

INORGANIC LIQUIDS USED FOR DIMENSIONAL PROCESSING THROUGH COMPLEX ELECTRICAL EROSION

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ABSTRACT: *In the processing through complex erosion conductive liquids are used (diluted solutions of the inorganic salts: nitrate potassium, sodium carbonate, sodium nitrate, sodium chloride and potassium perchlorate). The essential functions of the electrolyte used in the processing through complex erosion are: ensuring the presence of the electrical charge carrier within the space between the electrodes as well as the anodic dissolving of the piece to be processed. The electrolytes used in the processing through complex erosion have to ensure the initiation and promoting the process of anodic dissolving. On the other hand the cathodic process has to ensure a maximum efficiency, through a lower quantity of metallic ions deposit.*

KEYWORDS: processing, complex erosion, inorganic liquids, current density

1. THE ROLE OF INORGANIC LIQUIDS IN DIMENSIONAL PROCESSING BY COMPLEX ELECTRICAL EROSION

Conductive liquids are used in the processing through complex erosion (diluted solutions of inorganic salts: potassium nitrate, sodium carbonate, sodium nitrate, sodium chloride and potassium perchlorate) [1, 2].

The essential functions of the electrolyte used in complex erosion processing are: ensuring the presence of electric charge carriers in the space between the electrodes and the anodic dissolution of the piece to be processed. The obtained ions can participate in the reactions with the electrodes. Generally used electrolytes are aqueous solutions of inorganic compounds, but in some cases non-aqueous solutions may also be used.

At the anode, the electrolyte must ensure continuous dissolution of the piece to be processed and the composition of the electrolyte must be chosen in such a way to avoid the formation of insoluble reaction products that may cause passivation of the object to be processed. The properties of the electrolyte solution are largely influenced by the nature of the anions and cations present, very good results being obtained with electrolytes containing halogen ions (Cl⁻, F⁻) [3].

The reaction of the electrode occurring at the cathode is important because the release of the positive ions must not influence the anodic dissolution. Thus it is important to avoid the metallic ions discharge at the cathode [3].

The electrolytes used for complex erosion processing must ensure the initiation and promotion of the anodic dissolution process. On the other hand, the cathodic process must ensure maximum efficiency, by depositing a small amount of metal ions, as small as possible.

2. GENERAL CONSIDERATIONS ON INORGANIC WORKING ENVIRONMENTS USED FOR PROCESSING BY COMPLEX ELECTRICAL EROSION

When choosing the optimum electrolyte, it is necessary to take into account a number of factors that may not always be fully observed, which sometimes leads to compromises in choosing the electrolyte solution.

The characteristics of the electrolyte solutions used in processing through anodic dissolution are [4, 5, 6]:

a) Concentration of electrolyte solution

A concentrated solution has the advantage of low voltages due to the corresponding conductivity. At the same time, the electrolyte speed is high because the conductivity of a concentrated solution slightly changes with temperature. On the other hand, diluted electrolyte solutions result in a smooth processing surface and decrease the probability of crystallization. A super-concentrated solution can become saturated, thus causing the formation of crystals that can damage pumps, pipes, etc.

b) Electrolyte conductivity

This parameter depends primarily on concentration and temperature, and must be constantly monitored, as it directly affects the processing speed. At high conductivity penetration speed is also high. The electrolyte conductivity changes with temperature; for a NaCl solution, the conductivity is 100% at 700°C.

Figure 1 shows the effect of temperature on the electrolyte resistance for five electrolyte solutions. Any change in the electrolyte conductivity affects the OP geometry, because the processing depth depends on the conductivity. For these reasons the temperature must be kept under control. Maintaining a low temperature and a high current intensity requires cooling operations.

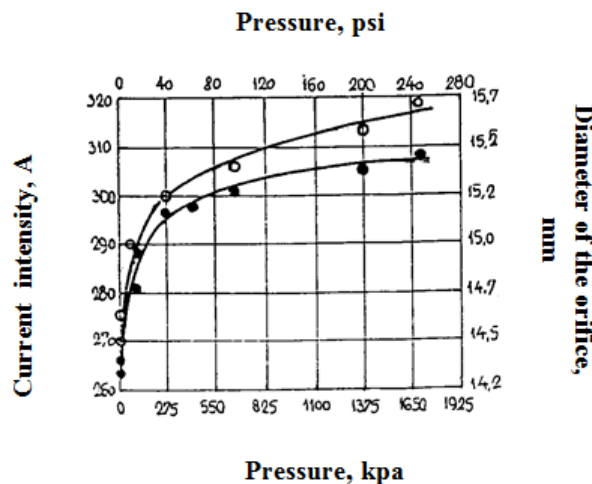


Fig. 1 The effect of temperature on the electrical resistance of the electrolyte

c) The electrolyte flow velocity

This parameter is particularly important because the electrolyte must remove heat and reaction products. The higher the flow velocity is, the more efficient is the removal of heat and reaction products. At the same time, with the increase of the electrolyte speed the cost of the pumping operation also increases, and the excessively high speeds can cause the erosion of the OT or the OP. Flow velocity influences surface finish and processing accuracy. High flow rates result in uniform metal removal. Slow flow rates cause sediment adhesion to the OP, which can cause changes in the flow regime and affect the working regime.

