

PROCESSING OF CHROME ALLOYED STEELS BY COMPLEX EROSION IN A SOLUTION OF SODIUM SILLICATE, KAOLINE AND SODIUM NITRATES

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ABSTRACT. At the processing by electrochemical and electrical discharges, an important influence has the working solution.
This paper presented the results obtained by applying of a mixture between colloidal and inorganic solutions that will remove the drawbacks of both media and lead to the increasing of the process efficiency.
For the best solution (silicate 30%+ kaolin 10% +$NaNO_3$ 5%), was analysed the process efficiency Q_p , at the processing by electrochemical and electrical discharges, of the steel bars with different percent of chrome. By comparing the obtained results has been established the best results for processing by electrochemical and electrical discharges steels alloyed with chrome.
KEYWORDS: Colloidal solution, sodium silicate, kaolin, process efficiency

1. INTRODUCTION

The working liquid, at the processing by complex erosion (electrochemical and electrical discharges) has an important influence on the surface quality. In the case of inorganic solutions the anodic dissolution is very important for removing the material. On the work piece surface is achieved a pellicle from oxides, hydroxides or salts, that protects the surface. In this case the surface is smooth, with a small roughness because the metal was removed by anodic dissolution.

In the case when the machining process takes place in colloidal suspensions of kaolin and sodium silicate, the protective pellicle is achieved by an adsorption phenomenon of the colloidal micelles on the work piece surface. The material is especially removed by electrical discharges and the obtained surface has a great hardness.

Most electrolytic media are sodium silicate solutions that have some drawbacks as an adherent and hard to remove pellicle on the work piece surface [2], [8]. Therefore was necessary to find some other solutions that lead to a protective pellicle easily to be removed and in the same time to promote the electrical erosion. The pellicle's type has a major influence on the processing by electrochemical and electrical discharges [1], [2].

This paper work examines mixtures of colloidal solutions with inorganic ones and the obtained results are better than in the case of the other solutions.

Mixtures of colloidal suspension with inorganic solutions improved the process by avoiding the obtaining of an adherent pellicle on the machine surface as well as the increasing of the process efficiency, reducing the processing time.

In the case of colloidal solutions of silicate and kaolin, because of the dielectric properties, the anodic dissolution is less important, the passive pellicle is achieved by selective adsorption of the colloidal micelle on the work-piece surface. Because these adsorption forces are weak the pellicle has a low stability and doesn't protect properly the work-piece surface so are promoted the electrical discharges. The material removing is mainly because of the electrical discharges and the obtained surface will have a great roughness [4].

The colloidal solution promotes the material removing and the increasing of the process efficiency and are preferred instead the inorganic solutions that have not only a low efficiency but also the possibility of a short circuit between electrodes.

Inorganic solutions are preferred when the obtained surface of the work-piece have to be smooth [3].

There have been tested many mixtures of colloidal and inorganic solutions and the best result taking into account the process efficiency and the processing rate, was obtained in an ad-mixture solution of sodium silicate 30, kaolin 10% and sodium nitrate ($NaNO_3$) 5% because of the following considerations:

1. The processing rate is high because sodium silicate is in excess;
2. Decreases the pellicle adherence on the processing tool surface, because a part of the connection forces are consumed to bond the colloidal micelles of kaolin;
3. Increases the solution conductivity as well as the anodic dissolution because of the inorganic solution of $NaNO_3$.

Taking into account the presented advantages it was considered that the mixture of sodium silicate, kaolin and sodium nitrate can be an optimal solution at the processing by electrochemical and electrical discharges of chrome alloyed steels: X210Cr12 (12% Cr), S6-5-3 (4.5% Cr) and 41Cr4 (1.2%Cr).

The colloidal solutions of sodium silicate and kaolin permits the improving of the processing by complex erosion by avoiding the obtaining of an adherent pellicle on the surface of the working machine as well as the increasing of the process efficiency by reducing the processing time.

In the case of the proposed solution, the obtained pellicle by kaolin anaphorese has worse electrical and mechanical properties, so it is necessary to use higher electrically current parameters.

The obtaining of the adherent pellicle on the work-piece surface is explained, in this case, by an adsorption process of the colloidal micelles on the metal surface. Because of the weak adsorption forces the pellicle has a low stability and does not protect properly the work-piece surface so will be promoted the electrical discharges in much more contact points.

