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Experimental investigation on the performance improvement of electrochemical machining process using oxygen-enriched electrolyte

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Abstract This paper investigates the performance enhancement of electrochemical machining (ECM) process by oxygenated aqueous sodium chloride (NaCl) electrolyte. It is experimentally found that the performance parameters such as material removal rate (MRR) and surface roughness (R_a) are greatly improved with this new mix of electrolyte. The oxygen gas is suitable to electrochemically react with aqueous NaCl solution to enhance the oxidation of metal oxides on the machined surface to increase the MRR. In this work, experimental investigations are conducted with both aqueous NaCl electrolyte and oxygenated aqueous NaCl electrolyte on the alloy steel specimen (20MnCr5). Largest MRR of 7.33 g/min with R_a of 1.90 μ m is obtained in oxygenated NaCl environment compared to MRR of 1.98 g/min and R_a of 3.13 μ m in aqueous NaCl environment with machining conditions of voltage (V) of 17 V, tool feed rate (F) of 0.5 mm/min, and electrolyte concentration (EC) of 142.5 g/l of water. Microstructure of surface of the specimen machined with oxygenated aqueous NaCl electrolyte is more homogeneous and promises a good surface quality.

Keywords Electrochemical machining (ECM) . Oxygenated aqueous NaCl electrolyte . 20MnCr5 alloy steel . Material removal rate (MRR) \cdot Surface roughness (R_a)

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Nomenclature

- V Voltage between tool and work piece (volts)
- EC Electrolyte concentration (grams/liter of water)
- F Feed rate (mm/min)
- IEG Inter-electrode gap between tool and work piece (mm)
- C Current (amps)
- t Machining time (min)
- U Flow rate (liter/minute)
- MRR Material removal rate (grams/min)
- Ra Surface roughness (μm)
- RSM Response surface methodology
- CCD Central composite design

1 Introduction

Electrochemical machining (ECM) is capable of machining materials which are very difficult to machine by conventional machining techniques. It is applied in aerospace, aeronautics, defence, die, and medical industries [[1\]](#page-8-0). ECM is a controlled anodic dissolution process at the atomic level of the work piece that is electrically conductive by a shaped tool through an electrolyte. In ECM, work piece is the anode and the tool is the cathode and the electrolyte is pumped through the gap between the tool and the work piece, while direct current is passed through the cell to remove metal in the form of metal hydroxides from the work piece. The anode work piece is dissolved according to Faraday's law. The metal hydroxides and other by-products generated in the process are transported from the gap by the high velocity electrolyte flow. ECM produces almost no tool wear (cathode), almost mechanical forceless machining, no thermally influenced machining zones, high surface quality and low roughness products. However, the fatigue value of ECM machined components

