High-Rate Pulsed Galvanostatic Anodic Dissolution of Chromium–Nickel Steels in Electrolytes for Electrochemical Machining: The Role of Surface Temperature

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Abstract—A pulsed galvanostatic anodic dissolution of chromium–nickel steels (types Kh18N10 (Cr18Ni10) and KhN35VT (CrNi35WT)) under the conditions of electrochemical machining is studied in chloride, nitrate, and mixed chloride–nitrate electrolytes at current densities up to 100 A/cm2. In all the considered solutions (except for the dissolution of CrNi35WT in chloride solutions), for relative pulse durations \( s \geq 2 \) (duty cycle \( D \leq 50\% \)), the faradaic rate of dissolution reaches a limiting value of \( \approx 0.18 \text{ mg/C} \), irrespective of pulse duration (from 20 µs to 2 ms), which translates into the current efficiencies of alloy dissolution of 50 and 68% for the Cr8Ni10 and CrNi35WT alloys, respectively. Using direct current for processing (i.e., \( s < 2 \)) boosts the current efficiency, and the rise in surface temperature is crucial to this effect.

Keywords: electrochemical machining, high-rate anodic dissolution, chromium–nickel alloys, pulsed processing, ECM electrolytes

INTRODUCTION

Electrochemical machining (ECM) is a modern method for materials processing based on high-rate anodic dissolution of metals and alloys in concentrated salt solutions [1–3]. The method has found a widespread use in machining of parts of aircraft engines, including turbine engine blades. The method is evolving and being perfected along the line of pulse machining. With pulsed current, anodic dissolution can be made more confined, and precision in transfer of the tool shape can be improved [2–9]. In addition, it seems to be nearly impossible to use ECM for processing large surfaces while not using pulsed machining. Typically, ECM is applied to chromium–nickel steels and, in particular, high-temperature alloys [2, 3, 10]; therefore, electrolytes often used in these processes are concentrated solutions of chlorides, nitrates, or their mixtures [1–3]. The Faraday law underlies calculation methods for processing rates, as well as their control and distribution across the surface to be processed; however, there are specific features to application of this law under ECM conditions. The applicability of this law depends on current efficiency \( \eta \), a quantity that markedly depends not only on the electrolytes used and processing parameters but it may also change on passing from direct current (dc) to pulsed current. In particular, when applying ultrashort pulses (typically, in the nanosecond range), a fraction of passed charge may not necessarily be related to Faradaic processes but to capacitive current due to the double layer at the interface. Double-layer effects underlie micro-ECM (or µECM), a special variant of ECM [11–13]. With ECM being an electrochemical process carried out under conditions far away from thermodynamic equilibrium, i.e., at high current densities and high potentials, thermokinetic effects based on the interplay between the rate of an electrochemical process and the surface temperature play an important part in controlling this process [14–16]. Studies [7, 17] showed the feasibility to control not only processing rates of chromium–nickel steels and alloys under ECM conditions but also their distribution along the surface being processed (with the purpose to improve processing confinement) using pulsed current with pulse duration in the microsecond range. However, the nature of observed effects is still a subject of discussions. In particular, the role of thermokinetic effects was not addressed because the surface temperature was not measured. In the present paper, we investigate the anodic dissolution rates of chromium–nickel steels under the conditions of
pulsed ECM, with the surface temperature being monitored during anodic dissolution.

**EXPERIMENTAL**

Here, for ECM processing, we used two types of chromium–nickel steels: the high-temperature type CrNi35WT steel and corrosion-resistant type Cr18Ni10 steel; their elemental composition is given in Table 1.

The data listed in Table 1 are the results of X-ray fluorescence analyses carried out before electrochemical processing on an XRS-FP instrument (Xenometrics, Israel). We used so-called activating (sodium chloride), passivating (nitrates), and mixed (chromium–nitrate) electrolytes. The concentrations of salts, as listed below, were such that the electrolytes had the same conductivity (0.15 S/m): 117 g/L NaCl and 230 g/L NaNO₃ for single-component electrolytes, and a mixed chloride–nitrate electrolyte contained 100 g/L NaCl and 80 g/L NaNO₃. The reason is that, under ECM conditions, the primary current distribution is typically observed, while the current efficiency and, therefore, the dissolution rate strongly depend on the anionic composition of the electrolyte [1–3].

