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Laser-Scan Lithography and Electrolytic Etching for Fabricating Mesh structures on Stainless-Steel Pipes 100 µm in Diameter

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ABSTRACT

Fine cylindrical micro-components such as stents and micro-needles are required. Here, laser-scan lithography and electrolytic etching were investigated for opening many slits on fine stainless-steel pipes with an outer diameter of 100 µm, a thickness of 20 µm and a length of 40 mm.

At first, a pipe coated with a positive resist was exposed to a beam spot of violet laser. Linearly arrayed 22 slit patterns were continuously delineated by scanning and intermittently moving the pipe in the axial direction. The same delineations of 22 slit patterns were repeated four times in every 90-degree circumferential direction. The pipe was exposed to the laser spot in lengths of 170 µm, and interval lengths of 100 µm were located between the exposed lengths. Thus, 88 slit patterns in total were delineated on 8 pipe surfaces.

Next, the pipes masked by the resist were electrolytically etched one by one. A pipe was used as an anode, and an aluminum cylinder was set as a cathode around the pipe. As the electrolyte, aqueous solution of $NaNO_3$ and NH_4Cl was used. Then, the resist was removed by ultrasonic cleaning in acetone. Sizes of etched 22 slits in a line were measured for each pipe using SEM (JEOL, JSM-5510). The average width and length measured at inner surfaces were 25.8 µm (σ=4.7) and 174.8 µm (σ=13.4), respectively. The width and length measured at the outer surface were 54.6 µm (σ=2.6) and 211.4 µm (σ=4.2), respectively. It was demonstrated that aimed mesh structures were successfully fabricated.

1. Introduction

Recently, micro-components with three-dimensional (3D) cylindrical shapes are required. They are used as contact-probe springs in testing systems of semiconductor integrated circuits[1], special syringe needles with surface textures for detecting their positions when they are stuck into bodies[2], medical stent[3][4][5], soft surgery tools[6] and others. For this reason, various methods for fabricating such 3D cylindrical shapes have already been proposed. For example, wire stent fabrication technique[3], texturing of stent surface using femtosecond laser[4], a method for entering balloon into micro structure fabricated on Ti substrate[5], CNC (Computer Numerical Control)

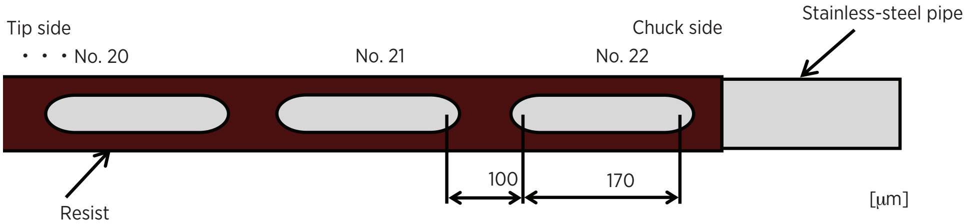

Figure 1. Programmed patterns for delineating a linear array of 22 slit patterns.

TAKE A LOOK INSIDE:

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EDITORIAL

A Great Time for Leading-Edge Masks!

Aki Fujimura, D2S, Inc.

It's amazing what the mask making community gets done, both every hour of every day and in the larger scale: taking on more and Moore of the error budget with a constant barrage of innovation from all angles despite the relatively limited budget of the $3B market. The mask maker's manufacturing orientation requires a conservative approach, carefully balanced by the need to be on the leading edge. BACUS and its members, both collectively and individually in their respective organizations, thread the needle, walk the tight rope, very quickly.

BACUS serves a critical role both in the individual organizational decisions and in the coordination of the collective community. The two eBeam Initiative surveys that we announce in September every year aim to help with that, too (www.ebeam.org/education). The Mask Maker's Survey is a factual survey about the masks made in the past year. The Industry Perceptions Survey is an opinion survey of luminaries in the semiconductor supply chain that gauges overall sentiment, mostly about the future. Luminaries' opinions are shaped by what they know, but can't share publicly, and also reflect how budgets are spent in their companies.

The Industry Perceptions Survey was definitive on EUV this year. When asked, "By the end of which year do you predict EUV will be used in high volume manufacturing?" 35% responded "Never" in 2014. That "Never" response has been steadily decreasing since, however, and only 1% said "Never" this year. By extension, actinic inspection's "Never" went from 21% last year to 7% this year. The trend is clear on EUV. In fact, EUV has been mentioned in all but one of these BACUS editorials this year.

To contrast, multi-beam mask writing is mentioned only in four BACUS editorials (now five). But it is just as significant a breakthrough. The Industry Perceptions Survey reflects strong optimism on both multi-beam writer readiness and the probability of near-term purchases. ILT on 193i was identified as the leading need for multi-beam. EUV and NIL were perceived as less in need of multi-beam. But I suspect this is because the general perception is that multi-beam excels where shape count is high because multi-beam write time is independent of shape count. A less-advertised benefit of multi-beam is its write time for slower resists, and both EUV and NIL require slower resists.