2. CONSIDERATIONS ABOUT THE PROPOSED WORKING SOLUTION

The sodium silicate and kaolin solutions permits the improving of the processing by complex erosion by avoiding the obtaining of the adherent pellicle on the surface of the working machine, as well as the increasing of the process efficiency by reducing the processing time.

In this case, the obtaining of the passive pellicle is explained by the anaphors process that consists from migration of the kaolin and silicate particles, negative charged toward the anode surface. The obtained pellicle having a superior mechanical resistance, concentrated the electrically discharges in a reduced number of peaks that corresponds to the most pronounced roughness, increasing in this way the quantity of material removed in a certain time.

The inorganic solution of sodium nitrate was added because promotes the obtaining of a smooth surface as well as the anodic dissolution. Because of its low mechanical resistance it can be easily removed from the work-piece surface and so the material removing by electrically discharges takes place on a greater surface not only at the peaks surfaces. The obtained surface will have a small roughness.

The proposed working solution of sodium silicate, kaolin and sodium nitrate is analysed taking into account the advantages and disadvantages [1]:

a) Sodium silicate: during the metal processing by complex erosion, sodium silicate promotes the obtaining of the passive pellicle by anodic dissolution as well as the electrically discharges because of the particles electrically charged.

In this case, sodium silicate has the module M =2.8-3.2 because in this interval the colloidal particles with negative charges are in a great number and by an electrophoresis process are deposited on the anode surface achieving the protective pellicle.

Sodium silicate in the processing by complex erosion (electrochemically and electrically discharges) have the following advantages:

- Obtaining of some viscous pellicle with high mechanical and electrically resistance;
- Dielectric properties that hinders the short circuit between the working piece and the processing tool;
- high process efficiency;
- Small usage of the working tool.

The drawbacks of sodium silicate are removed because of the mixtures with kaolin and $NaNO_3$:

- A rapid solidification in contact with air because of the water evaporation from the sodium silicate structure;
- Emanating of some poisonous gases.

b) Kaolin: It is one of the argyles suspensions applied at the processing by complex erosion. The obtaining of the passive pellicle is explained by the electro-phorese process when the particles electrically charged migrated towards the electrode under the influence of an electrically field [8].

The main component is kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) that are negatively charged so they will migrate toward anode.

The obtaining of the protective pellicle is because of the colloidal micelles resulted by kaolinite dissociation that due to theirs negative charges are fixed on the anode surface by adsorption forces. Because these forces are weak the pellicle has a reduced adherence and doesn't protect properly the work piece surface, but when kaolin is mixed with sodium silicate these drawbacks disappears.

By utilization of kaolin in the processing by electrochemical and electrical discharges (complex erosion) appears some advantages:

- Increases the process efficiency;
- The material removing from the work piece surface by electrical discharges is greater than in the case of sodium silicate. This

process is due to the pellicle with a low resistance;
- There are not emissions of poisonous aerosols;
- There is not achieved an adherent pellicle on the work piece surface.

c) Sodium nitrate ($NaNO_3$): The inorganic solutions at the processing by complex erosion has the rule to assure the presence of the electrically charges in the space between the electrodes as well as the dissolution of the work piece surface.

At the anode the electrolyte has to assure the dissolution of the work piece and the electrolyte structure must to avoid the obtaining of some insoluble products that can be deposited on the work piece surface.

By electrolytic dissociation [4] of the $NaNO_3$ solution results NO_3^- ions that under the influence of the electrical current migrates toward anode (work piece surface) where meets the metallic ions Me^{+z} resulted by anodic dissolution of the material. By chemical reactions that takes place on the work piece surface will be achieved a pellicle that includes also inorganic components. So at the anodic dissolution of steel the protective pellicle has in it's structure oxides (Fe_2O_3, Fe_3O_4, Cr_2O_3) and nitrates $Fe(NO_3)_3$, $Cr(NO_3)_3$.

These solutions applied at the processing by complex erosion have to assure the anodic dissolution without obtaining of some insoluble compounds that will hinder the process.

By adding of kaolin in sodium silicate is modified the structure of the protective pellicle from the work piece surface.

In the obtaining of the passive pellicle takes place 2 processes:

1) *The obtaining of the components from the pellicle* that consists from the following stages:
- dissolution of the sodium silicate;
- dissociation of the colloidal micelles of kaolin;
- dissociation of $NaNO_3$

2) *Adsorption of the obtained compounds on the work piece surface*

Because the solid pellicle achieved on the metal surface has a major importance in the processing by complex erosion, these stages will be analysed.

