Electrochemical Micromachining with Fiber Laser Masking for 304 Stainless Steel

Xiaohai Li¹, Shuming Wang², Dong Wang¹ and Han Tong¹

¹School of Mechanical Engineering, Jiamusi University, Jiamusi City, China
²School of Material Science and Engineering, Jiamusi University, Jiamusi City, China
Email: li_xh@jmsu.edu.cn

Abstract. In order to fabricate micro structure, the combined machining of electrochemical micro machining (EMM) and laser masking for 304 stainless steel was studied. A device of composite machining of EMM with laser masking was developed, and the experiments of EMM with laser masking were carried out. First, by marking pattern with fiber laser on the surface of 304 stainless steel, the special masking layer can be formed. Through X ray photoelectron spectroscopy (XPS), the corrosion resistance of laser masking layer was analyzed. It is proved by XPS that the iron oxide and chromium oxide on the surface of stainless steel generates due to air oxidation when laser scanning heats. Second, the localization and precision of EMM are improved, since the marking patterns forming on the surface of stainless steel by laser masking play a protective role in the process of subsequent EMM when the appropriate parameters of EMM are selected. At last, the shape and the roughness of the machined samples were measured by SEM and optical profilometer and analyzed. The results show that the rapid fabrication of micro structures on the 304 stainless steel surface can be achieved by EMM with fiber laser masking, which has a good prospect in the field of micro machining.

1. Introduction
Electrochemical machining is a method of removing metals by ion unit, which has a broad prospect in the field of metal microfabrication. At present, in order to overcome the problem of the stray corrosion during electrochemical micromachining (EMM), many scholars at home and abroad have carried out extensive research on EMM. For example, the ultra-short pulse current was used to fabricate micro metal parts by Schuster R[1] and Zhu D and so on [2], which achieved machining accuracy of sub-micron; Fan Z J[3] superimposed magnetic field during EMM, which is conducive to improve machining accuracy, surface quality and processing efficiency; Bao H Q[4] carried out EMM experiments by using pure water, the cation-exchange membrane was used to promote hydrolysis dissociation of ultra pure water, improve the current density of electrolytic processing and make micro holes on the surface of stainless steel; Zeng Y B[5] brought forward a new method of using dry film photosist with washed electrolyte to fabricate micro-dimple array on the surface of metal parts; Zhang C Y[6] proposed the laser-assisted electrochemical compound processing, the conductive transparent glass of indium tin oxide ITO was selected as electrolytic cathode, fiber laser scanning heating was adopted to remove the passivation film on the surface of 304 stainless steel during EMM and machine micro parts; Pajak P T[7] proposed the electrolyte jet nozzle with laser heating was used to fabricate micro parts, but the machining accuracy is low.
In this paper, in order to control the stray corrosion of EMM, the EMM with laser masking technology is adopted. Through laser surface modification technology, fiber laser masking pattern on the surface of 304 stainless steel are done by laser direct scanning, and the masking layer possessing corrosion protection can be formed. Then, the 304 stainless steel masked are used as the anode in the subsequent EMM. Due to the corrosion protection of masking layer, the localized machining can be controlled to fabricate the complex microstructures on the surface of 304 stainless steel.

2. Machining Mechanism

2.1. Principle of Making the Masking Layer

The developed device includes the unit of making the masking layer by fiber laser scanning and the unit of EMM. Two units are installed on the same three-axis feed table with resolution of 0.4 μm, which can solve the positioning problem during the EMM with laser masking, as shown in Figure 1. The pulsed fiber laser made in German IPG company is selected to form the masking layer, the galvanometer is the SCANLAB optical galvanometer made in German. The output power range of the fiber laser is from 0W to 20W, and the minimum diameter of laser spot is about 10 μm. The laser output frequency range is from 0 to 100kHz, and the output laser wavelength is 1.064μm. The laser focus can be controlled by focusing optical system of precision laser, three-coordinate precision worktable and the galvanometer, scanning along the planned path on the surface of the workpiece, direct writing and heating the patterns. The size and shape of the pattern can be strictly limited according to the set design. The patterns with complex shapes generate through laser surface modification, and patterns possess special properties as a masking layer in the subsequent EMM. Due to the small output power and ultra-short pulse output of the fiber laser with the only 100ns pulse width, the molten layer deposited by laser scanning is very thin and the thermal action region is very small, and the thickness of the masking layer formed is less than 1μm. In the process of EMM, the high-frequency pulsed power supply are used, the electrolyte is NaNO₃, and electrolyte circulation system is equipped for eliminating electrical corrosion products.

