Laser-Scan Lithography and Electrolytic Etching for Fabricating Meshed Pipes of Stainless Steel

Hiroshi Takahashi and Toshiyuki Horiuchi*

Graduate School of Engineering, Tokyo Denki University, 5 Senju-Asahi-cho, Adachi-ku, Tokyo 120-8551, Japan
*horiuchi@cck.dendai.ac.jp

Numerous micro-slits were opened penetrating through fine stainless steel pipes using laser-scan lithography and electrolytic etching, and meshed pipes were fabricated. Such micro-fabrication technology will be useful for developing bio-medical micro-stents, syringe needles, mesh filters, and others. As original materials, stainless-steel pipes with an outer diameter of 100 μm, a thickness of 20 μm and a length of 40 mm were used. At first, each pipe coated with a positive resist was exposed to a beam spot of violet laser, and multi-slit patterns were delineated by scanning and intermittently moving the pipe in the axial and rotational directions. After the development, each pipe masked by the resist film except the slit pattern parts were etched individually. Electrolytic etching was applied by using an aqueous solution of NaNO₃ and NH₄Cl as an electrolyte. As a result, mesh structures composed of four linearly arrayed 22 slits arranged at every 90° circumferential angle were fabricated.

Keywords: Laser-scan lithography, Slit pattern, Electrolytic etching, Stainless-steel pipe, Meshed pipe

1. Introduction

Recently, various 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], syringe needles with surface textures for detecting their positions when they are stuck into bodies [2], medical stents [3-5], surgery tools [6], micro-needles [7] and others [8-15].

For this reason, various methods for fabricating 3D cylindrical shapes are proposed. For example, a wire stent fabrication technique [3], pipe forming processes using hot indirect extrusion and multi-pass cold drawing of a magnesium alloy [4], CNC (Computer Numerical Control) manufacturing method [6], a micro-needle fabrication method by electroplating nickel on a resist mold [7], a biotemplating process [16], and cylindrical reactive ion etching with flexible stencil masks [17] are reported.

In our laboratory, two laser-scan exposure systems were developed for delineating patterns on wires and pipes placed horizontally and vertically, respectively [1,18]. Using the former exposure system, in which the specimens were set horizontally, nickel coil springs were fabricated by forming helical resist patterns on a stainless-steel wire with diameters of 80-100 μm using the laser-scan lithography, and electroplating nickel between the resist patterns [1]. However, it took long times to obtain sufficient nickel thickness by the electroplating.

For this reason, another new method using etching of pipes was developed. In the new method, helical patterns were delineated on stainless-steel pipes coated with a resist using the laser-scan lithography, and the patterned pipes were etched by an electrolytic method. As a result, helical micro-components such as coil springs and multi-hole pipes were successfully fabricated using pipes with an outer diameter of 100 μm and thickness of 20 μm [19].

On the other hand, it was confirmed that the latter exposure system in which the fine pipes were supported vertically was superior to the former exposure system in which the fine pipes were
supported horizontally, because the specimen pipes were not bent by their own weight.

Based on these backgrounds, fabrication of meshed pipes with fine numerous slit arrays are investigated using the latter exposure system and etching method in this research [20, 21].

2. Subjects and aimed meshed pipes

In the past research, distinct possibility for fabricating coils and pipes with multi-holes was demonstrated. However, they were works with continuous or homogeneous features. When patterns such as slits were arranged discretely on a pipe surface, homogeneous etching became difficult. And all the pipes were snapped at exceedingly etched places. For this reason, the main subject to be solved was the improvement of etching processes. However, because the etching performance also depends on the accuracy and homogeneity of resist pattern sizes, lithography processes should be managed carefully. That is, laser-scan lithography for delineating slit arrays are also earnestly reexamined.

At first, target shapes of meshed pipes to be studied in this research were discussed. It was considered that basic technologies should be developed using a general model. For this reason, considering the balance of difficulty and possibility, a meshed pipe with four lines of linearly arrayed 22 slits at every 90° circumferential angle was designed, as shown in Fig. 1. The unit of size values in the figure is “μm”. As the materials, stainless steel (SUS304) pipes with an outer diameter of 100 μm, a thickness of 20 μm, and a length of 40 mm was used. The materials are the same ones used for fabricating micro-coils and multi-hole pipes [19]. Designed width and length of slits on the outer surface were 50 and 200 μm, respectively. The designed interval between neighbored two slits in the axial direction was 70 μm. It was supposed that arbitrary slit meshes would be fabricated if the technology for fabricating meshed pipes with basic multi-slits was certainly developed.

