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Effects of Complexing Agent on Electrochemical Micro Machining of Stainless Steel

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Abstract: Problem statement: Electrochemical Machining (ECM) is a prospective technique in micro machining. The productions of work piece in ECM are precipitation of hydroxide, which will block the machining gap. To prevent the formation of hydroxide, acids were often used. To machining work piece which is not acid-resistant, acids are not suitable. **Approach:** This study is conducted to find the effects of complexing agent on Electrochemical Micro Machining (ECM) of stainless steel. Compared to acids, the complexing agent is non-toxic and non-corrosive. ECM of stainless steel by applying short pulses in sodium chlorate electrolyte added with complexing agent is researched. Ethylenediaminetetraacetic acid disodium salt (EDTA-Na2) is a kind of widely used complexing agent. The usage of EDTA-Na2 prevented the formation of hydroxide. On the other hand, without EDTA-Na2, the electrode was attached with precipitation of hydroxide and short circuit occurred frequently. **Results:** Experiments results indicated that EDTA-Na2 can avoid the short circuit and not increase the side gap of electrochemical machining. **Conclusion:** EDTA-Na2 can form complex compound with ions of anode and dissolved in electrolyte. It is a kind of effective complexing agent in electrochemical machining of stainless steel.

Key words: Electrochemical micro machining, micro hole, complexing agent, EDTA-Na2, non-toxic, non-corrosive, Ethylenediaminetetraacetic acid, sodium chlorate

INTRODUCTION

Micro machining technology is a research hotspot of modern manufacturing technology (Kirchiner *et al*., 2001; Iqbal *et al*., 2010). Electrochemical machining is appropriate for micro machining for it removes the rest material by electrochemical reaction, in which the material is dissolved at unit of single atom. The electrochemical machining has the advantage of excellent surface quality and no heat affected zone, no residual stress (Kim *et al*., 2005).

The electrochemical machining accuracy is not suit for precision machining. The accuracy is not certain and varies with the machining time and machining gap. This is because the stray current results the unwanted machining. To resolve the problem of stray current erosion, researchers used photo resist mask electrolysis technology to machining micro holes and other two-dimensional structures (Xiaohai *et al*., 2005; Kenney *et al*., 2004). Another method is applying ultra short voltage. It was successfully demonstrated for three-dimensional machining of copper and silicon with submicrometer resolution (Kozak *et al*., 2009; Kock *et al*., 2003). Here we apply this method to the machining of stainless steel.

The micro machining of stainless steel is difficult by electrochemical machining, especially in machining deep micro hole. The electrolyte properties play a significant role in controlling the dimensional accuracy and surface roughness in electrochemical machining. In electrochemical machining of stainless steel, the productions of work piece are hydroxide. To dissolve the hydroxide, acids, for example, hydrochloric acid, sulphuric acid are usually used as electrolyte (Schuster, 2007; Ryu, 2008). These electrolytes are toxic and corrosive. To avoid these problems, the complexing agent is added in sodium chlorate electrolyte, which is non-toxic and non-corrosive (Ahn *et al*., 2004).

In this study, ECM of stainless steel by applying short pulses in sodium chlorate electrolyte added with complexing agent is researched. The main component

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of electrolyte is sodium chlorate. Ethylenediaminetetraacetic acid disodium salt (EDTA-Na2) was used as an addition. A micro rotated cylindrical electrode was used as the cathode. It drilled holes in work piece by electrochemical machining. The usage of complexing agent can catch the metal ions of work piece, avoiding forming hydroxide (Kicrchner *et al*., 2001). In the machining process of deep hole, electrolyte is difficult to flash to the gap between electrode and work piece. The production of work piece will attach to the electrode and renders machining impossible (Hocheng *et al*., 2005; Chen *et al*., 2009). To machine deep hole, the electrode should be life up when machine a certain depth. It is helpful to let electrolyte flow to machining gap. Experiments results indicate that the addition of EDTA-Na2 did not increase stray corrosion of sodium chlorate electrolyte. The electrolyte is appropriate for electrochemical micro machining.