1) *The obtaining of the components from the pellicle*

a) *dissolution of sodium silicate* involved a chemical reaction with water:

$$Na_2O \cdot nSiO_2 + H_2O \rightarrow NaOH + Si(OH)_4 \qquad (1)$$

$$Si(OH)_4 \rightarrow SiO_2 \cdot nH_2O \qquad (2)$$

In the case of steels, iron resulted from the metal dissolution by anodic process, reacts with a part of silicic acid:

$$Si(OH)_4 + 2Fe^{+2} \rightarrow Fe_2SiO_4 + 2H_2 \qquad (3)$$

The obtained pellicle achieved on the anode surface has $SiO_2 \cdot nH_2O$, ferrous ortho silicate Fe_2SiO_4 and some traces of silicic acid $Si(OH)_4$.

b) *dissolution of the kaolin micelles* appears because kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ at the high temperature from the working space is transformed and the resulted colloidal particles migrates toward the work piece surface.

The obtaining of the protective pellicle because of the kaolin micelles can be explained by the following considerations:
- Kaolin does not dissociate in ions, it adheres on the work piece surface by adsorption of the colloidal micelles [9];
- Because of the weak adsorption forces the obtained pellicle is less stabile and does not protect properly the surface;
- The increasing of kaolin concentration promotes the electrical conductivity but hinders the electrolyte access in the working space;
- Electrolyte adding influences positively the increasing of the solution conductivity and promotes the obtaining of the anode pellicle.

c) *Dissociation of $NaNO_3$;* the presence of sodium nitrate ($NaNO_3$) in the working space intensifies the anodic dissolution that take place in the first stage of processing by complex erosion.

The global reaction that takes place is:

$$13NaNO_3 + 3Fe + H_2O \rightarrow 13NaOH + 3Fe(NO_3)_3 + NO + 3H_2 \qquad (4)$$

By chemical analysis of the obtained precipitate and of the protective pellicle from the work piece surface, for this working solution, it was be found that the obtained products by anodic dissolution are less in the protective pellicle and more in the precipitate as f ferrous nitrate $Fe(NO_3)_3$. It can be concluded that by adding $NaNO_3$ the anodic dissolution is significantly influenced but it does not appear in the protective pellicle.

2) *Adsorption of the obtained compounds on the work piece surface*

In the adsorption process an important influence has the migration rate of the obtained particles, so the colloidal micelles of kaolin with a high volume migrates slowly under the influence of the electrical current and it is promoted the adsorption of the particles resulted from sodium silicate dissolution.

In the first stage is adsorbed the silicic acid, ferrous ortho silicate and the silica gel, theirs particles are fixed on the anode surface by van der Walls forces.

The protective pellicle has a high mechanical and electrical resistance because of Al_2O_3 from the kaolin structure [5], [6], [9].

In the case of the working solution of sodium silicate 30% + kaolin 10% + sodium nitrate 5%, at the obtaining of the protective pellicle it can be concluded that:

- because of the greater thickness of the pellicle, it covers a greater surface from the work piece and the electrical discharges are achieved in a reduced number of contact points.

As a result the material removed from a certain surface is greater which increases the process efficiency. An important influence on the new pellicle has Al_2O_3 from kaolin structure, that assures a high mechanical and electrical resistance as well as the protective character of the pellicle;

- the adherence of the sodium silicate components from the pellicle is reduced, because a part of the adsorption forces are involved in bonding the kaolin particles, so that at the end of the processing it does not appear the white crust on the surface of the processing machine.

3. EXPERIMENTAL METHOD

The material used for this work is steels alloyed with chrome: X210Cr12 (12% Cr), S6-5-3 (4.5% Cr) and 41Cr4 (1.2%Cr), samples rods had 3 cm diameter and 30 cm length, time=5 min [1].

The chemical composition of the tested steels is presented in table 1:

Table 1 Chemical composition of chrome alloyed steels

Material	Composition, (%)					
	C	Cr	Mo	Mn	Ni	W
S6-5-3 (Rp4)	1.17-1.27	3.8-4.5	4.7-5.2	-	-	6-7
X210Cr12 (205Cr115)	1.9-2.25	11-12				
41Cr4 (40Cr10)	0.38-0.45	0.9-1.20	-	0.60-0.90	-	-

The steel samples were processed in the following conditions for the current intensity I = 75, 100, 125, 150 and 200 A.

