

Physical principles and miniaturization of spark assisted chemical engraving (SACE)

R Wüthrich¹, L A Hof², A Lal¹, K Fujisaki¹, H Bleuler¹,
Ph Mandin³ and G Picard³

¹ Ecole Polytechnique Fédérale de Lausanne, Laboratoire de systèmes robotiques,
CH-1015 Lausanne, Switzerland

² Delft University of Technology, Advanced Mechatronics, Mekelweg 2, 2628 CD Delft,
The Netherlands

³ Laboratoire d'Électrochimie et de Chimie Analytique UMR CNRS 7575, ENSCP,
11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

E-mail: Rolf.Wuethrich@a3.epfl.ch

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Abstract

Spark assisted chemical engraving (SACE) is an unconventional micromachining technology based on electrochemical discharge phenomena for glass and various ceramics. The limits of SACE with respect to small dimensions in the particular case of glass are explored. It is found, using a specially developed set-up based on an AFM, that even using extremely sharp tool-electrodes does not allow us to produce a smaller pattern than typically 25 μm . It is concluded that the gas film thickness, in which the electrochemical discharges take place, is the main limiting factor. Further experimental investigations on its formation are investigated. By adding surfactants to the electrolyte, in order to increase the wettability of the tool-electrode and therefore to reduce the gas film thickness, it is observed experimentally that the critical voltage reduces significantly. This observation may lead to a novel method of characterizing the gas film thickness in SACE.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Several applications in the field of micro-electro-mechanical systems (MEMS) need glass because of its unique properties such as chemical resistance, transparency, low electrical and thermal conductivity or biocompatibility. As examples can be mentioned micro-accelerometers, micro-reactors, micro-pumps and medical devices (flow sensors or drug delivery devices). The transparency of glass is very interesting for optical applications or applications where optical visualization of a process is needed.

The main limiting factor for glass machining and use in MEMS devices is its limited structuring possibility. Chemical etching technologies, such as HF etching, are well established, but remain too slow and expensive for many industrial applications. Thermal machining methods, such as laser machining, or mechanical methods such as abrasive jet machining, ultrasonic machining, water jet machining and

diamond cutting are other established technologies for glass machining. However, these methods are hampered by the difficulty in obtaining good surface quality and often lead to potential structural damage (micro-cracks). In general high aspect ratio structures are a challenging problem. Machining high aspect ratio micro-holes in glass would open several new possibilities in the MEMS field. In the particular context of microfactories alternative technologies become interesting if they avoid heavy machinery and ultra clean environments. A possible answer is spark assisted chemical engraving (SACE) [1]. SACE was presented for the first time in 1968 by Kurafuji and Suda [2] as electrical discharge drilling for micro-holes in glass. Various names are used for the process, like electrochemical arc machining (Kubota [3]), electrochemical discharge machining (Ghosh *et al* [4]), electro chemical spark machining (Jain *et al* [5]) and spark assisted chemical engraving (Langen *et al* [6]). The diversity of names illustrates the complexity of the process and the different explanations

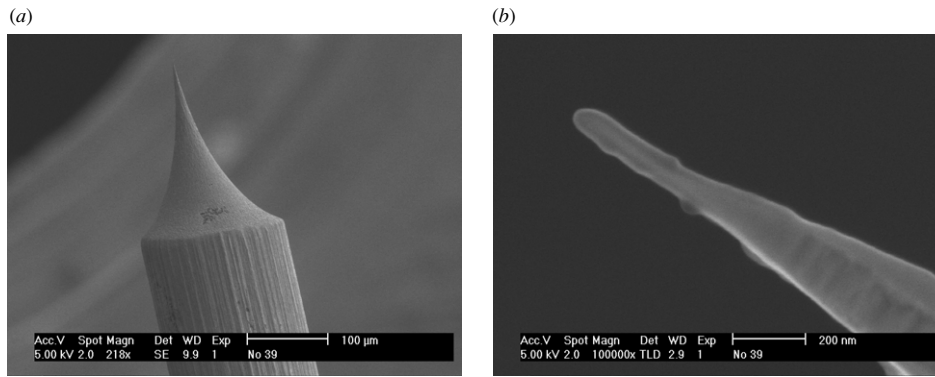


Figure 1. (a) Etched tungsten tip with initial wire diameter of 175 µm. The wire was immersed in 10%wt NaOH (immersion depth of 5.5 mm) and a voltage of 6 V was applied between tip and cathode. Etching time of about 5 min. (b) Radii of curvature of about 20 nm can be obtained.

proposed to describe the nature of the electrical discharges. In the following we will refer to this technology as SACE.

