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CEA (France)

New Characterizations at the MARS Beamline
(SOLEIL Synchrotron Radiation)

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New Characterizations at the MARS Beamline
(SOLEIL Synchrotron Radiation)

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MARS (Multi-Analyses on Radioactive Samples) is the X-ray bending magnet beamline of the French synchrotron facility SOLEIL dedicated to the study of radioactive matter by means of a multi-technique equipment [1].

The MARS beamline is the fourth dedicated beamline for studying radionuclides in Europe (after the ROBL beamline at ESRF (Grenoble, France), the INE beamline at ANKA (Karlsruhe, Germany) and the microXAS beamline at SLS (Villingen, Switzerland) and aims at extending the possibilities of synchrotron based X-ray characterizations towards a wider variety of radioactive elements (α, β, γ and n emitters). Thus, its specific and innovative infrastructure has been optimized to carry out analyses on radioactive materials with global activities up to 18.5 GBq per sample [2]. Particularly, it offers unique possibilities for studying γ and neutrons emitters’ samples with an activity up to 2 GBq. Nevertheless, such a possibility supposes to obtain special authorizations from French safety authorities (ASN) based on specific technical innovations to assure the confinement of samples and to reduce the dose rate during their manipulation on the beamline.

This beamline, which has been built thanks to a close partnership and support by the CEA, has been designed to provide X-rays in the energy range of 3.5 keV to 35 keV. Three main techniques are progressively proposed on MARS beamline: transmission and high-resolution powder X-ray diffraction (respectively TXRD and HRXRD), X-ray absorption spectroscopy (XAS) and X-ray fluorescence (XRF) [3].

After the preliminary experiences performed in 2009-2010 on un-irradiated samples [1, 3, 4], this presentation deals with recent results obtained at the MARS beamline, thanks, (i) to very powerful and useful improvements brought to the experimental set-up of the beamline (especially High Resolution diffractometer, fig. 1) and (ii) to various materials irradiated at high doses with ions (ODS up to 200 dpa) and also Zr based alloys irradiated with neutrons in Pressurized Water Reactors up to 5 PWR cycles.

The results obtained by X ray Diffraction on secondary phases evolutions as a function of irradiation doses for both ODS and Zr based alloys will be exposed, along with the very first XAS experiences performed on ODS materials.

Finally, future prospects and main objectives concerning the evolution of the beamline for our program on irradiated materials will be discussed; for example the milestone for 2013 concerning the analysis on ODS irradiated at high doses with neutrons.

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Fig. 1: High Resolution X Ray Diffractometer at the MARS beamline.

References

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* Multi Analyses on Radioactive Samples

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BRIEF OVERVIEW OF THE MARS BEAMLINE

National synchrotron facility, third generation source

29 beamlines foreseen
24 beamlines opened to users on 2nd semester 2012

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Energy</td>
<td>2.75 GeV</td>
</tr>
<tr>
<td>Circumference</td>
<td>354 m</td>
</tr>
<tr>
<td>Emittance H</td>
<td>4 nm.rad</td>
</tr>
<tr>
<td>Current Intensity</td>
<td>400 mA (430 mA in 2012)</td>
</tr>
</tbody>
</table>

Radioactive samples: Currently only allowed on MARS beamline

(1st beam in december 2008)
Multi-Analysis on Radioactive Sample (MARS) beamline, at synchrotron SOLEIL, is fully dedicated to advanced structural and chemical characterizations of radioactive matter (solid or liquid).

Energy range of the X-ray beam: **3.5 to 35 keV**

A multi-technique beamline infrastructure and optics optimized for: Absorption spectroscopy, Fluorescence, Diffraction

Sample maximum activity on MARS beamline:
- **✓** 18.5 GBq per sample for α- and β-emitters
- **✓** 2.0 GBq per sample for γ- and n-emitters
LAYOUT OF THE MARS BEAMLNE (SIDE VIEW)

A “hot” beamline inside a standard synchrotron building

- Global length: 40 m
- Restricted area: ~100 m²
- Low pressure: -80 Pa
- Fireproof: 2 h

Max. dose rate limitation:
- Inside 2 mSv/h and outside 0.5μSv/h
Collimating mirror Si/Pt
(110 x 1200 mm$^2$)

