

## CHAPTER ONE

### *Introduction*

Michael Faraday's early metallurgical researches, from 1818 to 1824, anticipated the developments which have led to the widespread use today of alloy steels. Of the innumerable applications of these materials, their service as cutting tools in machining practice has been recognised from the outset, and much effort has been expended to improve their performance. The aim has always been to yield higher rates of machining and to tackle harder metals which are developed (on the principle that the tool material must be harder than that of the workpiece which is to be machined). To that end, various heat-treatments and compositions of tool materials and

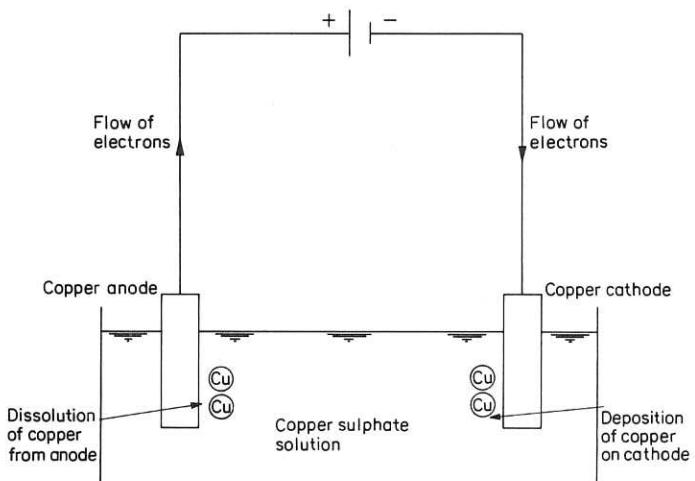


Fig. 1.1 Electrolysis of copper sulphate solution

formations of tools continue to be tried. Much progress has been made, but in recent years some alloys have been produced which are exceedingly difficult to machine. These have been prepared to meet a demand for very high-strength, heat resistant materials which, moreover, often have to take a complex shape. The evolution of suitable tooling has not kept pace with these advances, and accordingly, a search has had to be made for alternative methods of machining.

Electrochemical machining (ECM) has been developed initially to machine these alloys, although any metal can be so machined. Its basis is the phenomenon of electrolysis, whose laws were established by Faraday in 1833, and which, with his electrical studies, was mainly responsible for diverting his attention from his work on metals.

### 1.1 Electrolysis

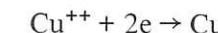
Electrolysis is the name given to the chemical process which occurs, for example, when an electric current is passed between two conductors dipped into a liquid solution. A typical example is that of two copper wires connected to a source of direct current and immersed in a solution of copper sulphate in water, as shown in Fig. 1.1. An ammeter, placed in the circuit, will register a flow of current; from this indication, the electric circuit can be deduced to be complete. A significant conclusion that can be made from an experiment of this sort is that the copper sulphate solution obviously has the property that it can conduct electricity. Such a solution is termed an *electrolyte*. The wires are called *electrodes*, the one with positive polarity being the *anode*, and the one with negative polarity the *cathode*. The system of electrodes and electrolyte is referred to as the *electrolytic cell*, whilst the chemical reactions which occur at the electrodes are called the *anodic* or *cathodic reactions or processes*.

Electrolytes are different from metallic conductors of electricity in that the current is carried not by electrons but by atoms, or groups of atoms, which have either lost or gained electrons, thus acquiring either positive or negative charges. Such atoms are called *ions*. Ions which carry positive charges move through the electrolyte in the direction of the positive current, that is, towards the cathode, and are called *cations*. Similarly, the negatively charged ions travel towards the anode and are called *anions*. The movement of the ions is accompanied by the flow of electrons in the opposite sense out-

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side the cell, as shown also in Fig. 1.1, and both actions are a consequence of the applied potential difference (or voltage) from the electric source.

A cation reaching the cathode is neutralised, or discharged, by the negative electrons on the cathode. Since the cation is usually the positively charged atom of a metal (in the above case, copper) the result of this reaction is the deposition of metal (copper) atoms. For copper, the reaction may be written



where e is one electron.

