

Electrochemistry

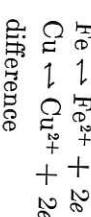
Electrochemical machining has been used predominantly in the gas turbine industry, where substantial savings in machining tough alloys offset the high tooling and facility investment and learning costs of the process. Research and development of the electrochemistry offers the most promising means of increasing ECM's manufacturing capabilities and reducing investment costs; thus leading to its general use in all metal working industries. One problem, for example, is the cost of masking areas of a component away from the intended machining zone, to prevent corrosion due to stray currents. Research led to the discovery that the problem is eliminated on ferrous alloys if sodium chlorate electrolyte is used. Electrolytes are needed which display similar properties in the machining of nickel alloys, titanium alloys, and so on. There is also tremendous need for improvements in process control, prediction of processing parameters, surface quality, accuracy, and machining rates. It is my hope that the following discussions may suggest useful lines of research for the advancement of electrochemical machining technology.

13.1 FUNDAMENTALS OF ELECTROCHEMISTRY

Before reviewing electrode polarization and passivation, which are significant in explaining ECM behavior and may hold the key to its technological advancement, it will be helpful to discuss some fundamentals of electrochemistry. This is concerned with the physical and chemical effects that occur when conducting *electrodes* are placed in conducting fluids, known as *electrolytes*. Unlike metallic conductors or conducting materials like graphite, in which passage of an electric current

comprises movement of electrons through the lattice structure of the material, the passage of electric current through an electrolyte is invariably accompanied by a movement of matter in addition to electrons. It is termed *electrolysis*. Electrolytes are molten salts or salt solutions. Neutral salts dissolved in water, such as sodium chloride, sodium nitrate, and so on, are used predominately in ECM, but acids such as sulphuric and hydrochloric or bases such as sodium hydroxide are used in specialized applications, (see Table 9.1). Electrical conduction through an electrolyte is possible because either all, or a large proportion, of its molecules split into negative and positive particles called ions, when in solution or in a molten state. It is perhaps more correct to use the concept that the negative ions, called *anions*, and positive ions, called *cations*, already exist as an electrically balanced stable array or lattice, when in crystal form. Dissolution in water, for example, breaks down the restraining forces so that the ions become free to move at random through the fluid; but the distribution of anions and cations remains uniform, so that the electrical potential at all points in the electrolyte is also uniform. Application of an electric field, however, will cause migration of one ion species with respect to the other. Since each ion carries a charge, this movement constitutes an electric current. Ultimately, ion concentrations will form to balance the electric field. If the field is established by applying a potential between two suitable conductors that are immersed in the electrolyte and joined by an external circuit, then the migration of ions will be continuous and current will flow in the external circuit.

It is the physical changes that occur at the electrodes, as electrons transfer between them and the electrolyte, that are of most interest to the electrochemist and, in the present context, are needed for the explanation and research of electrochemical machining phenomena. When an electrode is immersed in an electrolyte, atoms leave its surface to become ions, and ions are deposited as atoms in a continuous, balanced exchange. A potential called the *electrode potential*, then exists between a point just inside the surface of the electrode to a point just inside the electrolyte. Different electrode materials exhibit different electrode potentials. If two electrodes are placed in an electrolyte, for example, for ECM a copper tool and an iron work piece, then their difference in electrode potentials becomes the electromotive force of the cell so formed and may either assist or oppose the required flow of current.



difference

In the case of a copper electrode and iron work piece the emf is 0.749 V and will oppose the current in ECM, the copper tool being at a negative potential. This is the case with most electrode materials normally encountered in ECM work. The emf that must be applied between the electrodes to cause that current to just start to flow is the *decomposition voltage* of the cell; it will be negative or positive depending on the required direction of current flow. It is usually just larger than the difference in electrode potentials, provided that the electrodes are not polarized.

As current flows between the electrodes, several phenomena occur at the electrode surfaces that produce emf opposing the flow of current. They are termed the anode and cathode *overvoltages* and include activation polarization, concentration polarization, and ohmic overvoltage. They are illustrated in Figure 13.1.

When no current is flowing the electrochemical changes occurring at an electrode are in equilibrium; that is, ions discharge and atoms continually enter the electrolyte as ions. The electrode potential, between the electrode and electrolyte, acts as a barrier to a faster rate of reaction. To promote current flow, therefore, additional energy must be supplied so that ions discharge at the required rate. The effect is to cause an emf in opposition to the flow of current and is known as *activation polarization*; the potential required to overcome it is the *activation overvoltage*.

Concentration polarization also opposes the flow of current. Under the influence of the applied electric field, ions migrate towards the electrode surfaces and form concentrations. Each ion must pass through this concentration barrier to release its charge at the electrode surface, and newly formed ions have to pass through the concentration into the bulk of the electrolyte. The emf required for migration of ions through the concentration layer is the *concentration overvoltage*. It diminishes with electrolyte temperature, since the ion migration is aided by diffusion and thermal convection. The most beneficial agent in reducing concentration overvoltage, however, is electrolyte turbulence, since concentrations are rapidly dispersed away into the bulk of the electrolyte. In practically all ECM work high electrolyte flow velocities between electrodes are used; thus turbulent, rather than streamline, flow prevails.