is low due to the surface being stress free. Machining of metals particularly steels plays an important role in many industrial applications. The alloy steels preferably 20MnCr5 are used as good wearing resistance in the applications of boxes, piston bolts, spindles, camshafts, gears, shafts, and other mechanical controlling parts. High material removal rate (MRR) and low surface roughness (R_a) are the performance indicators of ECM. There are numerous investigations available on high anodic dissolution of steels during ECM process. Many chloride salts (LiCl, NaCl, KCl, $MgCl₂$, CaCl₂ etc.,) and NaNO₃ were used as electrolyte in ECM. Haisch et al. experimented with aqueous NaNO₃ (40 % by wt.) electrolyte for high anodic dissolution of 100Cr6 steel. Investigation on the mechanism of metal dissolution, gas evolution, and the solid surface film formation on the substrate of steel were undertaken. High current efficiency (η) was observed with current density of 21 A/cm² due to the formation of more $Fe³⁺$ ions [[2](#page-8-0)]. At low current density, exclusive oxygen evolution is observed. With increasing current density, formation of $Feⁿ⁺¹$ species is enhanced, while the oxygen evolution diminishes. At high current density, surface film formation is very less. However, $NaNO₃$ is a passivating electrolyte and for the same current density, the current efficiency is more with NaCl electrolyte solution. The anodic dissolution characteristics of iron metal with NaCl and NaNO₃ electrolytes were studied by Rosenkranz et al. and discussed the influence of pulsed current on the surface quality [\[3](#page-8-0)]. A transition from predominant oxygen evolution to predominant iron dissolution occurs in the range of 5 to 30 A/ cm2 current density for the electrochemical machining of steel in NaNO₃ electrolyte [[4](#page-8-0)]. A simultaneous formation of $Fe³⁺$ and $Fe²⁺$ with $Fe³⁺/Fe²⁺$ ratio up to 2 increases the dissolution of $Fe₃O₄$. Silkin et al. has presented that anodic dissolution of $St₃$ steel is increased in chloride solutions after electro-thermochemical treatment in nitrate containing electrolyte [\[5\]](#page-8-0). Koji Fushimi et.al examined the anodic dissolution behavior of titanium in chloride-containing ethylene glycol [[6](#page-8-0)]. High anodic dissolution of hafnium in water-isopropanol-glycerin chloride was studied by S.A. Lilin et al. [\[7\]](#page-8-0). The results indicate that hafnium anodic dissolution changes with an increase in either the anodic potential or the temperature of the bath in which the electrochemical machining is performed [\[7\]](#page-8-0). According to the literature, an electrolyte property plays a vital role in increasing MRR. Significant improvement in MRR and R_a was observed when the pulsating electrolyte with frequency of 10 Hz and amplitude of 0.2 MPa used in ECM [\[8](#page-8-0)]. MRR was accelerated more with an increase in pH value of electrolyte than the catalytic effect of hydroxide ions [\[9\]](#page-8-0). The change in anodic dissolution rate is also caused by the change in the composition and properties of oxide film on the metal surface. The participation of more hydroxyl ions as well as the change in the pH value of electrolyte is expected to increase the MRR. More corrosive behavior of electrolyte in addition to electrochemical dissolution provides more scope for improvement in MRR. This paper elucidates the effect of oxygenated aqueous NaCl solution on alloy steel

specimen (20MnCr5) in the electrochemical machining (ECM) in the direction of improving machining performance. Oxygenated aqueous NaCl solution has not been induced as electrolyte in ECM until now.

2 Experimental work

The schematic diagram of proposed ECM set up is shown in Fig. [1.](#page-2-0) It comprises of a power supply, electrolyte supply and filtering system, tool and tool feed mechanism, oxygen supply system, work holding and position system, control panel and frame and housing. A 5–30 V DC potential with current adjustable up to 300 A is applied across the inter-electrode gap (IEG) between a copper tool and an anode work piece. An oxygen cylinder is connected across the NaCl electrolyte flow pipe from tank. Pressure and flow rate of oxygen is controlled by regulator arrangement in the cylinder. Tool is fed against the work piece which is firmly fixed on the vice. Tool feed rate (F) and sufficient voltage (V) and current (C) is set in the control panel.

20MnCr5 alloy steel specimens were commercially obtained for the experiments. The composition of the steel is as follows: Iron 97 %, C 0.20 %, Mn 1.25 %, Si 0.25 %, $P \leq$ 0.035 %, S \le 0.035 %, Cr 1.15 %, and Al \le 0.020. Aqueous NaCl solution was used as basic electrolyte, and the electrolytes were axially fed in to the machining zone. Figure [2](#page-2-0) shows photographic view of the experimental setup. The copper tool with a circular end was used as the cathode. The tool and work piece interaction is shown in Fig. [3](#page-3-0). A crosssectional view of tool is shown in Fig. [4](#page-3-0). It has been reported that the ECM process parameters namely applied voltage, electrolyte concentration, electrolyte flow rate, and tool feed rate play a vital role on machining performances MRR and R_a [\[10](#page-8-0)]. The above selection of parameters has also been confirmed in some other investigations [\[11](#page-8-0)–[13\]](#page-8-0). Asokan et al. kept feed rate and electrolyte concentration constant and varied current, voltage, flow rate, and interelectrode gap in his work [[14\]](#page-8-0). Thanigaivelan et.al exposed that voltage and electrolyte concentration proved to be significant effect on the machining performance [[15](#page-8-0)]. It is learned from earlier works that the feed rate (F), voltage (V), and electrolyte concentration are the significant parameters in ECM. Therefore, these parameters were considered in this work and electrolyte flow rate (U) and interelectrode gap (IEG) were kept constant. A constant flow rate of 10 l/min ensured the uniform mixing with oxygen gas. The experiment was based on central composite design (CCD) of response surface methodology (RSM). RSM is a collection of mathematical and statistical techniques useful for modeling and optimizing the response variable models involving quantitative independent variables [\[16](#page-8-0)]. Twenty tests were required for three parameters with 8 cube points, 6 center points in cube, and 6 axial points to form CCD with α =2. Process parameters with their levels are