The Mask Maker's Survey highlighted the rapid adoption of MPC and the increase in data preparation time, contributing to the increases in turnaround time for the leading-edge masks.

In addition to EUV and multi-beam, those of us in computing are seeing another discontinuity opportunity in GPU acceleration. GPU acceleration combines very well with pixel-dose manipulation as required for multi-beam correction. Now, we can take advantage of multi-beam's per-pixel dose assignment to do linearity and printability correction by dose manipulation, not just by geometry manipulation. In addition to simulation and image processing, the power of GPU acceleration enables deep learning, another area of interest for the entire industry.

Looking forward to 2018, it's a great time to be on the leading edge in mask making!

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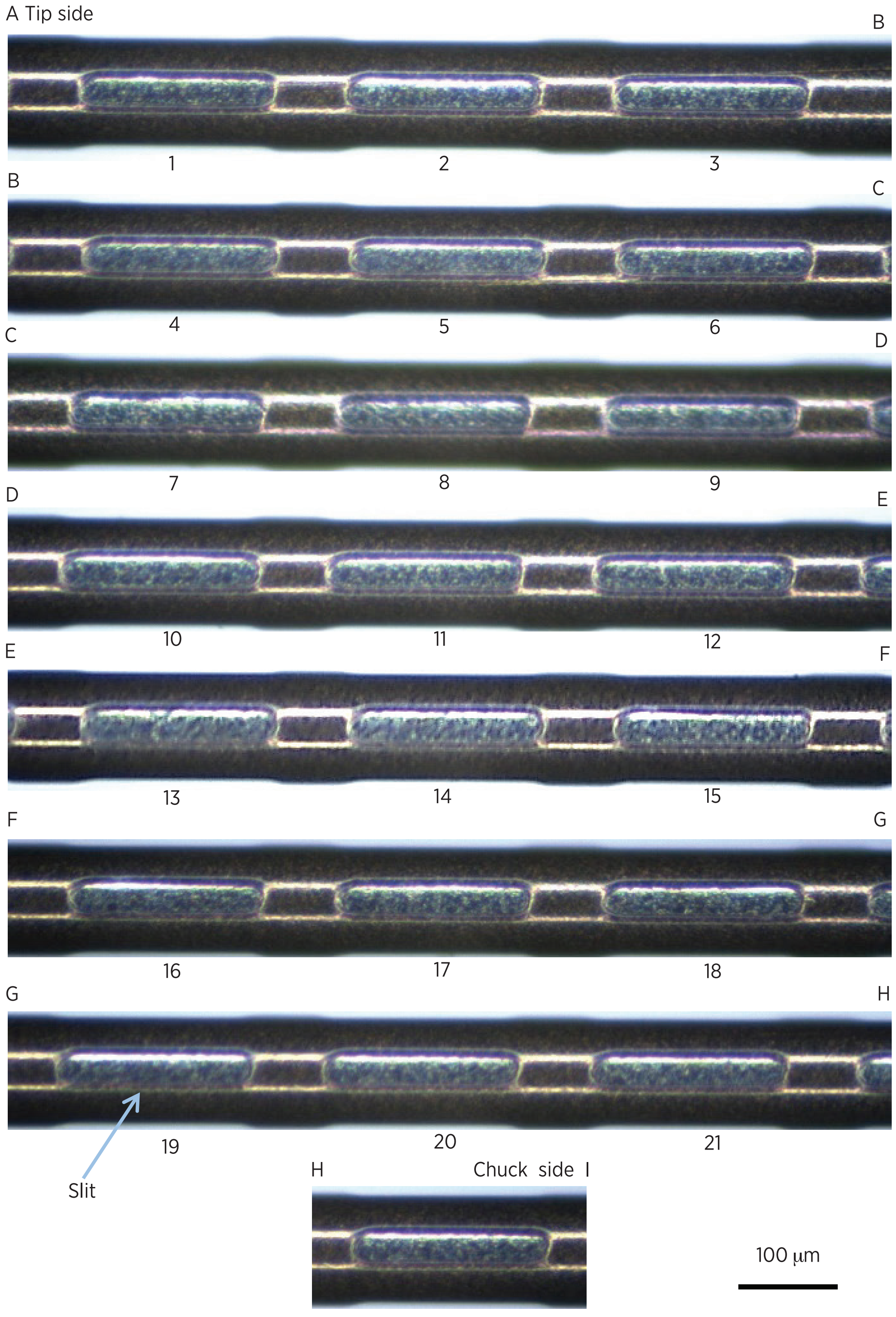


Figure 2. Actually delineated 22 slit patterns.

manufacturing method[6], a biotemplate method[7], and a patterning method using RIE (Reactive Ion Etching) with flexible stencil masks[8] are proposed. In our laboratory, two exposure systems were developed for delineating patterns on wires and pipes placed horizontally and vertically, respectively[1][9]. Using the former exposure system, in which the specimens were set horizontal, nickel springs were fabricated by forming helical patterns on a stainless-steel wire using laser-scan lithography, electroplating nickel, and pulling and thinning the wire[1]. However, it takes long times to obtain sufficient metal film thicknesses by the electroplating. In addition, it is difficult to ensure the uniformity and reproducibility of the metal film thickness.

