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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 using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now 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.

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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.

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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:** Study of the volatile fission products (Xe, I) behaviour in sintered TiN under annealing	**Experiment number**: CH/2889
Beamline: 30B	**Date of experiment**: from: 15/04/2009 to: 21/04/2009	**Date of report**: 25/11/2009
Shifts: 15	**Local contact(s)**: Olivier Proux	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

C. Gaillard[1]*, R. Bes[1]*, P. Martin[2]*, S. Gavarini[1]*, N. Millard-Pinard[1]*

[1] : Institut de Physique Nucléaire de Lyon, CNRS-IN2P3

[2] : CEA Cadarache DEN/DEC/SESC/LLCC

Report:

The aim of these measurements is to characterize the behaviour of xenon and iodine in polycristalline titanium nitride (TiN) at high temperature. Previous experiments led by RBS showed that these elements are strongly released from the TiN matrix at high temperature (up to 1700°C)[1] but the mechanisms involved is not known. For xenon, by comparison with previous works led in UO_2 matrix,[2] we can envision the formation of gas bubbles in the material but a migration by atomic migration through vacancies can not be precluded. The latter mechanism could also occur for iodine, but a sole volatilization of this element can also happen. We have thus carried out EXAFS and XANES experiments in order to gain insights into the Xe and I coordination sphere. For time reason during the allocated shifts, most of the analyzed samples contained xenon ; only a couple of iodine samples could be analysed. The influence of the TiN sintered pellets grain size and of the Xe/I concentration is investigated. Sintered TiN pellets are synthesised with three different grain sizes: 8 µm, 18 µm and 38 µm. Xe and I are introduced in the TiN samples at a 150 nm depth by ion implantation, before annealings under vacuum between 1400 and 1700°C. Two concentrations were investigated: 10^{17} at/cm² (8 atomic % at the maximum of the distribution) and 10^{16} at/cm² (0.8 at. % at the maximum of the distribution). The more concentrated samples were analysed by EXAFS while the low concentration of the latter samples could only allowed us to make XANES analysis. EXAFS and XANES experiments were led at the Xe K-edge (34.561 keV) and I K-edge (33.169 keV) on the FAME beamline at 10 K (helium cryostat) in fluorescence detection. A total of 27 samples were analysed during the 15 shifts allocated.

Looking at the XANES spectra, the Xe coordination in TiN after implantation does not depend on the grain size of TiN pellets, but a strong influence of the Xe concentration is observed (figure 1). After annealing, XANES spectra are the same for all samples, whatever the initial Xe concentration.
EXAFS measurements were performed on samples implanted at a 10^{17} at/cm² fluence. No oscillation was observed on as-implanted samples, as a sign that no long-range order exists in the samples. After annealing, Xe-Xe interactions are visible on the FT at a distance $R+\Delta \sim 4.0$ Å (figure 2), which intensity increases with the annealing temperature. This corresponds to the formation of Xe bubbles in our samples, for which the

number of Xe neighbours is characteristic of the bubble size while the Xe-Xe distance gives an information on the pressure inside the bubbles. In all Xe annealed samples, Xe-Xe distances were found to be 4.38 Å, which corresponds to the presence of unpressured bubbles. The number of Xe neighbours as a function of the annealing temperature follows two steps: first, we observe an increase of the Xe coordination number up to ~12 which corresponds to the increase of the bubble size. At this stage, the Xe release from the TiN is negligible under annealing. Then, the bubble size remains at its maximum value while the Xe release increases. When the Xe release from the sample reaches 40 %, a decrease of the Xe coordination number to ~6 is observed, hence the presence of smaller bubbles.

In the case of iodine sample, we have evidenced by XANES the presence of I(0) in our implanted sample. This probably correspond to the formation of I_2 species, which are highly volatile. We thus can conclude that the release of iodine from TiN at high temperature does not occur through diffusion but by a sole volatilization of I_2.

As a conclusion, those measurements have been very fruitful as they have allowed us to determine the state of xenon and iodine in TiN samples and as a consequence, the mecanisms involved in their release at high temperature.

