes, the meshed pipes were smoothed and homogeneously thinned. As a result, precisely meshed pipes were obtained.

3 RESIST PATTERN PRINTING

Using the reticle, meshed patterns were printed on SUS304 stainless-steel pipes with outer and inner diameters of 2 and 1.9 mm and a length of 50 mm. The thickness of the pipe wall was 50 µm. As a resist, the negative PMER N-CA3000 PM (Tokyo Ohka Kogyo) was used, and coated in approximately 10 µm thick in 20 mm area from the tip of a pipe one by one.

Although positive resists had high resolution, it was worried that the exposure doses between sensitized or not would change critically, and the exposure dose margin for the patterning became small. In addition, it was feared that the vague exposure influenced by the slit width and the pipe curvature led up to the contrast degradation of pattern images, and notable fluctuation of pattern widths and thicknesses occurred. In contrast, widths and thicknesses of the negative resist patterns tended to saturate if the exposure dose was sufficiently given. For this reason, it was thought that good patterning homogeneity would be obtained. Besides, negative resists with high transmittance were commercially available, and thick resist patterning durable for long-time etching with high speed stirring was applicable.

The reticle patterns were printed using a handmade exposure system, as shown in Figure 3. The typical exposure time for rotating the pipe 360º was 30 s.

An example of resist patterns on a pipe is shown in Figure 4. Mesh patterns are finely printed. Measurement results of pattern widths are shown in Figures 5 and 6. They show the width distribution in the axial and circumferential directions, respectively. It is known that pattern widths are very homogeneous. The 3σ deviation was 12.0 µm.

However, the mean width was 208 nm, and very wide comparing with the reticle pattern width of 130 µm. It was considered that this width increase was caused by the following reasons. One reason is that the actual projection ratio was not 1 but 1.13.

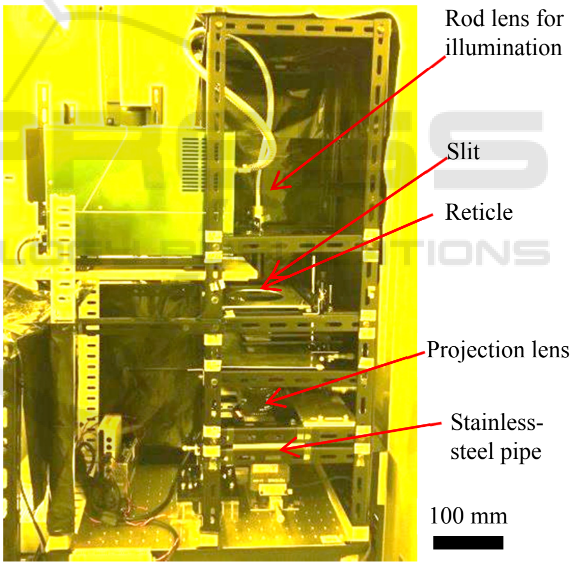


Figure 3: Handmade rotary scan-projection exposure system.

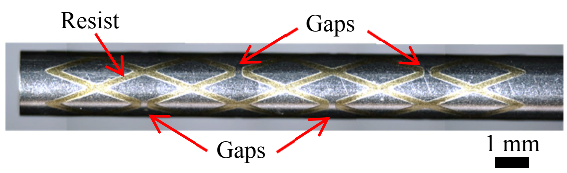


Figure 4: An example of resist patterns on a pipe.

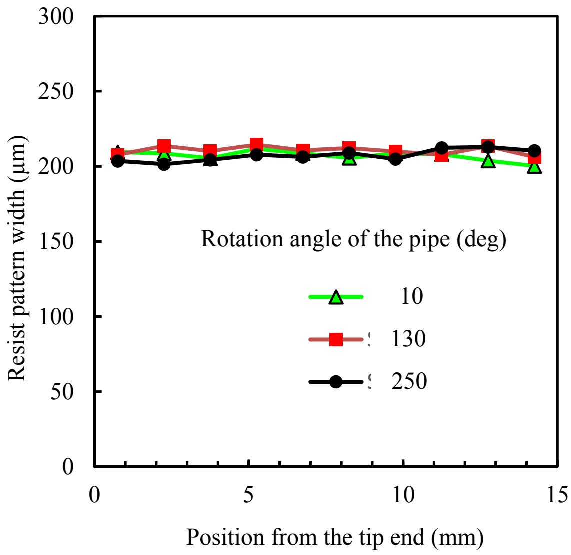


Figure 5: Width fluctuation of mesh resist patterns in the axial direction.