Processing glass with SACE is done as follows. The glass sample to be machined is dipped into an electrolyte (typically 30%wt NaOH). Between two electrodes a dc voltage is applied. If the voltage is higher than the so-called critical voltage U^{crit} , electrical discharges (sparks) occur through a gas film built around the tool-electrode and glass machining becomes possible by mainly thermal melting.

Even if SACE presents several interesting properties as described in [1], various open questions remain. One of them is the resolution of the process. How small can structures be machined with SACE and what is the limiting factor in obtaining the smallest structures? This problem is addressed in the present contribution.

The size of machined structures is linked to the tool and gas film thickness. In this contribution it will be analysed whether reducing the tool-electrode size to a few microns results in gas film thickness reduction as well and therefore in smaller machined patterns. As will be illustrated, the gas film does not scale down with tool size for extremely sharp tool-electrodes. Additional basic knowledge on the formation and behaviour of the gas film is needed if the thickness of the film has to be reduced.

2. Reducing the tool-electrode size

In order to analyse whether greatly reducing the tool-electrode size results in producing very small patterns in glass, some micro-electrodes in the form of atomic force microscopy (AFM) cantilevers were built. Electrochemical etching has been widely used for producing sharp probes for scanning tunnelling microscopy (STM) and AFM. This method is fast and the most convenient method to obtain cheap and reliable tips and is therefore chosen as the fabrication method.

Tungsten is a hard material featuring high elasticity modulus and chemical inertness compared to standard construction materials such as steel and aluminium. Therefore it is an appropriate material for the chosen fabrication technique.

2.1. Electrochemical etching of tungsten tips

The electrochemical etching process usually involves the anodic dissolution of the metal electrode. There are two different ways in which this can be done: an alternating current (ac) etch or a direct current (dc) etch according to the applied potential. Each procedure gives a different tip shape; the ac etched tips have a conical shape and much larger cone angles than the dc etched tips. On the other hand, the dc etched tips having the shape of a hyperboloid are much sharper than ac etched tips and are therefore chosen.

The dc drop-off method is described as follows: etching occurs at the air–electrolyte interface causing the portion of wire in solution to drop-off when its weight exceeds the tensile strength of the etched or necked down region of the wire. The upper part of the wire will continue to etch as long as it remains in the electrolyte under an applied voltage, also after the drop off of the lower part. This has a negative influence on the sharpness of the tip (upper part of the wire). It is therefore obvious that a very short cut-off time of the etching current will produce sharper tips and smaller radius of curvature. This can be realized by using an electronic circuit with small cut-off time, which is triggered by the sudden voltage drop when the lower part drops off.

Following the method and the set-up described by Ibe *et al* [7], an etching set-up was built in order to obtain tips with typical apex radii of 20–100 nm. Etching is done in 10%wt NaOH electrolyte. Typical etching times are a few minutes. The details of the design and the cut-off circuit are described in [8]. To build a cantilever from the etched tip, the wire was bounded on an auxiliary set-up [8]. Some typical results are shown in figure 1.

