

Marek St. Węglowski

## Electrolytic etching in welding metallography

### Introduction

An increase in the types of applied metals and the related growth of various requirements for structural materials used in welded structures or cast elements create a number of new metallographic issues such as, for instance, testing alloy steels, nickel alloys or titanium alloys. Proper preparation of metallographic specimens of such materials using classical etching methods poses numerous difficulties and sometimes proves impossible. In addition, when it becomes necessary to test a great number of specimens, e.g. in batch production, etching metallographic specimens is too time-consuming. Therefore, it is essential to implement new, more efficient methods. One of the ways of allowing a significant reduction of the time needed for etching metallographic specimens without deteriorating their quality is electrolytic etching. If materials have a complex chemical or, more importantly, structural composition, it is of great importance to develop proper etching procedures making it possible to reveal only selected microstructure components. And also for this purpose, one can use electrolytic etching.

### Principle of electrolytic etching

The process of electrolytic etching of metals is a complex electrochemical phenomenon. As an electric current flows through an electrolyte, strong polarisation and proper distribution of current density trigger elec-

trochemical phenomena which cause the surface of a metal, i.e. the anode, to dissolve. Cathodes play here the role of an element which enables closing the current circuit by the electrolyte and are responsible for proper distribution of the current density. Cathodes used in electrolytic etching do not wear even after a longer period of time [1].

This method can be applied for most metals and their alloys making it possible to obtain a properly etched surface. Figure 1 presents the dependence between the density of current flowing through a specimen and voltage. The process of etching takes place within a voltage range strictly specified for given conditions. Applying higher voltage is followed by a polishing process, whilst applying too high a voltage triggers excessive gas (oxygen) emission, causing non-uniform removal of specimen material and the formation of pits on the surface [2].

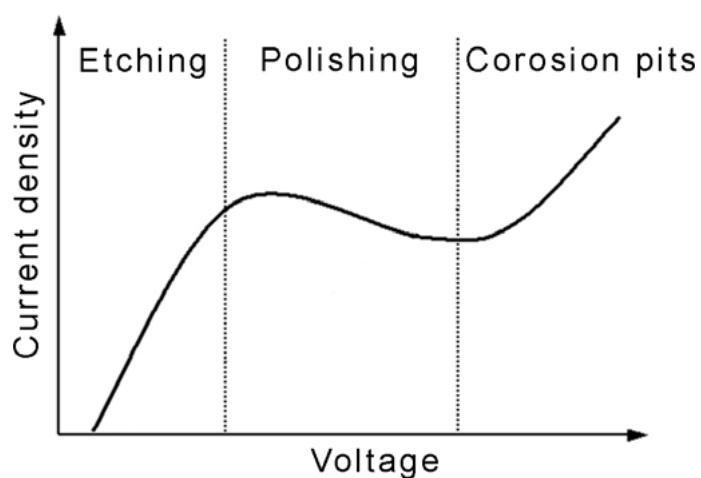


Fig. 1. Dependence between the density of current flowing through specimen and voltage [2]

One of the most popular theories explaining the phenomenon of electrolytic etching/ electrolytic polishing is the theory developed by Jacquet [3], according to which etching/polishing is caused by the anodal action of electrolyte on, first of all, the peaks of surface roughness of a metal subjected to etching/polishing and, to a lesser degree, on cavities. Such diversified dissolving can be explained by the formation of an anode film known also as a viscose film. This film covers the metal surface, with projecting surface roughness peaks being covered by a thinner film layer than the cavities (Fig. 2). The resistance of the thinner film layer (on the peaks) is lower than that of the thicker film layer (in the cavities).