Anodic dissolution (i.e., processing) was carried out using a rotating disk electrode (RDE) made of the material to be processed, and the electrolyte followed the electrode’s contours, as shown schematically in Fig. 1. A copper cathode with diameter $d = 3$ mm had a round bore with diameter $d_0 = 1.5$ mm to ensure removal of electrolysis products and heat away from interelectrode gap (Fig. 1) by the electrolyte flow. The RDE with a diameter of 3 mm had a sleeve preventing its side surface from dissolution. In measuring the surface temperature, we used a stationary disk electrode (SDE), which was flowed round by the electrolyte. In this case, a thermocouple was placed at the distance $\delta \sim 1-1.5$ mm (Fig. 1). Initially, the interelectrode gap was set to 0.2 mm. The rotational rate was set constant at 1000 rpm. The rate of electrolyte flow around the RDE and SDE was 0.5 L/min. With the electrode unit geometry adopted in this work, the linear ambient velocity for the working electrode was ~6 m/s. The experimental setup used was described in detail in work [17].

Electrochemical processing (anodic dissolution) was carried out under pulsed galvanostatic conditions, and the current density amplitude during current pulses was in the range of 1 to 100 A/cm²; the phase duration was in the range of 20 $\mu$s to 2 ms. Relative pulse duration $s$ varied between 10 and 1 (the latter corresponds to dc), and duty cycle $D$ varied accordingly between 10 and 100%.

A pulse train diagram (Fig. 2) shows that, for a given current density and pulse duration $T$, the average current density is $i_{av} = i_p/s$, $s = T/\tau_p$, $D = 1/s \times 100\%$, where $i = I/SA$, $I$ is the current in A, $i$ is the current density in A/cm², $S$ is the working electrode area in cm², $\tau_p$ is the phase duration in $\mu$s, $T$ is the pulse duration, $s$ is the relative pulse duration, and $D$ is the duty cycle (%; i.e., the fraction of pulse duration $T$ when the phase in on).

Linear dissolution rate $V_i$ is determined on the basis of Faraday’s law by the following formula:

$$V_i = \eta C i_{av}/\rho,$$

where $\rho$ is the metal density, $\eta$ is the current efficiency, and $C$ is the electrochemical equivalent of an alloy (mg/C or g/(A h)). Product $\eta C$, an experimentally measurable quantity, can be considered as the faradaic dissolution rate. Because quantity $C$ is usually a constant, current efficiency $\eta$ is the quantity to be measured experimentally. Parameter $C$ depends on the values for oxidation states of the alloy’s dissolvable components that were adopted in calculations, and these

