
**DUTCH-BELGIAN BEAMLINE AT ESRF**

**EUROPEAN SYNCHROTRON RADIATION FACILITY**


# Experiment Report Form

### Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

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| DUBBLE | **Experiment title:**<br>In-situ SAXS/WAXS studies of AC electrograining in aluminium | **Experiment number**:<br>**MA-666** |
| **Beamline**: BM26B | **Date(s) of experiment**:<br>From: 01-12-2008<br>To: 08-12-2008 | **Date of report**:<br>06-02-2009 |
| **Shifts: 9** | **Local contact(s)**: Giuseppe Portale | |

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## Report: (max. 2 pages)

In-situ SAXS data were collected for several AC electrograining experiments at the DUBBLE beamline. Previous small angle scattering (SAS) experiments were able to resolve a porous structure within the etch film (or smut layer), formed on aluminium sheets. It was also concluded that the pores were filled with gas during the graining process; the gas was then slowly released from the film after the potentiostat was turned off. The release of gas in the smut layer can be seen by using the invariant, obtained from each frame. Figure 1 is a plot of the invariant versus time for two different aluminium foils grained in different electrolytes. The peaks in the plot correspond to data collected whilst the galvanostat is on; pore size, with in the film, is constant throughout the process.

Small angle scattering experiments were performed at a detector distance of 8m at 15keV calculated from a wet rat tail collegen standard. An absolute intensity calibration was obtained using an eltex standard. Data was collected on two separate systems. The AC electrograining system was the first system under investigation. The two primary goals of these experiments were to 1)obtain the same data at grazing incidence and 2)obtain better resolution with respect to the amount of gas within the pores for different electrochemical conditions. Secondary goals included reproducibility of the data, the affect of drying on pore size and the influence of flow across the surface and DC offset.

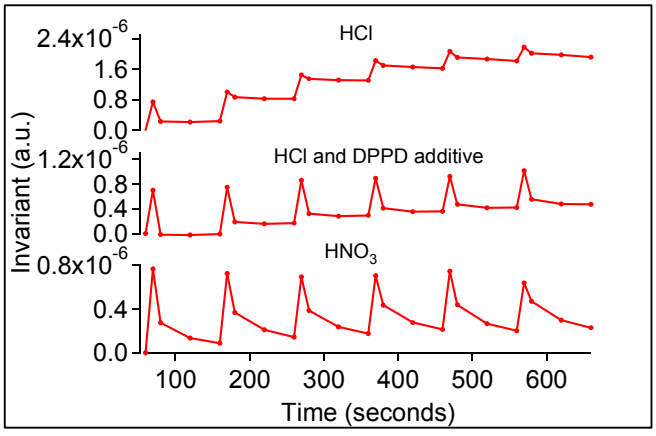


**Figure 1: Plot of the invariant of data collected from SAXS experiments at the DUBBLE beamline in 2007.**

In-situ electrograining experiments were performed in transmission geometry. Two separate "burst graining" experiments were performed. In one case, the galvanostat is turned off between bursts for 10 seconds; conversely, the same experiments were repeated with 100 seconds between bursts. These experiments were designed to evaluate the influence of gas, within the film, on film growth. Previous SAXS experiments have shown that after 10 seconds there is still gas within the film. During these 10 seconds the release of gas can be seen from a plot of the invariant, as in Figure 1. The galvanostat is then triggered after 10 seconds and film growth continues. The experiments, with longer wait times between graining allow the

complete release of gas in the film; therefore, when the galvanostat is triggered again, the graining restarts with electrolyte in the film, as opposed to gas. These two experiments should show a difference in film growth and pitting morphology. The release of gas is also seen from both. The electrochemical conditions were varied with these experiments by using HCl and $HNO_3$ electrolytes and varying the frequency and current density. The affect of flow, DC offset and drying were varied for aluminium sheets grained in HCl only. At the end of each transmission in-situ experiment, data was collected at different positions on the surface to evaluate the homogeneity of the pore size in the film.

In previous experiments a slight difference in pore size appeared between the ex-situ (dried) samples and the in-situ (wet) samples. There are several reasons why this may be. One possible explanation is that the pore size changes when the sample is dry. After the complete graining cycle was complete, gas flow was introduced into the cell and data was collected every 10 seconds for 120 to 200 frames. This data will allow us to see what happens to the pore size, as the film is dried. The drying sequence was performed after most cycles for aluminium grained in HCl only.

Burst graining experiments were also performed at grazing incidence. These experiments were designed to monitor the film growth in the plane perpendicular to the surface. The experiments were performed by filling the grazing incidence cell with electrolyte and triggering the galvanostat for 60 seconds and having it off for 60 seconds. This cycle was repeated four times. The cell was drained and data was collected for 60 seconds. Data collected from these experiments should tell us the pore dimension in the plane perpendicular to the surface.

Adsorption experiments were also performed on a copper and aluminium system. A slow, steady flow of organic molecules, in electrolyte, were passed over the surface, whilst varying the potential. To verify the molecules were adsorbing to the surface, differential capacitance was used with the SAXS data collection; the potential was scanned at a rate of 0.1 to 1mV/s between -1.4V to 0V. As the molecules were adsorbing to the surface, data was collected at different intervals. At first, data was collected every 200 seconds, as the signal was very low. Data collection then moved to shorter and shorter frames. Though not presented here, it was found that some differences in the data could be seen only when a fresh sample was prepared. The same experiments were also performed on an aluminium surface. Data collected from these experiments has not been analyzed yet.

A higher energy (15keV) was used as opposed to previous data (12keV). Scattering data from the electrograining experiments does appear to have much more noise than last time, but with better time resolution. Data collected from the DUBBLE beamline was compared with previous data collected there and data collected from the USAXS beamline at the APS. There are some small differences in the characteristic dimension of the pores, but well within experimental error. Approximately 7 times as much data was collected this time as was the previous. The SAXS will be analyzed with the aim at resolving the gas in the film as well as how different conditions effect the pore structure. Results from the analysis will be used to gain a better understanding of ionic transport across the film.

The collaboration between the University of Birmingham and the Vrije Universiteit Brussel concerning the SAXS/WAXS experiments done at the DUBBLE beamline in 2007 and 2008 will be presented during 2 conferences in 2009. A presentation entitled “In-situ analysis of etch products formed in aluminium AC electrograining using small angle X-ray scattering” will be presented by Josh Hammons at the ASST 2009 ($V^{th}$ Aluminium Surface Science & Technology Symposium) in Leiden (The Netherlands) in May 2009. An abstract entitled “In-situ synchrotron (USAXS) analysis of etch products formed during pitting of Al” has been sent to present our work at Eurocorr 2009 (the European Corrosion Congress), and will be most probably accepted as a keynote lecture in Nice, in September 2009.

Moreover, the collected data will be further discussed, and we are currently working on 2 papers to publish our work as soon as possible.

It is with great sorrow that our team has to announce the death of one of our members, dr. Orlin Blajiev. He passed away unexpectedly on the $27^{th}$ of January 2009. We will undoubtedly miss, amongst others, Orlin’s great contribution to the experimental sessions at ESRF, as well as his knowledge in the field of SAXS/WAXS.