

Micro Electrochemical Surface and Product Investigations during Electrochemical Machining (ECM) in NaNO_3

Santosh kumar¹, Samer Bahadur yadav², Chandra kant Trivedi³

Assistant Prof., M.Tech scholar Rama University Kanpur UP India.,

Assistant Prof., Department of Mechanical Engineering, Dr. Virendra Swarup Memorial Trust Group of Institutions, Unnao (U.P.) India.

Abstract: The surface structure of the sample was studied during electrochemical machining (ECM) of iron in neutral NaNO_3 solutions. From previous experiments, we expected a duplex structure: a solid oxide film of a few nm and, above, a highly stable and meta stable supersaturated iron nitrate film for MEC in NaNO_3 (current densities ranging from up to 100 A/cm². electrolyte flow) Total current (and charge) and dissolution products were measured during anodic pulses. The formation of Fe^{3+} and Fe^{2+} was followed by UV-VIS spectroscopy and allowed (for the first time) a quantitative determination of the product.

A transition from the predominant release of oxygen to the predominant iron solution in the range of 5 to 30 A / cm² was found. At current densities greater than 35 A / cm², the evolution of oxygen is reduced to a percentage of the total current. The formation ratio of $\text{Fe}^{3+} / \text{Fe}^{2+}$ increases to 2, which corresponds to dissolution of Fe_3O_4 .

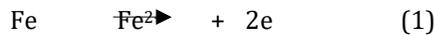
Keywords: A. Iron, steel; B. cyclic voltammetry; C. Transpassivity, passive films, interfaces.

1. Introduction

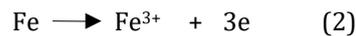
Electrochemical machining (ECM) is widely used to structure metallic materials. Initially sodium chloride solutions were used, but now a days mainly neutral NaNO_3 solution are used to yield products of high quality. ECM means the anodic dissolution of a work- piece with an especially formed cathode eat large current densities. The cathode is more or less the negative mold of the final shape of the work- piece. The advantages are obvious: almost no tool wear (cathode), almost force less machining, no thermally influenced machining zones, high surface quality, and low roughness without additional process steps. Typical ECM conditions are large current densities (about 100 A/cm²) and large electrolyte flow rates (some m/s) to remove products. Thus, an identification of the processes and the structure of the interface of the work-piece with the common electrochemical techniques is critical and requires new techniques. The structure of the metal/electrolyte interface is also open to discussion. Precipitated salt films [1,2], duplex (compact and porous salt) films [3], or super saturated viscous films with limited water dilution [4], or passive films [5] and combinations of these models were proposed. Landolt [6] distinguished 3 fundamental models:

- Rate limiting is the dilution / migration of dissolved cations,
- Rate limiting is the an ion discussion to the surface,
- Rate limiting is the water dilution to the surface

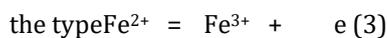
Landolt prefers crystalline precipitates, but supersaturated solution also remain possible. One crucial point is the identification of the products as they can reflect the composition of the surface. The anodic dissolution of Fe in neutral NaNO₃ solutions can follow



assuming an active or trans passive process. This reaction is normally used to calculate efficiencies. If the surface is covered by an oxide film, a passive dissolution according to



is probable. If both processes are involved reactions of



is probable. If both processes are involved reactions of



and can oxidize Fe²⁺ ions in the electrolyte. This process includes the formation of H⁺, and thus, an acidification of the surface. Altogether, four main products are possible,

Fe²⁺, Fe³⁺, H⁺ and oxygen. In the literature, efficiency data are always based on Fe²⁺ formation, a quantitative in situ analysis of the products seemed to be impossible. An interpretation of the data recorded from [7] in NaNO₃ and NaCl solutions indicated a different mechanism in both electrolytes. The current-potential curves extrapolate to values <1 V in NaCl, which is typical for a more or less active surface. In NaNO₃, however, we found values >2 V which are typical for Fe₂O₃ covered surfaces. Our aim was to identify the products quantitatively under ECM conditions at large current densities and under electrolyte flow.

