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REVIEW

Electrochemical machining

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To the end of 1974 the scientific literature contained over 1200 articles on electrochemical machining (ECM) [1]. Additionally approximately 100 papers appeared in 1975. Although a large number of those references appeared in what might be described as 'non-learned' journals, this still leaves the potential student with a difficult task if he wishes to review the state of the art. This is the first attempt to review thoroughly the literature in this field, although only a small proportion of those contributions are considered pertinent. The review will take the following form: after an introductory chapter there will be two chapters on dissolution kinetics, the second concerned with the kinetics as affected by the physical characteristics of the electrolyte; this will be followed by a section on the effects of electrochemically machined surface on the physical properties of a metal. Chapters 5 and 6 will deal with tool design and the optimizing of process parameters, after which will be a review of topics concerned with the application of ECM.

Contents

1. Introduction to ECM

The first practical application of electrochemical considerations to the removal of significant amounts of metal were made in Russia in 1928 [2, 3]. The early work was continued in Russia although it did not gain widespread interest, probably because the materials available up to, say, the 1950s were amenable to cutting and shaping by the traditional mechanical or chip techniques. A rather coloured account of the early history of ECM is available in the Russian literature [4], although more balanced articles are given by Moroz [5, 6] and others [7–10]. Scores of introductory texts on ECM are available, most of which are written in English and a few are recommended [11–21]; and a recent publication [22] reviews some of the theories of anodic dissolution. Furthermore, three books [23–25] have been published on the subject of ECM which will be of interest to anyone requiring a broad introduction to the problems associated with the subject. One of these books [23], recently reprinted, is in the form of a collection of introductory chapters by people working in the various areas important to ECM: electrochemistry, tool design, machine design, etc, and is a well-balanced contribution. Wilson [24] has produced a guide to the practice of ECM which enters in some depth the field of machine and tool design, provides extended machine operating parameters, and offers tips on

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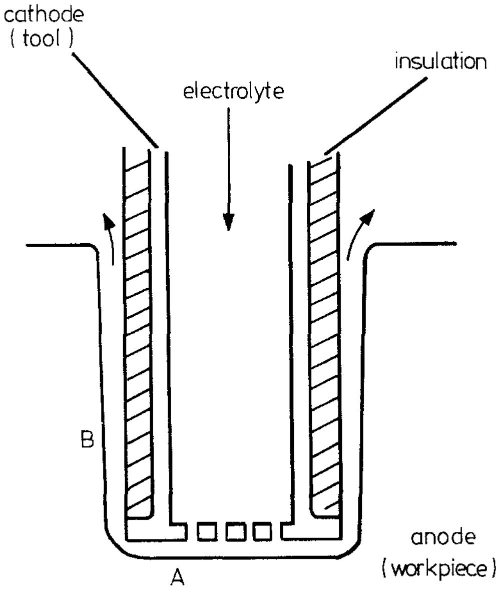

Fig. 1. Electrochemical drilling.

tool design without entering into the fundamentals of this topic, which is probably the biggest single problem in ECM. The third book, however [25], 'The Principles of Electrochemical Machining', is very much concerned with the fundamentals. Although this book is restricted to the consideration of only the ECM cell, and neglects such pertinent items as power sources, machines, electrolyte treatment, etc., it deals extensively with the fluidics within the cell, the electrochemistry, the interaction between the two, and with tool design.

Briefly, ECM is the use of an electrolytic cell with impressed current to corrode away an anodic workpiece, see Fig. 1. The gap between the two electrodes is kept as small as possible in order to maximize the amount of dissolution at A compared with B, i.e. to approach as near as possible, the mirror image of the tool in the workpiece, and also to minimize the ohmic voltage drop between the two. Electrolyte is pumped vigorously through the gap in order to: prevent boiling by Joule heat-

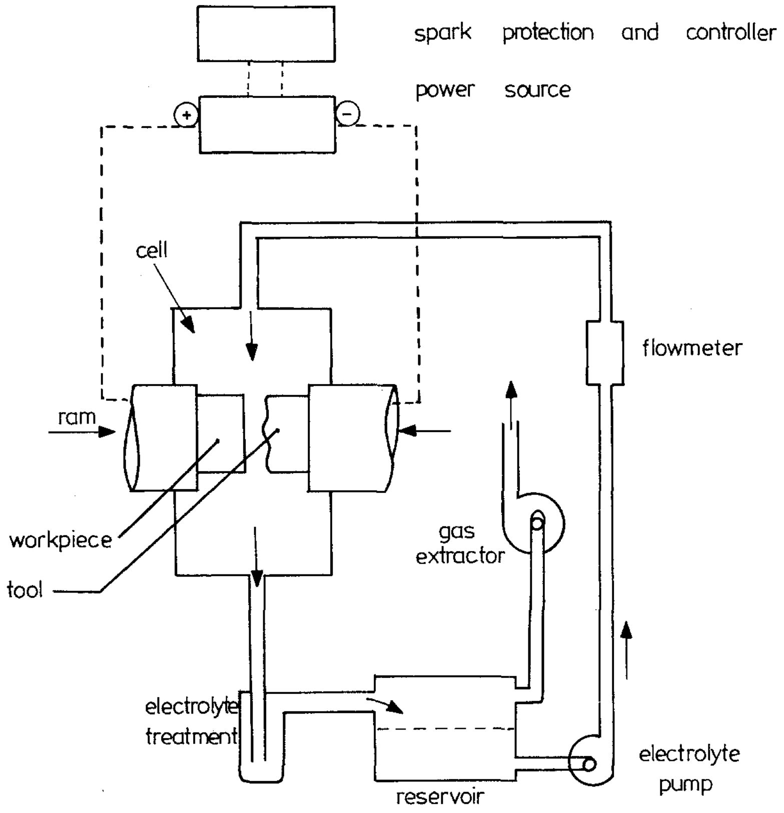

Fig. 2. Scheme for an ECM assembly.

ing – even although the gap is kept small there is still a finite resistance which leads to electrical heating at the high current densities used; and to sweep away the products of the electrode reactions – these products may be in solution, in a gaseous form, or be precipitated as solids [20]. The workpiece and the tool are brought together at a rate sufficient to balance the rate of dissolution, and thus an optimum working gap is maintained. The system is completed by the inclusion of a power source, usually a voltage-controlled rectifier and probably including a spark-detection device; an electrolyte circulation system, probably including an electrolyte treatment facility; and a gas extraction system because the cathodic reaction is usually the evolution of hydrogen. A system is shown schematically in Fig. 2.

It will be noticed that the cell arrangement in Fig. 2 is somewhat different from that displayed in Fig. 1. In the one example is a mode that is leading to the reproduction of a shape in the workpiece having a wavy cross-section, whilst the other example is of electrochemical drilling. One of the main advantages of ECM over other methods of machining is that in principle any shape may be produced in the workpiece by the appropriately shaped tool. The drill in Fig. 1 is not necessarily round in section but may be square, trapezoid, etc., and likewise the tool in Fig. 2 used for sinking may be virtually any shape.

The next major characteristic of ECM, and one that is a considerable advantage over many conventional machining techniques, lies in its applicability to the machining of a range of different metals and alloys. ECM is essentially governed by Faraday's laws of electrolysis and depends on the electrochemical equivalent of the metal but not on its hardness. Subsequently as modern alloys become harder, particularly those developed in the machine-tool and aerospace industries, the cutting rates by chip techniques fall accordingly. It will be shown later that ECM, competing with conventional techniques, finds its main application in the cutting of hard, exotic alloys and composites [26, 27].

These are some of the main characteristics of electrochemical machining and some of its many modes; other modes of operation of the process together with techniques closely associated with ECM, i.e. electrochemical grinding, electrochemical honing, electrochemical discharge machining, electropolishing, electrodescaling, electrolytic etching, and fine-hole drilling, will be discussed in further detail later in this article. These techniques all have their relative advantages and disadvantages and it may not be a simple task to decide which process to use for which application. A range of published articles are available comparing the principles and applicability of some or all of the mentioned techniques [28–33].

2. Kinetics of the dissolution process

2.1. *The anode–electrolyte interaction*

ECM is an anodic dissolution process and so is corrosion. This comment will give the reader some indication of the extent of the field and of the number of publications which are relevant to electrochemical machining. We shall be concerned here only with those studies at high dissolution rates except where it is considered that the work bears directly on the problems of high rate metal removal.

The cell reactions involved will depend upon the electrodes and upon the electrolyte, particularly its pH. The different electrolytes used in ECM will be reviewed later, but in the majority of applications low or neutral pH is preferred, the latter when plating out onto the cathodic tool is to be avoided. Pourbaix [34] has carried out a thorough study of the pH dependence of electrode reactions, and the thermodynamics indicate that in, for example, the case of iron, soluble ionic species are formed in simple acid/base reactions up to a pH of about 9. Above this pH, the formation of solid oxides or hydroxides occurs which inhibits metal dissolution and may even cause passivation. For some metals at very high pH a further zone of dissolution may occur [20, 25]. In indicating the conditions under which dissolution or passivation would be expected, Pourbaix diagrams (potential against pH) are a valuable aid in electrochemical machining, and the existence of anodic films is important both in restraining the dissolution process and in controlling the metallography of the machined surface obtained. The nature of the oxide film on iron, the most important metal to which most attention has been paid, is now accepted to be a form of

Fe_2O_3 overlying Fe_3O_4 [35], and this film leads to a 'true passivity' as opposed to the 'pseudopassivity' that would result in diminished corrosion rate caused by the precipitation of an insoluble salt as for example with lead in sulphuric acid [36]. Schwabe [37] further sub-divided 'true passivity' films into those like iron, cobalt, nickel, chromium, manganese and lead oxides which have good electronic conductivity, and those, for example, aluminium, tantalum, titanium, zirconium and beryllium, which have poor electronic conductivity. With this latter type of passive film a high overpotential is required for a redox reaction (such as oxygen evolution) to occur [38]. Hence this type of passivity is characterized by a quite broad passive region until a potential of 20 V or more is reached.

