MICROSTRUCTURAL EVOLUTION OF M5™ ALLOY IRRADIATED IN PWRs UP TO HIGH FLUENCES. COMPARISON WITH OTHER Zr BASE ALLOYS.


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Irradiation-induced microscopic defects and microchemical modifications can impact the in-service behavior of cladding tubes

- <c>-component loops are responsible for the growth phenomenon
  - D. Gilbon et al. ASTM STP 1245, 1994, pp. 521-548

- The level of alloying elements present in solid solution can impact the mechanical properties

The aim of this study was to assess the evolution of the matrix Nb content and of the <c>-component loop linear density versus fluence.
I. Materials of the study and irradiation conditions

II. Experimental Procedures
   - Analytical Transmission Electron Microscopy
   - Synchrotron Transmission X-Ray Diffraction at the MARS beam-line (Synchrotron SOLEIL facility, France)

III. Experimental Results
   - Native $\beta$Nb particles in M5™
   - Radiation-Enhanced Particles
   - $<c>$-Component Loops

Conclusion
I.- MATERIALS OF THE STUDY AND IRRADIATION CONDITIONS
This study is focused on fully RXA M5™ alloy with a homogeneous highly refined dispersion of $\beta$Nb phase precipitates.

M5™ is compared to Zr1%NbO and Zy-4 alloys also in a fully recrystallized state.

- **Zy-4**: standard RXA Zy-4 microstructure with hexagonal Zr(Fe,Cr)$_2$ Laves phases evenly dispersed throughout the matrix.

- **Zr1%NbO$_A$ and Zr1%NbO$_B$**: alignments of fine $\beta$ precipitates.

- If we except Zy-4, the chemical composition of these alloys differs mainly by their iron content in the range of 100 to 650 ppm.

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I. 2.- IRRADIATION CONDITIONS

All the samples were irradiated in PWR conditions

- Cladding-tubes of M5\textsuperscript{TM} and Zr1\%NbO\textsubscript{A}: fluence level up to about 15\times10^{25}\ n/m\textsuperscript{2}\ (E>1\ MeV)

- Free-growth test tubes of M5\textsuperscript{TM} and of Zr1\%NbO\textsubscript{B}: fluence level up to about 20\times10^{25}\ n/m\textsuperscript{2}\ (E>1\ MeV)

- Guide-tubes and free-growth test tubes of RXA Zy-4: fluence level up to about 20\times10^{25}\ n/m\textsuperscript{2}\ (E>1\ MeV)
II.- EXPERIMENTAL PROCEDURES

- ANALYTICAL TRANSMISSION ELECTRON MICROSCOPY (ATEM)

- SYNCHROTRON TRANSMISSION X-RAY DIFFRACTION (T-XRD)
  AT THE MARS BEAM-LINE
  (SYNCHROTRON SOLEIL FACILITY, FRANCE)
II. 1.- ANALYTICAL TRANSMISSION ELECTRON MICROSCOPY (ATEM)

- Observation and size distribution measurement of native and radiation-enhanced particles.

- Observation and size distribution measurement of radiation-induced defects as <c>-component loops

- Microanalyses of native second phase particles with a FEG STEM microscope and an EDX analyses system.

But for very tiny particles (on the nanometric scale) the use of synchrotron–based X-Ray technique is more relevant:

- X-Ray technique, with a bigger volume of the bulk materials simultaneously analyzed, is statistically representative.

- Synchrotron permits to analyze very tiny volume fraction of particles (composition and crystallographic parameters)
II. 2.- MARS A DEDICATED X-RAY BEAM-LINE FOR RADIOACTIVE MATTER AT THE SYNCHROTRON SOLEIL FACILITY

Multi-Analysis on Radioactive Sample (MARS) beam-line, at synchrotron SOLEIL (FRANCE), 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

**Sample maximum activity** *(after agreement from the French Nuclear Safety Authority)*: up to 18.5 GBq per sample for α- and β-emitters; including 2.0 GBq per sample for γ- and n-emitters (unique!)