2. Experimental set-up

The problem of potential control at current densities around 100 A/cm² was solved by reduction of the affected area of the sample. With our capillary based droplet cell [8], accessed electrode areas of <10—3 cm² become possible, i.e. we required absolute currents of less than 1 A which were delivered by a common potentiostat. Because of the immobile electrolyte in the previously used capillary cell, anodic products (oxygen bubbles and iron hydroxides) blocked the capillary after some ms. A redesign of the capillary cell fulfilled the following requirements

- Current densities up to 100 A/cm².
- 3-electrode arrangement for potentiostatic potential control.
- Electrolyte flow rates up to 10 m/s.
- Quantitative analysis of dissolution products.

The normal capillary was exchanged by a double barreled capillary. The partition was close to the mouth removed by etching, thus

we could realize a flow-through of electrolyte up to some 10 ml/min via a computer controlled gear pump. A schematic view of the set-up is presented in Fig. 1. More details of this special microcell set-up are given in [9]. The electrolyte outlet of the cell was connected to the flow-through cuvette of an UV-VIS spectrometer (HP 8452 A). The absorption coefficients of aqueous Fe²⁺ and Fe³⁺ ions are not very different and do not permit a simultaneous detection. Therefore, we added 1,10-phenanthroline, which forms complexes of different colour with both iron ions. These stable complexes also prevent an oxidation of Fe²⁺ by O₂. Due to the precise pump flow, concentrations and total amounts can be calculated and compared with the electrochemical charges.

3. Recent result

With the equipment described above we were able to detect all relevant parameters. The total charge q (calculated from current vs. time) is the sum of the charges of Fe²⁺ and Fe³⁺ dissolution and oxygen formation

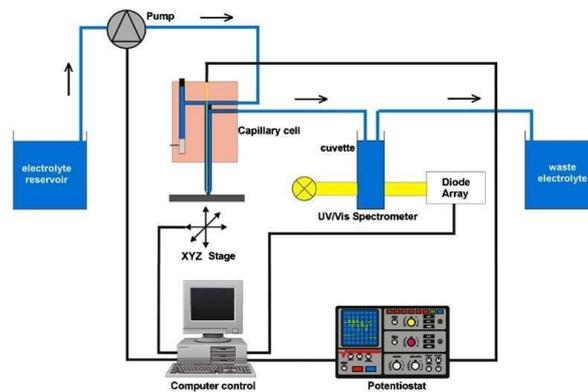


Fig. 1. Schema of the experimental set-up with capillary flow-through microcell and UV-VIS

$$q = q_{\text{Fe}^{2+}} + q_{\text{Fe}^{3+}} + q_{\text{O}_2} \quad (5)$$

If the amounts of Fe²⁺ to Fe³⁺ formation are detected

surprisingly low melting points (26–60 °C) and an extremely low tendencies to crystallize. It took some minutes to days until the first crystals appeared. These meta-stable melts were prepared in bulk amounts and their physical properties (conductivity, viscosity) were determined. They are of high density (around 1.5 g/cm³), highly water soluble, and intensely coloured [10]. Due to the short life-time in a moving electrolyte at large current densities a crystallization can be excluded. Instead, we must expect the formation of a viscous, supersaturated film with a thickness in the range of some 100 nm adherent to the surface during the process. The number of water molecules per ion is only around two. Accordingly, these phases represent a system in between melt and solution, which, accordingly, means a lack of adequate models for their description. The small number of water molecules will be bound to the ions (mainly cations) and, accordingly, the activity of free water will be extremely low. The rate of oxygen evolution will depend on this activity, as water is the educts (Eq. (4)). As already mentioned before, extrapolations of cyclic voltammograms to zero current always yield potentials in the range from 2 to 2.5 V. Clearly, a passive film remains at the surface with properties similar to the normal passive film of Fe₂O₃. This means a duplex

spectroscopically, the amount of oxygen formed can be calculated, i.e. we get a quantitative description of the process. The oxidation of Fe²⁺ by oxygen was prevented by adding a complexing agent (1,10-phenanthroline).