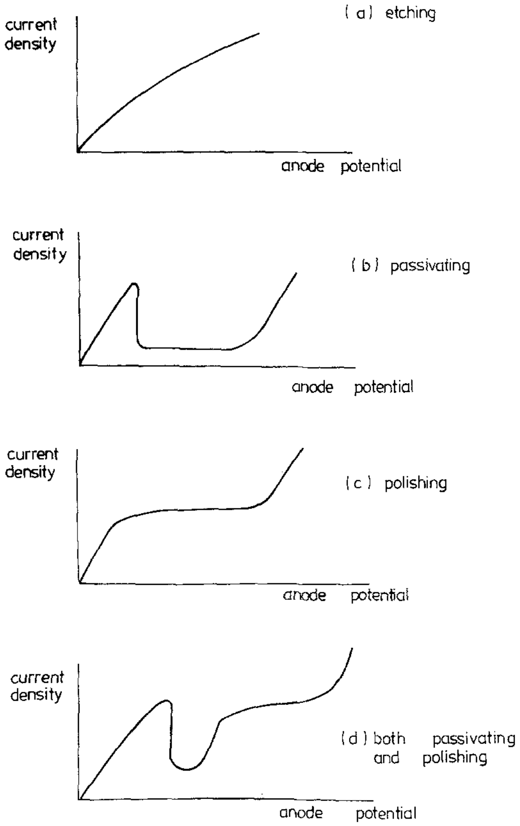

Fig. 3. Characteristic anodic polarization plots.

The discussion of dissolution kinetics so far has only been concerned with acid/base considerations, but another important feature must be considered. That is the possible existence in the electrolyte of agressive anions, such as the halides, which may modify the nature of protective films. This can be explained by reference to the anodic polarization curves shown in Fig. 3 [20]. Figs. 3(a) and (b) show the characteristic curves for active dissolution and passivation when an etched metal surface and an undissolved, film-covered metal surface will respectively be obtained. The third possibility, Fig. 3(c), is that electropolishing will occur and this may occur either via a mechanism involving a controlling viscous film or one invoking the existence of a solid, possibly an oxide, film. The viscous film theory of electropolishing was first suggested by Jacquet [39], since when there has been a great deal of evidence linking electropolishing with such a film [40] and standard electropolishing solutions have almost invariably involved a 'viscous-layer-forming' additive [41]. Subsequent work, however [42] indicated that the limiting current was brought about not just by the viscous layer which served to control the diffusion rate of metal ions away from the anode (or of aggressive species to the anode), but also by the existence of a solid film. The existence of a compact solid film in the classic system studied by Jacquet, i.e. Cu in H_3PO_4, has now been confirmed [43–45] and these findings have also been obtained for Cu in H_2SO_4 [46], Cu in KNO_3 and K_2SO_4 [47, 48].

In this mechanism the film is thought to dissolve at its outer surface and be created at its metal/film interface simultaneously. Other ingredients of many 'standard' electropolishing solutions are an oxidizing agent or film former, and an aggressive ion or film attacker [41]. Thus, whether or not the creation of a viscous film in some sys-

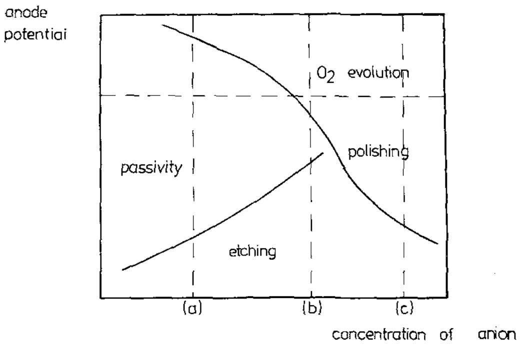

Fig. 4. The Hoar diagram.

tems is necessary for brightening or if the process invariably operates via a compact film mechanism is still open to some conjecture. Certainly brightening may be brought about in the absence of a viscous film and this is probably universally the case for high rate electropolishing (ECM). Furthermore, whether the control of the compact film thickness always occurs via a uniform creation/dissolution process or via a random pitting process, is again a matter of conjecture. An extensive study was made of the breakdown of passivating films by Hoar and co-workers [49–51] who constructed a graph relating the type of surface obtained with anode potential and aggressive anion concentration (see Fig. 4). An attempt was made to construct such a plot for the cases of Nimonic 80A and nickel dissolving in a chloride electrolyte [52]. The actual mechanism for anion breakdown of passivating films is not yet known conclusively, although many dissolution reactions involve local pH change [53, 54]; greater acidity in pits than in the bulk electrolyte has been reported [55] and a build-up of active anion concentration in pits is also expected [56]. Crystallographic pitting has been observed [57] although bright-bottomed hemispherical pits are more usual [49, 58]. A multiplicity of bright-bottomed, randomly-scattered pits may produce a polished, orange-peel finish [52]. Solid products have been observed covering the pits [57, 59], and it is thought that the ionic conductance of this product may be important in determining the life of the pit [60, 61].

The aggressive anions associated with pitting are usually the halides of which the chloride ion has received most attention [49, 51, 57]. Sulphate, perchlorate and nitrate ions are also known to produce pitting under certain circumstances [62, 63]. Kolotyrkin [62] evaluated the order of aggressiveness for a number of anions and found that for iron in neutral borate electrolyte the critical pitting potential, V_{crit}, became increasingly positive in the sequence $Cl^- > Br^- > I^- > ClO_4^-$. However, with titanium the order has been found to be the reverse: $I^- > Br^- > Cl^- > F^-$ [64]. The aggressive nature of the chloride ion in the presence of most metals and alloys has led to it being highly effective as an ECM electrolyte. It is also inexpensive – in the form of NaCl – and has become a commonly used electrolyte [23], particularly in respect of the machining of iron, steels, nickel and nickel-based alloys. A number of electrochemical studies have been made in chloride electrolytes under conditions of electrochemical machining [65–78]. Most studies indicate active dissolution of iron and mild steel in NaCl solutions, although at high electrolyte concentrations, inhibiting film formation occurs [71, 74] and surprisingly this film does not appear to be much affected by the speed of the rotating disc electrode. The film is porous and non-passivating and undoubtedly arises from precipitation of dissolution products. A similar film observed by Davydov *et al.* [69] was found to be dissipated by increased rotation speed. The evidence of Chin [74] is that the film was $Fe(OH)_2$, and the potential sweep work of Chikamori and Ito [70] suggests that the film is of an iron oxide or hydroxide. A similar mechanism for the inhibition of the dissolution of Al was also postulated [76] and with Ni in concentrated electrolyte [52], although in the case of Cr and Cr steels more tenacious films are formed which only break down at high potential [77, 78]. In the cases of Nb, Ta, V and Ti, and contrary to the normal degree of aggressive nature, bromides and iodides will be more effective than chlorides in bringing about machining [79–81].

Nitrates and chlorates have also been commonly used as ECM electrolytes [71–74, 82–89] and with iron as the workpiece produce anodic polarization curves showing the passivating behaviour of Fig. 3(b) but with rather high passive currents. The currents [72] were 2–8 mA cm^{-2} and the passive region 0 – 1·4 V (NHE) for 4·1 M $NaNO_3$ and 0·5 – 1·3 V (NHE) for 3·2 M $NaClO_3$. Both electrolytes show inhibition of the current compared with a halide electrolyte, but in the case of the chlorate, the passivation occurs with rising potential only after a period of active dissolution at higher current. A polarization plot of the type shown in Fig. 3(d) may be obtained [72, 74, 90, 91]. Here we have a region in which dissolution occurs to produce polishing, separated by a narrow potential range from a zone in which passivation occurs, and it was suggested by Hoare [90] that this rapid transition from passivity to transpassive dissolution is necessary in order that an electrolyte gives good dimensional cutting. In the case of NaCl electrolyte, a passivating film is not generated and the dimensional control is poor, i.e. there is a considerable amount of stray current attack. A comparison was made [71] between NaCl and $NaClO_3$ as electrolytes and it was found that stray attack was undesirable not just because of the poor dimensional control but because etched and pitted surfaces were obtained in this area [49–51]. It was shown [91] that the same effect of bringing about passivation in the stray current areas (low potential) could be achieved in NaCl electrolyte by the addition of a small amount of another salt to the electrolyte. The additive would be one, e.g. carbonate in the case of the machining of iron or nickel, which would form a sparingly soluble reaction product with the workpiece and hence bring about passivation by the precipitation of insoluble products in the pits of the stray current area. $NaClO_3$ has also been found suitable for the machining of cobalt [92]. In the case of the polarization of iron and nickel in nitrate electrolytes, the dissolution current is also inhibited compared with the chloride electrolyte [72, 84–87, 89, 93, 94] and again much better dimensional control is achieved. A current–time study of the passivation process [86] indicated that two dimensional nucleation followed by a monolayer of oxide occurred. Other work [89] refers to this film developing into a compact layer of Fe_3O_4 (on mild steel) which, with increasing anode potential, gradually breaks up revealing the underlying bare metal.

A number of comparisons of the nature of films formed on iron and mild steels have been made in NaCl, $NaNO_3$ and $NaClO_3$ electrolytes by Hoare and others [72, 83, 84, 90, 95] and also in other electrolytes, e.g. $Na_2Cr_2O_7$ [71, 72], $NaClO_4$ [96], Na_2SO_4 [97], $NaBrO_3$ [98]. Using dichromate, no machining was possible due to the formation of a tenacious passivating film of γFe_2O_3 [72, 99], although abrupt breakdown occurred at 1·5 V (NHE) accompanied by sparking and poor surface finish. It is likely that something similar occurs in Na_2CO_3 and Na_3PO_4 [71]. Na_2SO_4 also produces a protective film, brought about by a dissolution/precipitation mechanism, but which allows a small anodic current of about the same magnitude as that found in $NaNO_3$ and $NaClO_4$ [85, 100] and in $NaClO_3$ [71, 72]. With mild steel in $NaBrO_3$ [98] again a similar order of current density was obtained but in this case there was no abrupt change from the passive to the transpassive state and accordingly the dimensional control was found to be poor. It was concluded that a protective film of iron oxide is formed on mild steel in $NaBrO_3$ and that the film breaks down by a mechanical process to give rough, localized dissolution. What is required in ECM is the type of film formed in $NaClO_3$ which is a thin, porous oxide which allows random dissolution to give a polished finish. This condition probably also exists in $NaNO_3$ but in this case the film also happens to be electronically conducting such that anodic reactions take place other than metal dissolution and the subsequent efficiency of the dissolution process is very low [84]. In $NaClO_3$ the electronically-conducting film exists only at low current densities [101] where the efficiency is low, but at higher current densities the film takes on a porous nature and allows the efficiency to approach 100%.