MATERIALS AND METHODS

The mechanism of electrochemical micro machining of stainless steel: The mechanism of electrochemical micro machining of stainless steel is same as normal electrochemical machining. It removes the materials by electrochemical reactions. There are some differences between them. The normal electrochemical machining has higher voltage, higher current, higher electrolyte concentration and higher electrolyte flow rate. The electrochemical micro machining has lower voltage, lower current, lower electrolyte concentration and lower electrolyte flow rate, even in static electrolyte. The machining gap of normal electrochemical machining is above 0.1mm, in other wise, the electrochemical micro machining is lower than 0.05 mm and the smallest gap can reach 0.001 mm.

Schematic diagram of electrochemical machining is shown in Fig. 1. In the process of electrochemical micro machining, the reactions on the surface of electrode and work piece are listed in following equations. Equation 1 describes reaction on work piece in salt electrolyte without complexing agent. In the Eq. 1, the productions of the work piece are the precipitation of hydroxide $M(OH)_2$. The precipitation will attach to the electrode. It will decrease the efficient of electrochemical reactions and increases the frequency of short circuit. Equation 2 describes reaction on work piece in electrolyte with complexing agent. The productions of the work piece are some kinds of complex compounds MH_2Y, which are soluble in water. Equation 3 describes reaction on electrode, the production is hydrogen:

$$M + 2OH^- \rightarrow M(OH)_2 \downarrow + 2e^- \quad (1)$$

$$M + H_2Y^{2-} \rightarrow MH_2Y + 2e^- \quad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \uparrow \quad (3)$$

In the equations, M represents a kind of material with valence 2. H_2Y^{2-} represents a kind of complexing agent.

Experimental setup: The machining system is based on a 3-axises micro EDM machine. It consists of a precision servo system with 0.1 µm solution, an ultra short voltage pulse power, an electrolytic cell, a voltage detector system and an oscilloscope. For setting the beginning position of the work piece with respect to the tool electrode, the zero position was set as the short circuit of electrode and work piece. Then move the electrode to 10 µm above the work piece. The tool was a cylindrical metal wire, which can be made of tungsten, molybdenum, copper wire. The tool electrode was fabricated in the same micro machining system by EDM. The study piece is stainless steel. To prevent short circuit of electrode and work piece, an oscilloscope measured the voltage profile in machining. Stainless steel 304 plates is used as work material. Tool electrode is clamped by micro drill chuck.

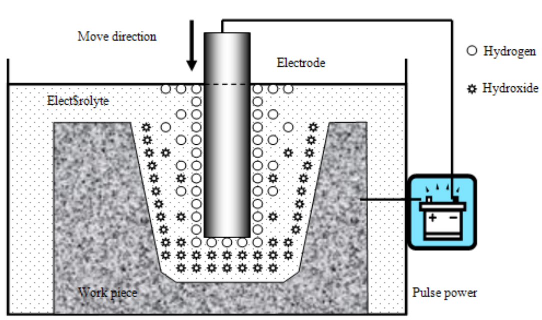


Fig. 1: Schematic diagram of electrochemical machining

Table 1: Experimental conditions

Voltage (V)	Frequency (Hz)	Pulse duration (ns)	Electrolyte (mol L^{-1})	Electrode	Work piece
6.5	1M	300	0.3 $NaClO_3$ + 0.05 EDTA-Na2	copper	304 stainless steel

Experimental conditions: The parameters of pulse power and the material of electrode and work piece are listed in Table 1.

RESULTS

The choice of complexing agent: To machine high aspect holes, it is difficult to machine in NaNO3, NaClO3 electrolyte. Machining speed in NaNO3, NaClO3 electrolyte is too slow and the fresh electrolyte is difficult to flush into the internal of hole. In the above condition, when the machining depth reached to 0.1 mm, short circuit occurred frequently. To circumvent this problem, a complex was chosen to the electrolyte.

