Research Paper

Electrolytic Dissolution of Mild Steel in High Current Density Region*

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(Received Feb. 3, 1970)

Polarization curves, current efficiencies and dissolution rates of mild steel in various electrolytes were obtained in the high current density region, that is, in the transpassive region up to current density 30 A/cm^2 , using specially designed electrolytic cell passing an electrolyte at a flow velocity 8.3 m/s .

In an electrolyte which gives a fine dimensional control in electrochemical machining (ECM), for example in sodium chlorate solution, mild steel dissolves quickly in the transpassive region though it hardly does in the passive region.

Criteria for good ECM electrolyte have been proposed. In order to obtain a fine dimensional control and minimize the possibility of the short circuit in ECM, the requirement for a desirable electrolyte is that its slope ascending toward right in the dissolution rate versus current density graph (Fig. 8) must be steep and sit at higher position as much as possible.

1 Introduction

Sodium chloride solution has been used almost exclusively as an electrolyte for electrochemical machining (ECM). However, after M.A. LaBoda and M.L. McMillan reported that sodium chlorate is excellent for ECM⁽¹⁾, such electrolytes as passivate iron and therefore had been scarcely paid attention became noticed again. And it has been confirmed from experiments that ECM is not necessarily impossible with such electrolytes as passivate iron⁽²⁾.

In the case of sodium chlorate solution, J.P. Hoare et al. suggested that the moderately strong passive film allowed ECM and that the sharp change from passive to transpassive state induced a fine dimensional control⁽³⁾. On the other hand, the authors found the evidences showing that ECM in sodium chlorate solution was done in the transpassive region as described in the previous report⁽⁴⁾.

Then, how the dissolution rate and the current efficiency in transpassive region vary as a function of the electrode potential?

What is the necessity for a good ECM electrolyte?

This report intends to obtain the answers to the above questions. In order to realize a high current density condition, a special electrolytic cell was constructed. With the electrolytic cell, the current density up to about 30 A/cm^2 could be obtained passing an electrolyte at a flow velocity 8.3 m/s . These experimental conditions are very close to those in practical ECM.

2 Experimental Method

The crosssectional sketch of the electrolytic cell is shown in Fig. 1. The electrolyte flows in the direction perpendicular to the paper. The electrolyte path is circular in crosssection at inlet and outlet but becomes narrow via ellipses to a rectangle of $2 \times 10 \text{ mm}$ at the center. The tip of the reference electrode capillary is placed adjoining to the mild steel (S 15 C) test electrode. The capillary was filled

Fig. 1 Crosssectional sketch of electrolytic cell

with agar-agar to prevent invasion of bubbles and electrolyte pressure. The counter electrode was made of 18-8 stainless steel and the main parts of the electrolytic cell were made of teflon. The test electrode and the counter electrode have the same shape, a $5 \phi \times 7 \text{ mm}$ cylinder, and one of the circular planes of the cylinder (0.2 cm^2) comes in contact with the electrolyte.

The experimental circuit is shown in Fig. 2. The maximum output current of the potentiostat is 10 A

* Electrode Processes in Electrochemical Machining (Part 3)

Fig. 2 Experimental circuit

and its output voltage is reinforced with the direct current source inserted between the potentiostat and the counter electrode. Other measuring instruments are the same as in the previous report¹⁾. A 200 W labo pump was used to circulate the electrolyte, which was kept at a temperature 40°C. Polarization curves were measured by changing the electrode potential manually from corrosion potential toward noble potential at a rate of about 0.05 V/s.

3 Experimental Results

Fig. 3 shows the influences of concentration and flow velocity on polarization curve in the case of sodium chloride solution. At a flow velocity 0.83 m/s, the current was limited by concentration polarization. At flow velocities above a few m/s, flow

Fig. 3 Influences of concentration and flow velocity on polarization curve

velocity hardly influenced the polarization curve. The difference in the polarization curve between the concentration 100 g/l and 300 g/l is thought to be due to the difference of electrolyte resistance between the test electrode and the capillary tip.

The polarization curve, current efficiency and dissolution rate of mild steel in sodium chloride solution are shown in Fig. 4. The current efficiency was determined by comparing the weight loss during the current-time curve measurement at a desired potential with the charge passed which was calculated by integrating the current-time curve. The dissolution rate is the product of the current density

Fig. 4 In the case of 100g/l sodium chloride solution at flow velocity 8.3 m/s

and the current efficiency. The open circles attached to the polarization curve were obtained by reading the steady state value of the current-time curve.