Films of solid materials forming on the electrode surface offer further resistance to the passage of current. The potential loss is known as the *ohmic overvoltage*. Those films such as metal hydroxides, which tend to be deposited on ECM cathode tools, probably offer a labyrinth of electrolyte passages for the migration of ions and make the path more restrictive. Loose oxide films at the anode surface will offer a

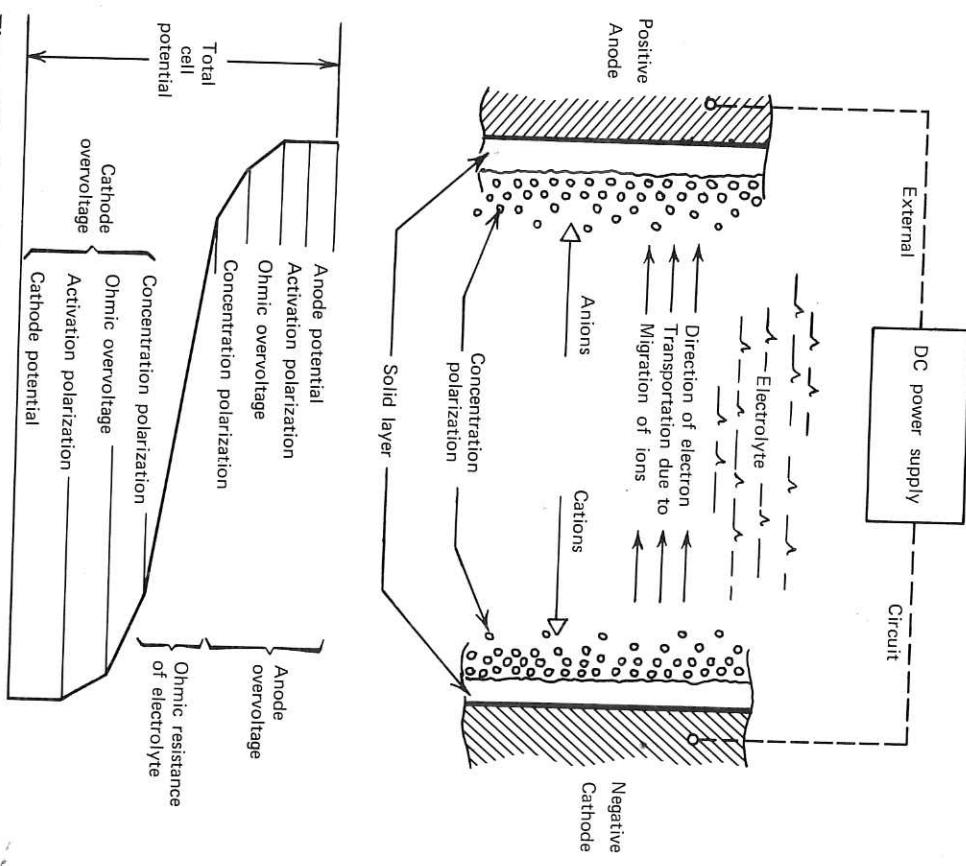


Figure 13.1 Potential profile in the machining gap.

similar resistance, but more dense tenacious oxide film will pass ions mainly by a slower process of diffusion. When an oxide film is such that it prevents ions reaching the anode surface, the electrode is said to be *passive*. The nature of anodic oxide films appears to vary widely with different electrode materials, electrolytes, and ECM processing parameters. It is the most significant factor in determining surface finish and accuracy of an electrochemically machined surface and will be discussed extensively later in this chapter.

Apart from the potential losses that occur at the electrode surfaces,

the ohmic potential loss occurs across the bulk of the electrolyte. This is the main voltage loss and is the only part of the circuit between the electrodes which appears to obey Ohm's law; that is, the potential loss increases uniformly with increasing current density. It is the single factor that makes ECM a stable, accurate, and predictable machining process. The machining process is self-stabilizing since, for a fixed rate of uniform movement of the cathode tool towards the anode work, the electrolyte gap will either increase or decrease so that the current density becomes just adequate to dissolve the anode at the same rate. For the same reason, because they are closer to the cathode, protrusions from the anode surface will be machined more rapidly. Calculations of tool shape to produce the required work geometry are also based on the assumption that the machining rate is inversely proportional to gap size, again in accordance with Ohm's law (see Chapter 7). This last assumption is substantially correct provided that the electrode overvoltages are either small or that they display only small variations in value with changing current density. In summary, the total cell voltage necessary to pass current between electrodes comprises the cathode electrode potential and overvoltage, the voltage drop due to the resistance of the electrolyte gap, and the anode potential and overvoltage.

13.2 ELECTROCHEMICAL REACTIONS

It is convenient to classify electrochemical reactions according to the three locations at which they occur: at the anode surface, at the cathode surface, and in the bulk of the electrolyte. The reactions vary depending on whether the electrolyte is acidic, neutral, or basic.

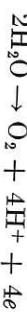
Anodic Reactions

As metal dissolves from the anode, electrons are left behind at a rate dependent on the metal valency. Thus for an iron anode:



This is the predominant reaction but may be accompanied, to a very limited extent, by the hydrolysis of water and liberation of cation electric charge.

In the hydrolysis of water oxygen is liberated and hydrogen ions are formed, so that there is a local increase in electrolyte acidity.



Although occurring at a higher potential, the liberation of the cation electric charge, rather than liberation of oxygen, appears to occur more readily in ECM.



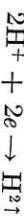
Both the foregoing reactions represent ECM process inefficiency, 5 to 10%, and in the latter the loss of cations depletes the strength of the electrolyte.

Cathode Reactions

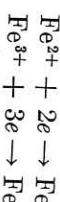
In neutral or basic electrolytes the main reaction at the cathode is electrolysis of water, causing liberation of hydrogen gas and local increased alkalinity because of the formation of hydroxyl ions.



Liberation of hydrogen, by neutralizing the charge on hydrogen ions, is the main reaction in acidic electrolytes.



Metal ions can also reach the cathode, particularly in acidic electrolytes, and be deposited there.

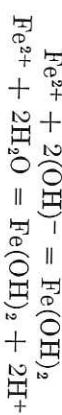


The deposit tends to adhere loosely and forms slowly if the electrolyte is weak in metal ions. That is why acid electrolytes used in ECM are frequently replenished, or a system, which periodically reverses the direction of the electrolyzing current, is used to deplate the deposits that accumulate on the cathode. Even in neutral electrolytes, where metal ions form insoluble hydroxides and are, therefore, not available in the vicinity of the cathode, a cathode deposit of about 0.001-in. thickness does form during electrochemical machining. The effect is probably due to electrophoresis, in which suspended particles of metal hydroxides become positively charged, migrate to the cathode, and tend to be deposited there. By the same principle other particles in the electrolyte will tend to migrate to one or other of the electrodes. Small air bubbles, for exam-

ple, will migrate toward the anode, an effect which may explain the tendency of titanium anodes to pacify with oxide films when machined using slightly airated electrolyte.

