EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

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.

ESRF	**Experiment title:** Nanotomography of aerogels	**Experiment number**: sc4154
Beamline: ID16A	**Date of experiment**: from: 18.11.2015 to: 20.11.2015	**Date of report**:
Shifts: 6	**Local contact(s)**: Julio Cesar Da Silva	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Lorenz Ratke[1], Barbara Millow*[,1], Marina Schwan*[,1], René Tannert*[,1], Ameya Rege*[,2], Mikhail Itskov[2]

[1]Institute of Materials Research, German Aerospace Center, Germany

[2]Department of Continuum Mechanics, RWTH Aachen University, Germany

Report:

Summary:

A. Targeted goals of the project:

a) Knowledge of porosity: SEM images give information about particles, not porosity. Standard techniques such as nitrogen adsorption tests are imprecise, defective, limited to pore sizes <100 nm, and imply pore shapes to be cylindrical. Such 3D reconstruction would give insights into pore sizes >100 nm.
b) Knowledge of the structure and connectivity: Besides providing precious data for nano-mechanical modelling (using the generated 3D structure data), it would be helpful towards tailoring the mechanical and thermal properties of aerogels.

B. Targets achieved:

a) First, this attempt is conclusive that carbon and resorcinol-formaldehyde (RF) aerogels can sustain radiation and can be tested at the ESRF beamline.
b) Using 60 nm voxel sizes, sharp images from volume reconstructions were obtained. Noise was generated due to the presence of the glass tube around the specimen, but this was worked upon during post-processing of the data.
c) The generated data gives insight to pores in the upper nano region (>200 nm) and lower micro region (<50 μm), which is very useful information. Pores at these scales cannot be obtained using nitrogen-adsorption tests (*e.g.*, BJH calculations) or using mercury porosimetry.
d) The 3D microstructure could be visualised with 60 nm voxel sizes, although the particle definitions could not be seen

C. Targets not achieved:

a) Images obtained at 10 nm voxel sizes were not very helpful. This was primarily because the specimen size was to too large for rendering nanotomographs at such low voxel sizes, and only a part of the specimen was captured. Although results were obtained, they do not help in understanding the underlying microstructure.
b) There was sample movement in some specimen (see, for instance, Figure 1b).
c) Pore shapes below 200 nm could not be visualised, due to the limitation on the voxel size, which, in turn was based on the specimen size.
d) The 3D nanostructure could not be visualised, due to the limitation on the voxel size based on the specimen size. Also - as mentioned above-, the microstructure is seen without particle definitions.

Detailed work report:

A. Sample preparation:

Four aerogels were synthesized for holotomography experiments: two resorcinol-formaldehyde and two carbon aerogels [1-3]. The monolithic carbon aerogels were dried and pulverized by means of a ball mill. Since they are softer, monolithic resorcinol-formaldehyde aerogels were ground with abrasive paper. No morphological changes in the network were observed in SEM after milling. After pulverisation, the powders were dried in an oven at 120°C over night to remove any water adsorbed from air.

Thin-walled quartz glass capillaries of 100 µm outer diameter and 10 µm wall thickness (Hilgenberg, Germany) were then densely filled with dried powder. The capillaries were then cut, sealed with paraffin wax, and fixed with Loctite Super Glue 3 onto sample holders for nanotomography.

B. Experimental setup:

The experiments were performed at beamline ID16A with X-ray energy of 17 keV at room temperature. During the tomographic scan the specimens were rotated around the vertical axis. The samples were imaged with 2000 projections at four different distances. Voxel sizes of 10 nm and 60 nm were used.

C. Data rendering:

3D reconstructions of aerogels tested at voxel sizes of 60 nm:

All four samples (soft and hard carbon aerogels, and soft and hard RF aerogels) have been tested and resulted in good 3D visualisations above 200-300 nm scale range. Pore sizes above 150 nm can be characterised, *i.e.* sufficient data on micro-porosity was obtained. In Fig. 1, one can observe the 3D structures of all four specimens along with their sliced/zoomed versions generated using Visual Graphics Studio MAX 2.2.

Fig. 1(b) shows the hard carbon aerogel sample, which is visibly moved during testing. Other three samples seem to be rather stable. The results show that the soft aerogels show larger pores and larger cavities, in comparison to their hard counterparts. This is only a first interpretation of the structure, while a more detailed analysis is ongoing.

3D reconstructions of aerogels tested at voxel sizes of 10 nm have not been shown, as no clear visualisations could be obtained.