2.2. *Efficiency of the anodic dissolution*

Efficiencies for the dissolution of mild steel in these two electrolytes ($NaNO_3$ and $NaClO_3$), and also in $NaClO_4$ and NaCl were measured by Mao [83, 84] and have been discussed by McGeough [25]. The differences in current efficiencies between mild steel and nickel in $NaClO_3$ were studied [102]. The behaviour of the two metals was somewhat different, thus reinforcing the suggestion that machining is highly dependent on the nature of the anodic film. The low efficiency for iron dissolution and the concomitant high rate of oxygen production in $NaNO_3$ arises from parallel anodic reactions occurring at the film/electrolyte interface. The electronic conductivity of the oxide film formed on iron in HNO_3 was found to be quite high [103]. The dependence of dissolution efficiency upon current density for Ni in $NaClO_3$ has been studied by Landolt [104], and for mild steel in NaCl, $NaNO_3$ and $NaClO_3$ by Chin and Wallace [87]. With mild steel in the chlorate electrolyte the current efficiency was zero at low current density, rising rapidly over a narrow range of current density to a figure approaching 100%. In nitrate the current efficiency again rose rapidly from 0% but this time reached a maximum of 80%. In the case of NaCl [105] the current efficiency was close to 100% at all current densities up to $\sim 2 \times 10^5\ A\,m^{-2}$, depending slightly upon the flow rate, when there is a small drop in efficiency probably caused by the oxidation of ferrous salts to ferric. This current density coincides with an improvement in surface finish from one that is rough to one that is polished, and also coincides with the reported [74] formation of a porous film brought about by the precipitation of anodic products. The efficiency of pure iron and pure nickel in 4 M $NaClO_3$ was studied by Hoare and Wiese [106]. Although the current efficiency for Fe was little affected by flow and current density between 500 and 3000 cm s^{-1}, and 5 and 50 A cm^{-2}, the values for Ni were greatly affected by both flow and current density. The current efficiency was measured for Ni at various current densities and values of flow of acidified $NaNO_3$ [94].

The current efficiencies referred to are Faradaic efficiencies, i.e. mass of metal removed/theoretical amount per coulomb x 100% where the theoretical amount is the electrochemical equivalent/96 500 C, and the e.c.e. involves a supposed value for the valency of the electrode process. Efficiencies of less than 100% indicate that some other process is competing, such as O_2 evolution etc. It is possible to calculate theoretical efficiencies, assuming that all of the reaction proceeds via the single mechanism, e.g.

$$\mathrm{Cu} \rightarrow \mathrm{Cu^{I}}$$

$$\mathrm{Fe} \rightarrow \mathrm{Fe^{II}}$$

$$\mathrm{Ti} \rightarrow \mathrm{Ti^{IV}}\ \text{etc.}$$

and this has been done for many metals and alloys [25, 107, 108]. Thus a 100% efficiency for the hexavalent reaction,

$$\mathrm{Mo} \rightarrow \mathrm{MoO_4^{2-}} + 8\mathrm{H^+} + 6e,$$

has been reported [109], and for the monovalent dissolution of copper in cyanide and chloride [110]. However, Kinoshita *et al.* [48] found that although the apparent valence was 1·0 due to the stabilization of the cuprous ion by complex formation in the Tafel (active) region, upon passivation the apparent valence increases to a maximum of 1·4 with increase in current density before reaching a limiting value of 1·2. This increase is due to a part of the reaction being

$$\mathrm{Cu} \rightarrow \mathrm{Cu^{II}}$$

In nitrate and sulphate active dissolution had an apparent valence of 2, but transpassive dissolution leads to lower apparent valence. This drop was thought to be due to the production of monovalent copper species. The dissolution of Fe and steel in NaCl usually occurs at efficiencies slightly below 100% and this is thought to be due to the formation of a little Fe^{3+} [111].

Current efficiencies higher than 100% may be obtained if incorrect assumptions are made regarding the valence of the dissolution reactions. Also it may be possible that particles of the anode, possibly due to extreme intergranular attack undermining grains, could fall away without undergoing electrolysis [112]. Chikamori and Ito [113] pointed out that a good ECM electrolyte must satisfy two main requirements: (a) the current efficiency should be high at the machining current density, and (b) current efficiency should be high at the high current density and lower at the low current density in order to maintain good dimensional control. They noted that $NaNO_3$ satisfied the second requirement but not the first, and attempted to improve on this electrolyte by the use of additions of other salts. These authors postulated that, as the electrode potential above which the current efficiency increases, coincides with that at which the evolution of oxygen begins, then this evolution reaction may well contribute to the rise in efficiency. The evolution reaction is probably

$$2\mathrm{H_2O} \rightarrow \mathrm{O_2} + 4\mathrm{H^+} + 4e,$$

and the increase in efficiency is thought to be brought about by the lowering of the pH (to shift the reaction to the corrosive domain of the Pourbaix diagram). The addition of oxidizing additives to the electrolyte is thought to promote this reaction. This local pH change was also used to explain the changes in efficiency for the dissolution of Ni in $NaClO_3$ [106]. At high c.d. and low flow, H^+ tends to dissolve the protective βNiOOH and thus expose the underlying Ni to attack.

2.3. *Mixtures of electrolytes*

Many studies have been made using mixtures of electrolytes. Most have been based on the philosophy of using an additive to create a controlling film, either a viscous film [114] or a passivating oxide, phosphate, etc. film, together with an aggressive anion to bring about breakdown. The film-forming anion mostly studied is nitrate [85, 115–117], although phosphate [91, 118], nitrite [93, 119, 120]. sulphate [100], ferricyanide[91], etc. have all been tried, as well as a number of the inhibitors that are commonly used in corrosion work [67, 121]. Surface active polyacrylamides [122] were found to improve the surface finish of mild steel dissolved in NaCl; and the use of carbonate additive to improve dimensional control has already been discussed [91]. The aggressive component most used is NaCl and a NaCl/$NaNO_3$ mixture was found to give a smooth finish on nickel-based alloys [117], and on chromium steels [116], although for mild steel such a mixture was not as good as for example $NaClO_4$ [115]. It was found that by mixing KBr with the NaCl electrolyte [120], although the rate of removal of Cr–Mn steel was not improved over NaCl alone, the surface finish was greatly improved. Hoare and Mao [100] differentiated between an oxide film formed on mild steel in $NaNO_3$/NaCl mixture and the dissolution/precipitation mechanism in Na_2SO_4/NaCl mixture. A third mechanism was identified for electrolyte mixtures in which perchlorate is the film-dissolver ($NaNO_3$/$NaClO_4$, Na_2SO_4/$NaClO_4$), and it was found that because the attack was an uniform film removal in the transpassive region compared with the rather localized attack of Cl^-, surface finishes could be improved. The effects of various additives to NaCl for the machining of a titanium alloy were monitored, [123] and it was found that the optimum electrolyte in terms of the surface finish contained chloride, nitrate, nitrite and bromide. Additives have also been used to control the pH of the electrolyte [124, 125]. Both the cathodic hydrogen evolution and the anodic oxygen evolution lead to changes in pH which may in turn convert the conditions of machining from favourable to unfavourable. For example, in unbuffered NaCl, Fe dissolves in the active state to a pH of about 12 but buffering may ensure transpassive dissolution and hence a better surface finish [126, 127]. Other means of controlling the anode kinetics have been sought through the use of complexing agents. These usually serve to prevent precipitation passivation, and hence increase dissolution rate, by sequestering the cations of the workpiece before precipitation can occur [128, 129], although problems then arise of the possibility of plating-out metals from solution just as in the case of using mineral-acids as electrolytes. If it is possible to discard the electrolyte frequently or if very small gaps are required for precise work, then citric acid or EDTA are useful sequestering agents for most steels and nickel-based alloys [23] and for tungsten carbon composites [130]. A variety of other sequestering agents have also been suggested [131]. In the case of the ECM of composite materials the various components may have completely different anodic reaction rates (this also applies to some multi-phase alloys – see later) and hence a compromise in the form of an electrolyte mixture is necessary. For WC–Co a variety of mixtures was studied [132] and equimolar proportions of NaOH and $NaNO_3$ were found to produce an uniform dissolution.

A completely new approach to some of the problems of electrode kinetics is possible by the use of non-aqueous media. Menzies and co-workers [133, 134] have electropolished a variety of metals in methanol-based and formamide-based electrolytes, and preliminary work [135] has shown that these systems may be used at high current densities to produce good surface finishes. Molten salts have also been used as ECM electrolytes [136] and these may offer potential in view of their high conductivities [137]. Basic potentiostatic work [138] on the dissolution of Ti alloys and Ni alloys in molten KNO_3 has indicated current efficiencies of less than 10%. However, Fe in chloride eutectic [139] dissolves actively at low current density but via pseudo-passivity at higher current density, a situation which looks promising for ECM.

2.4. *Concentration of active anion*

Hoar and co-workers [49–51] pointed out the importance of the concentration of the active anion in an ECM electrolyte following their studies on passivity and its breakdown. The Hoar plot was constructed (Fig. 4) and typical polarization plots for Ni in NaCl were obtained [91] at (a), (b) and (c) corresponding to those in Fig.s 3(b), 3(d) and 3(c) respectively. Evans and Boden also produced a Hoar plot for Nimonic 80 A in NaCl [52] and recognized a zone of imperfect polishing, which is virtually polishing except that the grain boundaries are visible and which occurred at lower anode potentials with increase in chloride concentrations. With nickel the imperfect polishing gave way to true polishing above chloride concentrations of ~ 3 M. At the higher electrolyte concentrations the solubility product of reaction products would be reached more quickly which led the authors to postulate a dissolution/precipitation mechanism of control. The absence of true brightening in the case of Nimonic 80A (Ni-68Cr-5Fe-2Co) was attributed to the formation of a soluble chromium chloride. A concentration effect was also found for Cu, Zn and brass in NaCl [140]. In all cases, however, the dissolution current was higher, the higher the electrolyte concentration, and this increase in the kinetics with increase in the number of active ions is a reason why electrolytes at high concentration are usually employed in ECM. Another reason is associated with the undesirability of large interelectrode ohmic drops; most electrolytes have increased conductivity up to high concentrations, frequently to their solubility limit [141]. On the other hand, film thicknesses will increase with increase in concentration [70, 100], and a compromise is usually required in the film former/film attacker ratio and in the overall concentration. Total concentrations of between 2 M and 3 M are usually employed [24]..

2.5. *Pulses and oscillations*

A method that has been used in ECM to bring about the breakdown of protective anodic films is the use of pulsed current. Potentiodynamic studies by Davydov *et al.*, [142] on WC/Co composites in $50\,g\,l^{-1}\,NaNO_3 + 5\,g\,l^{-1}\,NaNO_2 + 4\,g\,l^{-1}\,Na_2CO_3$ electrolyte indicated that a passivating film occurred after the passage of $5 \times 10^3\,C\,m^{-2}$. Using a bipolar pulsed current with the anodic pulse not exceeding this value, they successfully machined in the active region. Shikata *et al.* [143] also claimed that the use of pulsed current allowed passivating electrolytes to be used. Saushkin and co-workers [144, 145] claimed that the current pulses had an additional effect in bringing about extreme turbulence at the electrode surfaces and hence assisting dissolution (see later section on electrolyte pulsing); furthermore they found that accuracy and surface finish depended on the form of the pulse.