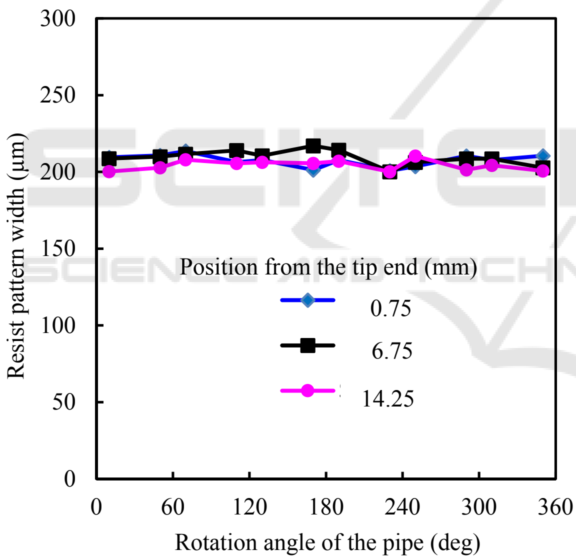


Figure 6: Width fluctuation of mesh resist patterns in the circumferential direction.

Accordingly, the projected width of mesh pattern becomes 130×1.13=147 µm. In addition, because the slit width was 800 µm and the mesh patterns were projected on the curved surface of the pipe, the pattern widths were slightly widened. Besides, projected positions were also shifted at the both outside ends of the slit. Since the slit width of 800 µm was also magnified to 800×1.13=904 µm, the angle θ between the ends A and B of the projected area from the centre line are calculated referring to Figure 6,

$$\theta = \sin^{-1}(0.904/2) = 26.9^{\circ}. \quad (1)$$

Therefore, the pattern width printed at the both outside ends of the slit becomes 147 µm /cos θ =165 µm.

On the other hand, the arc length L of the circumference MB of the pipe in the angle of θ is calculated to be

$$L = (26.9 \times \pi/180) \times 1000\ \mu m = 469\ \mu m. \quad (2)$$

Accordingly, the pattern at B is printed shifting 469-(904/2) =17 µm to the right outside. In contrast, the pattern at A is printed shifting 17 µm to the left outside. Accordingly, pattern width including the vaguely exposed parts become 165+17+17=199 µm. For this reason, if the resist is exposed sufficiently to stabilize the pattern widths, the widths become more than this width, and the widths shown in Figures 4 and 5 are within the reasonable range.

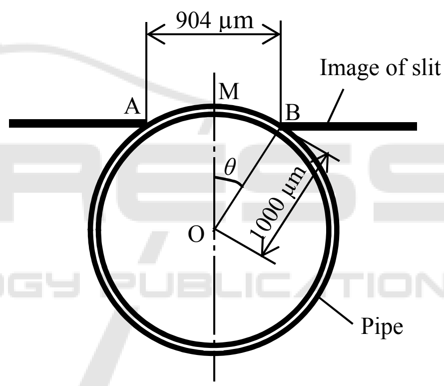


Figure 7: Figure for considering the pattern position shift and size change on the curved pipe surface.

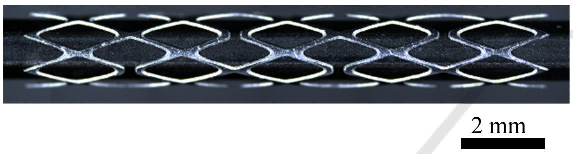
4 ETCHING AND CHEMICAL POLISHING

Patterned pipes were etched in an aqueous solution of $FeCl_3$ （Sanhayato, H-1000A） for 25 min at 40-45ºC. The etchant was stirred by a propeller stirrer rotating at 250 rpm. After the etching, the pipes were rinsed by pure water. The patterns on the pipe surface were remained as they were.