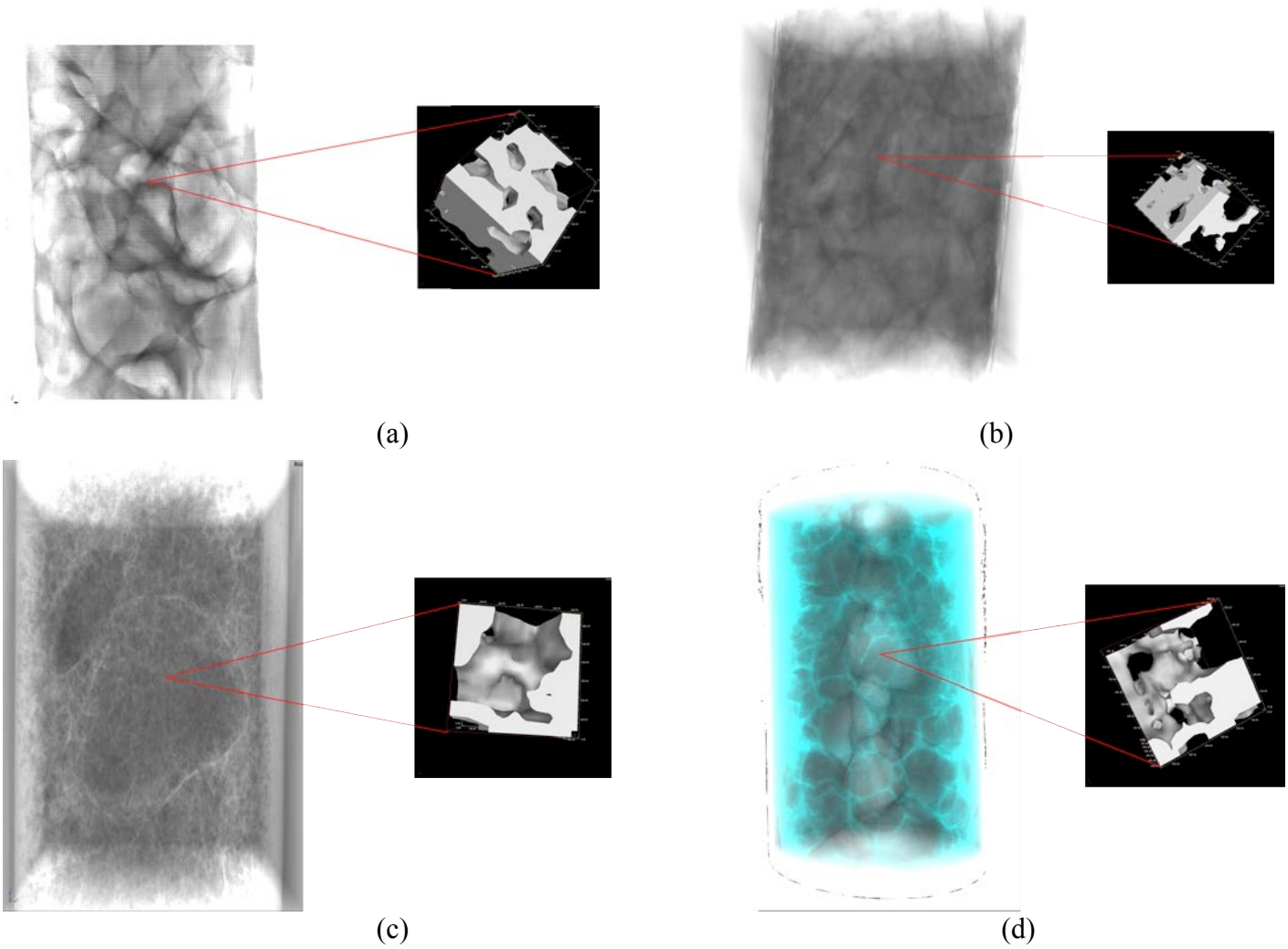

Fig. 1: (a) Hard RF aerogel, (b) hard carbon aerogel, (c) soft RF aerogel, and (d) soft carbon aerogel. These images show the complete cylindrical specimen (100 µm) along with their zoomed version (600nm).

Outlook:

We have applied for more time at the ESRF for nanotomography experiments. With our first experience, and guidance from the on site team at ID16A (especially our local contact Julio Cesar Da Silva), we will be improving our sample preparation techniques in order to suit experiments on ID16A more effectively. Smaller specimen (approx. 10 µm) will enable us to attempt going to low voxel sizes. Accordingly, we intend to capture particle definitions, and obtain good visualisations at the nano-scale (also identify nano-porosity).

References

[1] Pekala R. Organic aerogels frm the polycondensation of resorcinol with formaldehyde. Journal of Materials Science 1989;24:3221-7.
[2] Pekala R, Alviso CT. Carbon Aerogels and Xerogels. MRS Online Proceedings Library 1992:3.
[3] Schwan M, Tannert R, Ratke L. New soft and spongy resorcinol – formaldehyde aerogels. The Journal of Supercritical Fluids 2016;107:201-8.