

Review Article

Impact of Different Electrolytes on the Machining Rate in ECM Process

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Electrochemical machining is a nonconventional machining process in which the metal removal is achieved by the electricity and chemical solution known as an electrolyte. It is the reverse electrolysis process where the application of electricity facilitates the current travel in between anode and cathode. The mechanism of the ion movement is similar to the electrolysis process. Electrochemical machining (ECM) is a type of advanced machining process which employs electricity to perform the machining process on the workpiece. It is also known as a reverse electroplating process where metal removal is achieved instead of metal deposition on the metal surface. There are various parameters that affect the metal removal process in the ECM process, such as electrolyte, power supply, workpiece material, and tool material. The electrolyte is one of the key factors impacting the machining rate, surface finish, and reliability of the produced parts. In this project, a brief study is carried out regarding the electrochemical process and the electrolytes where the properties, functions, merits, and demerits are evaluated. The impact of the various electrolytes and their suitability for machining of various metals is also discussed. The findings of the effect produced by using the mixture of the electrolyte in the electrochemical machining process are discussed in this project. The effects of the complexing agents on the electrolyte and the electrochemical process as a whole are also reviewed.

1. Introduction

Electrochemical machining is a nonconventional machining process in which the metal removal is achieved by the electricity and chemical solution known as an electrolyte. Electrochemical machining is a modern and advanced metal removal technique that can produce metalworking for complex materials [1]. It is a very accurate machining process that can perform machining for any type of conductive workpiece. ECM finds its use in aerospace, construction, microsystems, medical equipment, and power supply systems [1, 2]. The electrochemical process is the noncontact metal removal process where no heat is applied, due to which the problems related to the conventional machining process are eliminated [2]. There is no tool wear due to which no defective layers are produced due to the tool on the workpiece [3], as shown in Figure 1.

1.1. Mechanism of ECM Process. ECM process is the reverse electrolysis process where the application of electricity facilitates the current travel in between anode and cathode. The mechanism of the ion movement is similar to the electrolysis process [2, 3]. For example, in the electrolysis of copper metal, the electrolysis process is conducted where the impure copper metal is kept to the anode material, and pure copper is kept as the cathode in the electrolyte of CuSO_4 solution. Copper atoms in the impure anode material are dissolved and travel to the cathode terminal via the electrolyte solution. The traveling is facilitated by a diffusion mechanism, and ions always travel from higher concentration regions to lower concentration regions to achieve chemical equilibrium. The concentration of the copper ion is high at the anode terminal, due to which they travel to the cathode terminal after getting attracted. Along with diffusion, the migration and convection also facilitate the

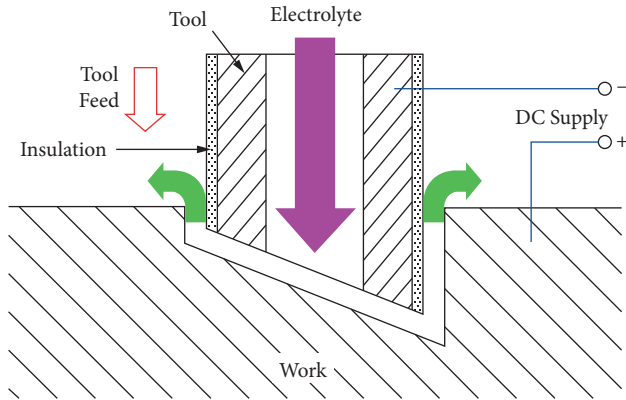


FIGURE 1: Electrochemical machine process.

complete electrolysis process. The migration mechanism is caused due to the potential field between the electrodes and the electrolyte. The third mechanism existing in the electrolysis and electrochemical process is convection which is caused due to the externally produced mechanical forces by stirring and bubbles in the solution [3]. The mechanism of copper purification is presented in Figure 2.