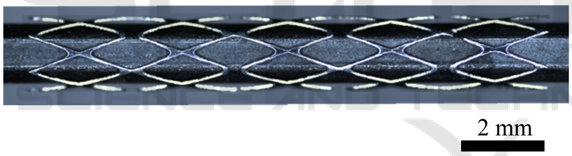
Next, etched pipes with the remained resist patterns were chemically polished in a chemical compound on the market (Sasaki Chemical, S-250) heated on a hotplate at 93-95 ºC for 1.5 min. During the polishing, the pipe was held by an L-shape tool handmade with a hard plastic material, and moved in the chemical compound by swinging it using the tool. The polishing was advanced at a speed of approximately 7 μm/min in width directions.

On the other hand, the resist began to be peeled off from approximately 40 s after beginning the polishing. Therefore, it was supposed that the polishing was advanced in the thickness direction also after that.

After the polishing, the pipes were rinsed by pure water. However, because resist fragments remained on the polished pipes were observed, they were removed by washing the pipes in acetone with ultra-sonic vibration. Figure 8 compares stent-like meshed pipes with and without the chemical polishing. In the case of a pipe etched only by $FeCl_3$, obtainable mean mesh width was 109μm, as shown in Figure 8(a). In contrast, when the chemical polishing was added, the mesh-part width was reduced to 83 μm, as shown in Figure 8(b).



(a) Pipe meshed by only etching in $FeCl_3$.



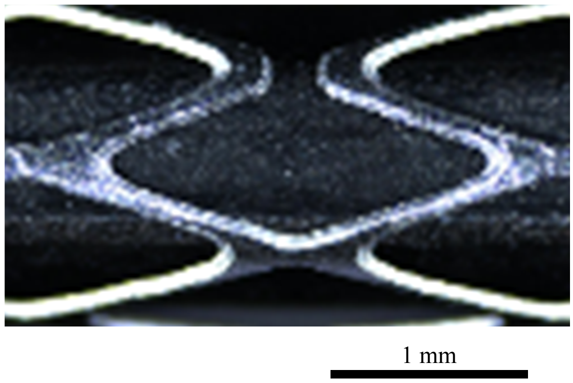
(b) Pipe finished by polishing in chemicals.

Figure 8: Comparison of meshed-pipe preciseness between with and without finishing by chemical polishing.

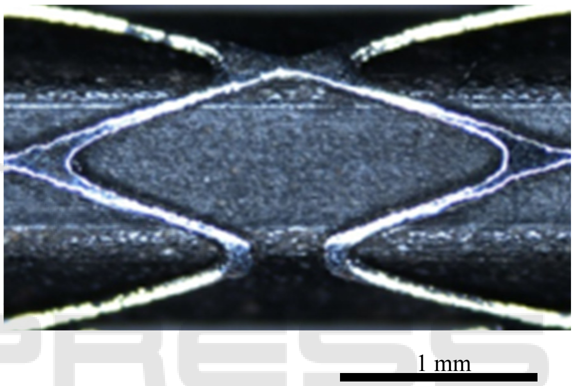
Besides, side wall roughness of the meshed parts was decreased from around 10 μm to 5 μm, as compared in Figure 9. It is known that the chemically polished pipes became smooth and sheeny.

In Figures 8 and 9, photographs of meshed pipes were taken by inserting a black hexagonal wrench into the meshed pipes. For this reason, only the front sides of the structures are shown. The vague horizontal lines in the photographs are the ridges of wrenches.

Next, to investigate the width fluctuation of stent-like meshed parts, mesh widths were measured at 4 sides of all 30 rhombuses. Measured width distributions are shown in Figures 10 and 11. It was clarified that the widths were almost homogeneous in both axial and circumferential directions. The 3σ deviation of width was 6.2 μm. This fluctuation



(a) Pipe meshed by only etching in $FeCl_3$.



(b) Pipe finished by polishing in chemicals.

Figure 9: Comparison of meshed-pipe roughness between with and without finishing by chemical polishing.

was far smaller than the 3σ deviation value of 13.5 μm obtained in the pipe shown in Figure 8(a) finished without adding the chemical polishing in the compound. In addition to the fact that the mean width was reduced, width fluctuation was noticeably decreased.

Components of S-250 are not made public. In the instruction manual, it is written that the chemical is composed of strong acid and gloss finisher. Judging from the description of “nitrous acid gas is generated”, it is supposed that the main strong acid is nitric acid. The gloss polisher is a dangerous goods class 4/class 2 petroleum. Pipe surfaces etched only by $FeCl_3$ without the resist was rough and not sheeny. The surface smoothness was inferior to that obtained by the polishing.