### Table 1. Elemental composition (wt %) of considered steel types

| Elements | Cr18Ni10 | CrNi35WT |
|----------|----------|----------|
| Cr       | 19.7     | 15.2     |
| Ni       | 10.4     | 33.4     |
| Mn       | 2.0      | 2.2      |
| Si       | 0.44     | –        |
| Fe       | 67.4     | 43.0     |
| Ti       | –        | 1.6      |
| W        | –        | 4.6      |
values can vary considerably depending on dissolution conditions. Therefore, we determined and used both \( \eta C \) (mg/C) and \( \eta \) in this work. In the latter case, the electrochemical equivalents of alloys were calculated assuming that the major components (i.e., Fe, Ni, and Cr) dissolve to give solution species with the lowest degree of oxidation, which is 2 for iron and nickel and 3 for chromium. The degrees of oxidation for W and Ti were taken to be 6 and 4, respectively. That being so, calculated values for the electrochemical equivalent characterizing dissolution of the type Cr18Ni10 and type CrNi35WT alloys were 0.345 and 0.266 mg/C. With pulsed dissolution, the surface temperature changes over the period of time \( T \) (Fig. 2). However, considering that the thermocouple response occurs over a finite period of time, the registered temperature was the average temperature over the processing duration. The time required for the temperature to reach a stable value did not exceed 15 s. Electrolyte temperature \( T_0 \) in the bulk of the electrochemical cell (unit) was maintained constant at 21 ± 2°C. Relative pulse duration \( \tau \) (or \( D \)) was varied in a broad range (from 10 to dc); however, this was achieved in different ways. When varying the relative pulse duration from 10 to 2 \( (D \text{ varied from 10 to } 50\%, \text{ respectively}) \), the phase duration was held constant at 20 µs. And, upon passing to the dc mode \( (D \geq 50\% \text{ and } \tau \leq 2) \), the pulse off-time was held constant (also 20 µs) while varying the phase duration (pulse on-time) up to 2 ms. The electrode used in anodic dissolution experiments was prepared by polishing it with sandpaper and followed by degreasing; before the experiments, the electrode was weighed on analytical balances with a precision of 0.05 mg. After processing, the electrode was dried and weighed again. The weight of material lost as a result of the applied processing was around 10–30 mg.

The surface temperature \( T_s \) was estimated by calculations from measured temperature \( T_m \) \( (T_s \geq T_m) \), because the temperature sensor (thermocouple) was at distance \( \delta \) from the electrode surface. In estimating this quantity, we considered that the heat transfer into the metal and the solution occurs by a thermal conductivity mechanism, and convective heat transfer in the solution was also taken into account.

The composition and morphology of a processed surface were studied using scanning electron microscopy (SEM) on a Hitachi TM 360 instrument equipped with an attachment for energy-dispersive spectroscopy (EDS) for elemental analysis.

**RESULTS AND DISCUSSION**

Results of measurements of faradaic dissolution rate (in mg/C) presented in Fig. 3 (pulsed current density of 50 A/cm² and \( s = 10 \)) show that \( \eta C \) remains constant in the entire range of phase durations, which fall into the microsecond range, irrespective of the nature of material, the type of anion (activating or passivating), and the pulse duration. This also means that the current efficiency remains constant and that it depends on neither the pulse duration nor the nature of anion. This result, i.e., that the current efficiency does not vary with the pulse duration, is of great importance in view of proving that the capacitive current and double-layer effects are immaterial here, otherwise (i.e., if these are present) the faradaic rate of dissolution and \( \eta \) would increase on increasing \( \tau_p \).

At the same time, the constancy of \( \eta C \) implies that the current efficiencies must differ substantially for different materials. With the assumed values for electrochemical equivalent, the current efficiency is 54% and 68% for dissolution of type Cr18Ni10 and type CrNi35WT steels. The values obtained for both the dissolution rate and \( \eta \) under pulsed conditions differ substantially from those observed under the dc conditions, with the current density being the same as the average current density under pulsed conditions (here, it is 5 A/cm²). Using dc instead of pulsed current leads to an increase in the current efficiency for the Cr18Ni10 alloy, whereas it decreases in the case of CrNi35WT alloy, as can be seen from Table 3. For
Table 2. Faradaic rates of dissolution observed when applying microsecond pulses with an average current density of 5 A/cm² (i_p = 50 A/cm²) are compared with those observed when using dc with the same current density.

| Steel type | Pulsed current η C, mg/C | dc η C, mg/C |
|------------|--------------------------|--------------|
| Cr18Ni10   | 0.185 ± 0.015            | 0.300 ± 0.005|
| CrNi35WT   | 0.182 ± 0.013            | 0.155 (chloride) |
|            |                          | 0.125 (nitrate,mixture) |

Table 3. Effect of dc current density on the current efficiencies in dissolution of type Cr18Ni10 steel in a chloride solution in the SDE and RDE variants.

| Current density, A/cm² | SDE | RDE |
|------------------------|-----|-----|
| 1                      | 78  | 78  |
| 5                      | 89  | 88  |
| 50                     | 95  | 86  |

Cr18Ni10, we observed only that η C did not depend on the nature of the electrolyte’s anion, as was the case under the pulsed conditions, but we additionally observed the influence of the nature of anion for the dissolution of CrNi35WT alloy (Table 2). The current efficiency for Cr18Ni10 increased to 88%, while it decreased to 47–58% depending on the nature of anion for the CrNi35WT steel.