To maintain the cathodic reaction, electrons are required to pass round the external circuit. These are obtained from the atoms of the metal anode, and these atoms thus become the positively charged cations which pass into solution. In this case, the reaction is the reverse of the cathodic. For the above example, it is



The electrolyte in its bulk must be electrically neutral; that is, there must be equal numbers of opposite charges within it, and thus there must be equal amounts of reaction at both electrodes. Therefore, in the electrolysis of copper sulphate solution with copper electrodes, the overall cell reaction is simply the transfer of copper metal from the anode to the cathode. When the wires are weighed at the end of the experiment, the anodic wire will be found to have lost weight, whilst the cathodic wire will have increased in weight by an amount equal to that lost by the other wire.

These results are embodied in Faraday's two laws of electrolysis:

- (i) the amount of any substance dissolved or deposited is directly proportional to the amount of electricity which has flowed;
- (ii) the amounts of different substances deposited or dissolved by the same quantity of electricity are proportional to their chemical equivalent weights.

The two laws may be combined to give the equation

$$m = \frac{AIt}{zF} \quad (1.1)$$

where m is the mass dissolved from, or deposited upon, the metal by a current I passed for time t. The reacting ions have atomic weight A and valency z, the quantity A/z being the chemical equivalent. F is

a universal constant known as the Faraday (or Faraday's) constant. It is the amount of electric charge necessary to liberate one gram-equivalent ( $A/z$ ) of an ion in electrolysis. Its commonly accepted value is 96 500 C.

When the product  $It$  is unity, i.e. one coulomb of charge has been passed, the value,  $m = A/zF$ , so defined is the *electrochemical equivalent* of the metal,  $e_a$ . For example, copper has an atomic weight of 63.57. When it is univalent, its equivalent weight is 63.57 g; when the metal is divalent, the equivalent weight is 31.78 g. The corresponding electrochemical equivalents are respectively  $66 \times 10^{-5}$  g/C and  $33 \times 10^{-5}$  g/C. Iron has an atomic weight of 55.85. In its divalent form this metal has an electrochemical equivalent of  $29 \times 10^{-5}$  g/C; trivalent iron has an electrochemical equivalent of  $19 \times 10^{-5}$  g/C.

A popular application of electrolysis is the electroplating process in which metal coatings are deposited upon the surface of a cathodically polarised metal. Current densities used are roughly  $2 \times 10^{-2}$  A/cm<sup>2</sup> and the thickness of the coatings is seldom more than about 10 µm. (Current density here is regarded as the current used over the area under treatment.) An example of an anodic dissolution operation is electropolishing. Here, the item which is to be polished is made the anode in an electrolytic cell. Irregularities on its surface are dissolved preferentially so that, on their removal,

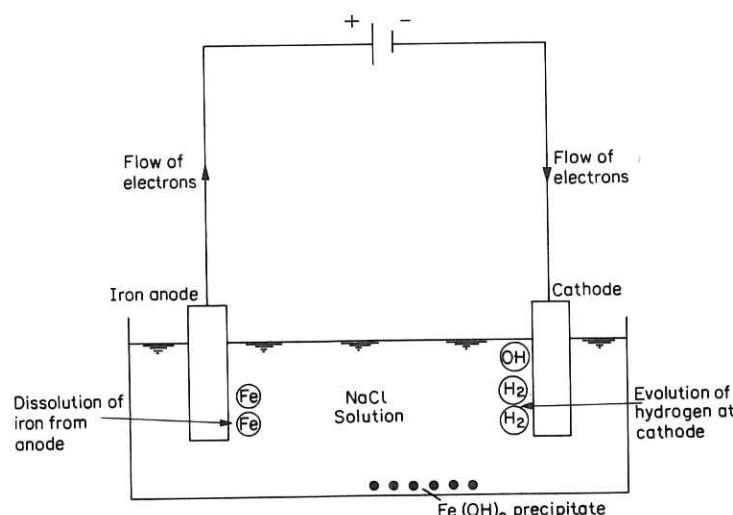


Fig. 1.2 Electrolytic dissolution of iron

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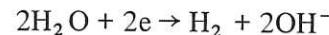
the surface becomes flat and polished. A typical current density in this operation would be  $10^{-1}$  A/cm<sup>2</sup>, and polishing is usually achieved on the removal of irregularities as small as  $10^{-2}$  µm. With both electroplating and electropolishing, the electrolyte is either in motion at low velocities or unstirred.