Compared with a steady-state current of $10\,A\,cm^{-2}$ where roughness was $> 8\,\mu m$ and the surface finish was patchy, using square-wave current of equivalent r.m.s. amplitude, an uniform finish of roughness $< 1{\cdot}5\,\mu m$ was obtained [146]. Duration of the pulses was ~ 3 ms and the interval ~ 10 ms. Ito [147] sees the pulse on mild steel and stainless steel in NaCl as an effect on the concentration polarization. An estimate of the effect of concentration polarization was made [148] from which the shape of the optimum pulse cycle was calculated. Concentration polarization was observed for Fe in NaCl under conditions of varying current sweep rate [149]. It was shown that the polarization characteristics depended considerably on the rate of the saw-tooth current pulse. Sedykin *et al.* [150] claimed that closer dimensional accuracy could be achieved by using a gap/pulse feedback system, whilst Levin and Nechaev [151] claimed that with WC/Co composites the pulse had the effect of reducing the dissolution overpotential of the carbide thus producing better surface finish and accelerated machining rates. Cook [152] found that once a pulse (50 V) had been used, machining of WC/Co in NaCl proceeded at 10 V, but allowing air oxidation after machining had been stopped necessitated a further pulse in order to recommence. Noble and Shine [153] examined the possibility of using a.c. and found that titanium and aluminium were suitable tool materials because they passivated readily on the anodic cycle, thus rectifying, and also offered high faradaic efficiencies below a frequency of ~ 300 Hz.

A number of workers have reported on the occurrence of oscillations during electrochemical machining [105, 154–156]. These oscillations manifest themselves as current oscillations under potentiostatic conditions [105, 154] and as potential oscillations under conditions of controlled current [155, 156]. Freer *et al.* [105] suggested that the fluctuations were caused by catastrophic rupture and replacement of a resistive layer on steel in a NaCl electrolyte. Postlethwaite and Kell [155], analysing a similar system, attributed the fluctuations to the presence of an unstable, porous, non-protective film (which was found to contain 70% Fe). Cooper *et al.* [156] analysed the characteristics of the oscillations on Cu in

$NaClO_3$ and deduced a two-phase anodic oxidation,

$$Cu + \tfrac{1}{2}H_2O \rightarrow \tfrac{1}{2}Cu_2O + H^+ + e$$

followed by $\tfrac{1}{2}Cu_2O + \tfrac{1}{6}ClO_3^- + H^+ \rightarrow Cu^{2+} + \tfrac{1}{6}Cl^- + OH^-$ and then by a build-up of dissolution products and an ultimate catastrophic rupture.

The cathodic reaction occurring during ECM in aqueous solutions is usually hydrogen evolution and inasmuch as this process might possibly be rate-determining for the overall cell process, some effort has gone into the study of H_2 evolution. It has been claimed that the evolution has a considerable effect on the equilibrium conditions within the cell [157, 158], although other work showed that the gas had only a slight effect on the electrolyte conductivity and on the process efficiency [159]. It was noted in the work of Mao [83, 84] that in most cases the current efficiency for the cathodic hydrogen evolution was close to 100%. However, in the case of nitrate electrolyte very little hydrogen was formed, and as ammonia, hydroxylamine and nitrite were detected, it seems that the main cathodic reaction is the reduction of nitrate. The current efficiency for nitrate reduction is likely to be affected by the cathode material as well as by the potential, and in fact a little H_2 was generated on Pt but none on brass, due to the lower hydrogen overpotential on the former. Photographic evidence [160] was presented that very little cathodic gas was produced in nitrate electrolyte on a copper cathode, and where gas was produced at high efficiency – in chloride electrolytes – it was concluded that the gas evolution had very little influence on the anodic processes below a flow rate of ~ 12 ms^{-1} at current densities up to 150 $A\,cm^{-2}$.

3. Further electrolyte studies

3.1. *Hydrodynamics and intrinsic properties*

In the last section the character of the electrolyte was considered where it was directly involved in the anode kinetics. In this section other electrolyte studies, i.e. hydrodynamics: flow, viscosity, etc. will be considered as well as those problems concerned with keeping the electrolyte consistently pure. However, for a theoretical discussion of hydrodynamics as it affects the ECM cell situation, the reader is referred to McGeough [25].

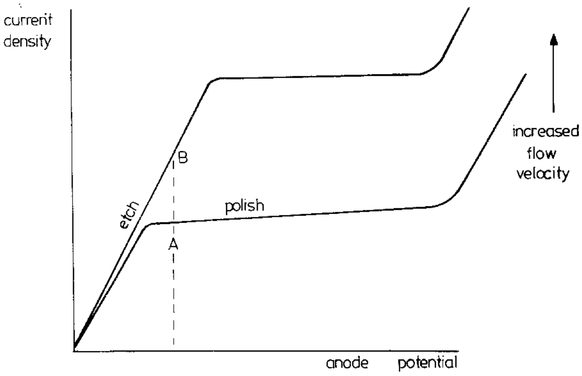

Fig. 5. Effect of flow on the surface finish.

Such matters that concern the electrochemical machinist as the corrosive nature of electrolytes or of the safety of their use will not be considered, except to say that aggressive anion salts like chlorides will tend to be more corrosive than film-forming salts like sulphates, nitrates, etc., and the use of chlorate (certainly perchlorate) presents a fire hazard compared with halide salts [23, 161–163]. Choosing the correct electrolyte to fit the job [164] is based primarily on electrochemical considerations, although solubility, conductivity and viscosity are also important, as is the choice of cathode reaction; electroplating is usually undesirable [165]. High rates of dissolution are usually required and to this end high temperatures, high pressures and high flow velocities are frequently employed [166]. In order that concentration polarization is kept low, and to ensure that reaction products are swept away, a high flow rate in the turbulent region is required (Reynolds number greater than ~ 2000) [167, 168]. In order that the flow profile is fully developed in the electrochemical cell, long inlet lengths are required [47] although in practice the ideal hydrodynamics are difficult to ensure and cavitation may occur [169, 170]. This phenomenon is likely to arise where an abrupt change in the direction of flow is encountered which brings about electrolyte starvation and produces poor surface finish and flow marks [171, 172]. One way of reducing the effect is to increase the cell outlet pressure [25] although other possibilities include the use of additives to the electrolyte which cause non-Newtonian behaviour and reduce the turbulent friction [122, 173]. A correlation between the orientation of grain boundaries relative to flow direction and electrolyte flow velocity during active dissolution was observed by Kops and Quach [174] although Ito *et al.* [147] on studying the dissolution of some steels in NaCl did not confirm this. Further work by the former authors using Scanning Electron Microscopy [175] showed that this was in fact the case for conditions of active dissolution, structures with grain-boundaries predominantly orientated perpendicular to the electrolyte flow dissolving more rapidly than otherwise. Other recent work [176] has confirmed this by showing that a variety of steels in NaCl at a fixed current density dissolved at rates dependent on the grain size, i.e. on the surface fraction of intergranular material. Freer *et al.* [105] suggested that local unevenness and striations could be attributed to fluctuation between activation and diffusion control of dissolution kinetics. A local increase in electrolyte velocity caused by some obstruction or secondary flow effect could cause the regime to change from polishing at A in Fig. 5 to etching at B. A polished hill then forms between etched valleys and thus accentuates the disturbances. Unevenness was found to be avoided by using sufficiently high velocities to remove completely anodic films from the surface of their steel samples. Similar effects were noted for the machining of nickel and Nimonic 80A [52] where it was noticed that a truly electropolished surface could only be obtained at relatively low velocities where a precipitated film occurred. The fact that the transition between grain boundary attack and polishing was found to occur at more positive potentials with increased flow rate suggested that low velocities removed concentration polarization effects but that these effects are restored with increase in dissolution rate. Nickel and a Nimonic alloy (Nimonic 90) were also studied by Larsson and Pyle [177] who observed the change in surface finish and considered that it corresponded with a change from activation to diffusion control of the kinetics. These findings are commensurate with the findings of others that anode potential requirement to maintain constant current fell with increase in electrolyte flow rate [178, 179], and that change in surface finish was accompanied by change in kinetics from activation-control to mass-transfer-control [94, 180]. A claim was also made [181] for a slight increase in current efficiency for the dissolution of Cu and Nimonic 80 with increase in flow of NaCl. For C-steels in NaCl a marginal effect was also observed [105] although this was less clear-cut for high carbon content alloys.

The most important single characteristic of an ECM electrolyte is a high electrical conductance so that ohmic losses in solution are minimized [182–184]. Extensive conductance data for NaCl have been tabulated [184] and plots of conductance change with concentration have been given together with nomograms to enable easy checks on the concentration of NaCl, $NaNO_3$ and $NaClO_3$, via their specific gravities, to be made [182]. A simple device for the determination of the conductance of an ECM electrolyte has been patented [185]. The conductance of an electrolyte is greatly influenced by temperature and by pressure [184, 186]. For a variety of concentrations of NaCl it was found [186] that at constant pressure conductance maxima were obtained with change in temperature. The maxima were obtained at ~ 300° C after an increase in conduction of more than a factor of four. Below approximately 250° C, pressure had virtually no effect on the conductance. Additionally, temperature will affect the electrode kinetics [187–189]. Sedykin [188] found that electrolytes heated above 40° C had a very undesirable effect on the surface finish, showing that it may be necessary to control electrolyte temperature. Kashcheev *et al.* [189] confirmed this during their studies on titanium and also noted that the dissolution anode potential fell by a significant amount with rise in temperature. Work has shown [159, 160] that although the effect is only slight, gas evolution at the anodes tends to 'dilute' the electrolyte and reduce its conductance. In order to redress this effect and also to reduce the occurrence of cavitation, high electrolyte pressures have been used [184, 190–192], in one case [192] the pressure being applied in the form of pulses. The purpose of this is to increase the turbulence in the electrolytic cell and hence help eradicate flow marks. To this same end the use of pressurized electrolytes purged with gas have been studied [193–195]. The gases used have been air [196], nitrogen [197], a mixture of the two [198], or CO_2 [199]. No difference between the nature of the gas was observed [195, 196], but above a maximum of 50 vol.% of gas, separation occurred which led to poor machining [197]. Separation also occurred at low flow rates [195]. Purging of the electrolyte with air has become so standard in the Soviet Union, that the optimum air/electrolyte ratio has been claimed [200] as one of the most important factors governing the ECM of steel. Improved accuracy has been reported [201–203] as a result of increased turbulence brought about by the mechanical vibration of one of the electrodes. Morozov and Zaidman [203] found a relationship between the accuracy of cutting and the degree of pulsing of the cathode, and Amirkhanova *et al.* [204] optimized the pulse rate at 50 Hz using a voltage of 4·5 for the machining of U8A steel in 10% $NaNO_3$. The improved cutting and reduced memory-effect was attributed to better electrolyte/workpiece contact. The use of ultrasonic vibrations has been found to increase the rate of electrochemical machining [205, 206]. Ivanov *et al.* [205] showed that in the absence of such treatment C-steel could be cut at the rate of 5 mm min^{-1} at a current density of $3 \times 10^6 A\,m^{-2}$, but with a proper combination of flow conditions and ultrasonic vibration this rate could be doubled. At a fixed frequency of vibration (20 kHz), Chaika [206] showed that the amplitude of the vibration had a considerable effect.