For this reason, a new method using the etching of pipes was developed. Helical resist patterns were delineated on stainless-steel pipes using the laser-scan lithography, and the pipes were etched by an electrolytic method. As a result, if the same-lot pipes were used, fluctuations of thicknesses were suppressed very small. For this reason, uniformly patterned micro-components such as helical springs and multi-hole pipes were successfully fabricated using pipes with outer and inner diameters of 100 μm and 60 μm, respectively[10].

To obtain technology for corresponding to various shapes, lithography and etching of discontinuous patterns are investigated here. Concretely, linearly arrayed 22 slits are formed in every 90-degree circumferential direction.

2. Lithography for Delineating Slit Patterns

At first, laser-scan lithography for delineating multi-slit patterns was investigated. SUS304 stainless-steel pipes with an outer and inner diameters of 100 and 60 μm and a length of 40 mm were coated with a positive resist PMER P LA-900 (tok) in 3-7 μm thick. Next, linearly arrayed 22 slit patterns with a length of 170 μm were delineated by setting intervals of 100 μm between them in every 90-degree circumferential direction, as shown in Figure 1. To delineate patterns, the laser-scan exposure system, which was developed in the past research, was used[9]. The exposure wavelength was 408 nm, and the delineation speed was 110 μm/s. The slit patterns were delineated near the pipe tips. The delineation was programmed using a personal computer, and executed by automatically moving and rotating the specimen pipes. The 22x~4=88 slit patterns were delineated on each pipe, and the same patterning was repeated for 8 pipes. Slit ends became round because the laser beam spot was circular. Before the etching, one of the pipes was picked out, and sizes of 22 slits in a line were observed and measured using an optical microscope (Arms system, LUSiS PA-20CU). The delineated slit patterns are shown in Figure 2. Distributions of width and length of delineated slit patterns are shown in Figure 3 (a) and (b). The slit sizes were measured at the bottoms of resist patterns, or on the surface of the pipe. The average width and length of the slits were 31.8μm (σ=1.4) and 188.0 μm (σ=2.7), respectively. Patterning uniformity is important, because resist pattern sizes strongly affect to the slit sizes obtained by etching the pipes significantly.

3. Etching of Pipes

The schematical set up used for the etching is shown in Figure 4. The pipe with slit patterns was set as an anode and an aluminum cylinder with an outer diameter of 80 mm, a thickness of 1mm, and a length of 60 mm was set around the pipe as a cathode. When a voltage was applied to the anode, electrolytic etching reactions were started at the parts where the resist was removed by the laser scan lithography.

In the past research, aqueous solution of NaCl and NH4Cl was used as the electrolyte[11]. However, all 17 investigated pipes were snapped during the etching or the removing of resist after the etching. It was clarified that the etching was especially concentrated at the chuck side, and pipes were snapped there caused by undercut. It was considered the current intensity distributed in the axial direction of the pipe, and the current intensity distribution caused the unevenness of the etching. For this reason, NaCl in the electrolyte was changed to NaNO$_3$ which was considered to improve the effect of current intensity distribution, and effects of adopting the newly prepared etchant composed of NaNO$_3$ and NH$_4$Cl are investigated.

To find out on appropriate etching condition, etching results for the conditions shown in Table 1 and 2 were compared in advance using other pipe specimens without including 8 pipes mentioned in chapter 2. As for the etching voltage, 5 V was better than 7 V. When the voltage was increased from 5 V to 7V, etching time was shortened. However, the etching speed became unstable, and the result were worse. Therefore, the etching voltage was fixed at 5 V. On the other hand, as for the etching time, slits were not penetrated entirely by the etching for 10 s. While, all slits were penetrated by the etching for 20 s. So, etching time conditions of 15-22 s (Table 2) were investigated. When the etching time was set for 22 s, all samples were snapped on the process of removing the resist after the etching. Among the etching time conditions of 15-20 s, 20 s was most appropriate, because differences of etched slit sizes between measured at outer and inner surfaces were the smallest.