ECM is similar to electropolishing in that it also is an anodic dissolution process. But the rates of metal removal offered by the polishing process are considerably less than those needed in metal machining practice. To find how ECM meets these requirements and, moreover, how it is used to shape metals, we study first another type of electrolysis, namely, that arising from iron in aqueous sodium chloride (Fig. 1.2).

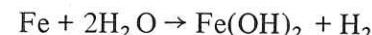
When a potential difference is applied across the electrodes, several possible reactions can occur at the anode and cathode. Certain reactions, however, are more likely to arise than others; this preference will be explained in Chapter 3 in terms of the *energy* that is available for each reaction. In the present example, the probable anodic reaction is dissolution of iron, e.g.



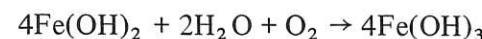
At the cathode, the reaction is likely to be the generation of hydrogen gas and the production of hydroxyl ions:



The outcome of these electrochemical reactions is that the metal ions combine with the hydroxyl ions to precipitate out as iron hydroxide, so that the net reaction is



(Note that the ferrous hydroxide may react further with water and oxygen to form ferric hydroxide:



although it is stressed that this reaction, too, does not form part of the electrolysis.)

With this metal-electrolyte combination, the electrolysis has involved the dissolution of iron from the anode, and the generation of hydrogen at the cathode, *no other action taking place at the electrodes*.

Certain observations relevant to ECM can be made at this stage:

- (i) Since the anode metal dissolves electrochemically, its rate of dissolution (or machining) depends only upon the atomic weight  $A$  and valency  $z$  of ions produced, the current  $I$  which is passed, and the time  $t$  for which the current passes. The dissolution rate is not influenced by the hardness or other characteristics of the metal;
- (ii) since only hydrogen gas is evolved at the cathode, the shape of that electrode remains unaltered during the electrolysis. This feature will be shown later to be most relevant in the use of ECM as a metal shaping process.

## 1.2 Development of the characteristics of ECM

These two aspects can be developed further by use of Equation (1.1). From that equation, and since  $m = v\rho_a$ , where  $v$  is the corresponding volume and  $\rho_a$  the density of the anode metal, the volumetric removal rate of anodic metal  $v$  is

$$v = \frac{AI}{zF\rho_a} \quad (1.2)$$

Suppose that a machining operation has to be carried out on an iron workpiece at a typical rate, say,  $0.026 \times 10^{-6} \text{ m}^3/\text{s}$ . For this removal rate to be achieved by ECM, the current in the cell must be about 700 A [on substitution in Equation (1.2) of the values  $A/zF = 29 \times 10^{-5} \text{ g/C}$  and  $\rho_a = 7.86 \text{ g/cm}^3$  for iron]. Currents used in ECM are of this magnitude, and indeed they are often higher, by as much as an order of magnitude. The corresponding average current densities are typically 50 to 150 A/cm<sup>2</sup>.

The means by which these high current densities are obtained can be understood from an examination of the other characteristics of an ECM cell, in particular, the electrolyte conductivity and the inter-electrode gap width. These parameters are related to the current through Ohm's law, which states that the current  $I$  flowing in a conductor is directly proportional to the applied voltage  $V$ :

$$V = IR \quad (1.3)$$

In the simple expression (1.3),  $R$  is the resistance of the conductor. The experiments on electrolysis, described above, demonstrate that electrolytes are also conductors of electricity. Ohm's law also applies

to this type of conductor, although the resistance of electrolytes may amount to hundreds of ohms.

Now, the resistance  $R$  of a uniform conductor is directly proportional to its length  $h$ , and inversely proportional to its cross-sectional area  $A$ . Thus

$$R = \frac{hp}{A} \quad (1.4)$$

where  $p$  is the constant of proportionality. If the conductor is a cube of side 10 mm, then  $R = p$ ;  $p$  is termed the *specific resistance* or *resistivity* of the conductor. The reciprocal of the specific resistance is the *specific conductivity*, often denoted by the symbol  $\kappa$ .