Focusing mirror Si/Pt
(110 x 1200 mm$^2$)

Double crystal monochromator
Si111 or Si220
(sagittal focusing)

First H/V slits

Secondary H/V slits

Beam catcher
(W block with 2 channels)

H alignment slit

Pb Bremsstrahlung wall

W beam shutter

Single crystal monochromator
Si111 or Si311
(2013 or later)
Two experimental stations are being used alternatively on the monochromatic branch

Standard Absorption station
XAS, T-XRD, XRF
Opened to users: 2010

High Resolution Diffraction station
HR-XRD with 4 circles diffractometer
Opened to users: 2011

Monochromatic branch:
Standard spot size (HxV) ~ 300 x 200 μm²
Flux 5x10¹¹ ph/s at 17 keV
with Si(220) and I = 400mA
Fuel cladding materials studied at the Nuclear Energy Division:

**Zr based alloys** for Gen2&3 reactors (PWR)

- M5™: Zr-1%Nb corrosion behaviour largely improved thanks to Nb addition
- β-Nb: natives + accelerated precipitation under irradiation

**ODS steels** for Gen4 reactors (SFR)

- Ferritic/martensitic steel: to reduce swelling, reinforced with nanometric oxide to reduce thermal creep

**6 PWR cycles**

Same goal for both studies: secondary phases (less than 0.5% vol. fraction) evolutions under irradiation
1 - Zr BASED ALLOYS IRRADIATED IN PWR CONDITIONS: 0, 1, 2 AND 5 PWR CYCLES (up to $11.10^{25} \text{n/m}^2 @ 330^\circ \text{C}$)

**XAS station used: Transmission X-Ray Diffraction**

**XRD analysis in transmission mode**
- Using a 2-dimensions image-plate detector
- Sample positioned on an 8-axis motorized stage

- **X-ray beam energy**: 17.038 keV
- **Beam size (H x V)**: 100 x 100 µm²
- **Exposure time**: about 240 s

Unirradiated/Irradiated sample: thin foil 3 mm in diameter and 100 µm thickness machined from the tube
The $\beta$-Nb diffraction peak after irradiation is the convolution of 2 contributions:

- Native $\beta$-Nb precipitates
- Radiation-enhanced $\beta$-Nb particles

With increasing irradiation doses:

- Paper accepted at ASTM 2013, 17th International Symposium on "Zirconium in the Nuclear Industry", February 03-07, 2013, Taj Krishna, Hyderabad, India
RESULTS (2/2)

➢ Analyses of the **initial β-Nb precipitates** vs irradiation dose

![Graph showing Nb content vs fluence](image)

Consistent with TEM analyses (S. Doriot, M. Griffith, V. Shishov, ASTM 1996) but with higher statistic and better accuracy.

Example of deconvolution: 2 PWR cycles

➢ Analyses of the **radiation-enhanced β-Nb particles** vs irradiation dose

Data not accessible by TEM: nanometric particles (less than 0.5 vol. fraction) can be analyzed using XRD at MARS beamline.

- Paper accepted at ASTM 2013, 17th International Symposium on "Zirconium in the Nuclear Industry", February 03-07, 2013, Taj Krishna, Hyderabad, India
**Scientific applications of HR-XRD can broadly classified as:**
- solving and refining of complex crystal structures,
- measurements of residual stress, textures,
- microstructure characterizations from analysis of peak shapes,…..

**1- A robust diffractometer (SMP)**
High precision stage $\Omega$, $2\theta$

**2 - A goniometer (CEA/DEN, Symétrie)**
With high precision, weight capacity of 5 Kg, a sphere of confusion of 40 $\mu$m between 3 rotation axes, $\Omega$, $\chi$ and $\varphi$

**3 - A detection system (CEA/DEN, COMAT)**
24 crystals analyzer Ge(111 crystals)
24 detectors
**Comparison** between the diffraction peak from the (100) reflection of the standard NIST LaB6 powder recorded at 17.038 keV with the PM1 detector of the multi-crystal analyzer and with a MAR345 detector.

Typically the FWHM linewidth is reduced by a factor of 10 with the use of the multi-analyser (FWHM are below 0.01°) compared to the MAR345 result.