Reactions Within the Electrolyte

In neutral or basic electrolytes, metal ions leaving the anode surface progress outwards into the bulk of the electrolyte, where they combine either with hydroxle ions or water molecules to form the metal hydroxide that is usually insoluble.



The immediate significance of these reactions is that the metal hydroxide precipitates can no longer play a significant roll in the electrochemical reactions, so that plating out at the cathode, which is very undesirable, is avoided. Also, the precipitates can readily be removed from the electrolyte by centrifugal separation or gravitational settling so that the electrolyte basically remains unchanged by the process. A very interesting phenomena, however, is the increase in hydrogen ions, and therefore acidity, in the area of the anode, particularly with neutral electrolytes. Acidity of pH 3-4 may be expected with an iron anode, since the ferrous and ferric ion remains in solution in more acid conditions. As acidity increases, the anions move further out into the electrolyte before forming the hydroxide. The local anode acidity increases with current density since more anions are then entering the electrolyte; but decreases with increased electrolyte flow and turbulence, since the hydrogen ions are then more readily dispersed. Thus the level of acidity may vary considerably at different locations on an anodic workpiece and may in turn affect the nature of oxide films and so influence machining rate and the nature of the machined surface.

13.3 TRANSFER OF MATTER

In the various electrochemical processes such as electroplating, electro-polishing, electroforming, and, of course, ECM, metals are deposited or dissolved at the electrodes, gases liberated, and so on. One would expect the quantity relationships of their products of electrolysis to involve temperature, type of solvent, concentration of electrolyte, and other factors. In fact, they are independent of these variables. The actual relationships are stated in Faraday's famous laws of electrolysis.

1. The amount of chemical change produced by an electric current, that is, the amount of any substance deposited or dissolved, is proportional to the quantity of electricity passed.
2. The amounts of different substances deposited or dissolved by the same quantity of electricity are proportional to their chemical equivalent weights.

The amount of a substance liberated by 1 A in 1 sec, a coulomb, is its *electrochemical equivalent* and is, according to Faraday's second law, proportional to its chemical equivalent weight. The proportionality constant $F = 96,500 \text{ C}$, or a faraday, is the quantity of electricity required to liberate the chemical equivalent weight, in grams, of a single element or molecule.

Iron, for example, has an atomic weight of 55.84; assuming that it exhibits a valence of 2 for the electrochemical reaction (that is, two electrons are given up to the anode as a single atom of iron enters the electrolyte), its chemical gram equivalent weight will be $55.84/2 = 27.92 \text{ g}$. Thus $96,500 \text{ C}$ remove 27.92 g of iron.

A 10,000-A EC machine will remove $(27.92 \times 10,000 \times 60)/96,500 = 174 \text{ g/min} = 22.1 \text{ cm}^3/\text{min}$ or $1.35 \text{ in.}^3/\text{min}$. Iron could also show a valence of 3 in the electrochemical reaction in which case the theoretical metal removal would be $0.90 \text{ in.}^2/\text{min}$. Many elements display a number of different valencies, but the valencies occurring during electrochemical machining are mostly unknown. Also, alloys, rather than pure metals, are more frequently machined and so it is difficult to precisely predict metal removal rates. Values for pure elements are given in Table 13.1.

If valencies of the alloying elements of a material are assumed, then a theoretical machining rate may be calculated. Let the alloying elements 1, 2, and so on have atomic weights A_1, A_2, \dots, A_n , valencies Z_1, Z_2, \dots, Z_n , and percentage composition x_1, x_2, \dots, x_n . Then (since 1 F removes $A/Z \text{ g}$, the electrochemical equivalent), 1 g of material will be removed from the anode by

$$\frac{F}{A_1} \left\{ \frac{x_1 Z_1}{A_1} + \frac{x_2 Z_2}{A_2} + \dots + \frac{x_n Z_n}{A_n} \right\} \text{ C}$$

and the machining rate:

$$\frac{\text{mass}}{\text{time}} = \frac{I}{F} \left(\frac{x_1 Z_1}{A_1} + \frac{x_2 Z_2}{A_2} + \dots + \frac{x_n Z_n}{A_n} \right)^{-1} \text{ g/sec}$$

where I = machining current and $F = 96,500 \text{ C}$.

Table 13.1 Theoretical Metal Removal Rates

Example

A nickel alloy has the following composition:

Element	Atomic weight	Valencies	Metal removal rate in. ³ /(min./10,000 Å)						
				C	Cr	Ni	Mo	W	Fe
Aluminum	26.97	3	1.26						
Antimony	121.76	5	1.46						
Beryllium	9.013	2	2.48						
Cadmium	112.4	2	0.62						
Chromium	52.01	6	2.45						
Cobalt	58.94	2	0.92						
Copper	63.57	2	1.37						
Germanium	72.60	4	2.57						
Gold	197.2	2	1.29						
Iron	55.84	2	1.93						
Lead	207.2	3	0.90						
Magnesium	24.32	2	3.46						
Manganese	54.93	2	2.65						
Molybdenum	95.95	3	1.39						
Nickel	58.69	4	0.70						
Platinum	195.23	2	0.47						
Silicon	28.06	4	0.90						
Silver	107.88	1	1.14						
Tin	118.7	4	3.90						
Titanium	47.90	2	1.54						
Tungsten	183.92	3	3.08						
Uranium	238.07	4	1.34						
Vanadium	50.95	6	1.01						
Zinc	65.38	5	0.64						

It has to be assumed that carbon, since it does not anodically dissolve, will leave the anode mechanically and so need not be included in the calculation.