The authors thought that the distortions of pattern sizes and the shifts of printed positions could be reduced by using a slit with a narrower width. However, the illumination optics had to be improved for collecting the light flux in the slit efficiently,

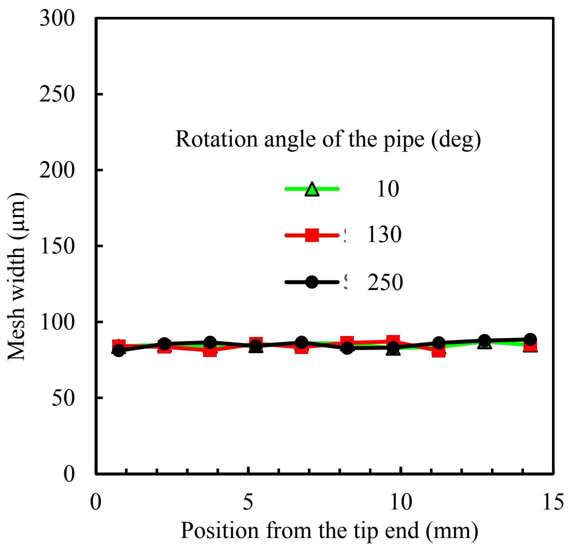


Figure 10: Width fluctuation of meshes in the axial direction after the chemical polishing.

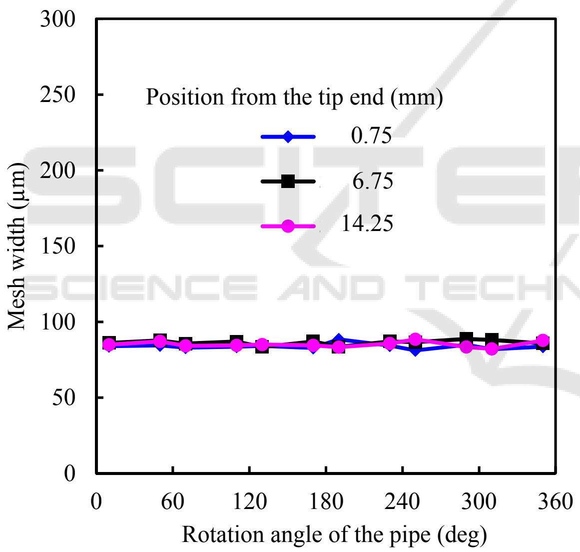


Figure 11: Width fluctuation of meshes in the circumferential direction after the chemical polishing.

because the exposure time was lengthened. In addition, since the meshed part widths were largely thinned by the undercut during the etching and polishing, printed wide mesh patterns were rather preferable.

Mechanical performance of the polished stent-like parts have not been investigated yet, and should be clarified hereafter. However, it was checked in the past research that a similar meshed pipe without polishing kept deformation linearity and elasticity when the pressing force was less than 0.6 N at least. Because the axial cross section of the stent-like part is 2×15=30 mm^2, pressing force of 0.6 N corresponds to the differential blood vessel pressure of 0.6/30 N/mm^2=0.02 MPa=200 hPa=150 mmHg, which is approximately the maximum differential blood vessel pressure.

5 CONCLUSIONS

Stent-like meshed pipes were successfully fabricated by a novel method using lithography, wet etching and chemical polishing. As a raw material, stainless-steel SUS304 pipes with outer and inner diameters of 2 and 1.9 mm, respectively, were used.

At first, resist patterns were printed on a pipe surface using a rotary scan-projection exposure system. In the system, stent-like mesh patterns on a reticle were continuously replicated on a resist film coated on a pipe by synchronously scanning the reticle linearly and rotating the pipe at a constant speed. After the patterning, pipes with stent-like resist patterns were etched in an aqueous solution of $FeCl_3$. Next, the meshed pipes were chemically polished using a chemical compound on the market.

As a result, very fine meshed parts with a mean width of 83 µm were obtained. Jogged edges of the etched pipes were smoothed, and the 3σ deviation of mesh widths was largely reduced from 13.5 µm to 6.2 µm. It was demonstrated that the subtractive process of stainless-steel pipes would be applicable to fabrication of minute complicated structures such as stents.