3.2. *Purity of the electrolyte*

The activity and viscosity of an ECM electrolyte depend very much on its degrees of purity, a fact recognized by Debarr and Oliver who devoted a chapter to the topic [23]. Since that chapter was written, however, a few other literature references have appeared which are worth noting. As ECM proceeds, the electrolyte will become increasingly laden with dissolved and suspended reaction products. Such materials as the hydrated oxides of iron and nickel will be precipitated out from non-acid electrolytes, and, if high precision is required, for example in the drilling of holes, these materials must be separated out. Kovalev [207] has reviewed the methods of separation and has compared the handling capabilities of equipment available in the USSR for sedimentation, centrifuging, electrostatic flotation and filtering. The performance of sedimentation tanks may be improved considerably by using a flocculant. It has been shown [122] that with 1–10 ppm concentrations of polyacrylamides the time of settling may be reduced to < 3% of that required in the absence of a flocculant. The use of a large-scale settling and centrifuging facility has been described [208], and designs for effective settling tanks and centrifuges have been patented [209]. Electroflotation [210] has been described but the main draw-backs with this technique are that it produces sludge which is wetter even than that from sedimentation in addition to requiring considerable electrical power. Filtration [207, 211] will produce a fairly dry effluent but this technique also requires considerable power.

The problem of reaction products in solution is very much more difficult to handle. Mauz [212] has discussed the 'ageing' [24] of an electrolyte which probably arises from a build-up of chromate ions in solution as a result of machining Ni–Cr or Fe–Cr alloys. The electrolyte usually improves in performance, but nevertheless a sulphide additive has been patented [213] in order to remove Cr^{6+} from solution by precipitation. The problem of undesirable build-up in solution only arises in the case of non-neutral electrolytes used for rather specialist applications [23], in which case such electrolytes are not purified but are discarded before build-up becomes a problem.

A third problem associated with the electrolyte is a possible change in character due to oxidation/reduction reactions at the electrodes such as the reduction of nitrate to nitrite and the generation of ammonium salts. This problem was noted by Mao [83, 84] and discussed by Mauz [212].

4. Surface and metallographic effects of ECM

4.1. *Surface finish: multi-phase and composite materials*

It has been pointed out that non-ideal dissolution conditions may produce an etched or uneven surface finish which in the case of certain materials may be severe. Many correlations between alloy composition or crystal size and surface finish have been made [175, 176, 214–216], and even defect density and microdistortions within the crystal lattice [217] have been shown to have an effect.

A major problem in ECM which has not yet been fully overcome is associated with the machining of more than one material at once, i.e. of composites or of multi-phase alloys. In the case of single-phase alloys, differential dissolution may occur in the active region of the polarization curve to give an etched finish, and the various controlling-film conditions have been proposed to avoid this. That crystallographic features manifest themselves during active dissolution has been deduced from a number of independent studies [77–79, 94, 177, 180] some of which [79, 177, 94, 180] showed that on passing to the transpassive mode this effect was diminished and a bright finish was obtained. Furthermore, plastic deformation [218] and work hardening [219] of the workpiece prior to ECM have been shown to influence the surface finish. Samples (of Cr–Ni steel) subjected to static work hardening were found to dissolve more rapidly than untreated samples [219], whereas cyclically worked (bending-rotation) samples showed the reverse effect. Two-phase alloys of particular interest to the EC machinist are the high carbon steels and cast irons. Voronenko and Moroz [220] and Freer *et al.* [105] noticed the poorer surface finish and the reduction in dissolution efficiency with increase in carbon content of C-steels. One group of authors [220] suggested that the increase in carbon leads to an increase in cementite content and that the dissolution of cementite requires extra electrical energy, whilst the others [105] suggest a stronger 'keying' of a surface film.

The inference here is that the film is electronically conducting and that other anodic reactions are occurring in addition to metal dissolution. Other work [221] has also shown that increase in carbon leads to poorer surface finishes of C-steels dissolved in NaCl, the ferrite dissolving more rapidly than the pearlite (a eutectoid of ferrite and cementite). A faster rate of dissolution of ferrite in alloy steels was also claimed by Pahlitzch and Dreesmann [222]. Mochalova [223] studied the relation between metallography and surface finish after ECM for some Cr steels and for some Cr–Ni steels. For Cr steels the best surface finish and lowest anode potentials were given by samples with the finely disseminated sorbite and troosite structures (as opposed to massive pearlite), and for the Cr-steels when the carbon was in solution as an austenitic structure. Hoare *et al.* [224] after studying the high rate dissolution of a series of alloys commented on the poor finish of high-Ni alloys in $NaClO_3$ due to preferential phase attack, and difficulty in machining Ti alloys without preferential attack was also observed [112]. The problem with machining cemented carbides is even more severe. These materials are extensively used in metal cutting and grinding and it is necessary to reshape them. In NaCl the corrosion potential difference between WC and Co, the usual cement, is 410 mV [225] and it would be unlikely that the WC would anodically dissolve in the presence of Co. However, it has been claimed [132, 226] that a mixture of NaOH and $NaNO_3$ produces a dense oxide film on the surface of the composite which leads to an uniform dissolution of both components. It was found [227] using this mixture with various Co/WC composites that with increase in the proportion of Co the rate of the dissolution fell and the roughness increased. WC and Co were found to undergo uniform dissolution in an electrolyte of 0·5 M Na_2WO_4 [228]. Analysis of the nitrate-based electrolyte after electrochemical grinding a tungsten carbide composite [229] showed that although most of the WC was present in the sludge, a significant proportion of the total tungsten was present in solution, presumably entering via the anodic oxidation of WC to tungstic acid.

4.2. *Secondary effects*

As undesirable, aesthetically as an etched surface may be, there is another important primary effect of ECM on metals in terms of their surface stress properties and the important secondary effect upon mechanical properties. A conference [230] was devoted to the consideration of residual stress in surfaces and the effect that electrochemical metal removal would have. The effect of ECM and other machining techniques on such a property has been termed 'surface integrity', and its importance has been emphasized by Kahles [231, 232], Bellows [233, 234] and others [235, 236]. Many texts on physical metallurgy or on metal working methods show the extent to which the metallography of the surface layers has been modified by conventional mechanical machining techniques. A variety of alloys were machined by a variety of methods by Field *et al.* [237] who found not just a 'smearing' of surface layers but such thermal effects as reaustenitized pearlite in C-steels and resolutioned α in two-phase Ti alloys down to depths of over 0·5 mm. On the other hand, the nature of the ECM process is such that no residual stresses are induced into the material and this method of machining leaves the workpiece in a state representative of the bulk material properties. Using an X-ray diffraction technique to study the crystalline structure of Nimonic 80A, Evans *et al.* [238] removed successive layers of a mechanically ground specimen by ECM and observed compressive stresses down to a depth of 0·20 mm.

A number of secondary surface effects produced by ECM have been recorded. Hydrogen embrittlement has been mentioned by several authors [237, 239] but no instance of this mode of degradation has appeared on record. This is to be expected because hydrogen evolution is usually the cathodic process and the gas is swept away before it is able to diffuse to the workpiece (anode).

Claims have been made that as a result of electrochemical machining, resistance to corrosion [240, 241], stress-corrosion [242] and corrosion-fatigue [243] may be improved relative to mechanically-prepared surfaces. This may be a result of removal of highly active high-stress layers. Improved wear resistance of a Ni–Cr–steel [244] after ECM has also been claimed. The tensile strengths of materials are little affected by ECM [245], although ECM or electropolishing of materials which are normally regarded as brittle may improve the tensile properties; thus Stephens [246] obtained marked improvement in the room temperature bend properties of tungsten. Electron microscope studies indicated that the improvement arose from the elimination of fine cracks which were present in the surface after mechanical preparation. Sedlatschek and Thomas [247] reported improvements in the tensile strength of tungsten after ECM, as did Fourdeaux and Wronski [248] whilst Ward *et al.* [249] showed improvements in the mechanical properties of beryllium due to electropolishing, and others [250] claimed improvement in the ultimate tensile strength of WC–Co composite. The same is true of the fatigue properties of materials, i.e. those improvements in fatigue life reported as a result of electrochemical treatment are restricted to brittle materials which are particularly notch-sensitive. For example, Bredin [251] reported increases in the fatigue life of coiled springs, Mondon [252] reported increases for high strength Ni–Cr–Mo steels and Ward *et al.* [249] for beryllium. A study of a high strength Cr–Mn steel (18KhGT) [253] showed that a great deal of surface damage was caused by mechanical polishing and ECM of the material caused the fatigue life to rise. A similar alloy in the form of rolling rolls (9Kh2MF) showed slight improvement [254] after ECM at stresses above the fatigue limit although very few experimental points were presented. Titanium alloys have also proved to be somewhat notch-sensitive compared with most common alloys [255] although ECM in these cases [112] did not raise the fatigue life. For most cases, the existence of a compressively stressed surface layer tends to aid fatigue life, and subsequent removal of this by ECM reduces the life [238]. It has also been shown [112, 256] that stress relieving the mechanically worked material by heat-treatment also reduces fatigue life. Different materials show variable sensitivity to fatigue life lowering: Inconel 718 [257] showed very little lowering, whilst other materials show up to a 25% reduction [245]. This lowering due to stress relief may also be aggravated by intergranular attack, although work on Nimonic 80A [238] and titanium alloys [112] showed that this was not excessive. That surface stresses represent the predominant reason for the lowering of fatigue life is supported by the fact that the fatigue life of EC machined samples can be retrieved by mechanical treatment. The data of Zimmel [see reference 239] were used to show this effect for steel 403SS by Debarr and Oliver [23]. Sand blasting and shot-peening are examples of post-ECM treatments that have been given to a variety of metals in order to recover lost fatigue properties [236].

5. Smoothing and shaping

In this section, we shall be concerned with the electrode/electrolyte interactions inasmuch as they affect the levelling and shape reproduction processes. The problem of designing a tool to produce a required shape is probably the single most important problem in ECM, and in practice, methods of design are still empirical even to the point of trial and error. An example of this approach has recently been given [258] for the radiusing of turbine blades in Mo steel. The topics of smoothing and shaping have been extensively dealt with by McGeough [25], so only the more important and the more recent publications will be discussed here.