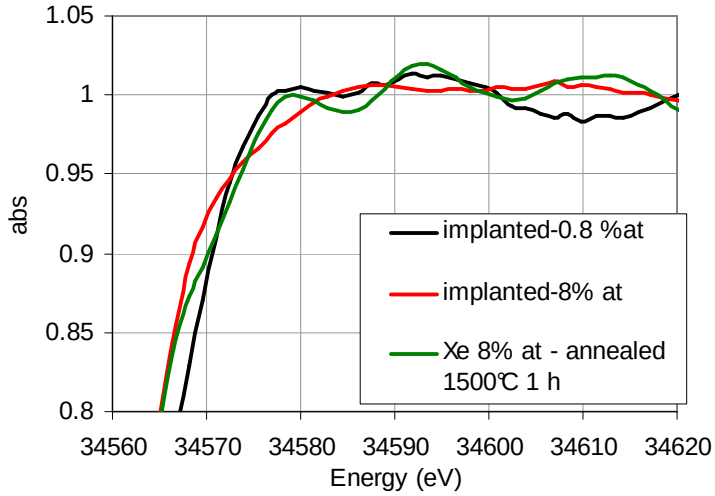

Figure 1: evolution of Xe K-edge XANES spectra as a function of the Xe concentration, before and after annealing.

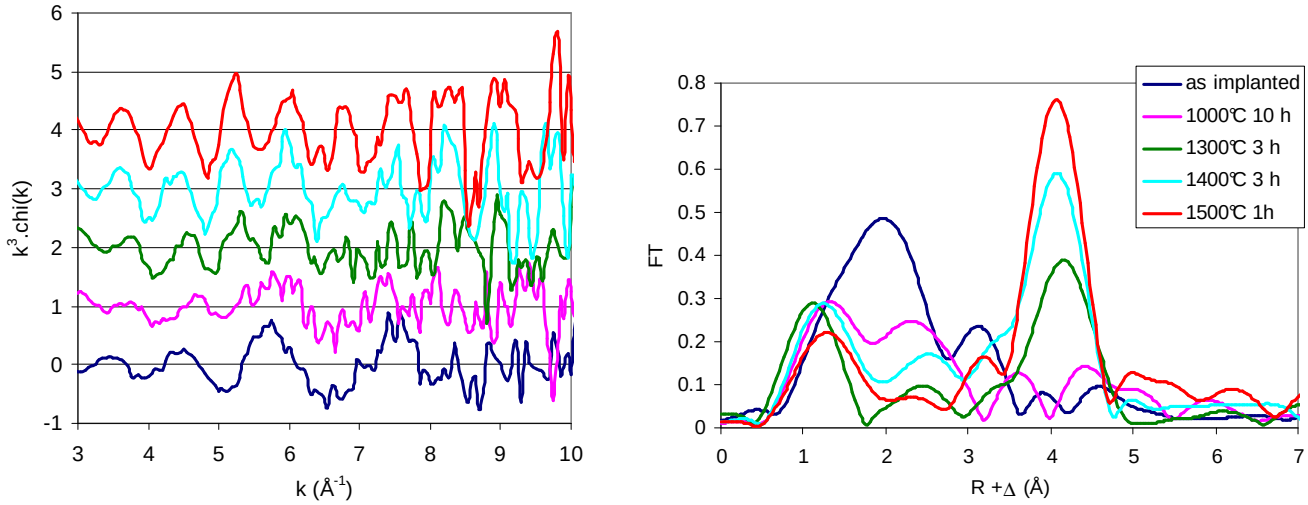

Figure 2: Evolution of the EXAFS spectra (shifted along the y-axis for sake of clarity) and FT as a function of the annealing time; TiN grain size = 38 µm

(1) Gavarini, S.; Toulhoat, N.; Peaucelle, C.; Martin, P.; Mende, J.; Pipon, Y.; Jaffrezic, H., *J. Nucl. Mater.* **2007,** 362, 364.

(2) Martin, P.; Garcia, P.; Carlot, G.; Sabathier, C.; Valot, C.; Nassif, V.; Proux, O.; Hazemann, J.-L., *Nucl. Instr. and Meth. in Phys. Res. B* **2008,** 266, 2887.