The geometry of the tool to be processed also influences the flow rate of the electrolyte. In order to obtain a smooth, uniform surface of the OP, the geometry of the tool must ensure a uniform flow rate.

The size of the interstice is directly proportional to the voltage and inversely

proportional to the feed rate and the electrolyte resistivity. If the voltage, feed rate and resistivity of the electrolyte can be maintained constant in the gap, then the space between the electrodes will remain constant. Unfortunately, the electrolyte resistivity cannot be maintained constant because in the electrolytes gas bubbles and a certain amount of heat are formed. The gases that are formed tend to increase their resistivity and the heat tends to decrease it. The conditions in the working interstice are also affected by the electric field, which in turn is influenced by the electrode shape. The intensity of the electric field and the current density are more pronounced around the electrode.

If the feed rate of the OT is higher than the rate of removal of the metal, the interstice becomes smaller and smaller. With the decrease of the interstice, the current, respectively the rate of removal of the metal increases proportionally. At some point the removal rate of the metal will be equal to the feed rate of the electrode.

At first, as the feed speed decreases, the interstice will increase. As a result, the current intensity will decrease due to the increasing of the resistance. Optimal accuracy is obtained by maintaining all the parameters constant.

In order to avoid corrosion of machining equipment and to ensure the highest reliability, both electrolytes and reaction products should not exhibit corrosive action. The choice of the electrolyte must also take into account its degree of toxicity so that it should have a minimal degree of danger and the reaction products resulting in the processing should be non-toxic, ensuring optimum processing conditions.

Thus, when choosing the optimum electrolyte, it is necessary to take into account a number of factors that may not always be fully observed, which sometimes leads to compromises in choosing the electrolyte solution.

d) The material of the object to be processed

The material of the object to be processed affects the removal speed of the metal and the current density.

3. TYPES OF ELECTROLYTES USED IN ANODIC DISSOLUTION PROCESSING OF VARIOUS ALLOYS

Mineral acids are good conductors of electricity due to the presence of hydrogen ion which has a high mobility. One of the advantages of processing with this type of electrolyte is that the predominant cathodic process will be the discharge of hydrogen ions, that of the metal ions having no significant weight [3, 4].

The release of hydrogen will cause the conductivity of the electrolyte solution to decrease over time, at the same time causing the lowering of the pH of the solution, which favors the deposition of metal ions at the cathode. Acid electrolytes are generally corrosive, which is why they are less frequently used.

For most metals, alkaline electrolytes are not suitable due to the formation of an insoluble anodic layer of reaction products which prevents the dissolution of the part to be processed. These electrolytes are more suitable for the processing of metals whose stable compounds are those in which the metal is present more in anionic form than in cationic form.

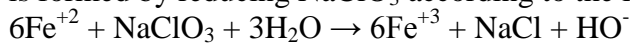
Aqueous salt solutions have lower electrical conductivity than acids and alkalis, but have a lower corrosivity. The anodic reaction leads to the formation of anionic metal compounds and the cathodic reaction involving the interaction of electrons and water molecules causes the release of hydrogen and hydroxyl ions. Anodic and cathodic products interact with the formation of insoluble metal hydroxides which are removed from the workspace by pumping the electrolyte solution [7, 8].

Among the inorganic working mediums, which favor the process of anodic dissolution in the processing through complex electrical erosion, we can mention [2, 3, 4]:

a) Sodium chlorate, NaClO₃

Sodium chlorate is one of the electrolytes that promote the anodic dissolution process when processing through complex electrical erosion. For this electrolyte most of the anodic dissolution process takes place at low values of potential; the iron dissolves in the form of bivalent Fe⁺² iron which can be oxidized by oxygen dissolved in trivalent iron, Fe⁺³. As the electrode potential increases, a critical value of the current density is reached, the surface of the anode being covered with an oxide layer, Fe²O³. By forming the oxide film, the anodic dissolution process is inhibited, the passivation state being installed.

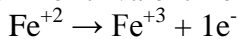
The cathodic reaction is the release of hydrogen. During the anodic dissolution process, NaCl is formed by reducing NaClO₃ according to the following reactions:



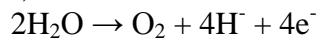
These results are determined by the oxide film formed on the surface of the anode, which is considered to be porous allowing the rapid passage of the cations, having small and randomly distributed pores. At the same time, the film acts as a barrier that prevents the reaction products from moving. The removal rate of the metal decreases over time depending on the thickness of the oxide layer.

The electrochemical processes that take place are the following:

The anodic reaction of oxidizing the iron which passes into the electrolyte solution in the form of trivalent iron:



By decreasing the amount of the metal removed, part of the current is used to generate oxygen, the electrode reaction being as follows:



With increasing current density, the oxide film becomes thin so that the metal removal rate increases. Because iron oxide has higher solubility at low pH values, the decrease of the oxide film thickness may be caused by low pH values near the anode surface.