In the ECM process, the workpiece is connected to the positive terminal, known as the anode, and the tool is connected to the negative terminal known as a cathode [2]. The gap is always maintained between the tool and the workpiece. ECM process works in the principle of Faraday's law of electricity and Ohm's law. In the ECM process, the electrical conductivity of chemical electrolytes across the gap is considered to be constant. The electrical potential of the circuit is also assumed to be constant at all machining periods [4]. The cathode terminal of the ECM setup transmits electrons and releases the hydroxide (OH^-) ions, whereas the anode terminal releases electrons and they eventually become the metal ions, as shown in Figure 3.

2. Electrolyte

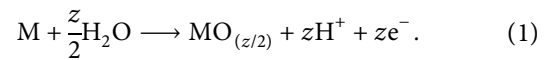
The electrolyte is the primary component of the electrochemical machining process. It has a significant role in material removal as well as tool wear. It has mainly three functions in the ECM process, carrying the current between workpiece and tool and removing the products of reactions from the interelectrode gap (IEG) [3].

The performance of the chemical machining process depends upon the selection of the electrolyte [5]. The electrolytes in the ECM process must have low corrosive nature and toxicity, high conductivity, and high electrochemical and chemical stability. The important properties of the electrolyte can be identified using the Polarization curve. Polarization curve is the graphical plot of the voltage or power density vs. current or current density of electrolyte cellular stack [6]. In the ECM machining process, the electrolyte is selected in such a way that no deposition of the material exists on the cathode. The deposition, if present, can deform the tool shape, and it can also impact the surface finishing of the workpiece. Moreover, the electrolyte also

should be able to take away the excess heat generated during the ECM process.

3. Mechanism of the Layer Formation

Depending upon the nature of the electrolyte and its selection process, the nature of the chemical reaction between the anode and cathode terminal can also be varied. The electrolyte can be categorized into two types, passivating electrolyte and nonpassivating electrolyte [3]. Passivating electrolyte facilitates passive layer development on the workpiece surface. This layer is composed of hydroxides and oxides, and it is formed after the current is passed between the workpiece and tool electrode terminals. Passive films can be electrically insulated and thus can hamper the chemical etching and dissolution process. But these films help in improving the machining resolution [7]. Nonpassivating electrolytes do not allow the film to be formed on the workpiece since the aggressive ions present in the electrolyte make the film unstable [3]. Nonpassivating electrolytes have a higher machining rate compared to the passivating electrolytes; however, the surface finish quality can be affected [8]. Passive layers on the workpiece are developed by workpiece metal itself along with the reaction from the surroundings. The water molecules are dissolved in the electrolytic solution and perform the following reaction forming the oxide layer as given below [9]:



Passive films can be insulators or noninsulators. The insulating film on the workpiece is self-subdued. The result is in the form of a thick and dense layer on the surface in a homogenous manner. However, the passive film can be cracked and distorted by the uneven electric field. The film can also be impacted by the addition of different functional ions [10].

4. Selection of Electrolyte

Electrolytes can be classified into four main categories depending upon their nature and physical form. They are neutral aqueous salts, aqueous acids, aqueous alkalis, and nonaqueous electrolytes, respectively. Neutral aqueous salts are mostly used electrolytes since they are relatively cheaper and are generally harmless to the working tool and machinery. The chlorides and phosphates of the metals such as Sodium, Potassium, Magnesium, calcium, etc., are some of the neutral electrolytes. Acidic electrolytes are used when the dissolution is not effective and possible by using other electrolytes. Some of the acidic electrolytes are sulfuric acid, hydrochloric acid, nitric acid, perchloric acid, etc. The interelectrode gap can be reduced to a great extent since the ions and other reaction products are firmly dissolved in the electrolytic solution. This also eliminates the problem of clogging. This is the reason why electrochemical micro-machining prefers acidic electrolytes [11]. According to the experimental investigation conducted by Yong et al. decided that the acidic electrolyte can produce very high machining