In sodium chloride solution the current efficiency is independent of electrode potential and keeps a constant value which is satisfactory close to the electrochemical equivalent for the dissolution as ferrous ion 0.289 mg/C. Therefore the dissolution rate varies as loosely as the polarization curve with the electrode potential.

Fig. 5 shows the polarization curve, current efficiency and dissolution rate in sodium nitrite solution. Because the current efficiency at 5.0 V is 7.5 times that at 1.2 V, the dissolution rate varies more sharply than the polarization curve. The mild steel was passivated so strongly in this solution that the weight loss in the passive region could not be measured, and the current efficiency and dissolution rate could not be determined.

Fig. 6 shows the polarization curve, current efficiency and dissolution rate in sodium nitrate solution. Corrosion potential in this case exists in an active region. The current efficiency is relatively high at

Fig. 5 In the case of 200 g/l sodium nitrite solution at flow velocity 8.3 m/s

Fig. 6 In the case of 200 g/l sodium nitrate solution at flow velocity 8.3 m/s

Fig. 7 In the case of 300 g/l sodium chlorate solution at flow velocity 8.3 m/s

electrode potential up to 1.3 V. After the current efficiency dropped at about 1.5 V, it increases with the increases of electrode potential. The dissolution rate increases sharply in the transpassive region.

Fig. 7 shows the polarization curve, current efficiency and dissolution rate in sodium chlorate solution. The mild steel was passivated from the beginning as in sodium nitrite solution. The current efficiency increases almost up to the value in sodium chloride solution with the increase of the electrode potential. The dissolution rate increases most sharply in the transpassive region.

4 Discussion

In the previous section the dissolution rate and the current efficiency have been considered as a function of the electrode potential. Under such high current density, however, it is very difficult to measure the electrode potential precisely because of the great contribution of the ohmic drop between the test electrode and the capillary tip. On the other hand, the difference between potentiostatic and galvanostatic measurement is not supposed to affect the result in the transpassive region remarkably, because there is no electrically unstable region as is seen at the transition between active and passive state. Therefore it would be more reasonable in this case to describe the results as a function of the current density, which can be measured precisely, rather than the electrode potential. The experimental results are summarized in this way in Fig. 8. In order to obtain a fine dimensional control in ECM, it is a

Fig. 8 Dissolution rates in various electrolytes as a function of current density (at flow velocity 8.3 m/s)

necessary condition that the current efficiency is lower at a lower current density in order to discriminate the dissolution rate between the machining area where current density is very high and the other area where some amount of stray current exists. In order to minimize the possibility of the short circuit and increase the removal rate, the dissolution rate must be large enough. Consequently the requirement for the desirable electrolyte for ECM is that its slope ascending toward right in Fig. 8 must be steep and sit at higher position as much as possible. The part under the current density of about 1 A/cm^2 may be neglected in this evaluation because the current density applied to ECM is several tens or hundreds of A/cm^2 .

Evaluating the electrolytes in Fig. 8 with the above mentioned criteria, the followings can be said. Sodium chloride solution provides the largest removal rate and the least possibility of the short circuit but the worst dimensional control. When logarithmic scaling of the axes is considered, it will be known that the dimensional control in the cases of sodium chlorate solution, sodium nitrate solution, and sodium nitrite solution will be considerably better than that in the case of sodium chloride solution. Moreover, the dissolution rate in sodium chlorate solution is very close to that in sodium chloride solution. The current efficiency in sodium nitrate solution is expected to increase more by increasing the current density more than that measured this time. Sodium nitrite solution has a handicap of the smallest dissolution rate.

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Above mentioned conjectures coincide fairly well with the results in a practical ECM experiment²⁾.

5 Conclusion

Above mentioned experimental results and discussion are summarized as follows. From the views of the dimensional control and the prevention of the short circuit, the requirement for a desirable electrolyte for ECM is that its slope ascending toward right in Fig. 8 must be steep and sit at higher position as much as possible. In other words, it is required to find out an electrolyte which passivates the work material but dissolves it quickly in the transpassive region.

Acknowledgment : Some part of this experiment was done at the faculty of engineering, Hokkaido University, taking the advantage of the floating researcher system sponsored by the Agency of Industrial Science and Technology. We would like to express our appreciation to Prof. Go Okamoto (at the present, Science University of Tokyo), Prof. Norio Sato at the university and the persons concerned for giving us guidances and facilities.

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