2.2. AFM set-up for SACE machining

The extremely small tool-electrode size demands a sensitive contact detection system. Therefore, an AFM set-up was realized which has a sensitive detection system during machining. Approaching the cantilever for contact detection demands low cantilever stiffness while SACE machining requires high stiffness in order to reduce tool-electrode vibrations. A compromise is made to satisfy both requirements

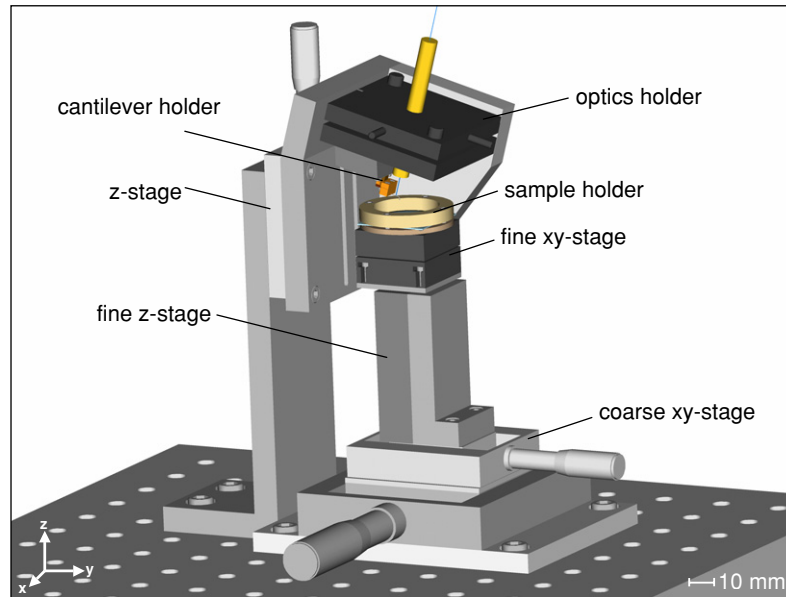


Figure 2. AFM set-up for SACE machining.

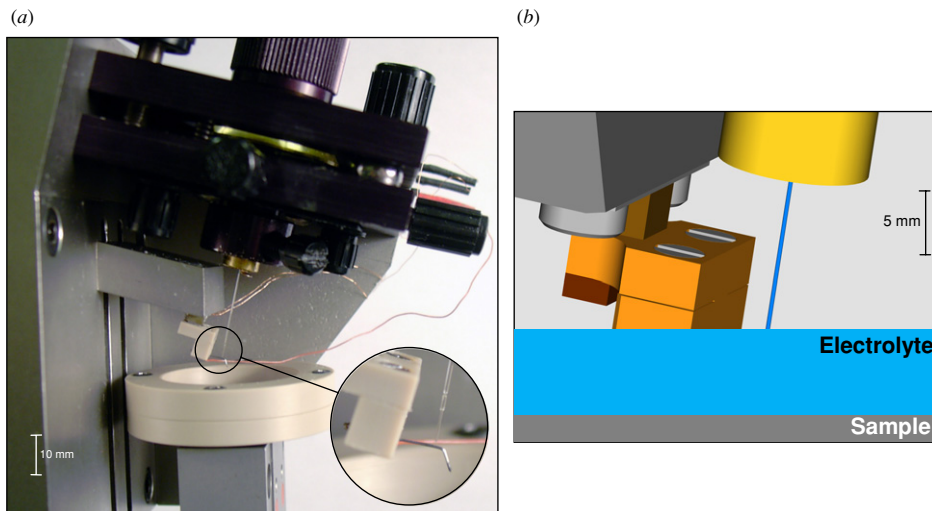


Figure 3. (a) AFM set-up with a cantilever mounted. (b) Schematic drawing of the cantilever and the fibre optics dipped into the electrolyte.

to the best. The developed set-up is drawn in figure 2 and described in detail in [8].

Because the procedure of machining with the AFM set-up differs from the conventional method, a short description is given for all steps involved in machining. The approach for contact detection of tip and sample is the same as used in tapping mode AFM.