Fig. 1 1 Electrolyte tank (NaCl solution). 2 Motor. 3 Pump. 4 Flow control valve of NaCl solution. 5 Pressure gauge for aqueous NaCl solution. 6 Filter and precipitator. 7 Flow meter for aqueous NaCl solution. 8 Three-way joint. 9 Flow control valve for oxygenated aqueous NaCl solution. 10 Flow meter for oxygenated aqueous NaCl solution. 11

shown in Table [1.](#page-4-0) In ECM, the current density is usually high. At low current densities, the metal removal rate is low. In order to have a high current efficiency, a higher current density of 70 $A/cm²$ was used.

In this work, MRR was measured based on weight loss during machining time.

$$
MRR = \frac{m}{t} \text{ grams/minute} \tag{1}
$$

where

cylinder

 m mass of material removed (grams)

 t machining time (minutes)

Fig. 2 Experimental set up of ECM apparatus with oxygen

Specimen masses were measured before and after the machining by weighing machine (BS423S, Sartorius) with least count of 0.001 g. Surface roughness (R_a) of the machined Machining chamber. 16 Workholding vice. 17 Work piece. 18 Tool. 19 Tool holder and feed mechanism. 20 Low voltage high current DC supply

specimen was measured using a surface roughness tester (SJ-201, Mitutoyo) with sampling length of 10 mm. The results are the average of measurements taken three times. Table [2](#page-4-0) shows the experimental results of aqueous NaCl and oxygenated aqueous NaCl electrolytes.

gauge. 14 Pressure gauge for oxygenated aqueous NaCl solution. 15

3 Electrolyte and reaction

3.1 Case 1: aqueous NaCl electrolyte

Aqueous NaCl solution was inducted in to electrochemical machining in order to compare its performance with new

Pressure gauge

Fig. 3 Tool and work piece interaction

oxygenated aqueous NaCl electrolyte. Flow rate of 10 l/min of aqueous NaCl solution was allowed in to the interelectrode gap of 0.2 mm. The electrolyte and water undergo ionic dissociation as potential difference is applied between the work piece (anode) and tool (cathode). The positive ions move toward the tool and negative ions move toward the work piece.

Aqueous NaCl solution dissociate as NaCl
$$
\rightarrow
$$
Na⁺ + Cl⁻ and H₂O \rightarrow H⁺ + (OH)⁻
(2)

The anode, which is a work piece (alloy steel), undergoes an oxidation reaction by which work piece atoms are ionized.

At current efficiency (η) =100 % for NaCl solution, divalent ferrous dissolution is occurred.

$$
Fe^{0} \rightarrow Fe^{2+} + 2e \tag{3}
$$

Trivalent ferrous dissolution occurs at current efficiency (n) <100 % for NaCl solution.

$$
Fe^{0} \rightarrow Fe^{3+} + 3e \tag{4}
$$

Hydroxyl ions (OH)[−] evolve oxygen at the anode as

$$
4OH \rightarrow O_2 \uparrow + 2H_2O + 4e^-.
$$
 (5)

This oxygen formation dominates if no metal dissolution occurs. For NaCl solution, oxygen formation is less.

The hydrogen ions will take away electrons from the cathode (tool) and form hydrogen gas at the cathode.

$$
2H^{+} + 2e^{-} \rightarrow H_{2} \uparrow
$$
 (6)

These hydrogen bubbles may sometimes choke the flow of electrolyte. However, this is avoided by the high velocity of

the electrolyte jet. Within the electrolyte, sodium ions would combine with hydroxyl ions to form sodium hydroxide.

$$
Na^{+} + OH \rightarrow NaOH
$$
 (7)

Ferrous ions would combine with hydroxyl ions and form Fe (OH) ₂ and get precipitated in the form of sludge.

$$
\text{Fe}^{2+} + 2\text{OH} \rightarrow \text{Fe}(\text{OH})_2 \tag{8}
$$

Some amount of Fe (OH) ₃ is also formed in a further reaction. In this manner, it can be noted that the work piece gets gradually machined and gets precipitated as sludge. Moreover, there is no coating on the tool, only hydrogen gas evolves at the tool or cathode. As the material removal takes place due to atomic level dissociation, the machined surface is of good surface finish and stress free.