Computer simulations of ion dilution and migration

[10] yielded extremely large concentrations of iron and nitrate ions in excess of 10 mol/l at the interface during machining. This is above the solubility limits. Structure, a solid oxide film of some nm and, above, a supersaturated nitrate film with concentration gradients of the products (increasing in direction to the surface) and water (decreasing in direction to the surface), which will be discussed later. In this paper we want to present quantitative product data of pulse experiments at large current densities and of process efficiency.

4. Pulse experiments

The experiments were carried out in a neutral electrolyte (250 g/l NaNO₃). Small sheets of Armco iron were used as electrodes. To get sufficient product amounts, relatively large capillaries with inner tip diameters of about 500 μm were used. Fig. 2 shows a typical flat hole produced with the capillary cell after a 1 s pulse of 10 V. Though we use the common potentiostatic 3-electrode arrangement, the current is mainly controlled by the potential drop between reference and working electrode and, thus, remains relative constant during the process. In Fig. 2 A mean current density of 28 A/cm² was detected. As our interest focused on the interface structure and the product composition, the shape and surface quality of the machined area was of minor interest. This surface was shiny in Fig. 1, but other preparation parameters yielded also black layers (Fe₃O₄ could be detected in some cases) or hydroxide precipitates, depending on the experimental conditions.

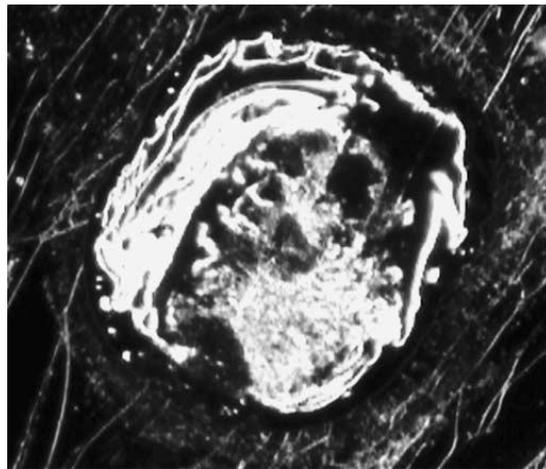


Fig. 2. Typical microscopic view of a flat hole (diameter 500 μm) produced with the capillary microcell (1 s pulse of 10 V). The surface of the hole is shiny in this case; other preparation parameters yield black layers or hydroxide precipitates, depending on the experimental conditions (current density, electrolyte flow, geometry of the cell).

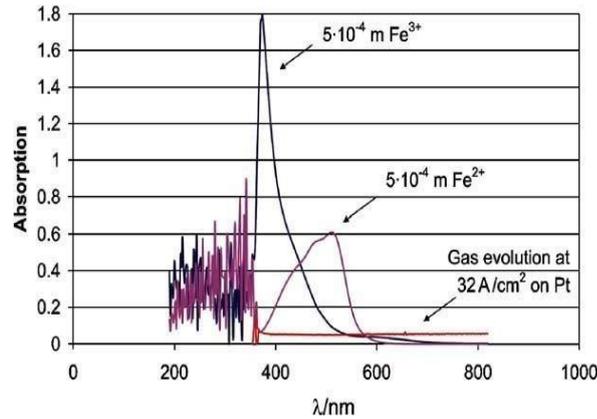


Fig. 3. Calibration spectra of the iron phenanthroline complexes ($5 \cdot 10^4$ molar solutions) from the UV- VIS spectrometer. The noise at wavelengths <350 nm are artefacts of the supporting electrolyte (phenanthroline and 250 g/l NaNO_3). Gas bubbles caused an almost wavelength independent absorption.