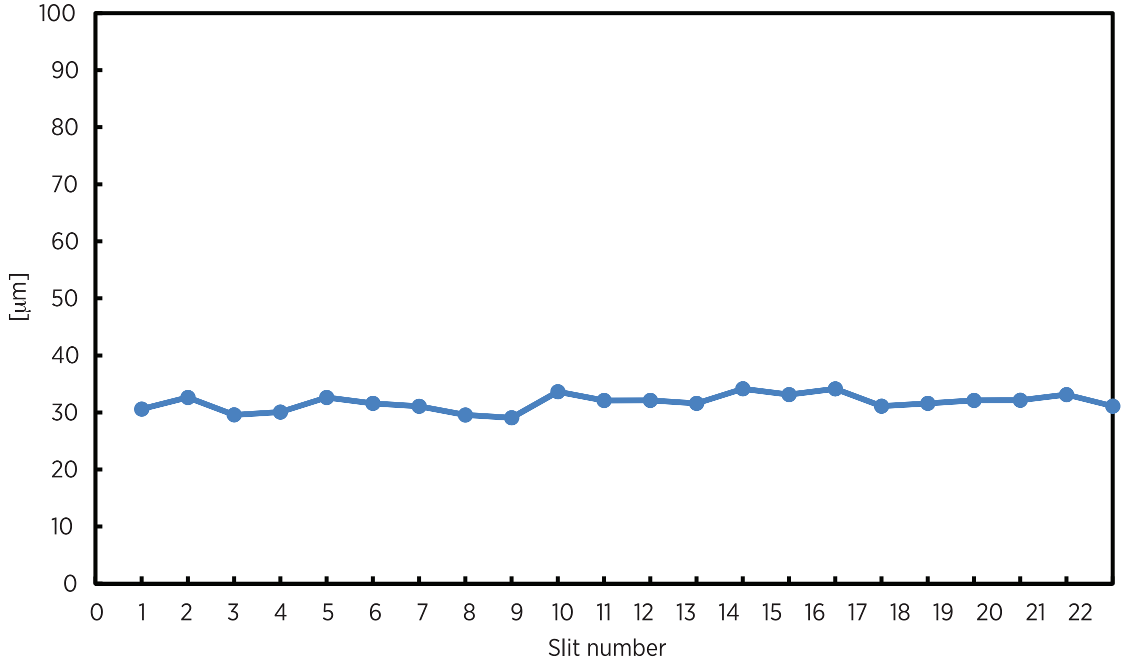
The remained 7 pipes with 88 slits patterns mentioned in chapter 2 were electrolytically etched one by one next. Electrolytes used for the etching were aqueous solutions of 5 wt% NaNO$_3$ and 5 wt% NH$_4$Cl. The pipes were etched for 20 s applying 5 V. These etching time and voltage conditions were the optimized ones by the experiments mentioned above. The etchant was kept at 20-22°C by placing the bottle on a hotplate during the etching. Slit shapes of the etched pipes are shown in Figure 5.

All slits were uniformly etched and opened. Concentration of etching at the chuck side was improved and all the pipes were not snapped. The sizes of 22 slits in a line were measured for all the 7 pipes using SEM (JEOL, JSM-5510) after the etching. The average widths measured at outer and inner surfaces were 54.6 μm (σ =2.6) and 25.8 μm (σ =4.7), respectively. The average lengths outer and inner surfaces were 211.4 μm (σ =4.2) and174.8 μm (σ =13.4), respectively. The average edge roughness measured at the inner surface was 4.3 μm. It was demonstrated that aimed mesh structure was successfully fabricated. Distributions of the width and length of slits in a line on one of the pipes are shown in Figure 6 (a) and (b). Strictly speaking, there still remained the tendency that the slit sizes at the chuck side was slightly larger than those at the tip side. It was considered that the still remained distribution of current intensity in axial direction was the cause of this tendency. If this problem is solved, accuracy of etching will be improved further.