When make the laser masking layer, the scanning mode and path of the laser filling pattern are planned in advance. Since the output mode of optical fiber laser is pulsed mode, the scanning path of laser consists of a series of circles with a certain spot diameter, as shown in Figure 2. The laser scanning line width is determined by the laser spot diameter, and the laser scanning path planning is determined by the laser scanning line width and line spacing. As shown in Figure 3(a), laser surface
modification are carried out first on the surface of 304 stainless steel. Fiber laser beam with high density energy begin scanning according to planned path and generate the masking layer with protective effect. Then, the EMM experiments with high frequency pulse current are done, micro sheet stainless steel metal is selected as the cathode of EMM, sheet metal of 304 stainless steel with laser masking pattern serves as anode. The distance between sheet metal electrode and the workpiece surface are kept unchanged, the cathode repeatedly scans above the anode, as shown in Figure 3(b).

![Figure 2. Laser scanning path planning as laser filling pattern.](image)

![Figure 3. Principle of electrochemical micromachining by laser masking.](image)

Because the no-machining areas treated by laser masking possess the temporarily protective masking layer on 304 the stainless steel surface and the machining areas are not be treated by laser masking, the electrolytic etching metal removal rate of masking area was evidently slower than that of no-masking area on 304 the stainless steel surface. Accordingly, the machining areas can be quickly removed through electrolytic corrosion, and micro electrochemical localized processing can be realized. The two-dimensional micro cavity with certain protective masking pattern can be obtained, as Figure 3(c) shows. The depth of the cavity at one time is very shallow, and it can also be processed by many times processes of EMM with laser masking and the machining depth of cavity is improved. The repetition accuracy of laser masking pattern is less than 2 μm. If the pattern of the masking layer is different each time, a micro cavity with a multilayer structure can be machined, as Figure 3(d), (e) and (f) show.

As shown in Figure 4, under conditions of 5W laser power and 20mm/s laser scanning speed, 304 stainless steel surface with the 8K mirror precision is marked to make the surface metal melt and form the recast layer. In the process of laser masking, the metal on the stainless steel is oxidized by air. Due to rapid thermal quench, the micro cracks appear on the surface of the workpiece. The laser heating can produce the metal melting layer on the surface of stainless steel. The grains of the melting layer can be refined, which can improve the surface performance of stainless steel and also enhance the corrosion resistance on the surface of stainless steel [8].
2.2. X-ray Photoelectron Spectroscopy Analysis of Laser Masking Layer

According to the processing condition of laser masking in Figure 4, the energy density of laser beam was adjusted, and the surface modification of 304 stainless steel workpiece was done by fiber laser. X-ray photoelectron spectroscopy (XPS) analysis are used to study surface characteristics and explore the mechanism of corrosion resistance enhancement of laser masking layer of 304 stainless steel. As shown in Figure 5, the XPS spectrum of the Cr composition varies with the sputtering time on the 304 stainless steel surface.

The laser masking layer test was carried out by ESCALAB 250Xi type X-ray photoelectron spectroscopy analysis. The thickness of the metal surface layer tested is related to the sputtering time, and the XPS spectrum of the inner layer on the metal surface can be obtained by using the longer sputtering time. The samples include two types: 304 stainless steel treated by laser masking and 304 stainless steel substrate without laser masking. As shown in Figure 5 (a), the peak energy of the binding energy decreases from 575.8eV (chromium oxide state) to 574.0eV (chromium metal state) as...
the sputtering time increases. This indicates that the Cr component on the surface of 304 stainless steel without laser masking is not modified as the sputtering time increases, which is coated with a very thin layer of chromium oxide. As shown in Figure 5 (b), as the sputtering time increases, the binding energy peak is fixed around 577.1eV, showing a chromium oxidized state of matter (Cr₂O₃, CrO₃). This indicates that there is a thick layer of chromium oxide layer (Cr₂O₃, CrO₃) on the 304 stainless steel treated by laser masking.

Figure 6 shows the XPS energy spectrum of Fe on the surface of 304 stainless steel with the change of sputtering time. With the increase of sputtering time, the binding energy peak decreases from 710.1eV (for iron state) reduced to 707.1eV (iron metal state) on the surface of 304 stainless steel substrate without laser masking, as shown in Figure 6 (a), which indicates that Fe valence does not change and there is a very thin layer of iron oxide layer on the surface of 304 stainless steel surface without laser masking. But as shown in Figure 6 (b), with the increase of sputtering time, the binding energy peak is fixed at 710.0eV (corresponding to the ferric oxide state), which indicates that the surface of 304 stainless steel treated by laser masking is covered with a thick layer of iron oxides (FeO and Fe₂O₃).