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REFERENCES

Ando, K., Ishii, K., Tada, E., Kataoka, K., Hirohata, A., Goto, K., Kobayashi, K., Tsutsui, H., Nakahama, M., Nakashima, H., Uchikawa, S., Kanda, J., Yasuda, S., Yajima, J., Kitabayashi, H., 2017. Prospective multi-center registry to evaluate efficacy and safty of the newly developed diamond-like carbon-coated cobalt-chromium coronary stent system, *Cardiovascular Intervention and Therapeutics*, Vol. 32, Issue 3, 225–232.

Caiazzo, G., Fabris, K. E., Serdoz, O., Mattesini, A., Foin, N., Rosa S. D., Indolfi. C., Mario, C. D., 2015. Absorb bioresorbable vascular scaffold: What have we learned after 5 years of clinical experience? *International Journal of Cardiology* Vol. 201, 129–136.

Haoa, X., Wang, L., Wanga, O., Guoa, F., Tanga, Y., Dinga, Y., Lua, B., 2011. Surface micro-texturing of metallic cylindrical surface with proximity rolling-exposure lithography and electrochemical micromachining. *Applied Surface Science.* Vol. 257, 8906-8911.

Horiuchi, T., Fujii, H., Yasunaga, K., 2015, Lithography onto Surfaces of Fine-Diameter Pipes Using Rotary Scan-Projection Exposure. *Journal of Photopolymer Science and Technology*, Vol. 28, No. 2, 273-278.

Horiuchi, T., Furuhata, T., Muro., 2016. Synchronous scan-projection lithography on overall circumference of fine pipes with a diameter of 2 mm. *Japanese Journal of Applied Physic*s, Vol. 55, 06GP13, 1-6.

Horiuchi, T., Ito, K., Kobayashi, H., Yanagida, A., 2019. Investigation on stainless-steel stents fabricated using projection lithography and wet etching, 2nd EUROPEAN BIOSENSOR SYMPOSIUM (EBS 2019), FLORENCE, ITALY, 240.

Ito, K., Suzuki, Y., Horiuchi, T., 2017. Fabrication of Cylindrical Micro-Parts Using Synchronous Rotary Scan-Projection Lithography and Chemical Etching. P*roceedings of SPIE*, Vol. 10454, 1045410, 1-6.

Kesavan, S., Strange, J. W., Johnson, T. W., Flohr-Roese, S., Baumbach, A., 2013. First-in-man evaluation of the MOMO cobalt-chromium, carbon-coated stent, *EuroIntervention*, Vol. 8, No. 9, 1012-1018.

Lee, D., Hiroshima, H., Zhang, Y., Itoh, T., Maeda, R., 2011. Cylindrical projection lithography for microcoil structures. *Microelectronic Engineering.* Vol. 88, 2625–2628,

Lim, H., Choi, K., Kim, G., Lee, S., Park, H., Ryu, J., Jung, S., Lee, J., 2014. Roll-to-roll nanoimprint lithography for patterning on a large-area substrate roll. *Microelectronic Engineering*. Vol. 123, pp. 18–22, 2014.

Nishi, S., Nakayama, Y., Ishibashi-Ueda, H., Yoshida, M., Yonetani, H., 2013. Treatment of rabbit carotid aneurysms by hybrid stents (microporous thin polyurethane-covered stents). *Preservation of side-branches*, Vol. 28, issue: 7, 1097-1104.

Rahal, J. P., Dandamudi, V. S., Heller, R. S., Safain, M. G., Malek. A. l., 2014. Use of concentric Solitaire stent to anchor Pipeline flow diverter constructs in treatment of shallow cervical carotid dissecting pseudoaneurysms, *Journal of Clinical Neuroscience* Vol. 21, 1024–1028.

Rebelo, R., Vila, N., Fangueiro, R., Carvalho, S., Rana, S., 2015. Influence of design parameters on the mechanical behavior and porosity of braided fibrous stents, *Materials and Design.* Vol. 86, 237–247.

Tammareddi, S., Sun, G., Li, Q., 2016. Multiobjective robust optimization of coronary stents, *Materials and Design*. Vol. 90, 682–692.

Varghese, T. G., Thomas, S. C., Revanka, V. R., 2015. Emergency stenting of unprotected left main coronary artery occlusion using bare metal stent with good long-term results, -A case report-, Journal of Indian college of cardiology, Vol. 5, 345-348.