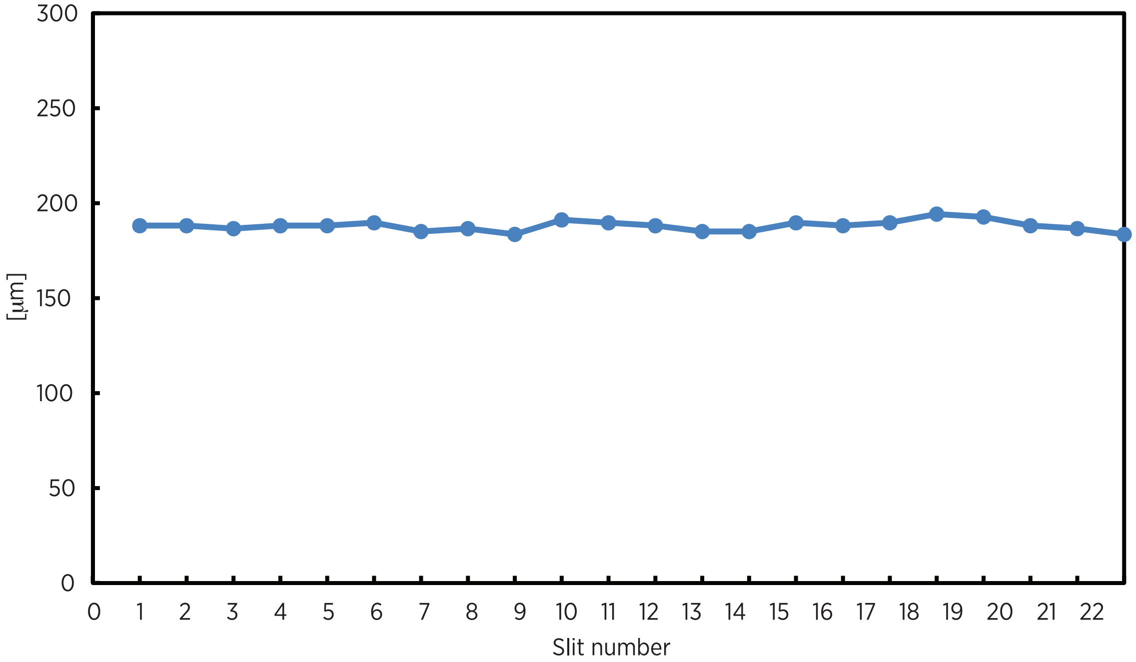
Distributions of the width and length of slits in the circumferential direction measured using the 11th slits of one of the pipes are shown in Figure 7 (a) and (b). The slit sizes were almost homogeneous in the circumferential direction.

4. Conclusion

Multi-slits were successfully penetrated stainless-steel pipes with outer and inner diameters of 100 and 60 μm by the combination of laser-scan lithography and electrolytic etching. Effects of changing the electrolyte from NaCl + NH$_4$Cl aqueous solution to NaNO$_3$ +



(a) Slit pattern width



(b) Slit pattern length

Figure 3. Distributions of delineated slit pattern sizes.

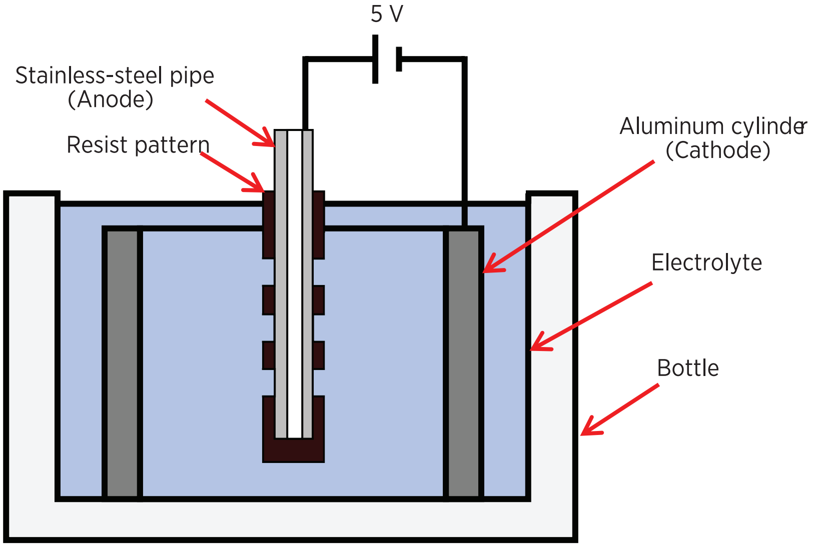


Figure 4. Electrolytic etching method.

Table 1. Rough comparison of etching results for various conditions.

Electrolyte	Voltage [V]	Etching time [s]	Results
$H_2O:NaNO_3:NH_4Cl=100:5:5$	5	10	Under etch
		20	Almost appropriate
	7	5	Under etch
		10	Unstable

Table 2. Search of appropriate etching time condition.

Electrolyte	Voltage [V]	Etching time [s]	Results
$H_2O:NaNO_3:NH_4Cl=100:5:5$	5	15	appropriate
		17	appropriate
		20	Most appropriate
		22	Over etch