Apart from the faradaic rate of dissolution, the measured surface temperature T_m also did not depend on the pulse duration (Fig. 4). The data of Fig. 4 pertain to the process of dissolution of Cr18Ni10 steel in a nitrate electrolyte. Similar values were obtained for Cr18Ni10 steel in a nitrate (36.7 ± 1.5°C) and for CrNi35WT (33.2 ± 5.4°C in chlorides and 33.6 ± 3.0°C in a nitrate solution). We note that, despite the scatter of measured T_m values, the average temperature observed in dissolution of the Cr35WT alloy proved to be lower than that for Cr18Ni10 in both chloride and nitrate solutions, which, as will be shown below, is related to the difference in thermal conductivities between these two steel types.

To analyze the results, we must have the data on the dissolution rates (current efficiencies) observed when using dc, and such data for the Cr18Ni10 steel are presented in Fig. 5 and Table 3.

The results presented in Fig. 5 and Table 3 show that the current efficiencies in both chloride and nitrate solutions, as measured in the SDE and RDE variants, differ. In the case of nitrate solution, the difference in current efficiencies is observed for all current density values applied, whereas the increase in measured η values for the SDE variant, compared to the RDE variant, is seen only at high i in the case of chloride solution (Table 3). The decrease in surface temperature that occurs when the electrode begins to rotate may be one cause behind the effect that the rotation of electrode being processed has on the faradaic rate of dissolution, as will be shown below.

For dissolution of the Cr18Ni10 and CrNi35WT steels, the results mentioned above reveal that there is a difference in measured values for surface temperature T_m. Such a difference is even more pronounced at higher T_m, e.g., when the relative pulse duration decreases (D increases accordingly), while the density of pulsed current (50 A/cm²) and τ_p (20 μs) are constant for D ≤ 50% and τ_off (also 20 μs) D ≥ 50% (Fig. 6). The presence of dependence shown in Fig. 6 results from the fact that the surface temperature, while rising...
during the period of a high-current pulse, does not have enough time to diminish during the pulse-off time $\tau_{\text{off}}$, and the decrease in surface temperature is smaller when the pulse-off time $\tau_{\text{off}}$ is less. At the same time, we can state that the measured surface temperature increases with increasing the average current density, because it grows linearly with increasing $D$ (decreasing relative pulse duration $s$) at constant $i_p$. But the data presented in Fig. 5 and Table 3 show that the current efficiency (and the dissolution rate) grow with increasing $T_m$ with the current density fixed at a certain value.

Average $T_m$ values for dissolution of considered steel types in the nitrate and chloride solutions are shown in Fig. 6. As can be seen, $T_m$ does not depend on the nature of anion, a conclusion based on the observed absence of dependence of measured temperatures on the nature of electrolyte used in dissolution, but it exhibits a strong dependence on the nature of material to be processed.

Evidently, the alloy thermal conductivity has a certain effect on temperature distribution in the sample, and the materials under study have different thermal conductivity coefficients ($\lambda_{\text{Cr18Ni10}} = 17 \text{ W/(m K)}$ and $\lambda_{\text{CrNi35WT}} = 13 \text{ W/(m K)}$ at 20°C). The most interesting result that follows from the data in Fig. 6 is the fact that, despite fairly high surface temperature values close to the boiling point, the rise in surface temperature does not affect the faradaic rate of dissolution (the current efficiency). For all the systems studied here, the average $\eta C$ value, with a precision of 5%, was constant (0.174 ± 0.009 mg/C) for $D$ values ranging from 10 to 50% and at temperatures indicated in Fig. 6. The $\eta C$ values for CrNi35WT in chloride-containing solutions were not included in the $\eta C$ calculations shown above. The steel of this type behaves differently in chloride-containing solutions, and the discussion of these differences is beyond the scope of our present study.