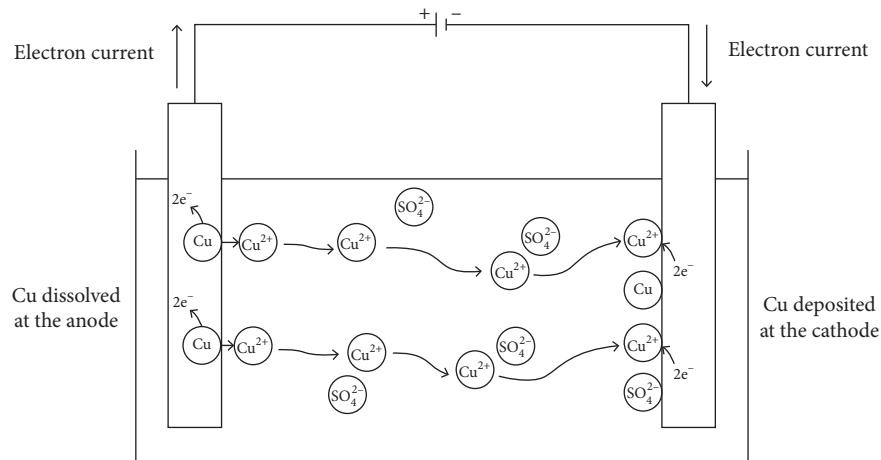


FIGURE 2: Diffusion of copper in copper sulphate and purification of copper.

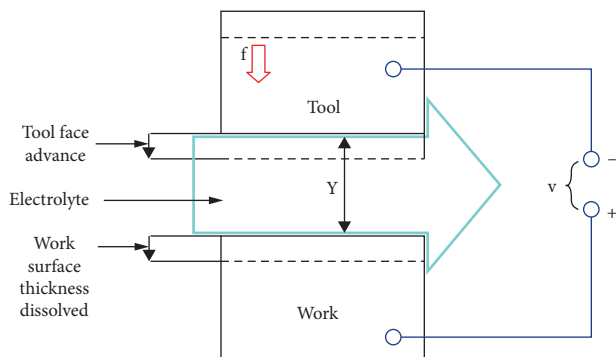


FIGURE 3: Mechanism of ECM process.

efficiency along with better surface quality [12]. Alkalis, including sodium hydroxide generally, are not recommended as electrolytes since they tend to promote the formation of the passive film. Due to the precipitation caused by the hydroxide ions, the IEG needs to be larger to accommodate the film thickness. The alkali electrolytes also tend to have the problem of clogging due to the precipitates. But some of the metal systems, such as tungsten carbide, are preferably soluble in the alkali electrolytes such as potassium hydroxide and can be used for particular metal systems only.

Nonaqueous electrolytes are nonpassivating electrolytes since they do not allow the oxygen molecules necessary for forming the passive oxide films. They are beneficial for the metals forming the metal oxides, but these electrolytes have the problem of dissolving the metal ions resulting in lower conductivities of the solution [3]. Some of the nonaqueous electrolytes are gel electrolytes, dry polymer electrolytes, ceramic electrolytes, ionic plastic crystals, etc. [13–15]. They can also operate at the small IEG since the gases and precipitation products are not produced. Solid electrolytes are already used in machining metal workpieces. Sjöström and Su have performed rapid micropatterning on the titanium using ethylene glycol electrolyte [16]. They also observed that there was no emission of gas and precipitation.

One of the most common electrolytes used in the ECM process is concentrated sodium chloride (NaCl). It is used

for machining stainless steel when a very shiny surface is required. Sodium chloride does not produce the layer on the stainless steel metal, and this allows the workpiece to be machined easily and quickly. Another electrolyte named sodium nitrate is normally used for machining the steel in case a very close replication of the tool is required. Sodium nitrate prevents stray corrosion, which helps to obtain a highly precise replica of the tool [3, 17]. The extent of current density also impacts the ECM process. For instance, in the case of sodium nitrate electrolyte, high current density leads to anodic dissolution, whereas the low current density increases passivation of the electrolyte [3].

