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

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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:** **Hydrogen cycling effect on the local order to high entropy alloys**	**Experiment number**: MA 5434
Beamline: ID15	**Date of experiment**: from: 19/01/2023 to: 21/01/2023	**Date of report**: 22/02/2023
Shifts: 6	**Local contact(s)**: Gavin Vaughan	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Nayely Pineda-Romero, PhD student at ICMPE CNRS

*Tales Ferreira, postdoctoral researcher at ICMPE CNRS

*Claudia Zlotea, researcher at ICMPE CNRS

Report:

We are currently studying several high entropy alloys $Ti_{0.30}V_{0.25}Zr_{0.10}Nb_{0.25}M_{0.10}$ with *M* = Mg and Cr, (ii) $(TiVNb)_{100-x}Al_x$ (x = 0, 5, 10) and (iii) $(TiVNb)_{100-x-y}Al_xMo_y$ (x, y = 0, 5, 10) for hydrogen storage applications. These alloys can reversibly absorb hydrogen at room temperature and form interstitial hydrides with high storage capacity. However, the hydrogen absorption/desorption cycling of our materials in the laboratory showed several behaviours depending on the alloy's chemical concentration: several alloys can lose up to 10 % of their initial capacity in the second cycle, whereas others are constantly decreasing the uptake, and few are stable during cycling. The reason of such behaviour is not yet known despite several reports on cycling behaviour of HEAs. Moreover, laboratory X-ray diffraction before and after cycling did not allow us to conclude about a possible structural change nor phase segregation. Therefore, the main objective of the proposal was to study the local crystal structure in various high entropy alloys as well as the induced modification during hydrogen absorption/desorption cycling by *in situ* X-ray total scattering and associated PDF analysis.

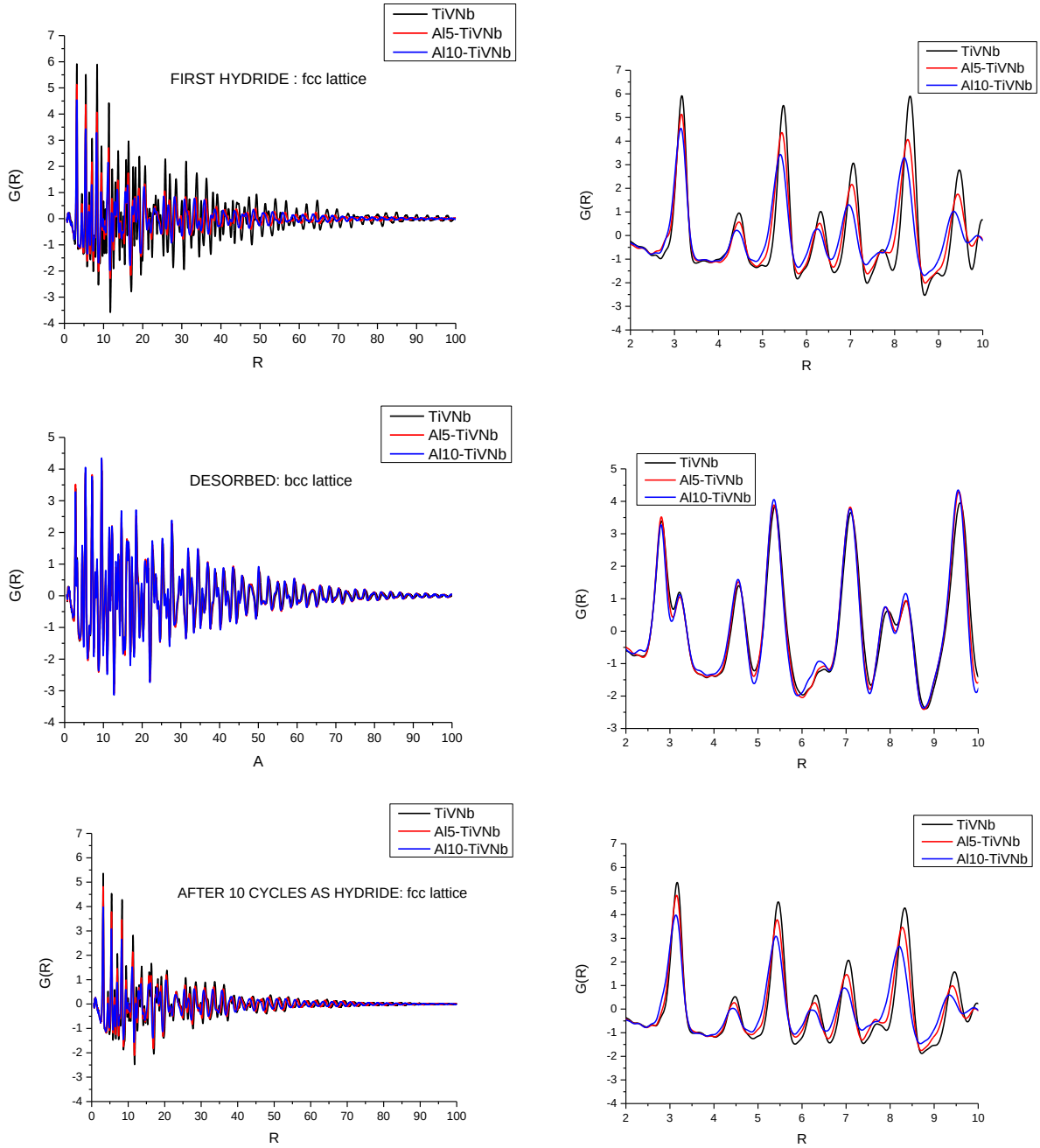
During these two days, we experienced some beam technical issues that hindered us to measure our samples for several hours. For this reason, we have performed exclusively ex situ measurements of powder samples inside capillaries. We have attempted one in situ experiment on the $TiVNbH_2$ hydride in the last 2 – 2 ½ shifts. We could follow the phase transformation during the hydrogen desorption under secondary vacuum by heating from 25 to 400 °C. However, during this step the surface sample get passivated because of small leaks in the vacuum system. Unfortunately, the surface passivation made the rehydrogenation of the desorbed phase impossible at room temperature under 10 bar H_2 pressure.