$$\text{removal rate} = \left[96,500 \left(\frac{0.155 \times 2}{52.01} + \frac{0.594 \times 2}{58.69} + \frac{0.16 \times 3}{95.95} + \frac{0.04 \times 6}{183.92} + \frac{0.05 \times 2}{55.84} \right) \right]^{-1}$$

$$= 3.02 \times 10^{-4} \text{ g/C}$$

The density of this alloy is 8.91 g/cm³. Thus using 10,000 Å the metal removal rate will be

$$\frac{3.02 \times 10^{-4} \times 10,000 \times 60}{8.91 \times 16.4} = 1.24 \text{ in.}^3/\text{min}$$

Until more information is available on the valencies displayed by elements during electrochemical dissolution, theoretical values of machining rate can only be considered as a rough guide. Similarly process efficiency would be expressed as:

$$\frac{\text{actual metal removal rate}}{\text{theoretical metal removal rate}}$$

which is rather meaningless. A process efficiency of 85 to 95% is probable, based on the limited information currently available. Inefficiency, in terms of metal removal, is due to liberation of gas at the anode, such as chlorine when using sodium chloride electrolyte. There is sometimes a gain in efficiency when particles of material, either grains which are machined much slower than surrounding metal or nonmetallic inclusions, mechanically become detached rather than dissolved from the anode.

13.4 PASSIVITY

Passivity is generally considered as a special condition of anode polarization that results in either a substantial reduction in current or an increase in valency of anodic dissolution. Although, in dealing with ECM, passivity must be considered additionally as any condition of polarization that limits anodic dissolution such that the moving cathode closes on to the anode. Concentration polarization can produce this condition if there is an inadequate velocity of electrolyte flow. It has been shown, for example, that in a "stirred" 1-N solution of hydrochloric acid, at 20°C, anodic dissolution of nickel is limited to 16.38 A/in.². The rate of machining is determined by the ion diffusion through the polarized layer. In practice current densities of 3000 A/in.² are readily attained in ECM. The high turbulence, created by forced circulation of the electrolyte, brings anions to the surface and washes away cations so that concentration polarization is small and no longer limiting. Poor flow in an ECM operation will tend to produce passivity; as closure of the electrode gap occurs, the metal hydroxides and gasses, resulting from the electrode reactions, displace electrolyte so that current flow is further impeded. Ultimately, closure of the gap will fail to produce dissolution at the anode commensurate with the rate of cathode advance. In this unstable condition the electrodes will touch with resultant process failure.

Passivity is more often associated with anodic solid films, mainly metal oxides. Special processing conditions change the anodic film so that it prevents or limits the passage of current. Increased anode potential may permit other reactions to take place, for example, renewed anodic dissolution, but at a higher valency. Oxidizing conditions tend to promote passivity, and reducing conditions develop activity. It is important to note that passivity can occur at high electrolyte flow velocities in ECM. The thickness of the oxide film may be dependent on the availability of oxidants. Increased electrolyte flow will supply more oxidizing ions, dissolved oxygen, and air bubbles to the surface, and so promote passivity. Alternatively, concentration of hydrogen ions can modify, either chemically or mechanically, the oxide film so that it readily passes the electrolyzing current. High flow velocities, by removing this agency, can induce passivity. In machining titanium components, passivity has occurred at points on the cathode tool corresponding to the highest flow velocities. The condition has then been overcome by screening entrapped air out of the electrolyte system. Presumably, air circulating with the electrolyte was the main source of oxygen. The surface of titanium alloys are normally in an oxidized condition because

of chemical action; in initiating machining a high cell voltage is required to break down the anode film. Even then, only local asperities on the surface start to machine at first, aided by a concentration of the electric field at these locations. The machining action slowly spreads from these points until the entire anode surface is active. If more asperities are created on the surface, for example, by grit blasting, then the anode surface becomes completely active in a shorter time. During machining the cell voltage may be reduced from 15 to 5 V without promoting passivity. A few seconds pause in the passage of current, however, immediately causes the return of the passive condition. This behavior supports the theory of the important role of the hydrogen ion in the anodic process.

13.5 CURRENT POTENTIAL CURVES

Since dissolution of the anode is of most interest in electrochemical machining, most of the remaining discussion in this chapter is concerned with phenomena that occur near the anode surface. In considering the effects of potential, therefore, it is more significant to use the potential between a point just inside the anode to a point just inside the bulk of the electrolyte. This will correspond to the discharge potential as current just starts to flow but will then increase because of anode overvoltage. It is known as the *anode potential*. Experimentally, it is usually measured by placing the end of a glass tube, that has been drawn down to a small capillary, close to the anode surface. The anode potential is then measured between the end of the tube and the anode. The current potential curve is a plot of anode current density against anode potential. The typical forms that this curve may take are shown in Figure 13.2a.

Theoretically flow of current should not occur until the discharge potential is reached, but, in practice, the presence of impurities in the anode material promotes some current flow at much lower potentials. A pure metal electrode should display a sharp rise in the curve as its discharge potential is reached, while with alloyed metals the change in slope of the curve should be more gradual, since the possible anode reactions will increase with anode potential, as the discharge potentials of different ion species are reached. As the anode potential increases, the current will increase within the limitations imposed by the back emfs because of activation, ohmic, and concentration polarizations. Provided that the polarization effects change quantitatively, but not in their characteristic behavior, then the anode potential curve will be similar to curve 1, in Figure 13.2a.