ECM process is improved by employing the oxygen-rich electrolyte. Murugan and Jain investigated the effect of the cathode on the distribution of temperature in the ECM machining process. They made use of sodium chloride along with the enrichment of oxygen. From the experimentation, they determined that the material removal rate got increased with the addition of oxygen to the mixture [18]. Trimmer and others have used 0.05 M of hydrochloric acid for creating submicron nanoresolution structures. It is obtained on the substrate of the nickel surface [19]. Research studies have determined that the more concentrated electrolyte in conjunction with an increase in current density increases machining, and tool performs overcutting of the workpiece [20]. Rathod et al. have found out that, with the increase in the concentration of electrolyte, the resolution of the machining process gets reduced. This was because, with the increase in the electrolyte conductivity, the ions available for the reaction would be in increasing number [21]. It has also been identified that the resolution of the ECM process can be easily improved by adding the electrolyte resistance across the solution [22].

Fan et al. noticed that the mixture of the sodium chloride along with the HCl acid brought an increase in the electrolyte concentration, which lead to the machining overcut [23]. This indicates that the positive correlation of the mixed electrolyte with the concentration of the electrolyte helps to increase the machining rate. Hence, the varying concentration of the electrolyte has its advantages and disadvantages. With the lower concentration electrolyte, chemical

etching is particularly lower compared to the highly concentrated electrolyte. This is particularly beneficial in the machining of micro-sized particles [24]. Moreover, the electrolyte concentration is found to have an impact on the current density, ultimately leading to the change in machining resolution. The lower concentration of electrolyte can therefore produce higher machining resolution [25]; on the other hand, the increase in concentration has its advantages. Ayyappan and Sivakumar concluded that the higher concentration of the electrolyte helped to increase the surface finish of the machined workpiece [26]. Zohoor et al. have researched the effect of electrolytes and their nature on the ECM process of 304 Steel [2]. They compared the working of electrolytes such as sodium nitrate, sodium chloride, and potassium chloride at different currents. From the research, they found out that the material removal rate (MRR) is higher for NaCl and KCl compared to the NaNO₃ at the same working conditions. Side gap was found to be highest for KCl, with NaNO₃ having the least side gap. Surface roughness was observed to be increasing with the current for sodium nitrate, but it was the opposite for sodium chloride and potassium chloride.

Researches show that when a particular amount of acid is mixed with the natural salt electrolytes, it tends to increase the side gap and material removal rate in comparison with the pure natural electrolytes. Moreover, the surface roughness is also found to be in decreasing trend with the mixed electrolytes [2]. But in the case of the alkali or oxidant electrolytes such as sodium bromate (NaBrO₃), the production of oxide passive layer negatively impacts the machining rate along with the dimensional and geometrical accuracy [27]. In the case of alkaline electrolytes, the mixing of two electrolytes can improve the machining accuracy of the ECM process. Sabahi and Razfar have investigated the effect of mixing of sodium hydroxide and potassium hydroxide on the machining efficiency of the electrochemical discharge machining (ECDM) process. They found out that the mixing of two alkaline electrolytes increased electrical conductivity. The mixing also helped to increase the microchannel depth and limited the stray erosion of the workpiece. They also noticed that the increased concentration was achieved due to mixing, and the surface finish was also observed to be better when the alkaline electrolytes were mixed [28].

5. The Solubility of Electrolyte with Complexing Agents

Complexing agents are mainly used for dissolving the electrolyte with the metallic ions in the ECM process. Complexing agents are highly soluble in water and have high complexing ability and low viscosity, which makes them suitable to be used in the ECM process. They have a ligand structure that gets attached to metallic and hydroxide ions. Some of the ligand structures are calcimines, complexone groups, polyhydroxy acid groups, etc. In the ECM process, the workpiece placed in the anode terminal gets oxidized into metallic ions. In case of reaction with neutral electrolyte, the workpiece forms the layer of hydroxide precipitate with

the electrolyte. When the complexing agent is added to the electrolytic solution, the ligand of the complexing agent gets intermixed with the hydroxide ions and oxygen molecule with the metal ion to produce the clathrate. This product, known as clathrate, is soluble in water. The complexing ability of the agent determines the stability of the clathrate product. Hence, in this way, the insoluble products in the ECM process get dissolved with the help of the complexing agents [29].