Therefore, the following results concern ex situ measurements carried out on capillaries.

We were able to measure the following samples:

i) $Ti_{0.30}V_{0.25}Zr_{0.10}Nb_{0.25}Cr_{0.10}H_2$, $Ti_{0.30}V_{0.25}Zr_{0.10}Nb_{0.25}Mg_{0.10}H_{1.6}$,
ii) $(TiVNb)_{100-x}Al_xH_y$, $(TiVNb)_{100-x}Al_x$ desorbed, $(TiVNb)_{100-x}Al_xH_y$ after 10 cycles (x = 0, 5 and 10),
iii)$(TiVNb)_{100-x-y}Al_xMo_yH_y$, $(TiVNb)_{100-x-y}Al_xMo_y$ desorbed and $(TiVNb)_{100-x-y}Al_xMo_yH_y$ after 10 cycles (x, y = 5, 10)

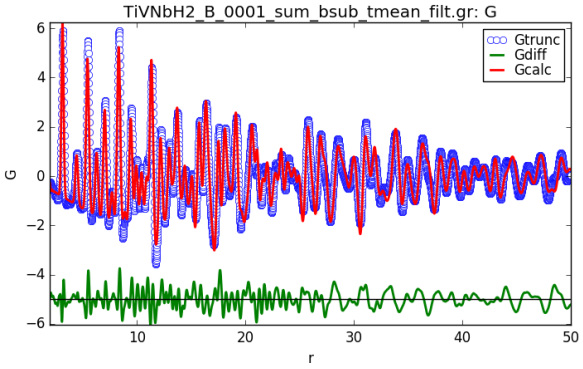
The figures below show the PDF profiles for the first hydrides, the desorbed phases, and the hydrides after 10 cycles:

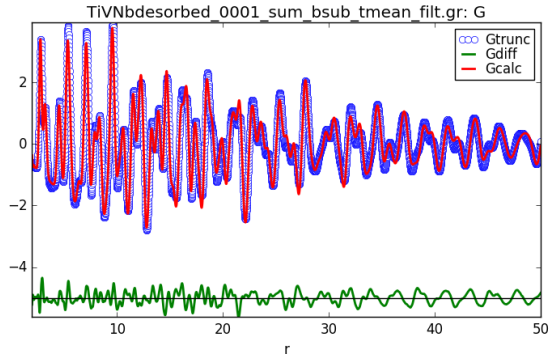


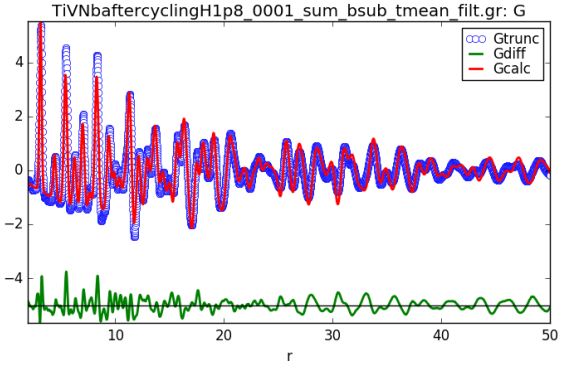
The first conclusions are:

- Al addition in TiVNb (5 and 10 %) decreases the intensity of PDF peaks as fcc hydride (first and after 10 absorption/desorption cycles) but not as bcc desorbed phase,
- The cycling seems to broaden the PDF peaks for all alloys,
- The PDF profile after 10 absorption/desorption cycles in TiVNb more rapidly decreases as compared to alloys with 5 and 10 % Al.

We have attempted to fit the PDF profiles for the $TiVNbH_2$, TiVNb desorbed and $TiVNbH_{1.7}$ after 10 cycles with the help of PDFgui program using a random distribution of metallic atoms within the fcc and bcc lattices. The fit results are shown below, and the refined parameters are given in the table below.







Sample	Structure	a (Å)	U_{iso} (Å^2)	Q_{broad}	Q_{damp}	χ^2	R_w
Hydride 1 cycle	fcc	4.448(1)	0.0105(3)	0.038 fixed	0,023 fixed	0.11	0.28
desorbed	bcc	3.221(1)	0.0189(6)			0.04	0.18
Hydride 10 cycles	fcc	4.438(1)	0.0189(7)			0.05	0.27

If the fit for the TiVNb desorbed is acceptable, there are some problems for the hydride phases, irrespective of the cycle number. Our local contact, Gavin Vaughan, is helping us to improve these fits by introducing defects into the description of the lattice.

The treatment of the rest of the data is in progress.