



**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.

(next page)



	<b>Experiment title:</b> In-situ Study of Pitting of Aluminium	<b>Experiment number:</b> <b>26-02-386</b>
<b>Beamline:</b> BM26B	<b>Date(s) of experiment:</b> From: 30-11-2007 To: 03-12-2007	<b>Date of report:</b> 30-01-2008
<b>Shifts:</b> 9	<b>Local contact(s):</b> Kristina Kvashnina	
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### Report: (max. 2 pages)

The overall aim of this project is to study the AC pitting or electrograining of Al by use of SAXS/WAXS. Pitting of Al has been studied extensively due to broad application of Al alloys as structural material often in environment (e.g. maritime) where chlorides can be present. Pitting of Al is also used as a surface process to create a well-defined roughness on the substrate. This is important for the creation of large surface areas Al capacitor foil and also for the formation of highly convoluted surfaces for improving the water retentive properties for Al litho printing materials. *Controlled AC electrochemical* processing allows creating different morphologies depending on the aluminium metal composition, the electrolyte composition and the applied potentials. After many years of research, some effects like the effect of metal composition, applied potential signal and electrolyte composition are clearly understood. Yet it has been shown in the research that the formation and deposition of etch products related with the pit formation plays a crucial role in the detailed pit structure. Depending on the nature of the etch products, more crystallographic attack according to the (100) planes is observed while in other cases the pit morphology is more in a smooth convoluted form. Changing the electrolyte composition, by adding passivating anions such as nitrate or sulphate affect immediately the resulting pit morphology and hence the overall created roughness. Also the effect of local pH variations is not understood. Prior investigations have clearly indicated that the pit morphology is highly dependent on the nature of the etch products deposited during the *AC electrochemical* pitting process. The pitting process was investigated so far using two approaches. By extensive ex-situ analysis using FE-SEM, FE-AES, XPS and SIMS the pit morphology was related with the nature of the deposited etch products. With in-situ approaches the etch products were investigated as a function of pH variations using solid state NMR and the changes in electrical and optical properties were analyzed with electrochemical impedance and in-situ ellipsometry. These studies have convinced us that the nature and structure of the etch film have to be studied in-situ during polarization in the appropriate electrolyte in order to understand better why and how the pit growth depends on the etch film. In addition, *AC electrochemical modeling* is used at the moment to model the deposition of these products. As the system needs to describe mass transfer through an ionic wet film, in-situ analyses are required.

In-situ and ex-situ graining experiments were carried out at DUBBLE. All ex-situ samples were prepared on site to ensure that samples were as fresh as possible. The procedures were the same as those employed in previous studies by XPS, AES, FE-SEM, SIMS, and TEM. SAXS-WAXS data were collected from the etch films that were scraped from their sheets and also as produced on an aluminum foil. Two types of Al electrodes were used; Al foil (60 µm) and Al thin sheets (0,1 mm). An in-situ electrochemical cell was

developed that permits data to be collected in transmission during the electrograining process. Data were obtained with a camera length of 1,5 m and 8 m.

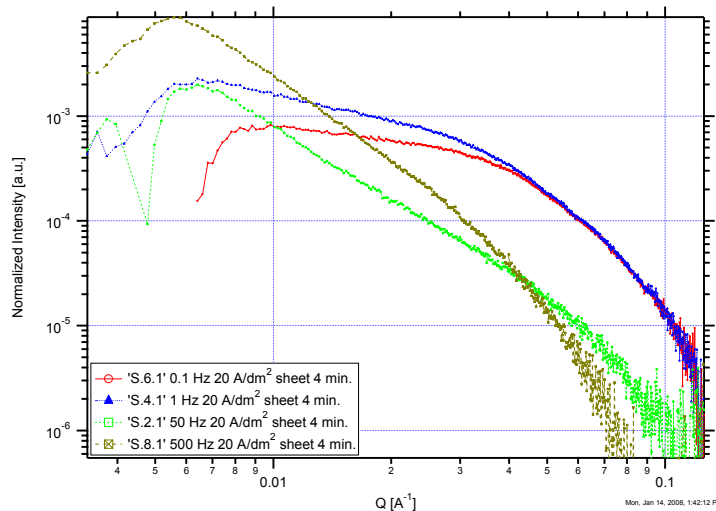
The initial aim was: 1) to determine if the SAXS experiments could resolve differences in the etch film formed under different conditions and 2) to investigate the length scale of the porosity of the smut layer since this will affect its transport properties. It was found that the data taken at a camera length of 8 m are most useful. Although data analysis is at an early stage, some conclusions have been made about both the ex-situ and in-situ experiments. In almost all SAXS data taken a small pore size population of  $\sim 10$  nm is seen. In some of the data larger pore sizes are seen. The volume fraction of the larger pores, with respect to the 10 nm pores, depends on the conditions of the respective electrograining process.