A flow through cuvette was connected to the outlet of the capillary cell and enabled an in situ analysis of the machining products. 1,10-phenanthroline was added to the electrolyte to yield convenient absorption spectra and to stabilize Fe^{2+} against oxidation by the dissolved oxygen. Calibration spectra of the iron phenanthroline complexes are presented in Fig. 3. Nitrate dominates the spectra at wavelengths <350 nm. Therefore, the spectrum of the supporting electrolyte was subtracted in all cases. Gas bubbles formed during the process yield an almost wavelength independent absorption which was demonstrated for oxygen evolution at an (inert) Pt electrode. So the spectral gas contribution was determined in the range from 700 to 800 nm and subtracted. Fig. 4 shows the results of a single pulse experiment. The current density during the 12 V, 5 s pulse is almost constant at 21 A/cm^2 . The delay of about 1 s between current and spectra is caused by the dead volumes of the tubes and the cuvette. The dissolution of iron is dominant in the beginning, then decreases and increases again. The absorption caused by gas bubbles (some oxygen from the sample, hydrogen

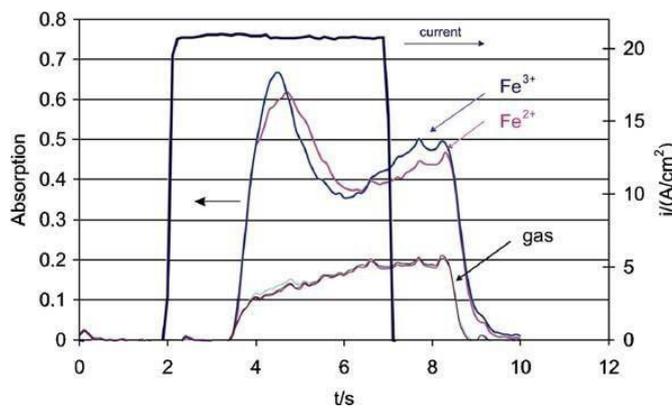


Fig.4. Current density and product absorption for a 12V pulse of 5s and an electrolyte flow of about 20 m/s

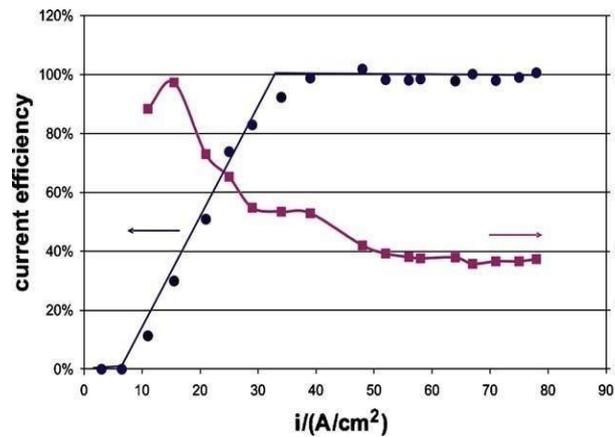


Fig. 5. Mean current efficiencies and mean Fe^{2+}/Fe^{3+} product ratio of 5 s pulses from 4 to 40 V. The current densities increase up to 78 A/cm², electrolyte flow 20 m/s.