If Equations (1.3) and (1.4) are combined, the following relationships are derived between the average current density, current, surface area to be machined, applied potential difference, gap width, and electrolyte conductivity, these quantities being denoted by the respective symbols  $J$ ,  $I$ ,  $A$ ,  $V$ ,  $h$ , and  $\kappa_e$ :

$$J = \frac{I}{A} = \frac{\kappa_e V}{h} \quad (1.5)$$

It has been pointed out that in practice  $J$  is often about 50 A/cm<sup>2</sup>. To obtain a current density of this magnitude, a cell could be devised with high values for  $\kappa_e$  and  $V$  and low values for  $h$ . Even for strong electrolytes, however,  $\kappa_e$  is small. If the current is high, power requirements, amongst other considerations, restrict the use of high voltages, and, in practice, the voltage is usually about 10 to 20 V. If values of 0.2 ohm<sup>-1</sup> cm<sup>-1</sup> and 10 V are taken for  $\kappa_e$  and  $V$  respectively, then for  $J$  to be 50 A/cm<sup>2</sup> the gap  $h$  must be 0.4 mm. It will be shown later that a gap of this size is also necessary for accurate shaping of the anode. As dissolution of the anode proceeds, this gap is maintained by mechanical movement of one electrode, say the cathode, towards the other. To maintain the gap of 0.4 mm, a cathode feed-rate about 0.02 mm/s would be needed, the values given above for the other process variables being retained.

The accumulation within the small machining gap of the metallic and gaseous products of the electrolysis is undesirable. If the growth were left uncontrolled, eventually a short circuit would occur between the two electrodes. To avoid this crisis, the electrolyte is pumped through the inter-electrode gap so that the products of the electrolysis are carried away. The forced movement of the

electrolyte is essential also in diminishing the effects of electrical heating of the electrolyte, due to the passage of current, and of hydrogen gas, which respectively increase and decrease the effective conductivity. These matters will be discussed in greater detail later, but at this stage, the Joule heating effect provides a simple, convenient way of estimating a typical electrolyte velocity. Without forced agitation to control the increase in the electrolyte temperature, boiling will eventually occur in the gap. If all the heat caused by the passage of current remains in the electrolyte, the temperature increase  $\delta T$  in a length  $\delta x$  of gap is, from Joule's and Ohm's laws,

$$\delta T = \frac{J^2 \delta x}{\kappa_e \rho_e c_e U} \quad (1.6)$$

where  $U$  is the electrolyte velocity,  $\rho_e$  the electrolyte density, and  $c_e$  its specific heat.

If, for simplicity, the increase with temperature of the electrolyte conductivity is neglected, integration of Equation (1.6) yields

$$U = \frac{J^2 L}{\kappa_e \rho_e c_e \Delta T} \quad (1.7)$$

where  $L$  is the electrode length and  $\Delta T$  is the temperature difference of the electrolyte between points at inlet and outlet to the gap.

Consider the typical values,  $J = 50 \text{ A/cm}^2$ ,  $L = 10^2 \text{ mm}$ ,  $\kappa_e = 0.2 \text{ ohm}^{-1} \text{ cm}^{-1}$ ,  $\rho_e = 1.1 \text{ g/cm}^3$ ,  $c_e = 4.18 \text{ J g}^{-1} \text{ deg C}^{-1}$ . Suppose, too, that  $\Delta T$  must be kept to  $75^\circ\text{C}$  to avoid boiling at the exit point, the inlet temperature being, say,  $25^\circ\text{C}$ . From Equation (1.7), the velocity to maintain this condition is calculated to be about  $3.6 \text{ m/s}$ . Velocities of the electrolyte solution through the gap in ECM usually range from about 3 to  $30 \text{ m/s}$ . The pressures required to achieve these velocities will be calculated in the next chapter.