Complexing agent is also named as chelating agent. It is a substance capable of forming a complex compound with another material in solution. The commonly used complexing agents are EDTA-Na2, citric acid, $K_4P_2O_7$, KCN. Compared to other complexing agents, EDTA-Na2 is non-toxic and non-corrosive, environmental friendly. EDTA-Na2 is a widely used abbreviation for the chemical compound Ethylenediaminetetraacetic acid disodium salt. EDTA-Na2 refers to the chelating agent with the formula C10H14N2Na2O8. EDTA-Na2 binds to metals via four carboxylate and two amine groups. EDTA-Na2 forms especially strong complexes with Mn(II), Cu(II), Fe(III), Pb (II) and Co(III). The EDTA-Na2 complexing property avoids the formation of insoluble deposition on the work piece surface and in the electrolyte solution. By adding EDTA-Na2 in electrolyte, the metal ions dissolved will not form hydrate deposition. So it can improve electrolyte renewing. There are two reasons to choose EDTA-Na2. The first is that EDTA-Na2 has high complex ability. It can complex with most kinds of metal ions. Table 2 lists the EDTA-Na2 complex compounds stability constant of main elements of work piece. The stability constants are all greater than 8, which proves its complex compounds is stable. The second reason is EDTA-Na2 complex ability is not decreased in a large range of PH value. This is useful in machining, in which the PH value of electrolyte will increase with the process. So EDTA-Na2 is chose to add in electrolyte for electrochemical micro machining.

The experiments of micro holes machining: In the experiment, we used two kinds of electrolyte. One kind of electrolytes is 0.3mol L^{-1} $NaClO_3$. Another electrolyte is 0.3 mol L^{-1} $NaClO_3$, with addition of 0.05mol L^{-1} EDTA-Na2. To avoid acid corrosion, acid was not selected to dissolve deposition.

Table 2: Stability constant of EDTA-Na2 complex compound

Element	Fe^{3+}	Ni^{2+}	Cr^{3+}	Mn^{2+}
stability constant	25.1	18.62	23.4	13.87

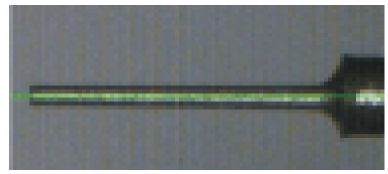


Fig. 2: 16electrode before machining

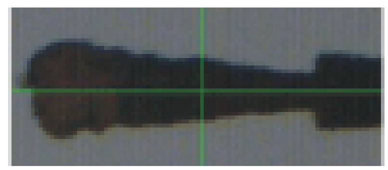
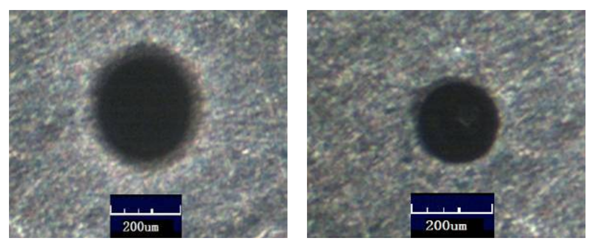


Fig. 3: Electrode after machining



(a) (b)

Fig. 4: Hole machined in 0.3mol L^{-1} NaClO3 electrolyte (a) Hole entrance; (b) Hole exit

The electrode before machining is shown in Fig. 2. The diameter of the electrode is 100 micrometer. In the electrolyte of 0.3mol L^{-1} $NaClO_3$, the electrochemical machining was short circuit frequently, especially when the machining depth was increased after 100 micrometer. This is because the electrolyte was hard to flash into the machining gap. With the machining undergoing, the production of work piece cannot diffuse from the gap, which resulted electrochemical machining cannot continue. The electrode after electrochemical machining of deep hole is shown in Fig. 3. The surface of electrode is covered with a lot of deposition. The compositions of the cover were hydroxide and oxidizing material of work piece. For the stay current, the diameter of hole entrance is bigger than its exit, as is shown in Fig. 4.