Application to irradiation defects in Zr based alloys
<br><c> loops density, directly linked to radiation induced growth of Zr alloys

Broadening of diffraction peaks (~micro-deformation) => work in progress
ODS alloys studied

Fe-9Cr-0.1C-1W + 10 wt% Y₂O₃ as modelling alloy at powder state

Fe-18Cr-1W-0.4Ti + 0.56 wt% Y₂O₃ as consolidated samples

CEA fabrication/ODS Project

Characterization of the nano-oxide dispersion

SANS

TEM (EDS and EFTEM)

TAP

nano-phases (~2–3nm)

What about the crystallographic structure, local environment during the process and before/after irradiation?

RESULTS: XRD ANALYSES AT DIFFERENT SCALES AND STEPS IN THE FABRICATION PROCESS (before irradiation)

**XAS station used: Transmission X-Ray Diffraction**

A single grain of powder mounted on an iron based tip and glued with silver lacquer

**Fe-9Cr-0.1C-1W + 10 wt% Y₂O₃ model alloy**

Global TXRD diffractogram obtained for a single grain of powder during the process

**Consolidated** thick rectangular bar annealed at 1300°C 1h

Fe-18Cr-1W-0.4Ti + 0.56 wt% Y₂O₃

Precipitation happens during the consolidation process with thermal annealing => Y₂O₃bcc cristallite sizing ~20 nm

(L Toualbi et al. JNM 2012)

Nano structured Y₂Ti₂O₇ pyrochlore type phase can be analyzed using XRD at MARS beamline, cristallite sizing ~15 nm (ML Lescoat et al. JNM 2012)
RECENT ANALYSES: X RAY ABSORPTION SPECTROSCOPY (XAS)

For previous materials: in fluorescence mode at the Y K<sub>α</sub>-edge (E ~17.038 keV) in a He flow cryostat running at ~10 K

X-ray Absorption Near Edge Spectroscopy (XANES)

Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS)

EXAFS spectra at 20°C on Fe-K edge (7.112 keV)

Fe<sub>18</sub>Cr<sub>1</sub>W<sub>0.8</sub>Ti<sub>+0.3</sub>MgO model alloy, after ion-irradiations (Jannus Saclay) at 500°C (ML Lescoat, 2012).

⇒ 50 to 215 dpa : quantitative analysis of the local atomic configuration as a function of irradiation dose

work in progress

9%Cr ODS alloy is very similar to the one from Y<sub>2</sub>O<sub>3</sub>-bcc reference, 18%Cr ODS alloy: coexistence of structures other than Y<sub>2</sub>O<sub>3</sub>-bcc, Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> nano-structured

CONCLUSIONS AND PERSPECTIVES

CEA/DEN sponsoring the MARS beamline since the beginning => first analyses for samples with activities < exemption limit (weakly activated materials) at room temperature using approved sample holders.

- Original results concerning secondary phases evolution under neutron irradiation (Zr based alloys, M5™ from 1 to 5 PWR cycles)

Beamline is operational using a standard focused beam (300x200\(\mu\)m\(^2\)) HR-XRD station and collimated beam (50x50\(\mu\)m\(^2\)) XAS station.

- HR-XRD station is in operation (irradiation defects have been quantified in Zr based alloy) ; adding off axis imaging plate geometry (excellent sensitivity).
- XAS station: Analyses using micro focused beam with KB optics (10x10 \(\mu\)m\(^2\)) are available => local analyses and small quantity of material can be studied (ODS powder grain, Zr metal/oxide interfaces,...).
- XAS station: XANES and EXAFS from 10K to RT, before/after irradiation (demonstration from charged particles-Jannus-irradiated ODS steels => D. Menut PhD 2012-2015).

Future:

Beamline should be opened for samples with activities above the exemption level and for low and high temperature conditions after authorizations from the French Safety Authority (ASN), September 2013.
Multi-crystal analyzer with 24 channels composed of Ge(111) crystals

Diffractometer with two coaxial high precision rotation stages ($\theta$, $2\theta$)

Goniometer with:
- Two high precision ($\chi$, $\varphi$) rotations (sphere of confusion of 40 $\mu$m in diameter)
-- Three translation stages ($T_x$, $T_y$, et $T_z$)

Incoming monochromatic X-ray beam

MAR 345 Imaging plate

sample