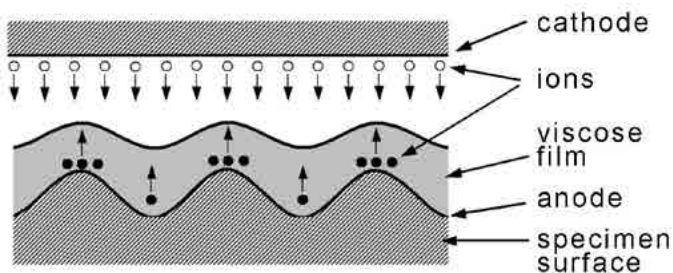


Fig. 2. The formation of anode film and distribution of ions in the inter-electrode space [3]

For this reason the peaks of surface roughness dissolve to a greater extent than the cavities. In this manner, the surface irregularities are gradually made even until polishing or etching. This theory clarifies the basic course of electrolytic etching or electrolytic polishing, yet it does not explain individual cases. The Jacquet theory is right only for a certain group of phenomena; it properly explains the processes of electrolytic etching/electrolytic polishing of copper and steel in an electrolyte composed of phosphorus acid and organic additions as well as electrolytic etching/ electrolytic polishing of steel in a chloric-acetic electrolyte. In these cases one can observe the formation of a dense colloidal or liquid film from the reaction products. Many theo-

ries have been developed in order to explain this and other phenomena. Yet they all share the same disadvantage, i.e. they explain phenomena in a temporary manner and are usable only in individual cases [3].

### Factors affecting electrolytic etching conditions

The most important factors affecting etching conditions include the potential difference (PD) and the density difference of current, electrolyte temperature, electrolyte stirring, surface pre-treatment, heat treatment of the specimens, treatment time, dimensions of the electrolyser used for etching and electrolyte consumption degree.

### Difference of current potentials and density

Usually during electrolytic etching it is possible to obtain better results if during the process the difference of potentials is permanently monitored rather than the density of current. Independent of the difficulty in maintaining constant current density, a longer time of electrolysis combined with heightened current density cause the emission of a gas which may trigger the formation of pits on the surface of a specimen. Moreover, at the initial stage of anodal dissolving, prior to the stabilisation of etching conditions, current density should significantly exceed the normal value for a period sufficient for the stabilisation of etching conditions. It is important that at the initial stage of etching the difference of potentials on the electrolyser should be within the boundary values used for etching.

### Temperature of electrolyte

The resistance of the electrolyte decreases along with an increase in temperature. Consequently, the voltage necessary for obtaining the same current density decreases. The voltage corresponding to a given cur-

rent density is defined by an experimentally determined equation:

$$U = \frac{K}{a \times T + b}$$

where:

$K$ ,  $a$ ,  $b$  – constants dependent on electrolytic conductance, electrolyser dimensions and current flowing through the electrolyser,  
 $T$  – temperature.

The equation reveals that the power necessary for maintaining given current density decreases along with an increase in temperature [1].

### ***Electrolyte stirring***

During the process of electrolysis in stabilised conditions, the products of the reaction accumulate around the electrode. In some cases the inflow of fresh electrolyte is insufficient, and stirring is necessary to remove some of reaction products. However, one should avoid excessive stirring as it could destroy the film and prevent the stabilisation of optimum etching conditions. Moving and stirring also prevents excessive local heating caused by the flow of current through the high-resistant layers on the anode and favours maintaining a more uniform electrolyte temperature. In many cases the best results are achieved by rotating and swinging the anode rather than by stirring the solution.

### ***Impact of heat treatment on the outcome of electrolytic polishing***

The structure of metal significantly affects its properties and consequently its behaviour during treatment. This impact is visible during mechanical working and in particular during electrolytic etching. The change of the structure and of the mutual relations of individual components causes changes both in the potential and dissolving degree, affecting the surface appearance. The difference is particularly evident while comparing the sur-

face of objects subjected and those unsubjected to heat treatment. The heat treatment has a positive effect on the quality of the surface intended for etching, provided it has led to the formation of a uniform structure. If a heat treatment has triggered the formation of carbides, as is the case with alloy steels during electrolytic etching for instance, the so-called point corrosion may occur as a result of the intense dissolving of areas around the carbides.