The electrochemical micro machining was carried on a 0.4 mm thick stainless steel. The electrode diameter was 0.1 mm. In the electrolyte of 0.3 mol L^{-1} $NaClO_3$, with addition of 0.05 mol L^{-1} EDTA-Na2, the time of short circuit is decreased. The machined depth with time was shown in Fig. 5. The initial machining gap was 10 micro meter. The terminal machining depth was 410 micro meter. The machining time in electrolyte added with EDTA-Na2 was 30 min and in electrolyte without EDTA-Na2 was 40 min. In the initial machining process, the machining state was stainable, with no short circuit occurrence. This is because the machining depth is small, the production of work piece can be flashed by electrolyte flowing. With the machining depth increasing, the short circuit occurred frequently in the electrolyte without EDTA-Na2, for the production is difficult to be flashed out of machining gap. The electrode should draw back. The Fig. 6 shows the holes machined in two kinds of electrolyte. The left hole with 280 micro meter in diameter was machined in electrolyte with EDTA-Na2 and the right with 180 micro meter in diameter was machined in electrolyte without EDTA-Na2. This is because the machine time without EDTA-Na2 is longer. So EDTA-Na2 can decrease the short circuit and not increase the side gap of electrochemical machining.

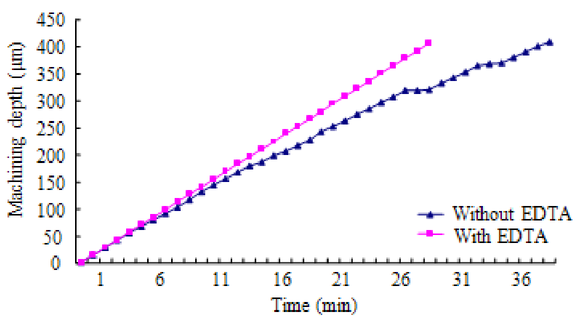
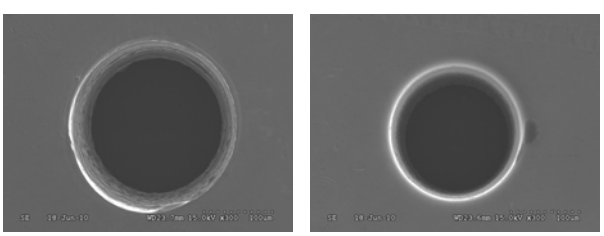


Fig. 5: The machined depth with time in two kinds of electrolyte

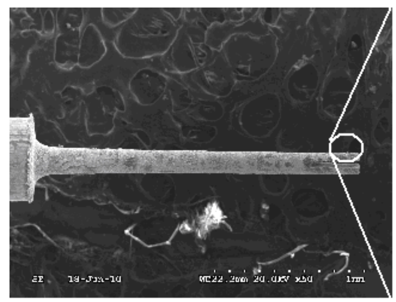


(a) (b)

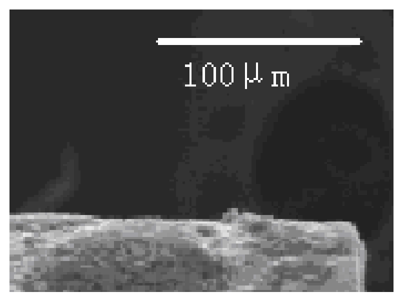
Fig. 6: The micro holes machined in 0.3 mol L^{-1} $NaClO_3$, 0.05 mol L^{-1} EDTA-Na2 electrolyte

DISCUSSION

The effect of EDTA-Na2 to the production of work piece: In sodium chlorate electrolyte, the production of work piece is precipitation of hydroxide. Figure 7 shows the electrode after machining in sodium chlorate electrolyte. The surface of the electrode was cover with some precipitations. On the other hand, the electrode used in the electrolyte with EDTA-Na2 was the same as before. Through X-ray photoelectron spectroscopy analysis in Fig. 8, the precipitation is consisting of C, O, Fe, Cr and Ni. They are the main elements of 304 stainless steel. It indicates that the precipitation is hydroxide of work piece.