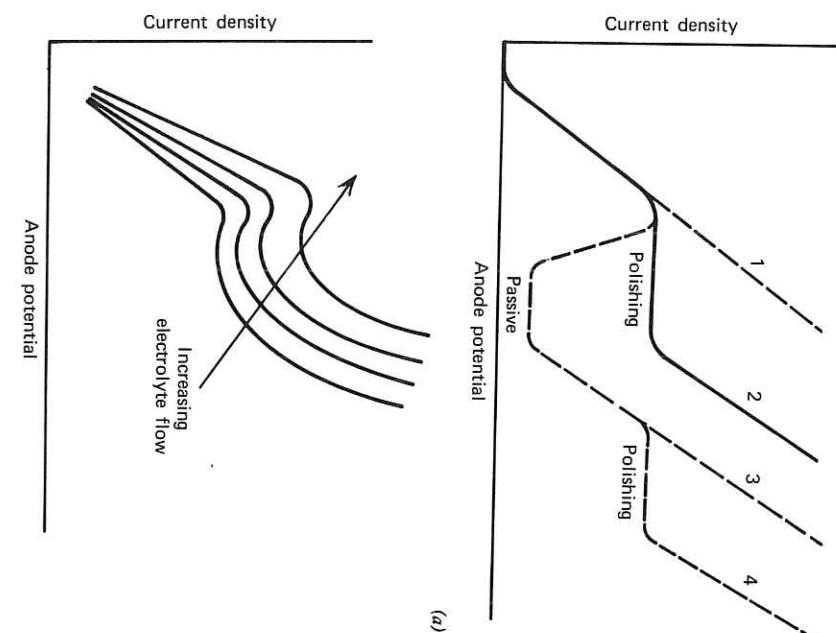


Figure 13.2 (a) Low current density part of a current potential curve. (b) The effect of electrolyte flow velocity on the current potential curve.

controlling factor. The anodic film, usually an oxide, then has a physical structure that permits passage of anions to the anode surface only by diffusion. The rate of diffusion is limiting, so that current density remains constant despite increasing anode potential. The anode film tends to be thick over microrecesses, but thin over microasperities, with corresponding reductions and increases in diffusion rates, respectively. The effect is to produce a smooth, polished anode surface. Further increase in anode potential produces evolution of oxygen, and this causes discontinuities in the film. At first, localized rapid dissolution at these discontinuities causes pits in the anode surface, but as the anode potential is further increased, dissolution becomes uniform, and a smooth, but not polished, surface is produced.

It is also possible for the anode film to be tenacious, continuous, and impervious to the diffusion of anions, so that no or very little current flows. This *passive* condition may occur by itself, as shown in curve 3, or together with the polishing plateau, as shown in curve 4, Figure 13.2a.

The current potential curve has been a basic experimental tool in electrochemistry and has contributed much to the development of electroplating, electropolishing, and similar electrolytic processes. It should be pointed out, however, that the classic polishing plateau and similar features of these curves, which have received close attention, all occur at very low current densities of a few amperes per square inch. Naturally, as such a familiar tool of electrochemistry, it is not surprising that researchers have used it as a base to start their investigations into ECM. This process operates at current densities of 50 to 5000 A/in.², and so there is little reason or experimental evidence that the low amperage region of current-potential curves is significant in the study of high current electrochemical machining conditions. The little work that has been done at higher amperage, and significant phenomena observed in the application of ECM, do indicate, however, that the high current range of the current potential curve could be of considerable significance. Since it has been suggested that the curve changes with different electrolyte flow rate, one would expect characteristic features of the curve to shift to lower values of anode potential in response to increased electrolyte flow. This is illustrated in Figure 13.2b.

The explanation of this effect is that loose or poorly adherent particles of the anode ohmic layer and concentrations of ions are more readily dispersed into the bulk of the electrolyte at the higher and therefore more turbulent, flow conditions. Thus at a particular current density, since the polarization effects are reduced, the anode potential will also

become smaller. Similarly, since polishing plateaus and so on are associated with the degree of polarization, these features of the curve will shift to higher values of current density.

It should not be assumed that a current potential curve, after displaying its polishing plateau or other characteristic features at a few amperes per square inch, will sweep smoothly upwards into the high current density regions. On the contrary, it is likely that there will be many sudden changes in gradient, plateaus, and so on as a result of different polarization mechanisms occurring. The full curve may still be expected to shift with flow velocity. Such a hypothetical curve is shown in Figure 13.3a.

These theories appear to be supported by phenomena observed during the practical application of ECM. A machined surface will sometimes display, in a localized area, corrugations that lie in the direction of electrolyte flow. They are usually termed *flow lines*. This is not a misnomer, but it is incorrect, except in very pronounced cases, to try to smooth the flow distribution over the tool to overcome the condition. It is naive to believe that it is practical to obtain absolutely uniform electrolyte flow velocities over a complexly contoured ECM tool. The corrugations are produced because the anodic polarization effects change rapidly with small changes in flow velocity. This can occur at a feature, such as a polishing plateau, as shown in Figure 13.3b. The point *B* will correspond to a polishing condition at the lower flow velocity. Since it is at a higher anode potential, it will produce a ridge on the anode along a low velocity flow line. Slight increase in flow shifts the curve so that although at the same current density, point *A* is a normal machining rather than a polishing condition. It displays a much lower anode potential and will correspond to a valley along the slightly higher velocity flow line across the anode. There are two corrective actions which overcome the corrugation or flow line problem. If the machining current is lowered, usually 10 to 20% in practice, point *B* moves to *D* and *A* to *C*. The anode potential difference for the same flow variation is now very small and corrugation effects on the machined surface becomes insignificant. Alternatively the flow velocity in the machining gap may be significantly increased. There are still likely to be flow variations but the higher velocity condition *A* moves to *A'* and *B* moves to *B'*, since the curves shift with increasing flow. Again the differences in anode potential are small, so there will be insignificant effect on the geometry of the machined surface.