1. Place the sample to be machined together with the counter electrode in the liquid holder.
2. Fix the cantilevered etched tip in the cantilever holder and put some electrolyte in the liquid holder.
3. Oscillate the cantilever at its resonant frequency by applying a sinusoidal ac voltage to the oscillation actuator (PZT).
4. Move the coarse vertical stage with cantilever downwards until it is in the range of the high resolution z-stage (range of 25 μm). This point is determined by using an optical microscope with eight times magnification.
5. Switch on the controller and move the high resolution z-stage upward using an offset voltage until contact between tip and sample takes place. This is seen as a decrease in oscillation amplitude.
6. Switch off the controller and choose the desired tip to sample height by varying the offset voltage for the piezo z-stage.
7. Apply a dc voltage ($U = 25 \text{ V}$) between tool and counter electrode for a certain time (typically 1.5 s).
8. Bring the tool at a height of 10 μm (to prevent destruction of the tip, due to roughness of the sample surface) and change x or y position to a desired value.

The machining steps from five up to eight can be repeated in order to produce a series of holes. When moving the x or

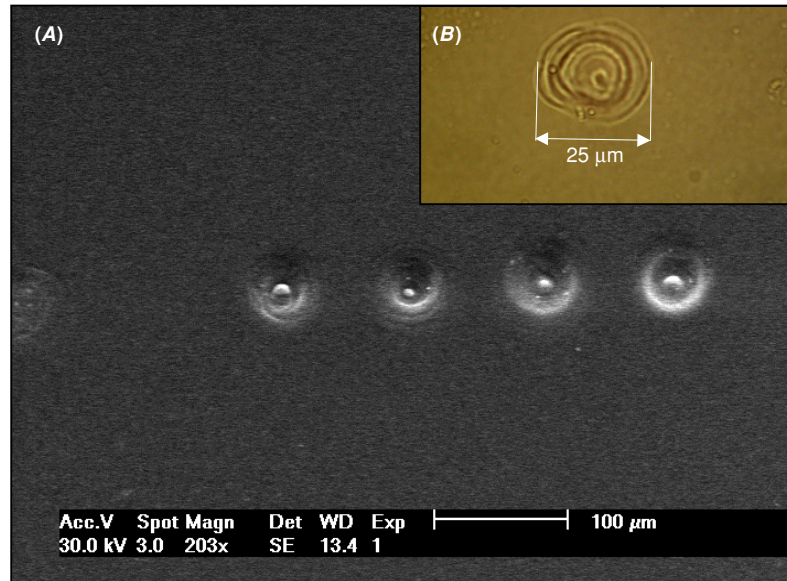


Figure 4. (a) Machining results with tip-sample distance of 2 μm . (b) Machining result with tool-substrate distance of 5 μm .

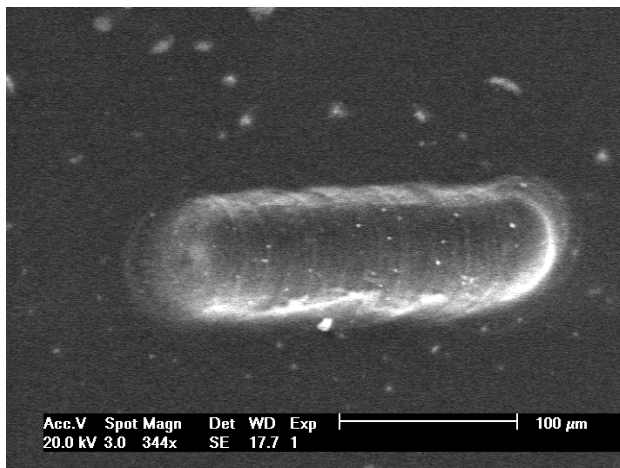


Figure 5. A line of about 200 μm length and 50 μm width and machined at a constant distance of 2 μm from the substrate. The cantilever was moved with a constant velocity of 10 $\mu\text{m s}^{-1}$.

y position during machining (after step seven) other structures like lines can be machined. Figure 3(a) shows the realized set-up and figure 3(b) gives a schematic drawing of the cantilever dipped inside the electrolyte together with the fibre optics for the cantilever displacement measurement.

2.3. Results

To investigate the machining results on the glass sample, several images were taken with a scanning electron microscope (SEM). Using non-conductive materials such as glass, a gold layer of about 100–300 Å thickness has to be deposited on the sample surface for optimal SEM imaging.