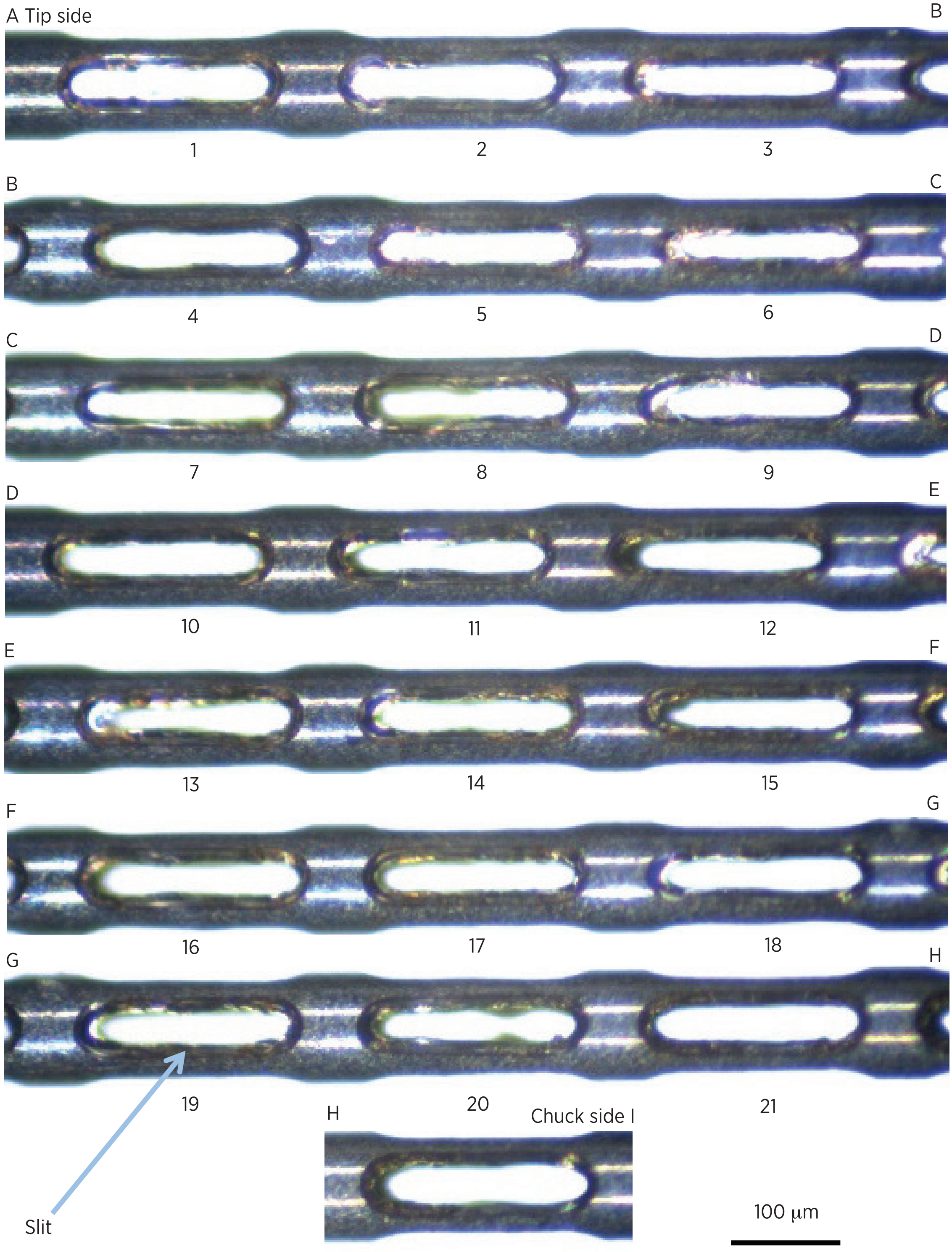
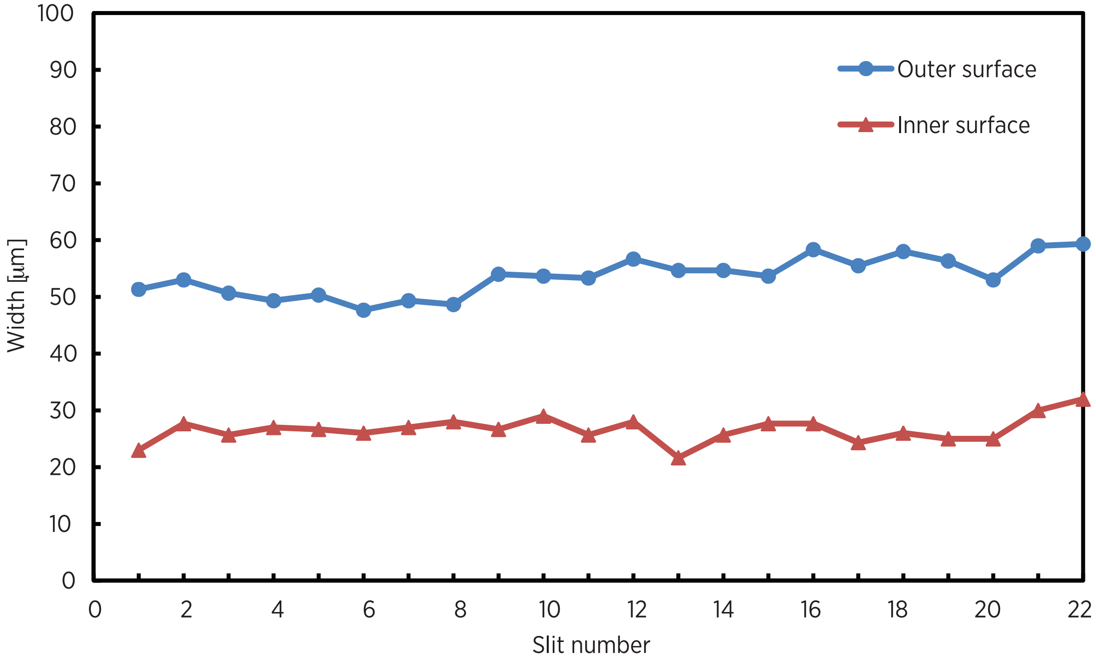