### ***Etching time***

The time of electrolysis necessary for obtaining the desired condition of the surface changes depending on a metal and electrolyte used. According to a general principle, the time of etching is inversely proportional to current density. In this manner, in the case of solutions containing orthophosphorous acid, for which low current density is used, the treatment requires a longer time than in the case of the solutions of tetraoxochloric acid, for which high values of current density are usually used. In general, etching lasts between several seconds and several minutes [1].

### ***Dimensions of electrolyser for etching***

An important factor associated with electrolytic etching is the dimensions of an electrolyser, as their changes may significantly affect the process conditions.

### ***Impact of electrolyte consumption***

During etching iron, for example, the content of Fe ions in the electrolyte increases gradually as the amount of metal deposited on the cathode is much smaller than the amount obtained from the dissolved anode. Depending on the shape and dimensions of the cathode, this amount makes up 5% - 15% of the dissolved anode metal. An increase in electrolyte density is accompanied by

a worsening quality of the surface subjected to etching. In consequence, the solution becomes useless. Although a slight etching effect can be observed, the phenomena accompanying the process render the microscopic observation of the etched specimen difficult. The etching ability of the solution can be slightly extended by using a slightly higher current density or by adding between 5 ml and 10 ml of distilled water per one litre of solution. A greater amount of water also worsens the etching effect.

While using chemical or electrochemical etching one should bear in mind that used chemicals ought to be disposed of in accordance with environmental protection regulations.

### **Preparation of specimens for electrolytic etching**

The quality of an electrolytically etched surface is much more dependent on the stage of mechanical polishing and grinding than that obtained through chemical etching. Electrolytic etching is a process which can be initiated only at a certain specified surface roughness. If the roughness is too high even properly selected process conditions will not result in a properly etched surface (the process of electrolytic etching "highlights" scratches formed as a result of mechanical polishing). This is probably because the film, instead of filling the surface cavities, covers both the peaks and the cavities with the layer of the same thickness. While considering the applied gradation of abrasive paper, prior to electrolytic etching surfaces should be precisely ground using abrasive paper, starting with the paper of the greatest granularity (e.g. 80 or 100), and next using paper of lower granularity (280, 500, 800 etc.) Each grade of abrasive paper should be used until all marks (especially scratches) coming from previously conducted grinding with the paper of a greater granularity are removed from

the surface of a metallographic specimen. This can easily be observed if upon changing the abrasive paper grade one also changes the grinding direction by an angle of  $10^{\circ}$ - $20^{\circ}$ . During grinding with abrasive papers it is necessary to neither deform nor overheat a specimen being ground. For this reason it is advisable to wet grind specimens using water-resistant abrasive paper and devices ensuring permanent wetting of a grinding area [4]. The process of precise grinding finishes with abrasive paper of a granularity dependent on the type of a material out of which a given specimen is made. It is assumed that such granularity should amount to 600 for steels and 1000 for non-ferrous metals.

The process of mechanical polishing is carried out with a rotating disk covered with a special cloth, onto which one applies diamond-based polishing materials of various gradation (e.g.  $6 \div 0.25 \mu\text{m}$ ). Polishing usually finishes with liquid slurry of aluminium oxide  $\text{Al}_2\text{O}_3$  (grade e.g.  $0.25 \mu\text{m}$ ). The procedure of polishing is strictly dependent on the type of a material being treated. The selection of optimum conditions requires preliminary tests. It may happen that due to improperly selected mechanical treatment, scratches after electrolytic etching are not removed but, on the contrary, become more visible. In such a case, the scratches that are revealed are those which during polishing were covered up by metal, which during electrolytic etching are dissolved more intensively than the remaining part of the specimen [3].

A better effect from electrolytic etching is achieved sooner if the surface to be etched is better prepared in the process of mechanical polishing. Objects intended for electrolytic etching should be carefully cleaned and degreased. If impurities such as aluminium oxide  $\text{Al}_2\text{O}_3$  remain, the films floating on the surface may disturb treatment by causing the formation of stains on the surface being polished.