A result of machined structures, a series of holes, is shown in figure 4(a). These holes are processed with a

tip-sample height of 2 μm in 30%wt NaOH and show a good repeatability of machining. Experiments show that the repeatability becomes poorer with higher tip-sample heights. The maximum tip-sample height where machining is still possible is about 5 μm . A hole machined with this height is shown in figure 4(b) and presents a diameter of about 25 μm . Some other machining results are presented in figure 5. The line was machined with a lateral speed of 10 $\mu\text{m s}^{-1}$.

In summary, it can be seen that even using extremely sharp tips of a few nm curvatures it seems not possible to obtain smaller patterns than around 25 μm with SACE technology. We attribute this effect to the thickness of the gas film, given by the bubble dynamics as described below, which most probably does not scale down indefinitely with the tool-electrode size. In order to analyse why the gas film does not scale down, more investigations are done on it (see below). It is interesting to see that machining is possible only if the tool-electrode is closer than 5 μm to the glass surface. This is smaller than in conventional SACE machining where this height limit for machining has been reported to be about 25 μm [9].

3. Mechanisms involved in the gas film formation

A first idea of the process forming the gas film can be seen on the static $I-U$ characteristics (figure 6). For voltages above the water decomposition potential U_d water electrolysis starts. A first linear region (Ohmic region) is observed, followed by a plateau at voltages higher than U^{lim} (typically around 10–12 V), before reaching the critical voltage U^{crit} where the gas film is formed. For more details see, for example, [10].

Recent works in electrochemistry clearly indicate that the gas film in SACE is formed by bubble coalescence [11, 12]. This is illustrated in figure 7. For voltages lower than the critical one, the bubble growth density p is lower than the percolation threshold and bubble coalescence results only in bubbles of finite size. For $U = U^{\text{crit}}$, the bubble growth density

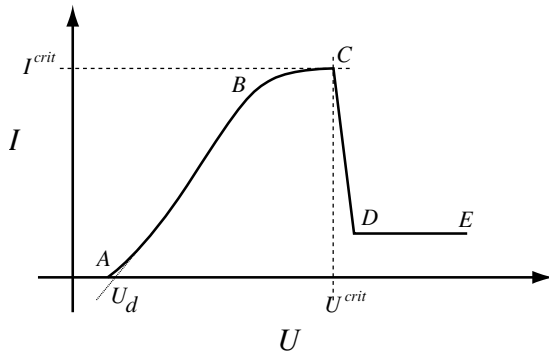


Figure 6. Typical static mean I - U characteristics of SACE. AB: Ohmic region; BC: limiting current region; CD: transition region; DE: electrode effects region.

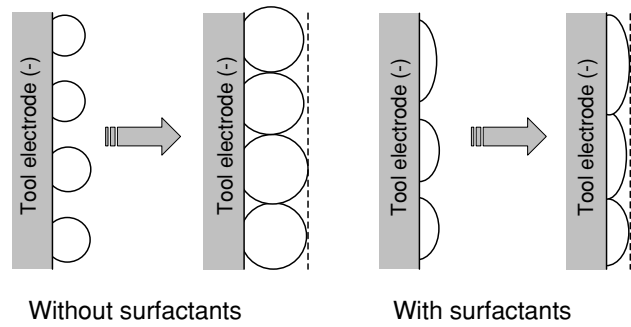


Figure 8. Schematic representation of nucleating bubbles at the tool-electrode surface. Left: nucleating bubbles in electrolytic solution without surfactants forming the gas film. Right: nucleating bubbles in electrolytic solution with surfactants forming the gas film.