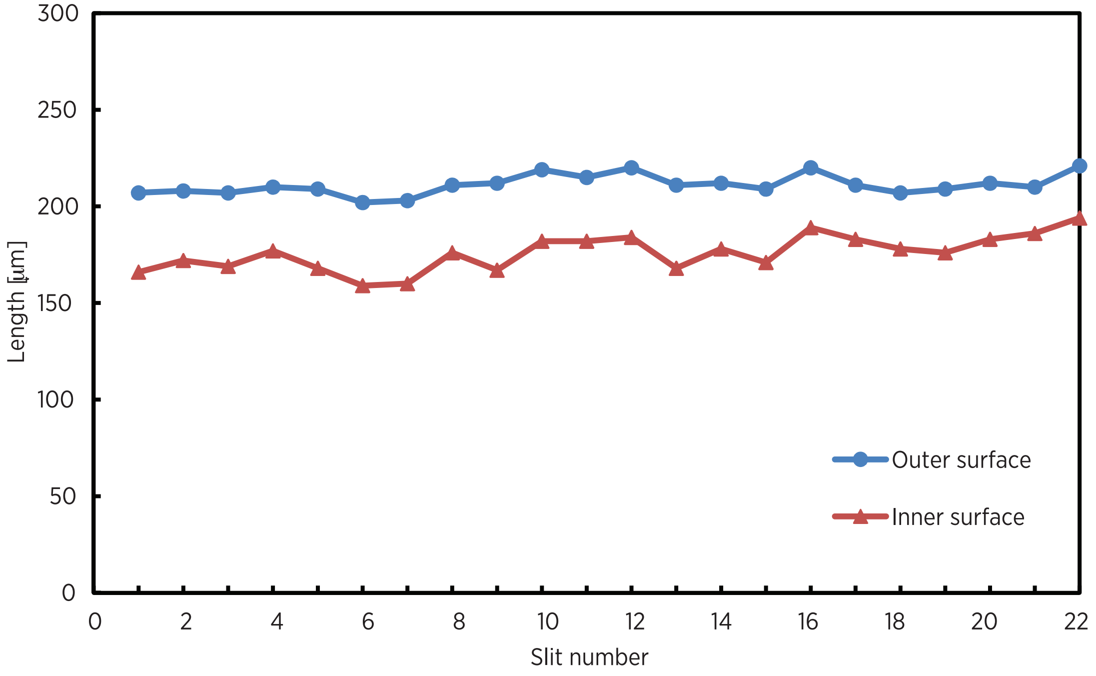