from the cathode) increases with time. Both species, Fe^{2+} and Fe^{3+} ions, are formed simultaneously .Fig. 5 compares the results from many experiments of this type up to current densities of 78 A/cm². The current efficiency was calculated according to Eq. (5). This efficiency respects, in contrast to most data in the literature, the different oxidation states of iron. The current efficiencies of iron dissolution and the Fe^{3+}/Fe^{2+} product ratios are mean values of the 5 s pulses. At current densities <5 A/cm², oxygen only is formed (and traces of Fe^{3+} At current densities up to 35 A/cm², the iron dissolution increases continuously. A similar transition from predominant oxygen evolution to predominant iron dissolution was also found by other authors (e.g. in [7] at 5–10 A/cm²), but this transition is strongly dependent on the experimental conditions (especially the flow rate). The current efficiencies of iron dissolution and the Fe^{3+}/Fe^{2+} product ratios, however, are almost independent of the flow velocity. The Fe^{2+}/Fe^{3+} ratio changes from a predominant Fe^{3+} formation to a Fe^{3+}/Fe^{2+} ratio around 2. This corresponds to a dissolution of an oxide film with the composition Fe_2O_3 at low current densities and Fe_3O_4 at current densities >35 A/cm². At these large current densities the efficiency of iron dissolution is close to 100%. Due to experimental errors in spectroscopy, however, we cannot exclude a further oxygen evolution of some % of the total current. The experiments shown in one figure are always carried out with the same capillary. The preparation of the capillaries yields specimen of slightly different shape. The shape has a significant influence on the flow rate and flow distribution in the tip. This has, however, only influence on the transition from predominant oxygen evolution to predominant iron dissolution, the efficiency and the composition of products at large current densities are not affected. So far, we expect a passive structure during ECM in $NaNO_3$. In technical applications, often pulsed ECM is used. Between the anodic dissolution pulses, short

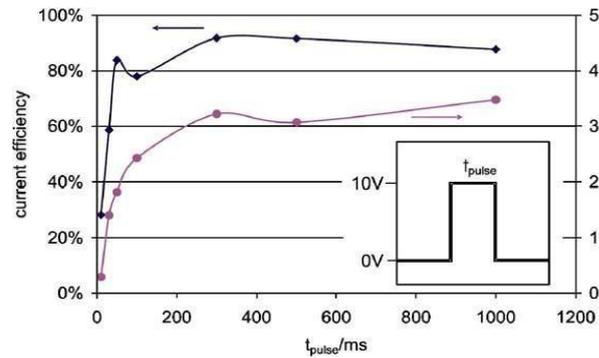


Fig.6. Meancurrent efficiencies and Fe^{2+}/Fe^{3+} production ratio for 10V pulses with different length from 10 ms to 1 s. The pulse experiment started in the active potential region with oxide free electrodes, electrolyte flow again 20 m/s.

pulses of reversed polarity are applied. If the electrode remains passive after the dissolution pulse, the adherent supersaturated layer is washed of and a solid passive film remains (Fe_2O_3 or Fe_3O_4). This can be reduced by the cathodic pulse. This means, starting with an active (layer free) surface, two processes must occur until a stationary dissolution is obtained: the formation of an oxide layer and a supersaturated film. To investigate this we tried to enhance the resolution in time. Due to the delay demonstrated in Fig. 4 caused by dead volumes, the spectroscopic analysis is slow. Therefore, we investigated short pulses of different lengths, starting with 10 ms. The product analysis can only determine the integral amounts of Fe^{3+} and Fe^{2+} for different pulse lengths. Fig. 6 shows the corresponding Fe^{3+}/Fe^{2+} ratios and efficiencies. Dissolution starts with predominant Fe^{2+} formation at low efficiencies. In longer pulses, after around 50 ms, a maximum is reached, and the contribution of Fe^{3+} increases rapidly. After 300 ms the system is stationary and passive and supersaturated films are formed.

5. Discussion and conclusions

We expect a duplex structure under ECM conditions (current densities up to 80 A/cm², strong electrolyte flow) in $NaNO_3$, a solid oxide film of some nm and, above, a highly soluble, supersaturated nitrate film with concentration gradients of the products (increasing in direction to the surface) and water (decreasing in direction to the surface). Our experiments showed. A transition from predominant oxygen evolution to predominant iron dissolution in the range from 5 to 30 A/cm²,

A simultaneous formation of Fe^{3+} and Fe^{2+} with Fe^{3+}/Fe^{2+} ratios up to 2, which corresponds formally to a dissolution of Fe_3O_4 .