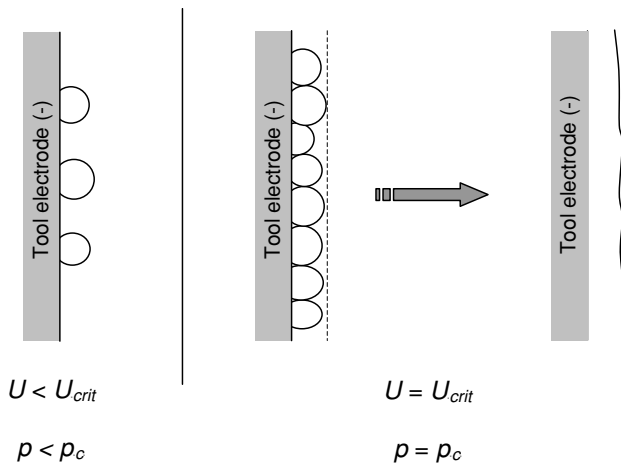


Figure 7. Gas film formation at the tool-electrode. When the applied voltage U is lower than the critical voltage U^{crit} , electrolysis happens and bubbles form on nucleation sites at the tool-electrode. The bubble nucleation site density p is lower than the percolation threshold p_c . When the applied voltage equals the critical voltage, $p = p_c$, the bubble layer transforms into a gas film.

reaches the percolation threshold p_c and a bubble of infinite size (the gas film) is formed [11]. If this model is able to predict the qualitative behaviour of the critical voltage as a function of the various parameters of the problem (tool-electrode geometry, electrolyte properties) it is not able to explain satisfactorily the plateau appearing prior to the critical voltage in the mean I - U characteristics (see region BC in figure 6). Such a plateau means that some mass transfer limitation takes place or that the active electrode surface is progressively shadowed by growing gas bubbles [13, 14].

To quantify the contribution of the bubble shadowing the active electrode surface, some additional experiments, where the surface tension of the electrolyte is changed, have been done.

It is well known that the addition of a surfactant, such as liquid soap, reduces the surface tension and modifies the wettability of interfaces. Water molecules do not bond as strongly with soap molecules as they do with themselves. Therefore, the bonding force that enables the molecules to behave like an elastic membrane is weaker. Assuming that the existence of the limiting region is due to bubble formation at

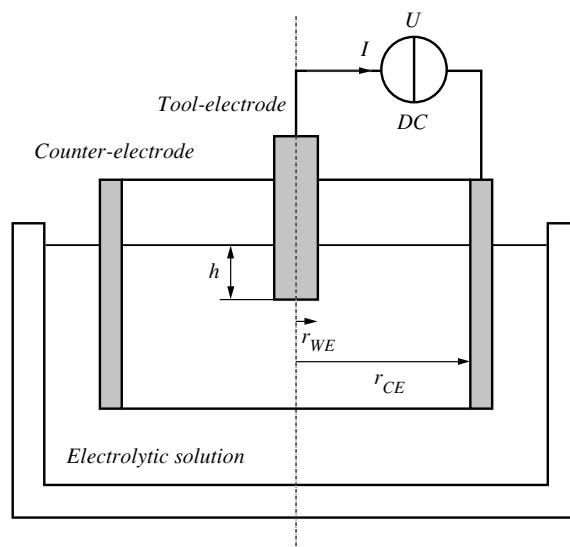
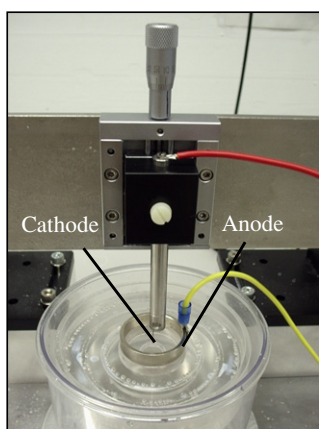


Figure 9. Set-up for the gas film characterization; h is the electrode immersion depth, r_{WE} the working electrode radius and r_{CE} the counter electrode radius.