Dissolution, we have seen, occurs through an anodic film, be it compact or diffuse, and the nature or thickness of this layer affects the ultimate surface finish [216, 259–261]. Estimates using the Navier–Stokes equation of the thickness of the diffusion layer [262, 263] show that the layer is very thin at the rates of electrolyte flow encountered in ECM (~ 0·003 mm) and is related to the inter-electrode gap attained. Current density varies inversely within this gap so that nearer points on the workpiece are points of vigorous action and are removed fastest [264], and this action is assisted by the diffusion layer thinning process on asperities. Petrov *et al.* [265] applied these considerations to the smoothing of micro-inhomogeneities in single- and multi-phase Fe alloys, and used photography to study the smoothing of small projections. They found, as did Parshutin and Zaidman [216], that high-C phases in C-steels and cast irons remaining as asperities could be reduced in roughness with increase in current density. Pronichev and Shmanov [266] developed a model for the levelling of titanium alloys allowing for the inhomogeneity of the alloys and the non-uniformity of current density and current efficiency over the surface. A simple experiment in fine-detail machining [267], i.e. in the avoidance of levelling, confirms that the current density (voltage) should be a minimum commensurate with satisfactory film generation/breakdown characteristics. This work also confirmed the loss of fine detail with increase in gap width. A mathematical solution to the plane, stationary problem of levelling by a solution of the two-dimensional Laplace was attempted simultaneously by Krylov and co-workers [268, 269] and by FitzGerald and McGeough [270]. With a dynamic model the situation is much more complicated although solutions have been attempted [270–272]. For a discussion of this treatment, the reader is referred to reference 25.

The hydrodynamic considerations pertinent to workpiece shaping in ECM are numerous. Ito and co-workers [170–172, 273] have made many observations on flow from electrolyte entries of circular and slit section. They found that cavitation occurred where the flow was high enough and starvation, where flow was too low. Korchagin *et al.* [274] observed a tendency to instability of the flow regime in very long cells which led to a related effect on the machining rate. Using more empirical approaches, slit entries have become favoured in the design of tools [24], and the electrolyte is usually fed out from these apertures in the tool although the cross-flow situation [275–277] and the reverse-flow arrangement [278, 279] have been described. With the solid-electrode [275–277], very careful hydrodynamic design is essential but this arrangement may be necessary where projections opposite the electrolyte entrance holes (or slits) cannot be tolerated. It has been found [278, 279] that in many ECM cells, reverse-flow of electrolyte produces fewer flow marks and ultimately a more uniform and predictable cut.

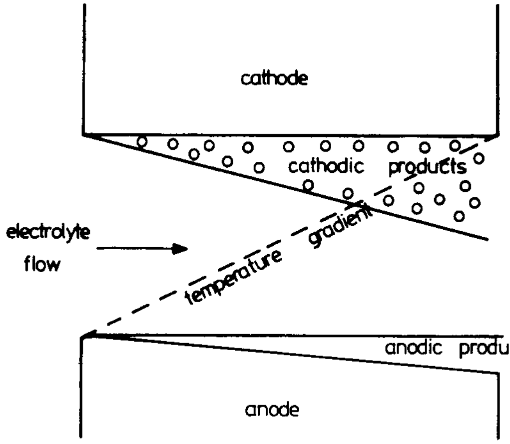

Fig. 6. Variation in gap across a cell.

In addition to the actual mass flow of electrolyte, there are two other important hydrodynamic considerations; they are the effect of temperature brought about by Joule heating of the electrolyte, and the effect of reaction products: hydrogen gas at the cathode and precipitated metal at the anode (sludge). The effect of sludge may be small, but the other two effects must be considered if progress is to be made in tool design. The increase in temperature of the electrolyte across the cell will have a two-fold effect: the kinetics of the dissolution will tend to be speeded up and the conductivity of the electrolyte will tend to be raised, both effects contributing to an increased rate of dissolution. On the other hand, the reaction products, particularly gas, will tend to dilute the electrolyte and have an opposing effect. This is shown diagrammatically in Fig. 6. When two electrodes approach one another in an ECM cell, an equilibrium gap situation is achieved due to the fact that material removal increases with increase in current density (Faraday's Laws) and that current density increases with reduction in gap (Ohm's Law) [23, 280, 281]. In studying this equilibrium process, Tipton [282] neglected the effect of gas and studied the effect of the temperature-dependent electrolyte resistivity on the variation of the simple cell. This approach was also taken by Zaidman *et al.* [283] and more recently by Dietz *et al.* [284]. Kawafune [285] and others [286, 287], on the other hand, neglected temperature effects and studied the effect of void fraction and gas compressibility. Hopenfeld and Cole [157] considered a quasi-steady process in which temperature effects were ignored and the effect of void fraction on current density distribution was determined. They produced photographic evidence for the two-phase, gas-electrolyte region next to the cathode and concluded that the effects were best minimized by increase in the electrolyte flow rate. A subsequent paper by these authors [288] took account of both temperature and gas on the variation of the equilibrium gap. The assumption of homogeneity of the two-phase mixture was made and they solved simultaneously the one-dimensional transport equations of mass, momentum, energy and charge. Numerical results compared favourably with experimental data. Feuillebois [289] has attempted to correct for inhomogeneity of the electrolyte/reaction product mixture, and similarly Ippolito [290] corrected for the non-linearity of the conductivity of the electrolyte with flow and current density. Thorpe and Zerkl Zerkle [291, 292] extended the approach to develop analytical solutions for the equilibrium conditions of rectilinear and radial flow configurations. These solutions allow a quantitative determination of certain limitations to ECM such as choking and electrolyte boiling. Another factor that the analysis techniques for shaping should consider is that of electrode polarization. As will be noted from previous sections of this review, this particular parameter is not fully understood and reliable data cannot be fed into analytical equations although FitzGerald and McGeough [270] attempted to consider the likely effects of both anodic and cathodic overpotentials. To date those approaches have not reached the point where they may be applied in the workshop and more empirical analyses have found more use. These are the approximate methods of shaping such as the 'cos θ method' and its derivatives [282, 284, 293–297]. The method is based purely on steady-state machining conditions and relies on the simple mathematical expedient of considering the equilibrium gap of surfaces approaching each other at an angle, θ, to be $g/\cos\theta$ where g is the equilibrium gap at the normal. Descriptions of the method are given in [23] and [25]. The other empirical technique of solving shaping problems is via the analogue methods. In the electrolytic tank variation [285, 298], shapes representing the tool and workpiece, possibly made from metal strip, are immersed in electrolyte and a probe connection, voltmeter and power supply used to derive the analagous shape for constant potential drop. A variation of this is described [299] using conducting paper. Numerical methods for solving the shaping problem also exist [299, 300] and are similar in principle to the analogue methods.

The very special case of shaping under conditions of pulsed current has been studied [144, 150, 301, 302] and improved accuracy has been claimed, probably as much a result of increased turbulence as anything. The velocity of a two-phase electrolyte was shown to change sign during pulsing [144] and advantages were found in momentarily widening the gap during the period of the pulse [302]. Pulsing of the electrodes has also been associated with improved levelling and shaping [201–204].

A large number of papers and patents exist on the actual mechanics of tool design, and it will be only possible here to refer to a significant few. Many of these publications pursue arguments such as whether more or less insulant should be used on a tool or whether the end of a drill should be hemispherical or paraboloid. Only the more novel contributions in these areas will be mentioned. For example, insulant materials have been suggested ranging from 'a high adhesive-strength rubber solution' [303], through plastic coatings [304] including Teflon [305] to the use of a passivating oxide film as insulant [306, 307]. Epoxy-resin insulants available in the USSR, and the treatment of an ECM tool, have been described [308].

Similarly, a range of recommendations on tool material exist ranging from Cu and stainless steel [304], through carbon and cast iron [309] to new copper-based alloys of the Cu–W type [310]. Tool wear becomes a problem, particularly for sophisticated and expensive tools, if sparking cannot be avoided and hence the types of materials used for EDM electrodes have been recommended [310]. Larsson and Baxter [311] carried out an analysis of tool wear relative to feed rate and voltage. Spark damage was found to be low, below a certain well-defined value of feed rate, and also to be reduced with increased sludge content of the electrolyte. An equation for minimum workpiece cost showed that, when using an expensive machine and low-cost tools, it is cheaper to work at high feed rates and accept tool damage. As wear is not normally, or should not be, a problem, Cu and brass are most frequently employed and a low-melting alloy for ease of manufacture by casting has been used [312]. Methods other than casting for the manufacture of tools have been suggested and these include electroforming [313] and shock-wave forming [314]. Other novel forms of tool manufacture include the use of bundles of tubes, the face of the tool being the ends of the tubes, shaped appropriately, through which the electrolyte passes [315]. A stack of thin plates has been used in a similar fashion [316]. If the individual components of a multicomponent tool are electrically isolated from one another, by switching and insulating, then the tool can be used in a multistage manner and large surfaces may be machined using a low-output power supply [317]. A variety of methods exist for protecting parts not required to be machined and these normally take the form of masking [305]. It was pointed out earlier in the review that the extent of stray current attack could be controlled to a certain extent by altering the throwing power of the electrolyte. Another way to do this is to use a Thief-anode, see Fig. 7, which steals away that current flux which is not normal to the tool face [318]. A variation on this idea is the use of electromagnetism [319].