There are many other surface defects such as bright spots and ripples that may appear under certain conditions of anode material, electrolyte composition, current density, and so on. Their spasmodic appearance

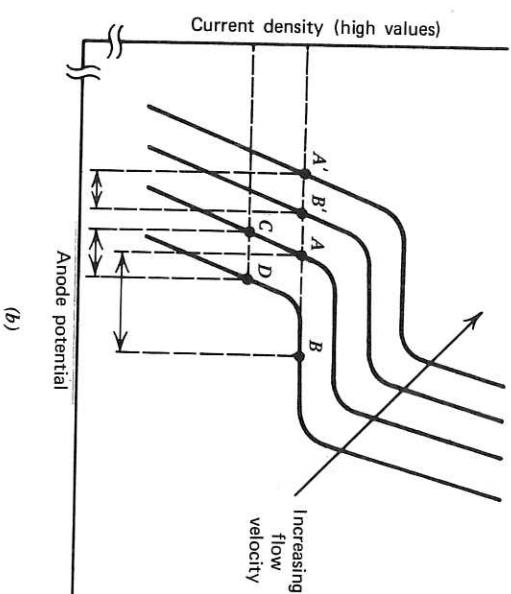
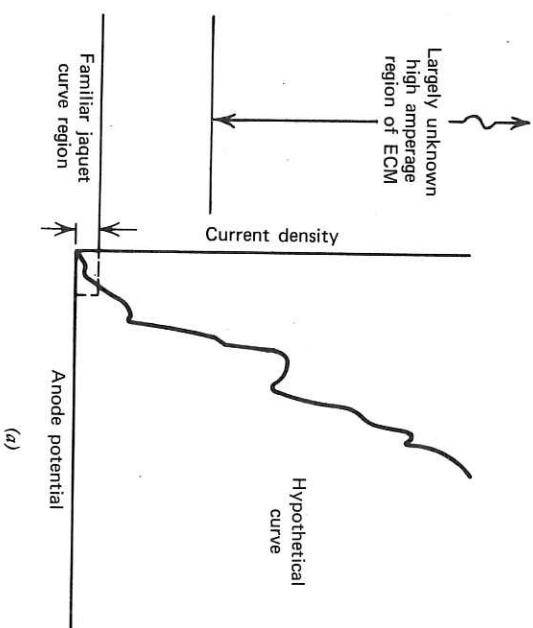


Figure 13.3 (a) A hypothetical current potential curve extending into high values of current density. (b) Anode potential changes with flow velocity and current density.

indicates that the machining conditions are close to a transition point on the current potential curve; in practice these defects disappear if significant changes are made in either machining current or electrolyte flow rate.

There is evidence that under certain conditions, instead of the anode potential decreasing with increasing electrolyte flow velocity, the converse is true. It would appear that some agency, which changes the degree of polarization, is removed more readily by the increased flow.

As discussed in Section 13.2, on electrochemical reactions, this agency is probably the hydrogen ion concentrations of which are indicated by observations of increased acidity adjacent to the anode surface. The acidity either changes the composition of the anodic film or alters its mechanical adherence.

For example, in the electrolytic dissolution of a zinc anode, dissolution occurs without formation of an anode solid film at pH values less than 8, but at values of 8 to 12, a nickel hydroxide film, $\text{Zn}(\text{OH})_2$, passivates the anode, and at higher values of pH a zinc oxide film, ZnO_2 , again permits dissolution. Relationships have also been established experimentally between anion concentration, anode potential, and the type of polarization phenomena occurring at the anode surface. In neutral and basic electrolytes the hydrogen ion concentration will be closely related to the anion concentration.

It has been speculated that by development of specialized electrolytes, possibly employed with potentiostatic methods of controlling anode potential, the conditions of the current potential curve polishing plateau may be duplicated during ECM processing. The prime interest in obtaining such a condition is that highly polished surfaces would then be produced. There is, however, a fundamental objection to this approach. Polishing, as already described, results from an essentially diffusion controlled migration of anions through the anodic film. Variation in potential does not then alter the rate of current flow and, therefore, the rate of anodic dissolution. The accurate machining action of ECM, however, is dependent on high potentials producing fast dissolution and low potentials slow dissolution. That is, at points of close proximity of the cathode and anode, machining will be fast, and, conversely, where electrodes are remotely spaced, machining will be minimal. The concept of a diffusion-controlled anodic dissolution is, therefore, not practical for precise metal removal by ECM. There are two possible exceptions. First, if a uniform layer is to be machined from an anode, then the uniformity of dissolution rate over the entire surface of the anode, as imposed by a diffusion controlled process, would be quite practical, for example, as may be required to enlarge the bore of a shaft. Second, the system

may be used just to brighten the anode surface, after the bulk of material has been removed by normal ECM processing. In this way the benefits of a highly polished machined surface could be realized without significantly reducing its dimensional accuracy.

13.6 THROWING POWER

In developing a formula for the prediction of cathode geometry to produce a contoured anode shape (Chapter 7), several assumptions were made. The most significant of these, from an electrochemistry point of view, was that anode dissolution (machining rate) was inversely proportional to the gap spacing between the electrodes. The assumption is valid for a limited range of gap variation, within the normal range of engineering dimensional tolerance. In predicting very close tolerances or if considering substantial variations in gap spacing, however, the assumption is not valid. In practice electrode overvoltages vary with current density, so that the voltage available to force current across the electrolyte film, which is substantially of linear resistance, is variable rather than constant. The condition of constant overvoltages would be needed for the principle, *machining rate inversely proportional to gap*, to apply strictly. By the concept of throwing power, electrolytes are compared as to their ability to machine areas of the anode remote from the cathode. The faster the metal removal at a remote area, compared to a near area of the anode, then the higher is the throwing power. In electroplating or electropolishing, high throwing power is desirable, since a uniform plated film or uniform degree of polishing are sought, despite complex component geometry. The required effect is produced by using electrolytes that promote concentration polarization. Thus the higher the current the greater will be the opposing back emf due to polarization. The reverse effect of low throwing power is most desirable for ECM. There are two aspects of the process in which this can be of significant improvement; first, in reducing the volume of metal removal to obtain a required anode geometry, and second, in confining anodic dissolution to areas of intended tool operation. At the start of machining the anode shape often has little resemblance to the cathode shape, particularly if a three-dimensional surface is to be produced. Hence there are points of close electrode proximity where dissolution is rapid and areas of remote spacing where dissolution occurs but at a much slower rate. The necessary depth of anode dissolution to achieve a stable, overall electrode gap geometry, within a dimensional tolerance commensurate with that required for the finally machined anode, will be dependent on the rate

of machining in these remote areas. An electrolyte displaying low throwing power will reduce the current falling in these remote areas, and so permit substantial anode to cathode conformity with less dissolution of the anode. The ideal condition would be that of complete anode passivity in remote areas, so that current flow would occur only at close electrode proximity.