3.2 Case 2: oxygenated aqueous NaCl electrolyte

In order to enhance the material removal, a new mix of oxygenated aqueous NaCl electrolyte was used. Oxygen was externally supplied with the rate of 0.018406 l/min to mix with aqueous NaCl solution. The ratio of aqueous NaCl solution flow rate to oxygen flow rate is 543. Oxygen flow rate was kept constant throughout the experiment. This rate was found optimal with lots of prior experimentation. Purity

Fig. 4 Cross-sectional view of tool

Table 1 Process parameters and their values at different levels

of oxygen supplied is 99.5 %. Since Oxygen is a strong oxidizing agent, it reacts with aqueous NaCl solution. During the process of ECM, the hydroxyl ions formation is important for machining because these ions react with work piece material to form metal hydroxide which is considered as material removal in this machining. In addition to the electrochemical reactions as discussed for aqueous NaCl solution, further reactions are possible due to more oxygenation. In the oxygenated aqueous NaCl environment, more oxygen is available to the cathode, and combines more with hydrogen ions and form hydroxyl ions (OH) .

$$
2H_2O + 4e^- + O_2 \rightarrow 4OH^-
$$
 (9)

Other possible reactions are the following:

$$
4Na^{+} + 6H_2O + O_2 \rightarrow 4NaOH + 4H_2O
$$
 (10)

$$
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{11}
$$

These hydroxyl ions react with positively charged work piece (alloy steel) ions and produce metal hydroxides.

 $Fe^{2+}+2OH^{-} \rightarrow Fe$ (OH)₂. The reaction further continues as the unstable Fe $(OH)_2$ reacts with more oxygen and form stable Fe $(OH)_3$ which is commonly known as rust.

$$
4Fe(OH)2 + 2H2O + O2 \rightarrow 4Fe(OH)3
$$
 (12)

 $4Fe + 3O₂ + 6H₂O \rightarrow 4Fe³⁺ + 12OH$ (overall reaction)

 (13)

Although NaCl is a non-passivating electrolyte, a small amount of FeO is possible on the machined surface. The ambience of oxygenated environment further oxidizes the FeO and ensures the fresh surface is exposed to the electrochemical dissolution.

Table 2 Results of material removal rate (MRR), and surface roughness (R_a) for different electrolytes

Sl. No	Voltage (V) Volts	Feed rate (F) mm/min	Electrolyte concentration (EC) g/1	Aqueous NaCl electrolyte		Oxygenated aqueous NaCl electrolyte	
				MRR g/min	$R_{\rm a}$ μm	MRR g/min	$R_{\rm a}$ μm
$\mathbf{1}$	14	$0.2\,$	95.0	1.14	3.05	2.83	1.90
\overline{c}	14	$0.4\,$	95.0	1.13	2.95	2.24	1.76
3	17	0.3	47.5	1.66	3.46	2.78	1.75
4	20	0.2	190.0	3.80	3.27	4.69	1.66
5	17	0.3	142.5	1.59	2.99	5.80	2.56
6	17	0.3	142.5	1.62	3.60	5.61	1.78
7	17	0.3	142.5	1.61	3.55	5.79	1.81
8	17	0.1	142.5	2.08	3.23	4.02	1.56
9	14	0.4	190.0	1.58	3.47	4.13	1.59
10	17	0.5	142.5	1.98	3.13	7.33	1.90
11	11	0.5	142.5	1.36	3.11	4.30	1.85
12	14	0.2	190.0	1.87	2.98	3.40	2.10
13	17	0.3	142.5	1.58	2.99	5.49	1.95
14	17	0.3	142.5	1.64	3.00	5.23	2.05
15	23	0.3	142.5	2.14	2.87	6.39	2.01
16	17	0.3	237.5	4.00	2.99	6.83	1.85
17	20	0.4	95.0	1.82	3.67	2.01	1.99
18	20	0.2	95.0	2.08	3.49	3.61	1.75
19	17	0.3	142.5	1.62	3.33	5.15	1.69
20	20	$0.4\,$	190.0	1.61	3.12	3.28	1.57