According to Faraday's law, electrochemical removal rate \( v_a \)

\[
v_a = \eta \omega I
\]  

where \( \eta \) is the machining current efficiency, \( I \) is current density, \( \omega \) is electrochemical equivalent. In Figure 7, the surface of 304 stainless steel treated by laser masking is coated with Cr, Fe and other oxides, so the resistance \( R_1 \) of masking layer is greater than the resistance \( R_2 \) of no-masking layer. Then, the current density \( I_1 \) between the electrode and the masking layer is much smaller than the current density \( I_2 \) between tool electrode and no-masking layer current density, and the material dissolved removal rate of no-masking region is much greater than that of masking region. Therefore, the oxide layer produced by the laser masking plays a major protective role in EMM and can realize the localized machining.

![Figure 6. Fe 2p spectra with change of sputtering time](image)

![Figure 7. Localized processing mechanism of electrochemical machining with laser masking](image)
3. Experiments of EMM with Laser Masking

The experimental researches on EMM with laser masking were carried out on the developed device of EMM with fiber laser masking. First, the surface modification of 304 stainless steel workpiece was treated by laser masking with suitable laser parameters, as shown in Table 1. The samples of 304 stainless steel treated by laser masking are fabricated by EMM in the electrolytic tank, the simple sheet electrode of stainless steel serves as the cathode electrode, 304 stainless steel treated by laser masking is anode, and the CNC system makes the tool electrode scan reciprocally above the stainless steel workpiece during EMM and strictly controls the unchanged distance between the electrodes in the process of EMM. The EMM parameters are shown in Table 2, the electrolyte is 1.8mol/L sodium nitrate solution, the electrolyte is powered by micro diaphragm pump to flow with high-speed through small nozzle jet, the electrolyte flow rate is 320ml/min, which makes electrolytic products fast wash out and makes electrolytic processing smoothly.

| Laser processing parameters | Value |
|-----------------------------|-------|
| Average laser power /W      | 5     |
| Frequency /kHz              | 80    |
| Laser scanning speed / (mm/s) | 20   |
| Beam diameter /µm           | 50    |
| Line spacing /µm            | 10    |

| Electrochemical processing parameters | Value |
|-------------------------------------|-------|
| Pulse width /µs                     | 50    |
| Pulse interval /µs                  | 750   |
| Machining voltage /V                | 9.5   |
| NaNO₃ electrolyte concentrations /mol/L | 1.80 |
| Interelectrode gap /µm              | 220   |
| Sheet electrode scanning speed / (µm/s) | 200 |

The cavity depth of one time EMM with laser masking is very small, and the depth of the machined cavity is remarkably improved by many times repeated processes of EMM with laser masking. Figure 8 is the samples fabricated through EMM with laser masking three times, and the cavity depth reach about 23µm, the width of the groove is about 120 µm in Fig.8(b). In the process of EMM with laser masking, the scanning speed of the laser masking is 20mm/s, and many samples can simultaneously be fabricated.

![Figure 8. Typical structural sample](image)

Figure 9 is a morphology of a cavity of figure 8 (a) measured by an optical profilometer, including the height difference, roughness, and sectional contour of the cavity. From Figure 9, the cavity side wall fabricated is very steep, micro cavity surface fabricated is very smooth, and the surface roughness Sa value is 0.263µm. The stainless steel surface formed by electrolytic corrosion at no-masking area is as shown in Figure 10. Because the electrode scanning speed of 200 µm/s during EMM and it is
unnecessary for the micro die-sinking electrode to be fabricated, so the efficiency of fabricating each cavity by EMM with laser masking is very high. The technology has a good prospect in respect of fabricating micro channels, micro mold cavities, etc.

4. Conclusion
The surface modification of 304 stainless steel surface was done by using fiber laser masking on the surface of 304 stainless steel to produce Fe and Cr oxide masking layer with corrosion resistant performance. A device of EMM with laser masking was developed to realize micro machining by combining laser masking with EMM. The experiments indicate that EMM with laser masking technology can rapidly fabricate the micro size cavities, which has a good prospect in micro machining.

5. Acknowledgements
The project is supported by National Natural Science Foundation of China(51375208) and Scientific and Technological Innovation Team of Jiamusi University (Cxtdpyn-2016-04).

6. References
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