Figure 5. Meshed pipe with 88 etched slits.

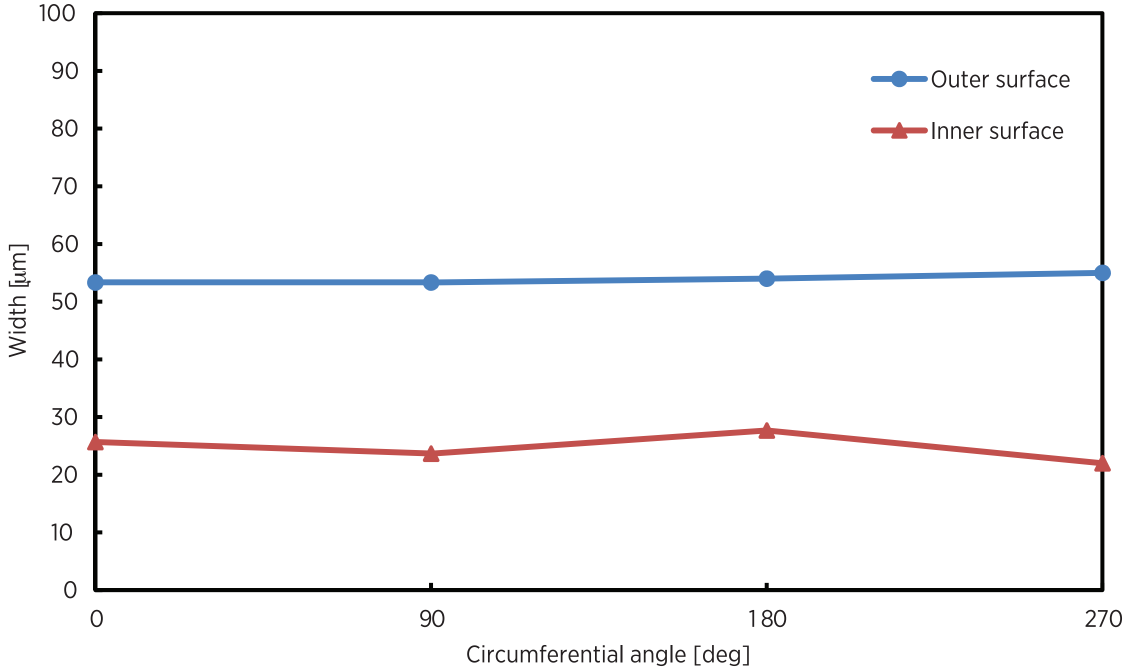


(a) Slit width

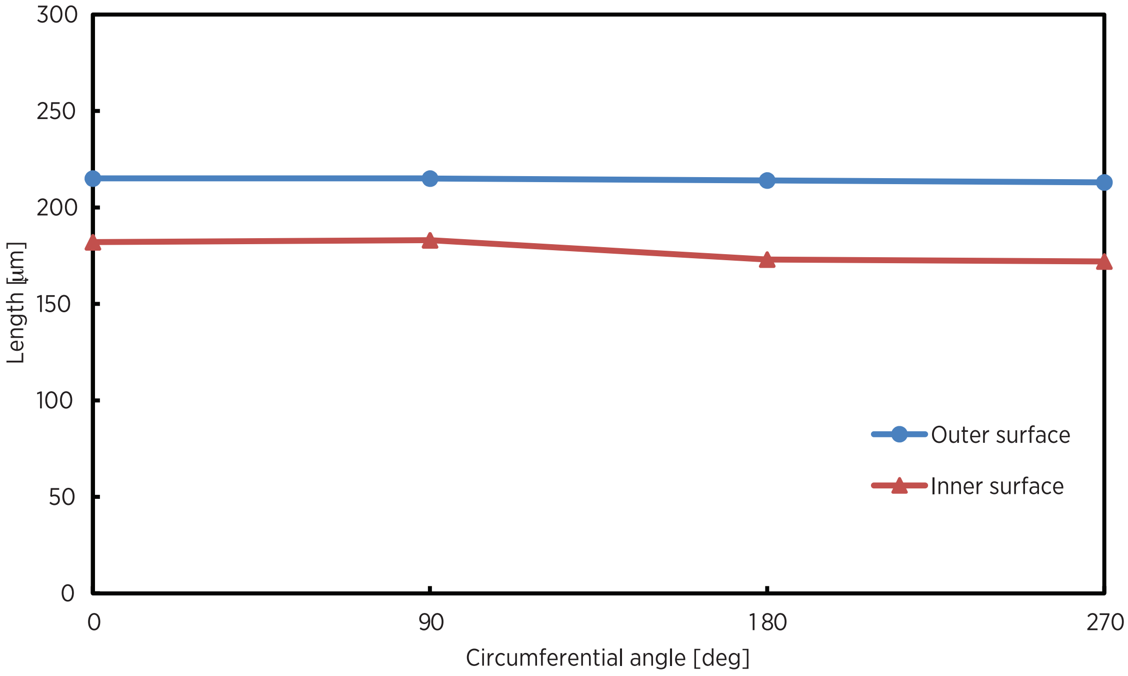


(b) Slit length

Figure 6. Distributions of slit sizes in the axial direction after the electrolytic etching.



(a) Slit width



(b) Slit length

Figure 7. Distributions of slit sizes in the circumferential direction after the electrolytic etching.

NH_4Cl aqueous solution were investigated using 7 pipes with 88 slit patterns. The pipes with slit patterns were electrolytically etched one by one in aqueous solutions of $NaNO_3$ and NH_4Cl by using a pipe as an anode and applying a voltage of 5 V for 20 s. Averages of etched slit widths measured at outer and inner surfaces were 54.6 μm (σ=2.6) and 25.8 μm (σ=4.7), respectively. Etched slit lengths measured at outer and inner surface were 211.4 (σ=4.2) and 174.8 μm (σ=13.4), respectively. As a result of changing the electrolyte, the etching concentration near the chuck side was drastically improved. It is considered that this technology can be applied to fabrication of fine cylindrical micro-components such as, syringe needles, stents, and meshed filter pipes.

5. Acknowledgements

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