Fig. 5 Effect of electrolyte concentration on MRR with feed rate of 0.3 mm/min and voltage of 17 V

All the experiments were done with current density of 70 A/cm2 . It is observed that MRR is higher with oxygenated aqueous NaCl for all tests. This is due to the formation of more active oxidation on the machined surface. The oxidizing agent oxygen facilitates the formation of hydroxyl ions which in turn oxidizes the work piece metal and forms sludge. During the electrochemical reaction, surface Fe-O bond strengths are higher than that of the O-O bond. Therefore atomic O is preferably absorbed more on to the metal surface rather than recombined to an O_2 molecule. Metal ion is oxidized to a higher valence state and it becomes more oxidizing (more electron attractive). The absorption of oxygenated intermediates on an oxide surface is tantamount to oxidize the metal active site to a higher valence state. Further supply of oxygen is tantamount to the decomposition of the higher oxide back to the initial oxidation state. Steels have high affinity to oxygen and thus electrolytic oxide films are formed on the surface. $Fe²⁺$ compounds are water soluble while $Fe³⁺$ compounds are insoluble. But a change in pH value of the electrolyte accelerates the $Fe³⁺$ compounds solubility. According to the current efficiency of each test it seems that more Fe^{2+} species are formed. Due to the continuous supply of oxygen, oxides formed on the surface are further oxidized and dissolved in

4 Results and discussion

4.1 Analysis of material removal rate

Faraday's law of electrolysis predicts the rate at which the material is removed from a work piece.

$$
MRR_{\text{theo}} = \frac{MI}{nF} \tag{14}
$$

where,

The current efficiency (η) for the 20MnCr5 alloy steel dissolution was then determined from the mass loss measurements assuming divalent metal ion (Fe^{2+}) formation. The experimental material removal rate $(MRR_{\rm exp})$ can be compared with the theoretical value (MRR_{theo}) calculated using the above equation. Then the current efficiency $(η)$ can be defined as follows.

$$
\eta = \frac{\text{MRR}_{\text{exp}}}{\text{MRR}_{\text{theo}}} \tag{15}
$$

Figure 5 shows the effect of electrolyte concentration on MRR with feed rate is 0.3 mm/min and voltage is 17 V. MRR

the electrolyte.

is directly proportional to feed rate. Higher concentration of salt allows more interactive reaction with oxygen thereby improving metal removal. At the feed rate (F) of 0.2 mm/ min and voltage (V) of 14 V, MRR is low for both the concentrations. MRR is more for the oxygenated aqueous NaCl. It is clear that the higher the voltage and electrolyte concentration, the higher the MRR. Electrical conductance is more at V of 17 V and electrolyte concentration of 237.5 g of NaCl per liter of water. Tenth test reading shows high metal removal with the test conditions of V of 17 V, F of 0.5 mm/ min, and EC of 142.5 g/l.

4.2 Analysis of surface roughness (R_a)

It is observed that surface roughness (R_a) is lower with oxygenated aqueous NaCl electrolyte for all tests. This is due to the uniform and active metal dissolution through the work piece. Deposition of reaction products mainly metal oxides on the metal surface are the reason for more surface roughness (R_a) . This is avoided by more oxygenation, which further converts the metal hydroxides and metal oxides in to a precipitated form. These precipitated products are washed by the electrolyte jet and filtered before reaching the electrolyte tank. This could be the main reason for less surface roughness (R_a) in oxygenated aqueous NaCl environment. Voltage change does not significantly affect the R_a values. Higher concentration of salt allows more interactive reaction with oxygen thereby improving the surface finish.

Influence of electrolyte concentration on R_a with F of 0.3 mm/min and V of 17 V is shown in Fig. [6.](#page-5-0) At a feed rate of 0.2 mm/min and voltage of 20 V, R_a is low for oxygenated NaCl electrolyte with a concentration of 190 g of NaCl per

Fig. 8 Microstructure (various lens) of work piece machined with oxygenated aqueous NaCl electrolyte. a $100 \mu m$ (×150) magnification). **b** 100 μ m (\times 200 magnification). c 100 μ m (×300 magnification). d 100 μ m (×750 magnification)

 (a) (b)

liter of water. With the same cutting conditions, except EC of 95 g/l of water, R_a is slightly high. It is observed from readings that Vand EC significantly affect the machining performance. It is clear that at higher voltage and electrolyte concentration, surface roughness (R_a) becomes lower. Participation of hydroxide ions in the electrochemical reaction is more at higher V and EC. It makes the perfect homogeneous dissolution and reduces the surface roughness (R_a) .