So far, the best model for the SAXS data is a poly-disperse system of pores. It is assumed that the pores are within the film and not hydrogen blisters on the aluminium plates or any other particles within the film. All of the grained samples show an approximate log normal distribution, with a mean size of 9-10 nm. Scattering from pores *ca* 10 nm is not observed in the etched aluminium, but is seen in the powders.

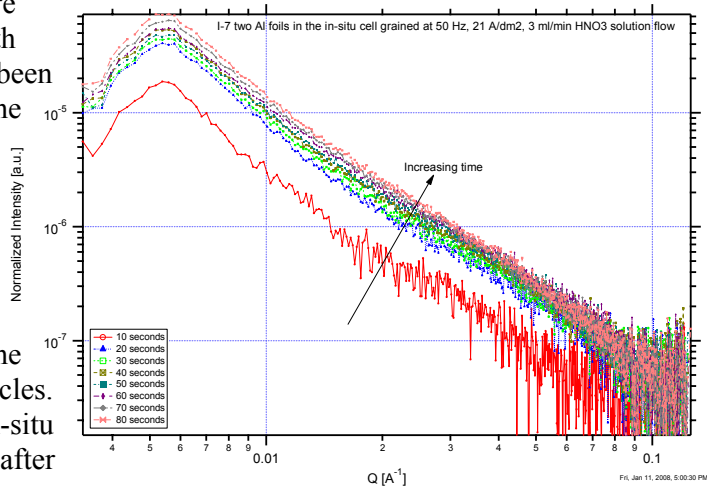
Four different sheets were grained in  $\text{HNO}_3 + \text{Al}(\text{NO}_3)_3$  at four different frequencies. As the frequency is increased, there is an increase in the volume fraction of pore sizes around 20 nm and shown in Figure 1. There are some other noticeable trends observed in the ex-situ experiments. Aluminium plates grained in HCl and HCl+DSPP show a reproducible decrease in pore volume fraction with increasing current density. However, there are some inconsistencies from samples grained in  $\text{HNO}_3 + \text{Al}(\text{NO}_3)_3$ .

All of the in-situ data indicate an increase in the pore volume fraction with time, as shown in Figure 2. The curves are similar to the ex-situ data showing the same size distribution at 9-10 nm. Current analysis from the in-situ experiments show that the pores are within the film and the volume fraction increases with film growth, which is something that has not yet been observed. The actual growth of the pores, within the film, is not resolved on the long time scales observed. Though data taken was successful, we believe that we can obtain time resolved data at each anodic and cathodic cycle instead of over several cycles. This will be accomplished by lowering the frequency from 0.1 to 0.01 Hz and taking images at every 5 seconds. At these conditions we will be able to resolve the growth of the pores during the anodic and cathodic cycles. Additional improvements will also be made to the in-situ experiments by including images of the Al electrodes after

the film has been removed for background subtraction; this was proven to be necessary for better background subtraction. Additionally, the grazing incidence cell will be used in order to ensure the pores are isotropic, with respect to the dimension not evaluated in transmission geometry. Based on results from these experiments, the frequency should be varied for each sample solution to clarify the trend in pore size distribution for different graining solutions (HCl and HCl+DSPP). From this point of view the data will be further discussed and it will be tried to publish a paper between the University of Birmingham and the Vrije Universiteit Brussel.



**Figure 1 is a plot of the SAS data taken for four different Aluminum sheets grained at different frequencies.**



**Figure 2 is a plot of the SAS data taken for one of the in-situ experiments. Other in-situ data are similar**