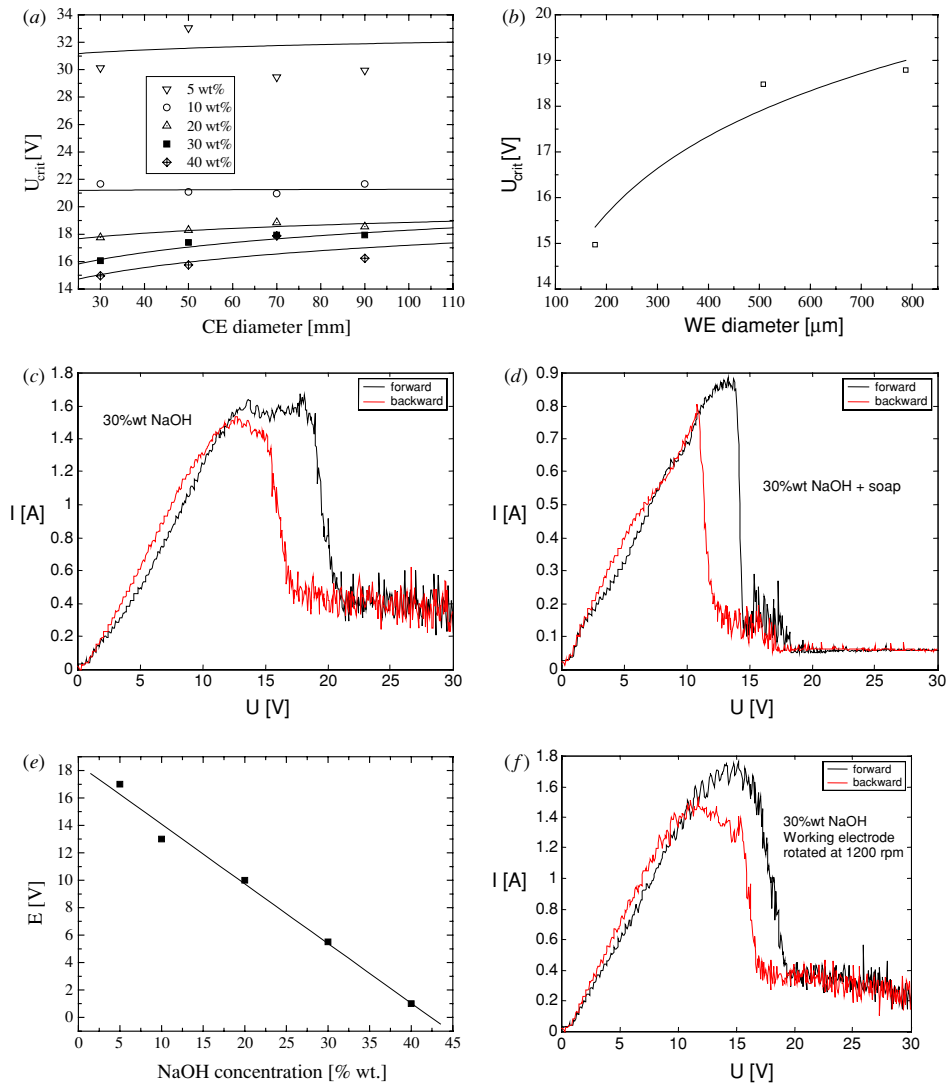


Figure 10. (a) Dependence of the critical voltage on the counter electrode (CE) diameter at a fixed working electrode (WE) radius of 508 μ m at various electrolyte concentrations. (b) Dependence of the critical voltage on the WE diameter at a fixed CE radius of 70 mm. (c) Typical $I-U$ characteristics in 30%wt NaOH. (d) Typical $I-U$ characteristics in 30%wt NaOH mixed with liquid soap (10:1). (e) Dependence of the extension of the limiting region of the electrolyte concentration. (f) Typical $I-U$ characteristics in 30%wt NaOH at rotating tool-electrode (1200 rpm).

the electrode surface, a change in physical properties (surface tension, viscosity) of the electrolyte should affect the size of this region. With reduced surface tension, the bubbles on the tool-electrode could more easily detach and therefore reduce the critical voltage. Additionally, the change in wettability changes the shape of the bubbles at the electrode surface, which is illustrated in figure 8. Increasing the wettability forces the formed bubbles to be more flat; the gas film thickness should therefore be reduced.

Rotating the tool-electrode affects the hydrodynamic state of the bubble film around the electrode and could therefore change the critical voltage as well.

