



# Investigation of 304L stainless steel in a NaCl solution using a microcapillary electrochemical droplet cell: Comparison with conventional electrochemical techniques

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## ARTICLE INFO

### Article history:

Received 1 July 2011

Received in revised form 20 October 2011

Accepted 20 October 2011

Available online 12 November 2011

### Keywords:

Microelectrochemistry

Microcapillary

Droplet cell

Corrosion

Stainless steel

## ABSTRACT

In this work a comparison has been made between a localized (micro scale) and a conventional (large-scale) corrosion study of 304L stainless steel in a sodium chloride solution using Tafel plots and electrochemical impedance spectra. Results show the high ability of microelectrochemical techniques for the local investigation of corrosion procedures on solid surfaces, something which is not feasible with conventional large-scale techniques. In the second experiment the microelectrochemical behavior of a faulty copper layer on 304L stainless steel was investigated using linear sweep voltammetry. Glass capillaries touching only small areas of the surface were used and the copper coated surface of the steel sample was scanned in a 9 by 6 matrix (54 measurements) while acquiring data. The obtained corrosion potentials for both defect and intact areas were used to map the surface. The surface plot shows the exact position of the defect point in the coating layer.

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## 1. Introduction

Capillary-based microcells are powerful tools for electrochemical surface investigations in the micrometer range. They can be used in the complete range of common electrochemical techniques, such as potential measurements, potentiostatic control in a three-electrode configuration, transient techniques including pulse and sweep techniques, and impedance spectroscopy.

Key differences between micro and macro scale systems confirm the high ability of microelectrodes in electroanalytical applications and also in kinetic studies [1–6]. Increasing the mass transport in micro systems is one of the most important differences between the two systems. By decreasing the surface area in micro systems the double layer capacitance is reduced and also micro systems obviously decrease the magnitude of the current passed [7] whereby small currents in the range of a few nA to some pA can be measured. Moreover, by applying different modifications to microcells, the evaluation and monitoring of additional parameters, such as pH, temperature, mechanical stress and electrolyte flow becomes possible [8].

A typical microcapillary cell is based on a standard three-electrode system containing a capillary in the range of  $\leq 1000 \mu\text{m}$ ,

which touches only a small area of a solid surface. In this setup the working electrode is the wetted area under the capillary tip. Therefore, measurements can be performed on selected micro areas of the sample. Different cell designs and capillary preparation methods have been discussed in the literature [9], along with various types of applications, including amongst other the microelectrochemical behavior of copper, 316L steel and aluminum, the investigation of aluminum–steel friction welds and a comparison of local electrochemical impedance spectroscopy of bi-electrodes and microcapillary cells [10–16].

In spite of the advantages, such as the study of microscopic surface areas and the direct evaluation of the initiation mechanism of localized corrosion [8], microcapillary techniques have some serious drawbacks, which sometimes makes their applications difficult [13]. Some of the most important limitations which have been considered in previous works are: the resolution of the potentiostat, the ohmic resistance specially in solutions with low conductivity and low concentrations, leakage and blockage of the capillary with oxidation or reduction products, such as oxygen and protons, and finally making capillaries with suitable tips for different aims (single measurement-surface scanning, etc.) [13,17,18]. The last mentioned limitation must be seriously considered when it comes to non-flat solid surfaces.

The objective of this work was to study the ability of a microcapillary electrochemical technique in the surface investigation of coated and bare 304L stainless steel and more specifically to make a comparison between localized and conventional large-scale

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surface analyses using voltammetric methods and electrochemical impedance spectroscopy. The first part of the work consists of the corrosion study of a bare 304L stainless steel sample in a sodium chloride solution in micro scale and so-called conventional large-scale cells. The second part of the work focuses on the surface mapping of the 304L sample under a faulty copper coating.

## 2. Experimental

### 2.1. Specimens and surface preparation

Both localized and large-scale measurements were performed on 304L stainless steel with the following chemical composition (wt.%): Cr: 17.65, Ni: 8.59, Mn: 1.75, Si: 0.41, C: 0.017, P: 0.032 and S: 0.005. The steel samples (coupons with a diameter of 12.5 mm and thickness of 2 mm) were mechanically grounded with silicon carbide paper down to 600 grit and then polished with alumina powder ( $<0.5 \mu\text{m}$ ), washed with distilled water and then rinsed ultrasonically in ethanol for 5 min.

For the second experiment, a thin copper layer was electrodeposited on a 304L stainless steel plate ( $2 \text{ cm} \times 3 \text{ cm}$ ). The latter was done according to the electrodeposition method described by Pardo et al. [19]. In brief the polished stainless steel plate was pickled in a mixture of  $\text{HNO}_3$  15 wt.% and HF 2 wt.% at  $60^\circ\text{C}$  for 2 min. The electrodeposition itself was performed in a saturated  $\text{H}_2\text{SO}_4/\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution using a potentiometric (galvanostatic) method with a current density of  $\sim 0.08 \text{ A}$  and a duration time of 300 s. A small defect point ( $\sim 300 \mu\text{m}$ ) was made in the center of the copper layer using a micro needle.