6. Process optimization

The various process parameters of ECM: temperature of electrolyte, pressure of electrolyte, flow rate, pH, conductivity, gap, tool feed rate, i.e. machining rate, voltage, current, etc. are all closely inter-related. We have seen how, unless film-formation occurs, cell current is proportional to voltage, flow rate, etc. Thus, all parameters have been controlled by information feedback of other parameters: conductance compensation by temperature control [320]; variation of gap to compensate for electrolyte conductivity [321]; gap control by electrolyte pressure [322], flow [323], voltage feedback [324], current feedback [325], hydrogen generation [326], etc. In the discussion on tool design and anodic shaping, the importance of many of these parameters on surface finish and shape reproduction was outlined [157, 280, 288–292]. But this is not the complete story because the EC machinist also strives for high metal removal rates, ease of operating the ECM process, and all of the other features that make the technique profitable. Cuthbertson and Turner [327] showed that high rates for the dissolution of nickel

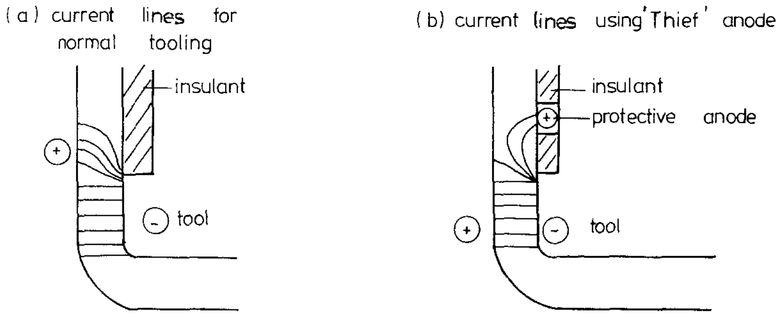

Fig. 7. Principle of the Thief anode [318].

alloys in NaCl could be attained if the electrolyte flow was high enough, and Loutrel and Cook [166, 328] found that very high removal rates could be attained at high voltage, high electrolyte pressure and high flow rate. Sorkhel *et al.* [329] discussed the maximizing of metal removal rate subject to the constraints of choking and boiling of electrolyte and pump capacity, and Gutikov *et al.* [330] studied this for the special case of the dissolution of the inner surface of a steel tube. These two constraints, boiling and choking, were predicted mathematically by Thorpe and Zerkle [331] for the cases of radial outflow (and radial inflow) for both flat-bottomed and spherically-bottomed tools. They constructed what they subsequently called [332] 'ECM characteristic curves', a generalized version of which is given in Fig. 8. The line labelled 'choke limit' separates the choking and non-choking ECM conditions. Aqueous electrolytes are somewhat compressible and are subject to choking; to the left and below this line the flow is not choked. To the left and above the line labelled 'boil limit', the electrolyte will not have been heated above the boiling point. Any tool feed rate greater than the intersection point 'm' will bring about either choking or boiling and this point moves to the right as inlet pressure is increased. This ECM characteristic curve may be determined by computer for any cell configuration provided the geometry does not become too complex, and for any configuration and inlet pressure the maximum metal removal rate is defined by 'm'.

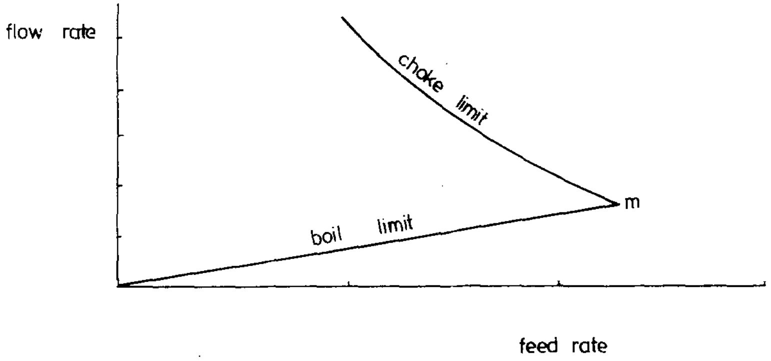

Fig. 8. ECM characteristic curve [332].

The problem of easing the operation of ECM has been tackled by a number of authors and optimum conditions derived from nomograms. Baldwin *et al.* [333] presented nomograms for equilibrium machining conditions for stainless steel (En 58J), and Schekulin [334] similarly rationalized machining parameters for some high temperature Ni alloys. René 41 was the alloy studied by Bellows [335, 336] who used data (feed rate, voltage, electrolyte composition, temperature and flow rate) and estimated response variables (gap, current density, electrolyte pressure, conductivity, temperature and viscosity) to construct triaxial nomograms. The electrolyte under study was NaCl. Electrolyte selection guides and other operating parameters for a variety of metals and alloys have been published [337–339]. Cross [340] has estimated optimum metal removal rates for some Fe-, Ni-, Co- and Ti-based alloys for various combinations of operating parameters including consideration of dimensional reproducibility of side and frontal cutting gaps. If the electrolyte is purged with air, as is becoming increasingly common in the USSR, then the other important quantity that must enter into the optimization tables is the air/electrolyte ratio. It has been claimed that this is one of the more important variables [200].

With the emergence of optimized conditions for ECM the economics of use of this technique should become more favourable. This was pointed out by Ratmansky [341], who also warned that the production engineer should be wary of cost-effectiveness in terms of component turn-round time, for example, which is reflected in good machine design. ECM machines have tended in the past to be large and rigid devices, reflecting the needs of a conventional machine. Many of the characteristics applied to such a machine have served to make it unnecessarily expensive and rather too inflexible [342]. These latter authors [342] contend that ECM should be concentrated on the areas of application for which the technique excels: sophisticated shapes, hard materials, mass production, and that only small jobs should be undertaken in order to pre-empt the likelihood of high tooling costs. Some successful applications of this sort have been reviewed by Allison [343], and the economic use of ECM compared with electrical discharge machining has been made [344]. The applicability of ECM to large production runs rather than for 'one off' jobs arises directly from the cost of tooling. Meleka [345] carried out an economic assessment of the application of ECM to the production of a jet engine component compared with its production on a copy milling machine, and an economic study has been made by the Production Engineering Research Association of Great Britain [346] on the total cost of producing a firm's annual output of ten different sizes of turbine wheel. Great savings using ECM were achieved in the study because integrally-bladed turbines could be made. The production cost graph shown in Fig. 9 gives the lowest unit cost (in pence mm^{-1}) to produce the firm's entire output for particular combinations of feed rate and number of blades machined simultaneously per machine. All costs are on a one machine-one operative basis, and it is seen that if a number of blades are machined simultaneously, the econ-

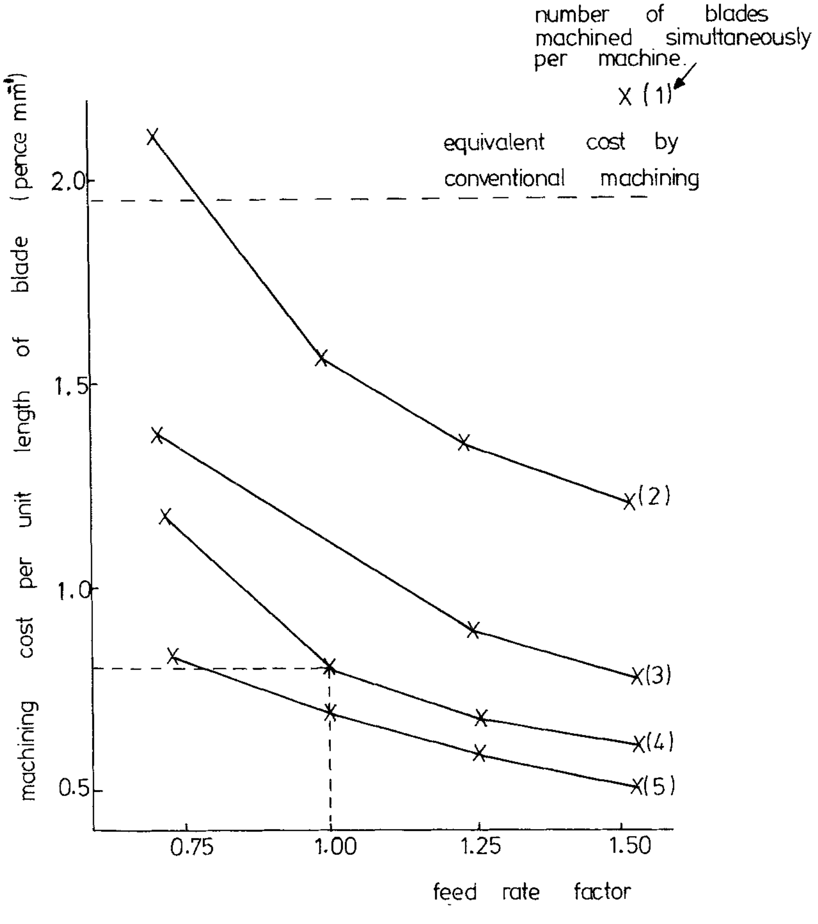

Fig. 9. Cost of producing integrally–bladed turbine wheels [346]. (This figure is reproduced by permission of the Production Engineering Research Association [PERA], Melton Mowbray.)

omics of using ECM rapidly become more favourable than the conventional chip-machining techniques. A number of other examples have been given [347–349] where ECM can make substantial savings over other techniques provided the many process variables are optimized.

7. Applying the ECM process

7.1. *Modes of ECM and related techniques*

As mentioned in the introduction to this review, the two most important modes of application of ECM are drilling and sinking (shaping). Important examples of EC shaping are in the production of turbine blades [350, 351] and discs in thin-section [352, 353]. EC drilling is of general applicability but recently it has gained a certain importance in the drilling of fine holes, particularly as long, fine holes are required in the production of some gas turbine blades [354]. A process known as Shaped-Tube Electrolytic Machining (STEM) has been pioneered by workers at the General Electric Company [355, 356] in which an insulated tube of any cross-sectional shape may be used to drill holes down to a 'diameter' of 0·25 mm and a length : diameter ratio of 100 : 1. Non-parallel holes (and even curved holes) may be drilled using tube-guides [356] or by using curved tubes, and holes may be drilled in otherwise inaccessible places, as shown in Fig. 10. An extension of this drilling arrangement is found in a technique called 'stream drilling'. In one form of stream drilling (SD), the tube is made entirely of insulating material, for example, glass, and the cathode is placed some distance away. The tip of the tube then becomes a 'virtual electrode' [357], the shape and size of the hole is then dependent upon the shape and size of the end of the tube and may be very small indeed. The distribution of current between the mouth of the tube and the workpiece will be the same as if the mouth were the actual metallic electrode. A series of patents [358] and a publication [359] described this process as one which would facilitate the drilling of long, fine holes in hard materials at a very high rate. The electrode is shown in Fig. 11. Kelly and Nutting [360] used a similar jet of electrolyte to prepare their samples for metallographic study and a recent patent application [361] by workers at Rolls-Royce has described another form of SD where only the jet of liquid, and not the insulating tube, is inserted into the hole being drilled. In this way it is hoped

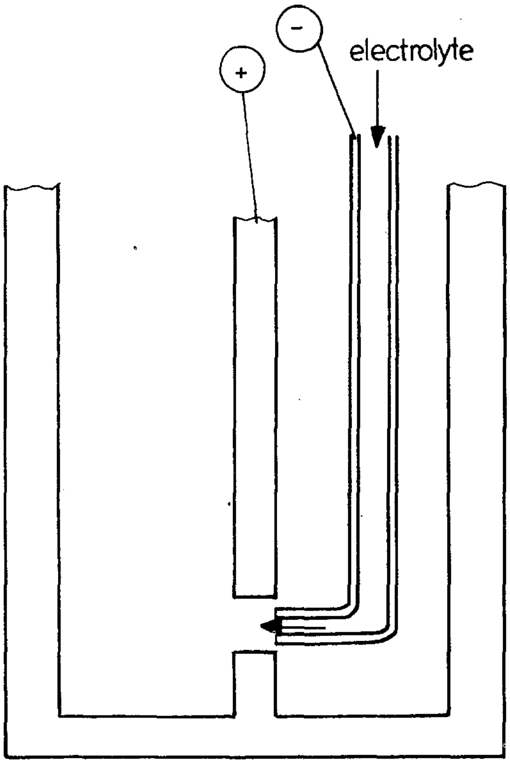

Fig. 10. Drilling in inaccessible places.