The results corroborate the conclusion established above (Fig. 3). Evidently, neither increasing the pulse duration at low surface temperatures (Fig. 3) nor the rise of surface temperature during ultrashot (20 $\mu$s) pulses (Fig. 6) can raise the dissolution rate (current efficiency) under the pulsed conditions. The dissolution rate proves to be fairly limiting (~0.18 mg/C). For the Cr18Ni10 and CrNi35WT alloys, this implies the presence of a limiting value for the current efficiency, which is ~50 and ~68%, respectively. The cause of this limiting behavior is not clear.

Such limitations can be circumvented by simultaneously increasing the pulse duration and surface temperature, which can be achieved under the conditions approaching dc-based processing, i.e., for $D$ values in the range of 50 to 100% ($s$ between 2 and ~1, accordingly) (Fig. 7). As was mentioned above, the experiment for which the results are presented in Fig. 7 was carried under the conditions in which the pulse-off time was maintained constant (20 $\mu$s) and $D$ was made large by increasing phase duration $\tau_{\text{p}}$. As a result, the measured surface temperature $T_m$ rose almost linearly with increasing $D$ (Fig. 6), and, in contrast to the experimental conditions with $D \leq 50\%$, we observed an increase in the current efficiency to values close to 100% (Fig. 7). For both Cr18Ni10 and CrNi35WT steels, $\eta$ grew linearly irrespective of the type of electrolyte used (chloride- or nitrate-containing one). It seems obvious that the effect of temperature on the dissolution rate (current efficiency) can be thought of as thermal activation.

A dependence shown in Fig. 8 serves as proof that this is actually the thermal activation. As can be seen, there is a single dependence of $\eta C$ on the surface temperature, which does not change with the natures of material and electrolyte.

The effect of $T_m$ on the dissolution rate (Fig. 8) can be related to changes in the average current density, inasmuch as the surface temperature grows with increasing $i_{\text{av}}$. However, upon varying the average current density, we did not observe (Fig. 9) a dependence similar to that shown in Fig. 8.

The dependences shown in Figs. 7 and 8 were registered when using the SDE, because the surface temperature was measured specifically under these conditions. However, the actual surface temperature may differ from its measured counterpart $T_m$, and this is indicated by a number of factors: (1) the influence of the nature of steel to be processed on $T_m$, which results from different between thermal conductivities, and (2) the difference in the dissolution rate (current efficiency) between SDE and RDE (Fig. 5 and Table 3). It seems obvious that this may result from the differ-
ence in $T_m$ values, which were not measured in the case of RDE.

$T_s$ values were estimated from the measured $T_m$ values by calculation. Considering the experimental facts described above, we performed calculations while taking into account different heat fluxes: heat flux into the metal and heat fluxes directed away from the surface of dissolving metal into the solution. In doing so, we considered heat removal from the rotating disk and convective heat removal due to a laminar flow passing through the channel.

As shown schematically in Fig. 1, heat-flux density $q$ (W/m²) evolving at the electrode–solution interface can be presented as the sum of the heat fluxes:

$$q = q_1 + q_2 + q_3,$$

(2)

where $q_1 = \lambda (T_s - T_m)/\delta$ is the heat-flux density into the metal caused by thermal conductivity, $q_2 = \alpha_a (T_s - T_0)$ is the heat-flux density due to heat emission into the electrolyte and is related to flow around the anode, $T_0$ is the temperature of incoming flow, $\alpha_a$ is the heat-transfer coefficient for a flat-parallel channel with width $\Theta$, $q_3 = \alpha_d (T_s - T_m)$ is the heat-flux density related to heat flow off the RDE surface, and $\alpha_d$ is the heat-transfer coefficient for the rotating disk.