An electrochemical machining operation may be one in a series of other manufacturing processes required for the completion of a component. During machining, current not only flows to anodic surfaces in advance of the cathode to achieve the intended dissolution, but also strays onto adjacent surfaces. These may be in a finished condition, so that the *wild cutting* or *stray machining* as it is often termed degrades both dimensional and finish qualities of these surfaces. Currently available corrective measures have been described in Chapter 7 and comprise either masking and similar tooling techniques, or a rearrangement of the overall component processing so that metal removal by conventional methods is performed after ECM. Both approaches are inconvenient and costly; they do not always provide a complete correction for wild cutting. The effect is not limited to the component; it eventually destroys anodic fixturing parts. Again, a low throwing power electrolyte will minimize these effects, and a passivating condition, occurring at areas remote from the cathode, will eliminate them.

Considerable interest in throwing power has resulted from the discovery that sodium chlorate electrolyte can be used to machine ferrous materials with practically no wild cutting. Good machining at high current density areas has been demonstrated, while anode surfaces more than 0.050 in. from the cathode have, under certain experimental conditions, shown no dissolution. The electrolyte has been used in accurately enlarging bores and reducing rod diameters using stationary electrodes. Other confirmatory laboratory evaluations have also used stationary electrodes, however, and so the very good results obtained are not necessarily fully applicable to moving electrodes. Increased accuracy can be expected because of the confinement of dissolution to anode areas close to the cathode, and substantial anode to cathode conformity will occur earlier during machining; but the accuracy of the finished anodic area, in the direct path of cathode movement, may not be improved.

The presence of oxide films on surfaces remote from the cathode when sodium chlorate is used, but absent when sodium chloride is used, indicates that passivity in these areas is a condition for low throwing power. This is further substantiated by the very much lower throwing power exhibited by sodium chloride, when known passivators, benzotriazole (BTZ), or potassium dichromate, are added to the solution. The additives

do not, however, appear to affect the dissolution characteristics in high current areas. Many references have been made to an apparent improvement in machining performance as electrolytes age with use. This may be due to chromium ions entering the electrolyte, so that a low throwing power results, since many alloys contain this element. There has been no precise explanation for the low throwing power of sodium chlorate, but it is probable that as potential gradients decrease with increasing electrode spacing, a limiting value of anode potential is reached below which passivity will occur. In the higher potential areas the high currents may be self-sustaining, in that the resultant increases in acidity and temperature at the anode surface may inhibit anodic passivity.

The importance of this aspect of electrolytes cannot be overemphasized; it is hoped that electrochemists will continue their research of low throwing power electrolytes, especially for use with iron, nickel, and titanium alloys.

13.7 SURFACE FINISH

There appear to be two electrochemical phenomena that, either separately or together, determine surface finishes produced by ECM, using various anode material and electrolyte combinations. In one, variations in the etching characteristics of different phases of the alloy crystalline structure determine the surface texture. In the other, sporadic breakdown of the anodic film permitting intermittent machining at localized sites is the controlling factor. In either case, increased potential gradient across the electrolyte film improves surface finish as does increased current density.

Since the entire anode surface uniformly advances before the approaching cathode, individual sites of different metallurgical structure, because of their different etching characteristics, will vary in their distances from the cathode surface. Thus an individual grain that readily etches will be recessed into the anode surface, while the material at a grain boundary, less readily etched, will protrude from the surface and thus be exposed to the potential necessary for it to achieve the dissolution rate common to the overall anode surface. A fine grained structure will tend to produce a smooth surface, a large grained structure a rougher surface, and so on. The greater the variation in etching characteristics of the phases within the structure of an alloy, the less refined will be the surface texture. A single phase material, or better still a single crystal component, will produce the best finishes.

Other conditions being constant, the potential gradient close to the

anode surface will control surface texture. The higher the potential gradient the better will be the finish; since phases of the material, with poor etching characteristics, will then need to project less from the anode surface to experience the potential needed to maintain their dissolution rate at the common level. If the peaks of the surface texture are contained within the anodic layer (estimated to be about 0.0001 in. for ECM), then the potential gradient across this layer will be the main factor determining finish. Current density is the process variable that substantially controls potential gradient within the anodic layer. Hence improvement of a "fair" surface finish is best achieved by increasing current density. If peaks of the surface texture protrude beyond the anode layer, then the potential gradient across the bulk of the electrolyte will be the main factor controlling surface finish. Improved finish will be obtained, therefore, by either increasing current density (with reduced gap or increased voltage and increased cathode feed) or reduced electrolyte conductively and increased voltage. Areas remote from the cathode are likely to show improvement only if the latter course is taken.

The methods that might be used to improve the dissolution in these remote areas, are worth exploring further since there appears to be little difficulty in obtaining quality finishes on anode surfaces machined at high current density.

A hypothetical curve of potential gradients occurring at points close to the anode surface, which may be expected for an anode having a select area machined by a moving cathode, is shown in Figure 13.4. The gradient will be at its highest value under the cathode and diminish as surfaces are more remote. The different etching characteristics of the phases comprising the metallographic structure of the anode, will

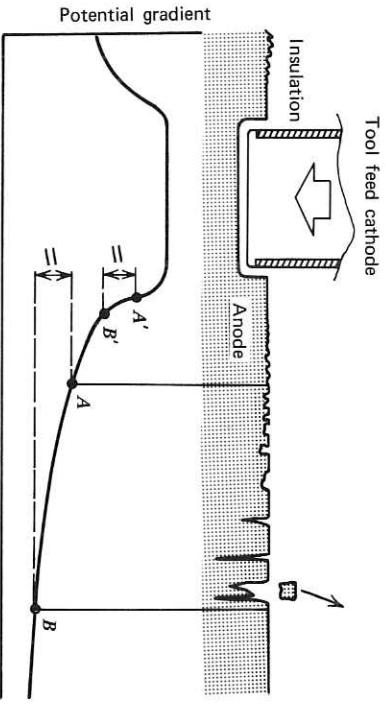


Figure 13.4 Surface finish profile over the area of cathode influence.