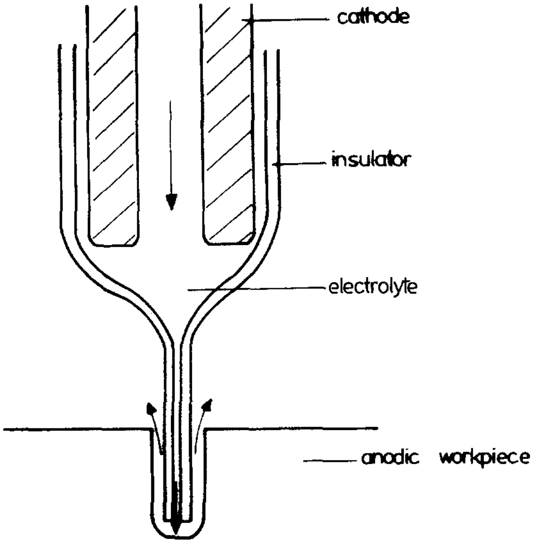

Fig. 11. Stream drilling with a remote cathode.

to produce even finer holes. The secret of the exceptionally high rates of machining possible with both of the forms of SD [358, 359, 361] probably lies in the fact that sufficiently high voltages are used to bring about a glow discharge [362].

Other modes of ECM are turning [363, 364] and milling [365, 366] where the workpiece and tool are moved laterally relative to one another and where ECM has made a valuable contribution in respect of both external and internal surface cutting. In EC wire-cutting, a travelling wire [367, 368] or a fine-tube with holes for the passage of electrolyte, is used to slice through metal just as a cheese wire passes through cheese.

A range of machining and finishing techniques exist which are variations on the ECM process, and whilst it is not the purpose of this section to review them, they will be briefly described.

Electropolishing is used extensively as a finishing technique; it is anodic dissolution at low rates to produce a bright finish and has been reviewed by Tegart [369]. Electrogel machining is a variation on ECM or electropolishing in which a gel electrolyte, possibly based on cellulose acetate [370], has been used to cut fragile metal honeycomb. Electroetching is a technique that has been extensively patented [371] for the marking of, for example, cutlery or razor blades. The technique has also been used for the graining of aluminium foil [372] which finds extensive use in the capacitor and lithographic plate industries. Stencils are frequently employed in the marking applications and the electrolyte is frequently contained in a sponge or in a gel. Electrochemical techniques have also been used for descaling, of, for example, ship hulls [373], for electrolytic cleaning [374], or for electrolytic stripping [375] of perhaps one metal from another.

Combining ECM with electrical discharge machmachining is a process called electrochemical discharge machining, ECDM, which utilizes spark discharges through a conducting electrolyte [376]. In its most popular form, the technique employs a profiled wheel possibly made of graphite or a metal, and the workpiece removal is thought to be brought about principally by the electrochemical process with the sparks serving to break-up passive films. This is also thought to be the mechanism responsible for the high removal rates in electrochemical grinding. In ECG the passivating and rate-controlling films are dispersed by the action of an abrasive but conducting wheel with the mechanical process accounting for perhaps as little as 10% of the metal removal [377]. Cole [378], and more recently Grodzinsky *et al.* [379], studied the effect of machining parameters on the efficiency of metal removal and found that 100% Faradaic efficiency could not be achieved. The wheels are made from abrasive particles set in a conducting matrix, frequently cobalt, and the interelectrode gap is determined by the size of the particles. A variety of abrasive wheels have been used, including SiC, Al_2O_3, diamond, etc. [380]. ECG is most suited for the cutting and shaping of very hard materials, particularly the types of composite materials (WC–Co, TiC–Co, etc.) that are used for tool and drill tips. Lately EC form-grinding has been described [381, 382]. Related to ECG is electromechanical machining in which no abrasive particles are used to separate the workpiece from the tool and the tool is allowed to contact the workpiece [383]. Thus, for many applications, a cheap steel disc may be used to replace the more expensive grinding wheel. A mode of ECG is the use of an abrasive slurry to replace the wheel and electrolyte [384, 385] and in another application, often termed 'barrel finishing', components to be deburred are turned in a barrel, across which is an electric field, containing an electrolyte and a number of small conducting or non-conducting spheres [386]. A mode of ECG of importance to the internal combustion engine industry is 'electrochemical honing' [387]. The main application of this technique is in the finishing of engine bores.

7.2. *Some applications*

It has been noted that the main advantages of ECM over other machining techniques lie largely in: (a) its ability to produce stress-free cutting; (b) its ability to machine hard metals, and (c) its applicability to the machining of sophisticated shapes. A few applications in these three categories will be considered, followed by a number of specific or novel applications of ECM, but first a number of publications will be mentioned which will serve as an introduction to the possibilities of ECM [388–391].

Where fragile or very thin-sectioned components are to be produced, ECM has proved to be very useful. For example, the electrolytic saw has been described [367] for removing thin slices of metal crystals, and this has been extended to the removal of crystal slices of germanium of defined crystal orientation [392], to the study of residual stresses by shaving off thin slices [393] and to the study of diffusion through tungsten by electrochemical sectioning [394]. Furthermore, the thinning of transmission electron microscope samples by ECM has been described [395]. An application of importance to the aero-engine industry where weight must be saved wherever possible, is the production of thin-section blades and compressor discs [396].

The application of ECM to the machining of advanced alloy steels and hardened spring steels [388–391] and to chromium- [397], tungsten- [398] and carbon- [399] die steels has been described. Cobalt-based alloys [356, 400] (René, Udimet) and nickel-based alloys (Inconels, Nimonics, Monels, Waspalloys) [401, 402] have been satisfactorily machined, as have tungsten, molybdenum, tantalum and their carbides [403]. Niobium alloys have also been machined [404] although only successfully in the active dissolution region at low current density. As noted earlier, there are limitations in the application of ECM to titanium alloys due to the poor surface finish obtained. However, such alloys are used extensively in the aero-engine industry and both single- and multi-phase alloys are machined electrochemically [405].

A number of complex shaping operations carried out using ECM have been reviewed by Movich [406]. Most applications in this respect are in the field of turbine blade or engine casing manufacture, or for the production of tool dies and many of these have been described by Wilson [24]. However, impossible or difficult shapes have been produced by other techniques, such as deep holes [357], gun bores with or without rifling [366, 407] and narrow grooves [303]. The ECM of a turbine blade has been described by Molloy [408] and the forming of shaped cooling channels in turbine blades by Bairamyan [409]. The manufacture of other gas turbine components by ECM has been reviewed by Cross [410]. The production of forging dies electrochemically and the problems of electrolyte flow in the process have been discussed [278]. Another important use of ECM is in deburring and many applications of the deburring of castings, forgings, aerospace components and gear wheels, have been given [411–414]. The application of ECM to the continuous production of the cutting edges on razor-blade strip has been presented in a number of patents [415]. A rather novel application describes the machining of Al–17%Si alloy [416]. An engine block is diecast in this material and the cylinder bores are electrolytically treated to reveal the wear-resistant silicon. The pistons are of aluminium coated with iron and a useful life has been obtained provided fine control of the Si content, and of its coarseness and distribution, is maintained. The formation of helical screws [417] and of gears [418], and the finishing of steel rolling rolls [419] and compression springs [420] have been described amongst the many other applications of electrochemical machining.

7.3. *ECM machinery*

Early literature on ECM consisted largely of descriptions of commercially available machines [421, 422] or of accounts of their behaviour in use [423]. The first machines were very large and rigid to compensate for electrolyte pressures and had very stiff and precise feed mechanisms in order to operate at very small interelectrode gaps and attain maximum precision. In order to attain this stiffness, and to reduce machine corrosion problems, machines were built using large concrete castings [424]. However, Billing [425] rejected this approach in devising a low cost pulse-feed mechanism. The stepwise advancement of about 10% of the gap width was found to have no detrimental effect on the machining, and subsequently vibrating tools [203–206, 426] have been used to produce a claimed improvement in machining. Furthermore, Billing [342] directed his attention to the production of a low-cost machine by designing for small component machining and making use of stainless steel and fibreglass to defy corrosion.

The second requirement for an ECM assembly is a power source. These are usually voltage-controlled d.c. units capable of supplying up to 30–50 V at currents ranging up to ~ 10000 A [23]. Much care has been taken in the design of power supplies to eliminate ripple although there is no practical evidence that this has any effect, in fact a.c. machining has been attempted [142–153] and power supplies have been made available for this purpose [427]. A controlling device for the supply of a.c. has been described [428] in which no current passes whilst the tool and workpiece are in contact, but pulsed current commences the moment they are separated. A feature of particular importance regarding the electrical circuit is adequate detection of metal/tool contact or sparking which might damage the tool. In the case of machining with sophisticated and highly expensive tools this is of particular importance. The requirements of an ECM system to reduce risk of sparking, including an adequate filtering system, have been reviewed by Williams [429], and a number of electronic circuits suited to this purpose have been patented [430].

The remaining important facility in ECM is an electrolyte supply system and the usual arrangement is shown in Fig. 2. The system may be furnished with an electrolyte purification assembly [207–212] and possibly also a purity monitoring device [185].

The design of the cell assembly will depend on the application, and a number of different modes of operation of ECM were described earlier in this review. Additionally, a number of novel cell arrangements have been published: cutting using rotating discs [431]; the electrochemical treatment of small parts with a hand-held stylus [432]; and a device for the precise thinning of discs [433]. The opposing-tool arrangement (two cathodes) used to produce turbine blades was the subject of a number of patents [434] and this cell arrangement has been further described by Wilson [24]. The description of section-by-section machining of large components by transferring the electric field from one section of the cathode to another has been given [435]. The principle of electrochemical shaping by reference to a master has also been the subject of patents [436]. In this case the master component provides the shape as in conventional copy machining and the tool then takes the form of a very simple and cheap drill. In many respects numerical control is a form of copy machining of this kind where the master copy has been replaced by a mathematical model. The possibility of using NC proper was suggested by Williams [437] but the marrying of ECM and NC has only very recently been attempted [438]. Thus, it seems that with the many applications of ECM and the many up-to-date developments described in the literature, the immediate future for the technique is assured.

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