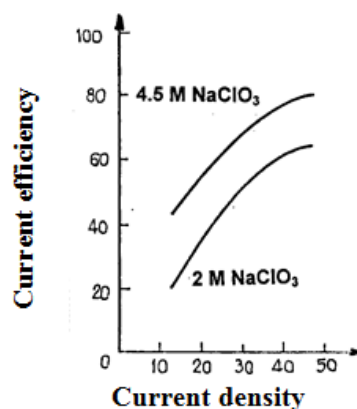


Fig.2 Current efficiency at dissolution of the bivalent iron ion according to the current density

From Figure 2 it is shown that the addition of sodium perchlorate, NaClO₄, in an electrolyte based on sodium chlorate, NaClO₃, causes an increase in the current efficiency. The oxide film formed is influenced by the concentration of the new electrolyte solution. The

main effect of adding the NaClO₄ solution is to decrease the oxidation power of the sodium chlorate solution.

At high concentrations of NaClO₄, this compound will attack the oxide film causing the phenomenon of pitting (a concentration higher than 0.25M). The processing through complex erosion of iron and steel in electrolytes based on NaClO₃ is different from the processing of nickel in the same electrolytes.

Under identical operating conditions the maximum nickel processing speed is half the steel processing speed. Measurement of the roughness of the obtained surfaces resulted in values ranging from 0.25 ÷ 0.39 μm for nickel as opposed to 0.026 ÷ 0.052 μm for steel. These results are in accordance with the measurement of the polarization phenomenon, which indicates that at high current potentials, , under similar conditions, the thickness of the anodic film on nickel as opposed to the oxide film on steel becomes thinner, more uniform.

b) The mixture solution, consisting of sodium perchlorate, NaClO₄, and sodium nitrate, NaNO₃

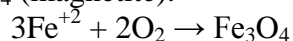
In this case, the influence of the electrolyte solution on the processing through complex electrical erosion was also pursued. Thus in a 2M and 4M NaClO₄ electrolyte solution at a current density of between 26 ÷ 47 A/cm², the current efficiency at hydrogen generation is almost 100%. At the anode, the current efficiency at metal removal and oxygen generation is almost 90%. The small amount of oxygen released in a NaClO₄ - based electrolyte solution compared to that released in a NaClO₃ - based solution is due to the thinner oxide film that is formed by using this type of solution.

c) NaNO₃ sodium nitrate

The results obtained for the processing based on the anodic dissolution in a NaNO₃ electrolyte are totally different from those obtained in other electrolytes. The cathodic reaction in this case is the reduction of nitrate, observing the occurrence of ammonia, hydroxylamine and nitrite during processing through complex erosion.

The current efficiency obtained is much lower than in the case of using the electrolyte based on NaClO₃, some of the current being consumed for oxygen release at the anode.

The oxide film formed with a passivizing role in a sodium nitrite electrolyte is based on Fe₃O₄ (magnetite):



A part of the iron can be dissolved in the form of ferric ions, and a part of the oxygen is consumed when oxidizing the reaction products in order to form the iron hydroxyl.

The properties of the working medium based on sodium nitrate, NaNO₃, can be improved in order to favor the formation of the oxidizing layer with a passivizing role, by adding chemical compounds (additives).

Japanese specialists have shown that by adding additives to the sodium nitrate solution the performances obtained at high current densities can be improved.

The presence of inorganic substances playing the role of additives in the electrolyte based on NaNO₃, contributes to the acceleration of the anodic dissolution process of the metal during the processing through complex electrical erosion, which has a positive influence on the formation of the passive film.

4. CONCLUSIONS

The use of inorganic working mediums in the processing through complex electrical erosion, determines an intensification of the processes of anodic dissolution of the OP metal.

Electrolytic dissociation of inorganic salt solutions contributes to the formation of a

large number of electric charge carriers in the workspace. Under the influence of the electric current the negative ions NO_3^- and ClO_3^- move towards OP connected to the anode, where they meet the metal ions Me^{+z} resulted from the anodic dissolution of the part. Following the chemical reactions that take place on the surface of OP, a film based on inorganic compounds will be formed which can have different structures. Thus, upon the anodic dissolution of the steel in the PP composition, oxides are found: Fe_2O_3 , Fe_3O_4 , compounds based on nitrates $\text{Fe}(\text{NO}_3)_3$ or chlorates $\text{Fe}(\text{ClO}_3)_3$.

The use of inorganic working liquids has the following advantages:

- due to the preponderance of the electrochemical phenomenon, of anodic dissolution, the obtained surface of the OP has a small roughness, it is smooth and no further finishing processing is required;

- no deposits are formed on the surface of the processing machine.

However, the disadvantages of these types of working mediums limit their use for dimensional processing through complex electrical erosion. Major disadvantages include:

- the low mechanical and electrical resistance of the PP determines the increase of the leakage component of the electric current, leading to inaccuracies of processing;

- the productivity of processing decreases;

- due to chemical reactions, corrosive compounds are formed and they cause the wear of the machine:

- harmful aerosols are released.

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