### 2.2. Preparation of the sealed microcapillary

The microcapillaries were obtained by heating glass Pasteur pipettes (2 mL) until the glass melting point and then pulling them in a special manner. The tip surface of the prepared capillaries was polished using first 600 and then 1200 grit silicon carbide (SiC) papers. This way tip diameters of  $100 \mu\text{m}$  (first set of experiments) and  $600 \mu\text{m}$  (second set of experiments) were obtained. In order to prevent leaking of the electrolyte, a silicon gasket was attached to the capillary tip. The latter was prepared by dipping the capillaries into silicon rubber, after which a stream of nitrogen was flushed through the microcapillary to keep the tip of the capillaries open without destroying the gasket. An optical microscope was used to monitor the procedure. By repeating this procedure for 2 or 3 times, thin layers of silicon were applied onto the tip of the capillaries (Fig. 1). Depending on the type of the surface analysis, the sealed microcapillary can be attached to the solid surface before drying for a single measurement or can be used after drying for surface scanning.

### 2.3. Electrochemical set-up

The localized microelectrochemical measurements were performed using a homemade microcapillary cell (Fig. 2) attached to an Autolab Eco Chemie potentiostat (PGSTAT 10). The setup is based on a common three-electrode system containing a thin platinum wire as counter electrode, a saturated Ag/AgCl reference electrode and a sealed microcapillary with a silicon gasket and with ground tip diameter of  $600/100 \mu\text{m}$  which touches only a small part of the solid sample placed on a platinum plate and forms the working electrode. The platinum plate itself is attached to a fiberglass plate with a number of holes and plastic screws, which makes it possible to fix different samples with different sizes on it before measurement (not shown in Fig. 2). To minimize the ohmic resistance during the measurement the counter electrode (here platinum wire) was placed near the tip of the microcapillary.

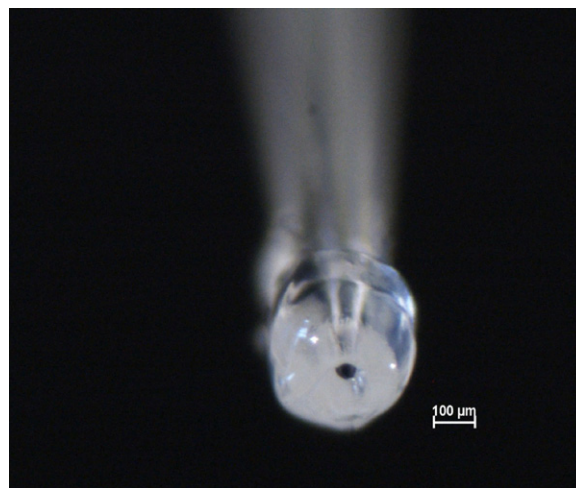


Fig. 1. Optical image of a microcapillary with silicon gasket.

The large-scale electrochemical measurements were performed using the same potentiostat in a three-electrode cell with a saturated Ag/AgCl/KCl reference electrode and a platinum plate as auxiliary electrode.

Both localized and large-scale electrochemical impedance measurements (EIS) were performed in a 1 M NaCl solution using a frequency range of 20 kHz–0.01 Hz. An amplitude of 50 mV at open circuit potential was used to decrease the noise and obtain smooth graphs. Nyquist plots of the sample were recorded before and after potentiodynamic polarization of the wetted surface. The latter was performed using linear sweep voltammetry. The potential range was between  $-1.5$  and  $1.3 \text{ V}$  (vs. Ag/AgCl) for the both micro and large-scale techniques.

In the localized surface mapping of the second experiment, the microcapillary was scanned in a  $9 \times 6$  matrix (54 measurements) across the surface while acquiring data for voltammetric technique (Fig. 3). For this the sample surface was divided into little squares of ca  $2 \text{ mm} \times 2 \text{ mm}$  using a marker, which allowed us to position the microcapillary for each measurement. The scanning was done by moving the sample. At each point a voltammetric scan in the potential range of  $-1.5$  to  $1.3 \text{ V}$  (vs. Ag/AgCl) was performed. The

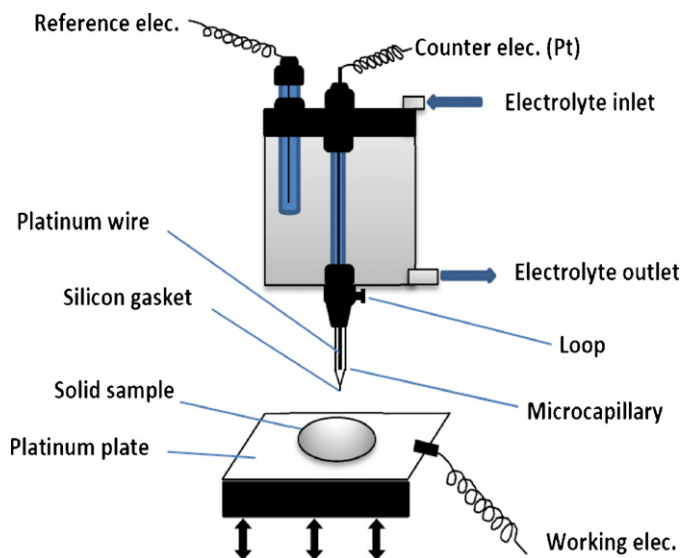


Fig. 2. Schematic drawing of the set-up of the capillary-based droplet cell.

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