The addition of the complexing agents can drastically improve the metal removal rate of the ECM process. The experimentation was conducted by Yong et al. on various composite electrolytes along with some of the natural electrolytes such as NaCl, NaNO₃, and NaClO₄. They observed that the metal removal rates of natural electrolytes, including NaNO₃ and NaClO₄, were identical. They added complexing agents and additives to the natural electrolytes and observed the metal removal rates of the ECM process. They found out that the MRR of natural electrolytes having the EDTANA₂ and tea as additives or complexing agents got improved by 22% and 10%, respectively. Moreover, the addition of complexing agents, namely sodium citrate, sodium gluconate, and sodium tartrate in the electrolytes increased the MRR by 35%, 43%, and 34%, respectively [12].

The electrolyte also plays an important role in the removal of excess heat from the reaction zone. Excess heat originated during the reaction can severely affect the tool and electrolyte. Excessive heat during the reaction also produces bubbles across the IEG and can cause boiling of the electrolyte [3, 23]. Electrolyte heat dissipation is necessary because the high amount of heat during the ECM reaction also leads to the poor surface quality of the machined workpiece. Research conducted by Bannard also indicates that the temperature of the electrolyte above 40 degree Celsius produced a gradually poorer surface quality of the workpiece [30]. Hence, it is very important to avoid the boiling of electrolytes. For prevention of boiling, the temperature of the electrolyte must be lesser than the boiling point of the electrolyte. N. K. Jain and V. K. Jain [31] have presented the equation for the temperature constraint of the electrolyte in the ECM process, which is given as follows:

$$T_b - T_{in} + \frac{1.0}{\alpha_K} \left[1.0 - \left(1.0 + \frac{S_k}{(1.0 - \alpha_{vo})^n} \frac{f^2}{U} \right)^{0.5} \right] \geq 0.0, \quad (2)$$

where T_b = boiling temperature of the electrolyte, T_{in} = electrolyte temperature at the inlet, α_K = temperature coefficient of electrolyte, f = tool feed rate, and U = electrolyte flow velocity.

6. Conclusion

According to this research study, it is presented that different reviews and experiments in electrochemical machining are already conducted. The electrochemical process, including the importance of electrolytes in the machining process, is reviewed. The most important component of the ECM process, known as the electrolyte, is also discussed in detail

and the importance of the mixing of electrolytes is also reviewed. The chemical properties and function of different electrolytes and the impact of passive films on the machining process are also discussed.

While it is very difficult to select the particular type of electrolyte for general use in the ECM process due to the variation of properties of different electrolytes and workpieces, it is possible to find out more suitable electrolytes for certain applications. Acidic electrolytes such as HCl and H₂SO₄ are preferred in electrochemical micromachining due to higher machining efficiency and accuracy of surface finish. Natural electrolytes such as NaCl and NaNO₃ are nontoxic and do not cause any harm to the tool and workpiece. They also ensure that the passive film on the workpiece does not exist. Solid electrolytes such as gel, polymer, and ceramic electrolytes are used when the passive film is highly undesirable, and IEG is small.

Mixed electrolytes formed by intermixing of electrolytes with the complexing substances are highly efficient compared to the traditional electrolytes. Mixed electrolytes are found to be better in terms of machining rate, surface finish quality, electrolyte solubility, etc. Other mixed electrolytes formed by mixing two electrolytes are also found to be higher in concentration compared to the individual electrolytes. The electrolyte concentration also is found to be positively correlated with the machining rate and surface finish quality.

From the study, it is evident that the intermixing of different electrolytes can improve the various process parameters of the ECM process. Further research regarding the complexing agents and their impact on the solubility of various electrolytes are also necessary.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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