Surface temperature $T_s$ was determined by solving Eq. (2) and using measured $T_m$ values, and the corresponding heat-transfer coefficients were found in the following manner. Heat-transfer coefficient $\alpha_c$ was calculated from dimensionless equation (3) for laminar flow [18]:

$$\text{Nu} = 0.15 \text{Re}^{0.33} \text{Pr}^{0.43} \left(\text{Pr}/\text{Pr}_s\right)^{0.25},$$

(3)

where $\text{Nu} = \alpha_c \Theta / \lambda_s \Theta$ is the interelectrode gap, $\lambda_s$ is the thermal conductivity of a fluid, and $\text{Re} = \rho \Theta \nu$ (where $\rho$ is the linear flow velocity and $\nu$ is the viscosity of electrolyte). With the value calculated for volume flow rate $V$, we calculated $\rho$ using the following expression for the flow cross section: $F = \pi (d + d_i) \Theta / 2$ ($\rho = V/F$). The calculated value for $\rho$ was 5.9 m/s in all the experiments. The values for parameter $\text{Pr}$ varied between 1.75 and 5.1 [18] depending on temperature. These values were calculated for the temperature that was an average between the solution temperature and $T_m$. We calculated $\text{Pr}_s$, which is for the surface temperature, because the surface temperature was higher than the electrolyte temperature. To calculate $q_3$, we

$\text{Fig. 7.}$ Current efficiency as a function of $T_m$ characterizing the dissolution of (1, 2) Cr18Ni10 steel and (3, 4) CrNi35WT steel in (1, 3) chloride and (2, 4) nitrate electrolytes.

$\text{Fig. 8.}$ $\eta \mathrm{C}$ as a function of measured surface temperature in dissolution of (1, 2) CrNi35WT steel and (3, 4) Cr18Ni10 steel in (1, 3) chloride and (2, 4) nitrate electrolytes.

$\text{Fig. 9.}$ Effect of average current density ($i_{av} = 50 \mathrm{A/cm}^2$) on $\eta$ CrNi35WT steel in (1, 3) chloride and (2, 4) nitrate electrolytes.
used the heat-transfer coefficient for a disk rotating at 1000 rpm and \( \alpha_d = 5.6 \times 10^4 \text{ W/(m}^2 \text{ K)} \) [14, p. 37].

Heat-flux density \( q \) was calculated for pulsed conditions as a product of the average current density and voltage \( U \) (V) measured experimentally under these conditions. At high thermal loadings, \( T_r \) was not calculated because of difficulties associated with evaluating the heat source and determining the heat-transfer coefficient.

Results of calculations are summarized in Table 4. We highlight that the listed \( T_m \) values are average values of this quantity for chloride- and nitrate-containing solutions. We note that the corresponding measured values were similar. For instance, the temperatures found for the dissolution of Cr18Ni10 at an average current density of 25 A/cm\(^2\) (50 A/cm\(^2\) and relative pulse duration \( s = 2 \)) were 95 \( \pm \) 1.5 and 91.7 \( \pm \) 0.5\(^\circ\)C in the nitrate and chloride electrolytes, respectively.

| Electrode, alloy | \( i_{avr} \), A/cm\(^2\) | \( U \), V | \( T_m \), \(^\circ\)C | \( T_r \), \(^\circ\)C |
|-----------------|-----------------|--------|-----------------|-----------------|
| SDE             | 5               | 1.8    | 35              | 32              |
| Cr18Ni10        | 10              | 2.2    | 54              | 47              |
|                 | 25              | 2.9    | 93              | 93              |
|                 | 50              | -      | 178             | -               |
| RDE             | 5               | 1.8    | -               | 29              |
| Cr18Ni10        | 10              | 2.2    | -               | 38              |
|                 | 25              | 2.9    | -               | 78              |
|                 | 50              | -      | -               | -               |
| SDE             | 5               | 1.8    | 27              | 28              |
| CrNi35WT        | 10              | 2.2    | 34              | 38              |
|                 | 25              | 2.9    | 70              | 82              |
|                 | 50              | -      | 125             | -               |

Cr18Ni10 and CrNi35WT steels is \( \sim \)7% on average (Table 4).