3.1. Measurement set-up

The layout of the experimental system is shown in figure 9. A voltage ramp (scan rate of 10 $V s^{-1}$) is applied between the working electrode (cathode) and counter electrode (anode) from 0 to 40 V. The current in the cell is measured with a current

sensor with a 200 kHz bandwidth, which can measure currents up to 4 A (an in-house made device based on a commercial Hall sensor). The measurements are controlled and recorded by a PC on which the mean of 50 scans is computed to get the static $I-U$ characteristic. The temperature is controlled at $T = 55^\circ C \pm 5^\circ C$ with a commercial temperature feedback system.

Because the material composition of the two electrodes influences the behaviour in the electrochemical cell, all measurements are done with cylindrical nickel electrodes, which are chemically inert in NaOH. The cylindrical geometry was chosen for this fundamental study as it allows us to get several electrodes with the same geometry in order to compare them.

3.2. Results

A typical mean $I-U$ characteristic in 30%wt NaOH is shown in figure 10(c). Measurements are done with a working electrode

of 508 μm diameter and a counter electrode with a diameter of 70 mm. Clearly a hysteresis effect according to a forward and backward voltage scan (10 V s^{-1}) can be seen. The theoretical interpretation in terms of gas film growth dynamics is presented elsewhere [15].

The dependence of critical voltage on counter and working electrode diameter is shown in figures 10(a) and (b).

The effect of the bubbles shadowing the active electrode surface is clearly demonstrated comparing figures 10(c) and (d), where the characteristics with 30%wt NaOH and 30%wt NaOH (200 ml) mixed with liquid soap (20 ml) are shown. The critical voltage is decreased significantly (from 20 V to 15 V) and the plateau has nearly vanished. A similar effect can be obtained by rotating the working electrode (figure 10(f)).

Measurements of the extension ΔE of the limiting region (region BC in figure 7) as a function of the electrolyte weight concentration in the case of NaOH are shown in figure 10(e). A linear dependence is found which still has to be theoretically investigated.

3.3. Discussion

The following possible explanation of the plateau in the I - U characteristic of the SACE process can be given. It is observed that the plateau is reduced by higher electrolyte concentrations. For electrolytic salts, such as sodium hydroxide, with sufficiently high concentration the bubble coalescence is inhibited [16]. For low concentrated NaOH the first two parts of the I - U characteristic can be explained as follows. After the decomposition potential, a linear increase of current with increasing voltage is observed due to the electrolysis reaction at the electrodes and hydrogen gas is formed. When the growth density of these bubbles is sufficiently high, they coalesce into larger bubbles. These bubbles are covering a large part of the electrode and thus reducing the active electrode surface. For higher concentrated NaOH, bubble coalescence is inhibited and no shadowing of the active electrode surface will occur. The plateau extension will decrease.

The results indicate that increasing wettability of the electrode (by adding some surfactant) results in a decrease of the critical voltage and the extension of the limiting region in the I - U characteristics. According to figure 8 the gas film thickness is expected to decrease. It may, therefore, be speculated that the critical voltage and the length of the limiting region are indicators of the gas film thickness (decreasing of these values meaning decreasing of gas film thickness). This aspect looks to be a promising method to characterize in a simple way the gas film thickness in SACE and is therefore worth investigating further [17, 18].

4. Conclusion

It was analysed how the gas film in spark assisted chemical engraving (SACE) does scale down with the tool-electrode. It is found that even by using very sharp tool-electrodes, the resolution limit of features in glass machining by SACE is around 25 μm . It is concluded that the resolution depends essentially on the gas film thickness at the tool-electrode.

The parameters influencing this thickness and the dynamics of bubble growth and coalescence into a gas film are therefore being investigated in depth. First results show that the surface tension of the electrolyte significantly affects the gas film thickness and thus the resolution of machining. The link between the gas film thickness and the current-voltage characteristics has been established. Surface tension and electrode wettability in turn are dependent on electrolyte concentration. They can be further influenced by the addition of surfactants such as liquid soap. A significant influence of this additive on machining results has been established experimentally and in theoretical interpretation. These results are promising for the further characterization and development of the SACE process.

Acknowledgment

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