cause a degrading of surface texture as the potential gradient falls. At some point, A, the available potential will fall below the dissociation potential of one phase so that it no longer dissolves and remains as small plateaus on the surface. Successive phases will stop machining as the distance increases. Remaining phases, occupying a small proportion of the anode surface, are subject to field concentration of the stray current and so rapidly dissolve, forming deep pits or crevices. In the latter case particles may become completely detached from the anode. At the point B, the potential falls below the dissociation potential of the remaining active phase, so that at greater distances from the cathode no dissolution of the anode takes place. If the cathode remains stationary then the different surface etching conditions and their lines of demarcation will be seen clearly on the anode surface. In the case of a moving cathode, having all but operative surfaces insulated, the three characteristic bands of surface texture will travel across the anode surface following the cathode movement. In this way the most destructive process occurring between A and B will be spread over a larger surface. Initially the extent of surface damage is time limited so that with rapid cathode movement some improvement in surface texture may be evident.

Two possible ways of modifying the electrolyte to reduce the selective etching problem (in the region between A and B) are presented. The width of the selective etching band determines the time a section of the anode surface will be exposed to this adverse machining condition during an ECM operation. If it is wide, then the surface pits and crevices will be deep; but if narrow, the short time exposure, as the condition sweeps across the surface, may limit the depth of the defects to acceptable values. The etching band will be narrower if the spread of dissociation potentials for the different phases is reduced. Thus if one phase prominently projects from the surface, then a more active electrolyte or an additive may make this phase dissolve more readily. Similarly, an oxidizing electrolyte might prevent dissolution occurring too rapidly at a grain boundary.

Alternatively, an electrolyte that produces a high overvoltage due to polarization will increase the potential gradients needed for the various material phases to enter solution. The selective etching band is displaced into a higher potential gradient area that is nearer the cathode. In Figure 13.4 the band A, B, will shift to A', B'. It will be very narrow, since the rate of change of potential gradient is rapid in this region; the degrading effects on the surface will reduce correspondingly.

The presence of an oxide film on the surface of a material can be predominant in determining the surface finish produced by machining. It is usually beneficial, since, as it is highly resistive, it tends to control

uniformly the electrolyzing current passing to the anode surface. To do this, however, the film itself must have uniform properties such as thickness, composition, anode adherence, and so on. In machining some alloys, it is difficult to select an electrolyte that promotes the formation of a stable anode film. Titanium alloys, for example, exhibit very unstable oxide films. Local variations in anode potential have been observed during machining, which appears to proceed sporadically at localized sites on the surface. There are few sites in low current density areas, and these become saucer-shaped pits, while adjacent areas of the anode surface remain unmachined. At higher current densities the sites are more numerous and merge to form a totally machined surface. Concentrations of the hydrogen ion at the anode surface appears to play an important role in modifying the tenacity of the oxide film. As the electrolyzing current is initiated, machining is confined to a few favorable locations, such as sharp protrusions, edges, or stressed areas of the anode surface. The generation of hydrogen ions causes breakdown of the oxide film and so promotes continued electrolytic action at these local sites. Factors, which either increase the number of active machining sites or increase hydrogen ion concentration, will improve surface finish. Grit blasting a surface prior to machining increases the number of active sites at the start of machining and is very beneficial to the quality of surfaces subject to stray current. Higher current density and higher potential gradient, which promote greater hydrogen ion generation and more active sites respectively, improve surface finish. Acidic electrolytes are likely to promote a more stable machining condition and therefore better surface finish, since the anodic dissolution is then less dependent on process generated hydrogen ions.

13.8 RATE OF MACHINING

Is there a fundamental factor that will limit the penetration rate of electrochemical machining? There have been several theories used to predict limiting rates, but these rates have now been exceeded. One theory, for example, proposes that there are a finite number of sites on the cathode surface at which the cathode reaction can proceed, the limiting electrolyzing current occurring when all available sites are active. In practice the limiting machining rates, projected from this theory, lie in the middle of rates currently used in industrial applications of the process. Rates an order higher than these (1 to 5 in./min) have been recorded under special laboratory conditions. Researchers in this field currently think that there is no foreseeable limit to the penetration

rates obtainable, apart from engineering difficulty. It is interesting to explore, however, the engineering and process changes that may be necessary to extend machining rates past their present superficial limitations.

Increased anodic dissolution must be accompanied by a proportionate increase in current flow. Higher electrolyte conductivity, using molten salts, for example, or smaller machining gaps, will offer less resistance to the electrolyzing current and so improve machining rates. Change in cell voltage offers more, however, since presumably it may be increased until the dielectric strength of the electrolyte film is reached. As the electrolyzing current becomes larger, more heat will be dissipated in the electrolyte; machining products, particularly hydrogen, will build up; and polarization will grow proportionately. Any of these effects may stop the machining process. Higher velocity electrolyte flow, however, will remove heat and gasses faster, and because of greater turbulence, it will disperse polarizing concentrations of ions into the bulk of the electrolyte. Additionally, pressurization will suppress vaporization of the electrolyte and compress gas bubbles so that they offer less interference to the passage of the current.

Diffusion of ions through the solid anode layer may tend to limit the electrolyzing current. Such films, however, tend to break down with higher potentials. There may be some advantage in superimposing a high spiked voltage waveform over the normal cell voltage to break down the anode layer, without appreciably altering the mean cell voltage. Following the same reasoning, laser and ultrasonic vibration energies have been focused on the anode. The laser appears to be ineffective because of diffusion of the light by the electrolyte. Ultrasonic vibration will dislodge loose oxide films with a marginal increase in machining rate, but otherwise is also ineffective.

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Appendix