In combination with \( \eta C \) measurements (Fig. 3, constancy of \( \eta C \) for \( s \geq 2 \)), the results presented in Table 4 show that the increase in surface temperature does not affect the faradaic rate of dissolution, i.e., thermal activation is absent, in all the cases in which the rise in surface temperature does not reach the boiling point. Further studies are required to determine to what extent it is attainment of the boiling point that leads to thermal activation.

We also highlight that the transition to a film boiling state does not occur at high heat loadings, though the difference between \( T_r \) and the boiling point can be as high as \( \sim \)80\(^\circ\)C, which is a consequence of peculiarities of boiling under the conditions of forced convection (i.e., a high mass flow rate and a relatively small area of the heat surface).

Crucial to this study is the fact that we experimentally observed the conditions in which \( \eta C \) (the faradaic rate of dissolution) remains constant under pulsed conditions in a broad range of \( T_s \) values (spanning from temperatures close to room temperature to those not exceeding the boiling point), and it also does not change with the nature of metal to be processed and the type of electrolyte. We note that \( \eta C \) is the mass of material removed per unit of charge passed.

Such a limitation can be avoided by performing processing under dc conditions. At the same time, this means that there are two aspects to the limiting processing rate under pulsed conditions: a decrease in the average current density and a decrease in \( \eta C \). This phenomenon was demonstrated here by considering (by way of example) the behavior of two materials with similar compositions in the passivating and activating solutions. Further research is required to establish to
what extent this experimental fact can be observed in other systems.

Meanwhile, we can state that the dissolution process under dc conditions becomes a thermally activated process as a result of the rise in surface temperature. It must be borne in mind that it is the rise in surface temperature—and not the increase in current density, including its average value under pulsed conditions (Figs. 5, 7, 8, Table 3)—that ensures the increase in dissolution (processing) rate. It seems obvious that the observed effects should be considered in developing techniques that both boost the rate of pulsed processing and improve its spatial resolution, which determines the precision of tool shape transfer.

The experimental facts revealed in this study have not given us a clue to their nature, yet. We can only hypothesize that the electrochemical formation of anodic oxides on the surface being processed (i.e., the dissolving surface) must be important, or maybe crucial, to our understanding of the peculiarities of the observed phenomena. The morphology and elemental analysis of the surface of a sample subjected to dissolution in a mixed chloride–nitrate solution in the SDE variant under dc conditions (current density of 50 A/cm²) are shown in Fig. 10. In this case, as well as in other cases in which the SDE was used, the morphology and composition of the surface at the periphery and in center of the sample were markedly different, because the local current density is low at the center, which is located directly under the bore in cathode, while the periphery was characterized by the highest current density. As can be seen, on passing to the highest current density, the oxide surface changes from porous to smooth, and the processed surface does not contain any elements other than those inherent to the steel subjected to processing, including the oxygen in the form of an oxide film.

**CONCLUSIONS**

In processing the considered types of chromium–nickel steels in the ECM electrolytes by applying microsecond current pulses with current densities up to 100 A/cm², we found that double-layer effects can be neglected and all the current passing through the system can be considered as faradaic current.

We showed that the faradaic rate of dissolution of the steels has a limit (~0.18 mg/C) under pulsed conditions and it does not change with the nature of electrolyte, type of steel, pulse duration, and relative pulse duration for relative pulse durations $s \geq 2 (D \leq 50\%)$). The limiting dissolution rate that we revealed here corresponds to current efficiencies of 50 and 68% for the corrosion-resistant type Cr18Ni10 steel and the high-temperature type CrNi35WT steel.

A boost in the dissolution rate and current efficiency can be achieved by switching to dc conditions while applying the same current density (higher $D$ or, equivalently, lower the relative pulse duration). In the meantime, the rise in surface temperature (thermal activation) is crucial here.
We showed the feasibility of implementing ECM under conditions when the temperature of solution exceeds its boiling point, which results in the formation of vapor near the electrode; yet, we did not see the process evolve to reach a state similar to film boiling.

We hypothesized that, in pulsed ECM, anodic oxide films are determinant for the dissolution rate and current efficiency to reach specific values.

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