3. Delineation of slit patterns using laser-scan lithography

Delineation of multi-slit patterns using laser-scan lithography was investigated using the latter exposure system developed in the past research [18]. The exposure wavelength was 408 nm. Approximately 20-mm parts of the pipes were coated with a positive resist of PMER P LA-900 (tok) in 5±2 μm thick. Slit patterns were delineated by setting the pipes one by one in the chuck of the exposure system. At first, linearly arrayed 22 slit patterns were delineated by moving a pipe 170 μm intermittently in the vertical direction. The intervals were set to 100 μm. The delineation speed was 110 μm/s. After one linear array of 22 slit patterns were delineated, the pipe was rotated 90°, and the second array was delineated. Thus, four linear arrays of slit patterns were delineated sequentially on each pipe. The delineation was programmed using a personal computer, and executed by automatically moving and rotating the specimen pipe. The slit patterns were delineated near the bottom tip of each pipe held vertically.

The length of scanning the laser spot or moving the specimen was set smaller than the target slit length. This is because the slit ends became round depending on the circular shape of laser beam spot. Delineated 22 slit patterns in a line were observed using an optical microscope (Arms system, LUSiS PA-20CU), as shown in Fig. 2. In addition, their sizes were measured at the bottoms of resist patterns, or on the pipe surface. Distributions of widths and lengths of the delineated slit patterns are shown in Figs. 3 and 4. Pattern widths were measured at three positions for each slit, and the average width was plotted. The total average width and length of 22 slits were 31.8 μm (σ=1.4 μm) and 188.0 μm (σ=2.7 μm), respectively.

Patterning uniformity is very important, because sizes of slits obtained by etching the pipes are strongly affected by the resist pattern sizes.
Although the accuracy should be improved some more in the future, it was clarified that the variations of widths and lengths were adequately small, and within almost acceptable ranges.

Fig. 2. Linearly arrayed 22 slit patterns delineated using laser-scan lithography. As a resist, positive PMER P LA-900 (tok) was used.

Fig. 3. Homogeneity of slit pattern widths investigated in the axial direction.

Fig. 4. Homogeneity of slit pattern lengths investigated in the axial direction.

4. Electrolytic etching of stainless-steel pipes

Stainless-steel pipes masked by the resist with the 88 slit patterns were etched by the electrolytic etching method. A schematic figure of etching set-up is shown in Fig. 5. The pipe with slit patterns was set as an anode and an aluminum cylinder with an outer diameter of 80 mm, a thickness of 1 mm, and a height 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 and wet with the etchant.

In the past research, an aqueous solution of NaCl and NH₄Cl was used as an electrolyte [19].
Fig. 5. Experimental set-up used for electrolytic etching.

However, when the past research was retaken by repeating the same etching experiments as the past research using the new slit patterns shown in Fig. 2, all of tested 17 pipes were snapped before the slits were sufficiently opened or penetrated. An example of snapped pipe is shown in Fig. 6. Although the etching conditions were variously changed, all the pipes were snapped if etching was continued till all slits were sufficiently opened.

For this reason, etching distribution and partial irregularity was investigated by etching a pipe for a half of the regular time. As a result, it was found that the pipes were excessively etched on the chuck side [20]. It was considered that the main cause was the distribution of etching current density along the etched pipe, and the etching current density was high at the chuck side.

To solve the problem, NaCl in the electrolyte was changed to NaNO₃. Because the value of current efficiency (actually etched weight / theoretically etched weight) of NaNO₃ is smaller than that of NaCl, it was thought that the influence of current density distribution in the axial direction would be mitigated. Therefore, an aqueous solution of 5 wt% NaNO₃ and 5 wt% NH₄Cl was used as a new etchant.

At first, influence of etching voltage was investigated to find out appropriate etching conditions. The etching was executed at room temperature of 22-25°C. When the voltage was increased from 5 V to 7 V, etching time was shortened. However, the etching speed considerably varied pipe by pipe. Therefore, the etching voltage was fixed to the conventional value of 5 V.

Next, influences of etching time were investigated. By preparatory experiments, it was clarified that the slits were penetrated by the etching for 20 s. So, detail etching time conditions of 15-22 s were tested. As a result, when the etching time was set for 22 s, samples were over etched and snapped in the process of removing the resist after the etching. Under the etching time conditions of 15-20 s, slits were appropriately etched. However, it was clarified that 20 s was most appropriate, because differences of etched slit sizes measured at outer and inner surfaces were the smallest.