(a)



(b)

Fig. 7: The electrode after machining in electrolyte without EDTA

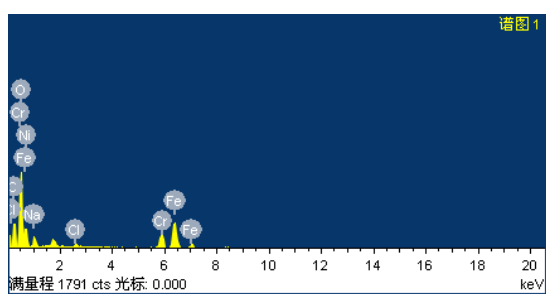


Fig. 8: X-ray photoelectron spectroscopy analysis of precipitation

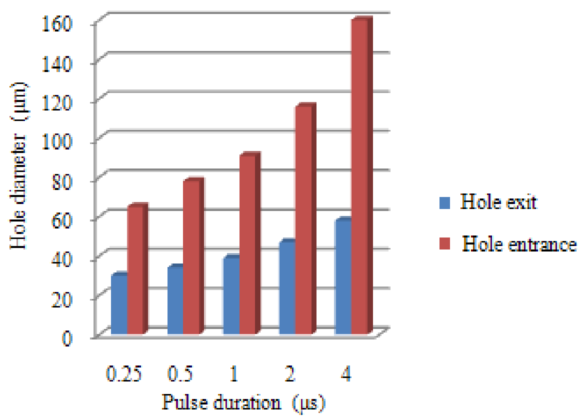


Fig. 9: The hole entrance and exit dimension with pulse duration

The effect of pulse duration on machining gap: To compare the effect of pulse duration on machining gap, different pulse durations were applied in electrochemical machining of deep hole. To avoid the short circuit occur, the machining was divided into several part. The electrode would withdraw after feeding 100 micrometer. So the machining of 400 micrometer thick stainless steel was carried in 4 times. The minimum pulse duration was 0.25 microsecond, the maximum pulse duration was 4 microsecond. The hole entrance and exit dimension with pulse duration was shown in Fig. 9. The machining voltage is 6.5V and feed rate is 6 μm min^{-1}. The machining accuracy is not affected by frequency. The frequency only affected the machining speed. To decrease machining time, high frequency should be selected. But to let electrolyte renew, sufficient pulse off time is needed.

Electrochemical micromachining with short voltage pulses is based on the charging time constant of the double-layer capacitance of electrode surfaces. According to electrochemical theory, when an electrode is immersed in electrolyte, a double-layer structure which is similar to the parallel capacitor would form at the interface between the electrode and the electrolyte. As current flows the electrodes and electrolyte, it renders tow processes, electrochemical reaction and charging the double-layer. In the equivalent circuit, we disregard electrochemical reactions resistance. So the potential drop on double layer varies by the local time constant, which is the product of electrolyte resistance and total capacitance. Assumed the capacitance and the electrolyte conductance are uniform everywhere, the time constant depends on the length of current path through the electrolyte, which is approximately equal to the separation between the electrode and work piece. So the potential increases faster where the distance is small. The machining rate, i.e., electrochemical reaction rate, is exponentially proportional to the over potential between work piece and electrolyte, which is approximately equal to the potential drop on double layer. By the application of ultra short voltage pulses, the potential drop on the double-layer is higher where the time constant is little.

CONCLUSION

To electrochemical machining of deep hole, two kinds of electrolyte were chosen in experiments. The EDTA-Na2 was chose as complexing agent added to sodium chlorate electrolyte. In the electrochemical micro machining of holes, EDTA-Na2 can avoid the short circuit and not increase the side gap of electrochemical machining. The production of work piece in the electrolyte without EDTA-Na2 will attach to the electrode. Its components are elements of work piece. EDTA-Na2 complexing agent avoids the formation of insoluble precipitation on the electrode surface and in the electrolyte solution and it is helpful to machining stability.

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