An indication of properly conducted degreasing is uniform water wetting of the whole specimen surface after its rinsing. The specimen should be subjected to electrolytic etching immediately after the last rinsing as it prevents accidental soiling and corroding of the surface [3].

### Exemplary results of electrolytic etching

Table 1 presents examples of electrolytic etching results (device ElektroMat ET1).

Table 1. Exemplary results of electrolytic etching

<p>Alloy steel; X5Cr-Ni18-10, electrolytic etching, HCL + methanol, time 4 s, voltage 4 V</p>	<p>Austenitic weld, electrolytic etching, HCL + methanol, time 4 s, voltage 4 V</p>	<p>Hasteloy C-2000, electrolytic etching, 5ml H<sub>2</sub>SO<sub>4</sub>, 95 ml H<sub>2</sub>O, time 2 s, voltage 6 V</p>	<p>Hasteloy X, electrolytic etching, 5ml H<sub>2</sub>SO<sub>4</sub>, 95 ml H<sub>2</sub>O, time 2 s, voltage 6 V</p>
<p>Steel 18-8, electrolytic etching, HCL + methanol, time 6 s, voltage 3 V</p>	<p>Transition zone of steel grade 18-8, electrolytic etching, HCL+ methanol, time 6 s, voltage 3 V</p>	<p>Steel 1.4404, electrolytic etching, HCl + methanol, time 4 s, voltage 3 V</p>	<p>Steel 1.4404, electrolytic etching, HCl + methanol, time 4 s, voltage 3 V</p>

### Device for electrolytic etching

In order to satisfy customers' requirements, Instytut Spawalnictwa has developed a device for electrolytic etching ElektroMat ET1 (Fig. 3) [5]. The device is of complex portable modern design ensuring the full repeatability of electrolytic etching process parameters. In addition, ElektroMat ET1 is resistant to operating conditions usually present in the industry.

A simple easy-to-use design guarantees failure-free operation also for less experienced personnel. This is a unique selling point and a competitive edge over devices offered by other companies. A person carrying out tests can precisely adjust etching time and voltage.

The device for electrolytic etching ElektroMat ET1 can be used in the following institutions:

- metallographic laboratories of universities and research institutes,

- industrial quality control laboratories,
- industrial DT laboratories.

The device can be used for most metals and their alloys. It ensures obtaining a properly etched surface and allows electrolytic etching of the following materials:

- iron alloys i.e. alloy and unalloyed steels,
- aluminium alloys,
- nickel alloys,
- titanium alloys,
- copper alloys.



Fig. 3. Device for electrolytic etching ElektroMat ET1

The ElektroMat ET1 is composed of an adjustable laboratory power supply unit and a system of electrodes with a vessel for conducting the electrolytic etching. The device does not require a complicated installation procedure, and its design features high-power transistors. The electronic control system ensures operation with optimum efficiency and output parameters. The output voltage can be adjusted in an infinitely variable manner within a 0 V ÷ 30 V range. The device operation (etching time) control is set up by means of an electronic time relay, ensuring the repeatability of an electrolytic etching process. The device operation status is signalled by means of LEDs placed on the front panel. In addition, the operator can read out current and voltage values on a digital display.

## Summary

Using highly-alloyed materials, developing technologies for welding structures of critical importance, and manufacturing products meeting more and more demanding customers' needs has caused that the recent years have seen an increasing role of microscopic metallographic testing. For this reason it is necessary to develop proper testing procedures for parent metals and

welded joints in order to eliminate errors already at the stage of specimen preparation as such errors could adversely affect the interpretation of obtained test results. To this end, while carrying out microscopic metallographic tests, it is essential to pay particular attention to the manner of metallographic specimen preparation. It is especially important to use a proper etching technique so that on the basis of microscopic metallographic observations one can reveal the presence (or absence) of a given microstructural component. In many cases chemical etching is insufficient or so problematic that the only solution is to use electrolytic etching. Yet, also in this case, the use of a proper metallographic reagent is insufficient and should be supported by a proper device for conducting electrolytic etching.

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