Based on the results of above mentioned preparatory experiments, pipes with 88 resist slit patterns with homogeneous sizes equivalent to those shown in Figs. 3 and 4 were etched finally. The etchant temperature was 20-22°C, and pipes were etched for 20 s applying 5 V. As a result, all slits were uniformly etched and opened. A bird’s-eye view of a meshed pipe is shown in Fig. 7, and a plane view of a slit array in a line is shown in Fig. 8.

Fig. 6. A stainless steel pipe broken caused by the local excessive etching. Almost all the pipes are snapped at the end slit (Number 22 slit).

Fig. 7. A bird’s-eye view of a meshed pipe fabricated by using the new etchant.
Biased concentration of etching at the chuck side was improved, and pipes were not snapped by applying the etchant using NaNO₃ instead of NaCl. The sizes of 22 slits in a line were measured, and plotted as shown in Figs. 9 and 10. The average of slit widths measured on outer and inner surfaces were 53.7 μm (σ=3.4 μm) and 26.6 μm (σ=2.2 μm), respectively. The average of lengths measured at the outer and inner surfaces were 211.1 μm (σ=5.0 μm) and 178.8 μm (σ=9.0 μm), respectively. The average edge roughness measured at the inner surface was 4.3 μm (σ=1.5 μm).

Fig. 8. Plane view of a meshed pipe with 88 slits fabricated by the electrolytic etching using the new etchant.

Fig. 9. Etched slit width homogeneity investigated in the axial direction.

Fig. 10. Etched slit length homogeneity investigated in the axial direction.
Distributions of slit widths and lengths in the circumferential direction were also measured using the 11th slit. The results are shown in Figs. 11 and 12. The slit sizes were almost homogeneous in the circumferential direction also.

Fig. 11. Etched slit width homogeneity investigated in the circumferential direction.

Fig. 12. Etched slit length homogeneity investigated in the circumferential direction.

5. Discussion

It was demonstrated that aimed mesh structures were successfully fabricated. Strictly speaking, there still remained an imperfection that the slit sizes at the chuck side were slightly larger than those at the tip side. It was considered that remained slight distribution of current density in the axial direction was the cause. If this imperfection is improved further, higher etching accuracy and homogeneity will be obtained.

Because the same tendency is always obtained, size correction of delineating resist patterns may be effective also. If the scan speed of delineation is changed, slit pattern width is controllable to some extent. And, pattern length is freely changeable by assigning the scan length. Therefore, if the target shape of the meshed pipe is fixed, it will not be difficult to compensate the resist pattern sizes as the etched slit sizes become uniform in the axial direction.

On the other hand, pattern sizes varied larger on the inner surfaces than the outer surfaces. It is considered that these phenomena are caused by the difference of slit width transition between the outer and inner surfaces. Slit widths are widened according to increasing the etching time by the undercut. However, because the etching proceeds almost equally in all directions, undercut to horizontal direction becomes larger at the inner surface than at the outer surface, as shown in Fig. 13, and the opened slit sizes change fastest when the etching reaches the inner surface. Therefore, the pattern sizes on the inner surface varies larger than the outer surface. Therefore, to reduce the slit size difference between the outer and inner surfaces, and to decrease the fluctuation of slit sizes at the inner surface, it is effective to increase the etching time, and make the slit side walls near vertical by etching the pipe sufficiently. However, to obtain the same slit width, narrower resist patterns should be delineated homogeneously.

Fig. 13. Difference of slit width transition between the outer and inner surfaces.
6. Conclusion

88 arrayed slits were successfully opened through stainless-steel pipes with an outer diameter of 100 μm and a thickness of 20 μm by the combination of laser-scan lithography and electrolytic etching. The pipes were etched one by one using a pipe as an anode and applying a voltage of 5 V for 20 s. As a cathode, an aluminum pipe with a diameter of 80 mm was used. As a new electrolyte, an aqueous solution of NaNO₃ and NH₄Cl was used.

Averages of etched slit widths measured on outer and inner surfaces were 53.7 μm (σ=3.4 μm) and 26.6 μm (σ=2.2 μm), respectively. Etched slit lengths measured on outer and inner surfaces were 211.1 μm (σ=5.0 μm) and 178.8 μm (σ=9.0 μm), respectively. As a result of using the new electrolyte, the local etching concentration on the chuck side was improved, and all the slits were successfully opened through the pipes before the pipes were broken or snapped by the partial excessive etching at the chuck side slits.

Although the reproducibility and the size accuracy should be improved some more, the developed technology would be applicable to fabrications of various fine cylindrical micro-structures, such as stents, filters, and others.

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