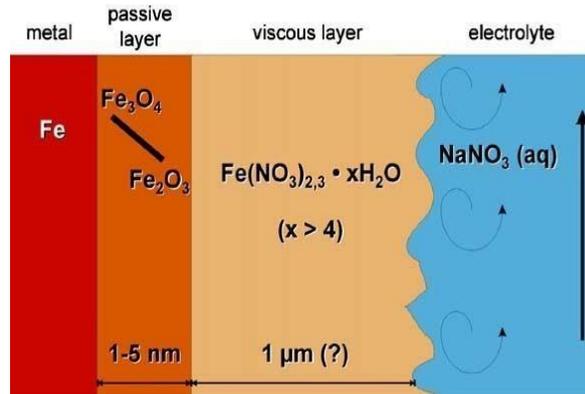


Fig.7. Tentative scheme of the sample surface during electrochemical machining. The thickness data are speculative.

Time resolved pulse experiment starting with an active surface showed a transition time of about 300 ms until stationary conditions are obtained. From former unpublished experiments a total charge of at least 1 mC/cm² was estimated to build up the viscous film. If we assume a time from 30 to 300 ms to get these final conditions we obtain charges from 0.7 to 7 mC/cm² using a mean current density of about 20 A/cm². Due to the electrolyte flow, parts of the viscous supersaturated film are washed of and, hence, the charge of the adherent part must be smaller. A charge of 1 mC/cm² corresponds to a film thickness of some 100 nm (Fig. 7).

The suppression of oxygen evolution is caused by different effects:

1. The depletion of water in the viscous film. The concentration of water, which is around 55 mol/l in diluted solutions, will be much lower in this film as the water molecules are strictly bound to the cations in the supersaturated solutions. Accordingly, the activity of free water will be extremely small, perhaps even 1 mol/l.
2. The pH shift according to Eq. (4) lowers the current density.
3. The formation of oxygen can be kinetically hindered at Fe₃O₄ surfaces.

The depletion of water is the most important. With increasing current density oxygen evolution changes from a process at a surface of Fe₂O₃ in an aqueous solution to a formation at Fe₃O₄ in a salt melt with a very low concentration of free water. Therefore we must assume that the rate determining step is the diffusion of water to the surface, similar to [4]. This can also explain the formation of Fe₃O₄ instead of Fe₂O₃. Fe₂O₃ requires 1.5 H₂O per Fe, Fe₃O₄ only 1.33H₂O per Fe.

References

- [1] M. Datta, H.J. Mathieu, D. Landolt, J. Electrochem. Soc. 131 (1984) 2484.
- [2] M. Datta, D. Landolt, Electrochim. Acta 25 (1980) 1263.
- [3] R.-D. Grimm, D. Landolt, Corros. Sci. 36 (1994) 1847.
- [4] S.H. Glarum, J.H. Marshall, J. Electrochem. Soc. 132 (1985) 2872; M. Matlosz, S. Magaino, D. Landolt, J. Electrochem. Soc. 141 (1994) 410.
- [5] M. Datta, H.J. Mathieu, D. Landolt, Electrochim. Acta 24 (1979) 843.

- [6] D. Landolt, *Electrochim. Acta* 32 (1986) 1.
- [7] T. Haisch, E. Mittemeijer, J.W. Schultze, *Electrochim. Acta* 47 (2001) 235.
- [8] M.M. Lohrengel, A. Moehring, M. Pilaski, *Fresenius J. Anal. Chem.* 367 (2000) 334; M.M. Lohrengel, A. Moehring, M. Pilaski, *Electrochim. Acta* 47 (2001) 137.
- [9] M.M. Lohrengel, I. Kluppel, C. Rosenkranz, H. Bettermann, J.W. Schultze, *Electrochim. Acta* 48 (2003) 3203.
- [10] Software by J. Deconick, B. Van den Bossche, ElSyCa N.V., Kranenberg 6, B-1731 Zellik, Belgium.
- [11] Strode I. and Bassett M.B. The effect of Electrochemical machining on the Surface integrity and Mechanical Properties of cast and Wrought Steel wear, 109,171-180, 1966
- [12] Hewidy M.S. controlling of metal removal thickness in ECM Process, *Journal of Materials Processing Technology*, 160,348-353, 2005.