5 Microstructure analysis

The surface structure of the sample and the electrochemical reactions taking place during ECM are strongly dependent on the electrolyte used. The tenth test conditions show a large difference in MRR and R_a for both the electrolytes. Thus, the microstructure of the test specimen at this condition is discussed here.

5.1 Case 1: aqueous NaCl electrolyte (tenth test)

Figure [7](#page-6-0) shows the microstructure of test specimen machined with aqueous NaCl solution with test conditions of voltage of 17 V, feed rate of 0.5 mm/min, and electrolyte concentration of 142.5 g/l. Even though a black solid surface film is formed on the 20MnCr5 alloy steel specimen during electrochemical machining, it is washed away with the high velocity of electrolyte jet. Heterogeneous surface structure is formed with aqueous NaCl solution. White spots in the image are ferrite. Black dots on the surface structure show the metal carbides in the steel matrix. Some irregularities such as troughs are found on the surface. These irregularities are formed due to the deposition of small amount of oxide film (FeO) on the surface. That is the main reason for high surface roughness (R_a) values. More number of Fe^{2+} species takes hydroxyl ions and forms Fe $(OH)_2$ and deposited on the work surface. Small amounts of $Fe³⁺$ species are also produced during the machining.

Largely, this trivalent yellow color ion leaves the surface with the turbulence of the electrolyte.

5.2 Case 2: oxygenated aqueous NaCl electrolyte (tenth test)

Figure [8](#page-6-0) shows the alloy steel microstructure with oxygenated aqueous NaCl solution for the tenth test readings. More carbide particles are clearly visible in steel matrix because of the high anodic dissolution and chemical reaction of ferrous molecules. The surface is a well-defined homogeneous structure. Major contribution of supplying oxygen is to enhance the oxidation of metal oxides on the surface and formation of OH¯ ions. With the turbulence of electrolyte, the electrochemical products on the surface are completely removed from work piece. Black dots on the structure are carbides and small amounts of non-metallic inclusion compounds. It does not electrochemically dissolve. The $Fe²⁺$ ions form solid reaction products, such as $FeCl₂$, Fe (OH)₂, FeO, and other solvated species. Continuous supply of oxygen transforms the unstable Fe $(OH)_2$ to stable precipitate of Fe $(OH)_3$. These reaction products $(Fe_xO_yCl_z)$ are the main components of the surface layer. But it is mainly washed away with the electrolyte jet. No surface layer is found on the images given below.

Figure 9 refers the picture of the test specimen machined with two electrolytes. Machined area in image (b) looks better than image (a). Some deposition preferably oxides can be seen in image (a) but that was completely removed by oxygenated environment due to further oxidation.

6 Conclusion

In this work, electrochemical machining with oxygenated NaCl electrolyte is presented as a way to increase the MRR and reduce R_a for 20MnCr5 alloy steels. Based on the experimental investigations, the following conclusions can be summarized as follows:

- 1. MRR substantially increased with the addition of oxygenated aqueous NaCl electrolyte. This is due to the formation of more hydroxyl ions which in turn produced more metal hydroxides (sludge). Further, due to the affinity of steel toward oxygen, more FeO are formed. Due to the high oxygen content of the electrolyte, the FeO is further oxidized and washed away by the electrolyte jet. Thus, MRR greatly improved.
- 2. Feed rate is significantly affecting the MRR at all test conditions for both electrolytes.
- 3. Higher voltage setting and higher electrolyte concentration produces better MRR and surface roughness.
- 4. Surface roughness is more with aqueous NaCl environment. Though NaCl is a non-passivating electrolyte, a small amount of surface binding such as FeO is possible due to some oxygen formation during the process. Because of less oxygen environment, further conversion of FeO is limited. This irregular presence of oxides on the surface is the reason for more surface roughness. Surface microstructure of the work piece machined with oxygenated aqueous NaCl electrolyte appears to be homogeneous and good surface quality.

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