### 1.3 Basic working principles

ECM has been founded on the principles outlined in Sections 1.1 and 1.2. As shown in Fig. 1.3, the workpiece and tool are made the anode and cathode, respectively, of an electrolytic cell, and a potential difference, usually fixed at about  $10 \text{ V}$ , is applied across them. A suitable electrolyte (e.g. aqueous  $\text{NaCl}$  solution) is chosen so that the cathode shape remains unchanged during electrolysis. The electrolyte, whose conductivity is about  $0.2 \text{ ohm}^{-1} \text{ cm}^{-1}$ , is also

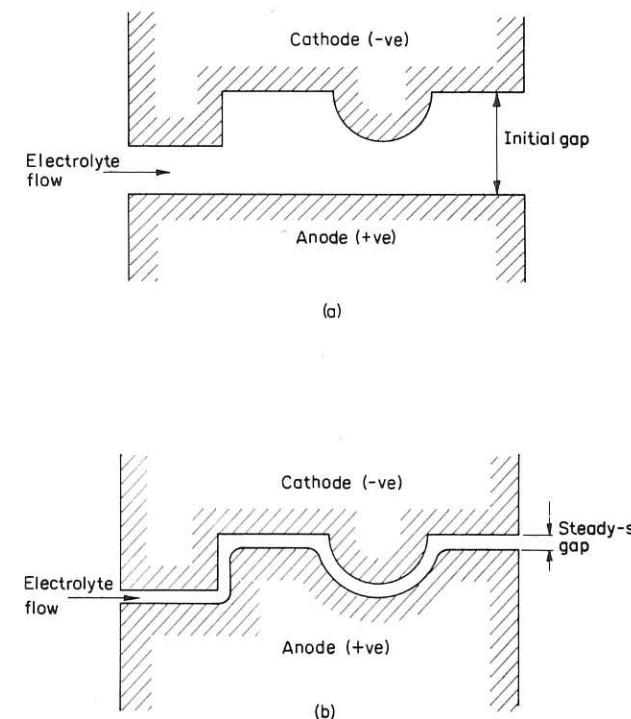


Fig. 1.3 (a) Initial electrode configuration for ECM. (b) Final electrode configuration for ECM

pumped at a rate, roughly 3 to  $30 \text{ m/s}$ , through the gap between the electrodes to remove the products of machining and to diminish unwanted effects, such as those that arise with cathodic gas generation and electrical heating. The rate at which metal is then removed from the anode is approximately in inverse proportion to the distance between the electrodes. As machining proceeds, and with the simultaneous movement of the cathode at a typical rate, say  $0.02 \text{ mm/s}$ , towards the anode, the gap width along the electrode length will gradually tend to a steady-state value. Under these conditions, a shape, roughly complementary to that of the cathode, will be reproduced on the anode. A typical gap width then should be about  $0.4 \text{ mm}$  and the average current density should be of the order of  $50$  to  $150 \text{ A/cm}^2$ . Moreover, if a complicated shape is to be formed on a workpiece of a hard material, the complementary shape can first be produced on a cathode of softer metal, and that

cathode can then be used to machine electrochemically the workpiece. In short, the main advantages of ECM are:

- (i) the rate of metal machining does not depend on the hardness of the metal;
- (ii) complicated shapes can be machined on hard metals;
- (iii) there is no tool wear.

### Bibliography

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## CHAPTER TWO

### **Basic Fluid Dynamics**

In the first chapter, the need for electrolyte flow in ECM was established. An understanding of the fluid dynamics involved in the process can be obtained from the analysis of five basic equations, which describe the likely patterns of the flow. In particular, these equations provide a guide to the significance of flow velocity profiles. From such studies the pressures can be estimated that are required to pump the electrolyte at specific rates down the gap between the two electrodes, and useful information can be obtained about the variation in electrolyte velocity across the gap.

In the treatment of such matters in this chapter emphasis is given to flow along rectangular channels and circular pipes since these flow channels are common in ECM. Nevertheless, the principles which are discussed are applicable also to other flow configurations, such as those arising with the rotating disc. The use of that type of configuration in both fluid dynamics and electrochemical (including ECM) studies is well known [1, 2].

#### 2.1 Basic assumptions and definitions

Investigations concerned with real, as distinct from perfect, fluid motion rely heavily on two assumptions. The first is that, wherever the fluid is in contact with a solid boundary, there is no motion or slip, relative to that boundary, of the fluid particles adjacent to it. In the second assumption, the shearing (i.e. tangential) stress between adjacent layers of fluid of infinitesimally small thickness is taken to be proportional to the rate of shear in the direction perpendicular