For these values was achieved a slot inside the steel bar to measure the breadth of the cut on a depth equal with1/2 from the sample's diameter. For the experiments was used the proposed solution of sodium silicate 30% + kaolin 10% + sodium nitrate 5%.

This colloidal solution promotes the processing by electrochemical and electrical discharges obtaining of an anodic pellicle with a high mechanical and electrical resistance. The process efficiency *(Qp)* was established using the standard mathematical relations [7]:

$$V_{OP} = \frac{\pi}{4} \cdot d_{OP} \cdot b \qquad (5)$$

where V_{OP} is the volume of removed material from work piece in [mm3 /min.]; d_{OP} = final diameter of work piece in mm, b= the slot's breadth in mm.

$$Q_{OP} = \frac{V_{OP}}{t} \qquad (6)$$

t- processing time [min.]

The obtained values for the process efficiency obtained in this type of working solution for steels S6-5-3 and X210Cr12, are presented in the table 2, table 3 and table 4:

Table 2 Dependence of the process efficiency on the current intensity for steel S6-5-3

sodium silicate 30% + kaolin 10% + $NaNO_3$ 5%	
I[A]	Q_p [mm^3/min]
75	529,87
100	1059,75
125	1177,5
150	1180,3
200	1413

Table 3 Dependence of the process efficiency on the current intensity for steel X210Cr12

sodium silicate 30% + kaolin 10% + $NaNO_3$ 5%	
I[A]	Q_p [mm^3/min]
75	706,5
100	1059,75
125	1115,52
150	1324,68
200	1418

Table 4 Dependence of the process efficiency on the current intensity for steel 41Cr4

sodium silicate 30% + kaolin 10% + $NaNO_3$ 5%	
I[A]	Q_p [mm^3/min]
75	567.29
100	639.34
125	730.56
150	890.12
200	958.09

4.RESULTS AND DISCUSSIONS

With the obtained results have been achieved a comparative analysis of the process efficiency Q_p [mm^3/min] in correlation with the electrical current intensity I [A] at the processing of steel bars alloyed with chrome.

In figure 1 is achieved a comparative analyses at the processing of steel bars of type X210Cr12, S6-5-3 and 41Cr4 in the colloidal solution of sodium silicate 30% + kaolin 10% + sodium nitrate 5%.

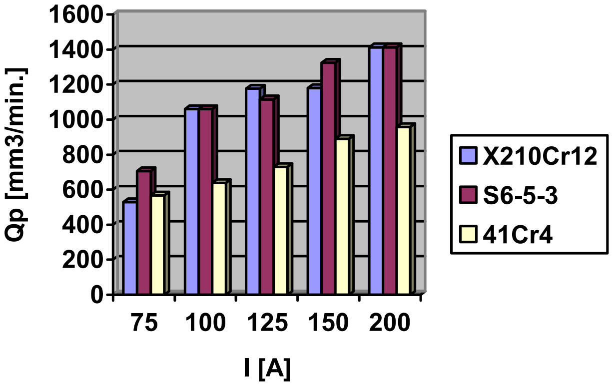

Figure 1 Dependence of the process efficiency Q_p on the current intensity I for steels X210Cr12, S6-5-3 and 41Cr4

5. CONCLUSIONS

The proposed mixture of colloidal and inorganic solutions has many advantages at the processing by electrochemical and electrical discharges:

- High processing rates because of the sodium silicate in excess;
- Decreases the pellicle adherence on the work piece surface because a part of the adherence forces are involved in bonding the kaolin micelles;
- Increases the solution conductivity as well as the material removing by anodic dissolution because of the inorganic solution, $NaNO_3$.

In the case of the working solution sodium silicate 30% + kaolin 10% + sodium nitrate 5%, the anodic process is less important, material removing takes place mainly because of the electrically discharges.

A positive influence of this type of working solution at the processing of steel X210Cr12 can be explained not only by an intensification of the anodic dissolution (because of the inorganic solution) but also by achieving of a protective pellicle that has in its structure oxides Fe_2O_3 and Cr_2O_3.

The presence of sodium silicate and kaolin promotes the obtaining of the protective pellicle and the inorganic solution ($NaNO_3$) 5% intensifies the anodic dissolution.

An important advantage for this working liquid is the fact that sodium silicate is not the only component of it and because of that is not achieved the solid crust on the work piece surface that can be hardly removed. Another advantage is the decreasing of the dangerous substances that are emanating when it is used only the sodium silicate.

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