**Sample maximum dose rate** < 2 mSv/h (yellow zone) inside the experimental hutch; <0.5 μSv/h outside (public area)

Development of dedicated experimental set-up including radiologic shielding and specific sample environment to prevent workers from contamination risk

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II.2.- MARS A DEDICATED X-RAY BEAM-LINE FOR RADIOACTIVE MATTER AT THE SYNCHROTRON SOLEIL FACILITY

Standard Absorption station

*XAS, T-XRD, XRF, XES*

Opened to users: 2010

High Resolution Diffraction station

HR-XRD with 4 circles diffractometer

Opened to users: 2011

Two experimental stations are being used alternatively on the monochromatic branch

**Monochromatic branch:**

Standard spot size (HxV) ~ 300 x 200 µm² Flux 5x10¹¹ ph/s at 17 keV with Si(220); Si(111) for lower energies and I = 430 mA

2 symmetric rows of 12 Ge(111) crystals associated with 12 NaI(Tl) scintillators coupled on fast PM tubes giving a 24 channel point detector
II.2.- MARS A DEDICATED X-RAY BEAM-LINE FOR RADIOACTIVE MATTER AT THE SYNCHROTRON SOLEIL FACILITY

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T-XRD

Standard spot size (HxV) ~ 300 x 200 µm²
Flux 5x10¹¹ ph/s at 17 keV
with Si(220); Si(111) for lower energies and I = 430 mA

Monochromatic branch

Powder diagram → X-Ray line profile

Sample holder
II.2.- MARS a dedicated X-ray beam-line for radioactive matter at the synchrotron SOLEIL facility
Whole-pattern profile matching analyses of the unirradiated M5™

- Peaks are described by a linear combination of a Lorenzian and a Gaussian function (pseudo-Voigt)

- Mean size of the coherent diffracting domains, usually related to the mean size of the particles for precipitates without micro-strains or defects, were evaluated from a Scherrer function
III.- EXPERIMENTAL RESULTS
• Particle size increases from 35 nm to about 50 nm and then remains constant from the fluence 4x10^{25} n/m^2.

• Number density is about 1x10^{20} m^{-3} and shows a slight continuous decrease during irradiation.
III. 1.- NATIVE $\beta$Nb PARTICLES IN M5™ T-XRD ANALYSES

Zoom of the whole–pattern profile matching analyses of the M5™ with increasing irradiation fluence level (range 22.9°-25.3°)

There is a broadening, and a shift toward smaller angles of diffraction.

That means an enlargement of the lattice parameter and a corresponding lowering of the Nb content.
III. 1.- NATIVE $\beta$Nb PARTICLES IN M5™ AND IN Zr1%NbO$_A$: Nb CONTENT BY TEM AND T-XRD

**Nb content (wt %)**

- Decrease of niobium content until it reaches an « equilibrium » value of about 55-60 wt% at the fluence of $\approx 8\times10^{25}$ n/m$^2$ [observed by TEM, confirmed by T-XRD and previously observed on extraction replica by Shishov and al.]

- The total Nb content in the native $\beta$Nb particles is about half the total Nb content of the original alloy and is unchanged by irradiation (no Nb rejected into the matrix).

**Total niobium content (calculated from volume fraction and Nb content)**

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III. 2.- RADIATION-ENHANCED PARTICLES
SYNCHROTRON X-RAY DIFFRACTION ANALYSES OF THE $\beta$Nb (200) DIFFRACTION LINE

Whole pattern profile matching decomposition of the $\beta$Nb (200) diffraction line of M5™

Un-irradiated sample  after 1 cycle

- Before irradiation contribution of mainly native particles
- After irradiation rise of a new kind of $\beta$Nb particles (supposed to be radiation-enhanced particles).
- We have modeled the different line contributions to get the line position and to deduce the crystallographic parameter and the Nb content of the particles.
III. 2.- RADIATION-ENHANCED PARTICLES
(A) LATTICE PARAMETER AND Nb CONTENT BY T-XRD

After irradiation, radiation-enhanced nanometric particles were observed for the three materials containing Nb.

T-XRD analyses confirm they are $\beta$Nb particles and they form with the « equilibrium » Nb content under irradiation (~ 60 wt%).

Nb content (wt %) deduced from the lattice parameter for $M5^{\text{TM}}_A$ alloy, from T-XRD analyses
III. 2.- RADIATION-ENHANCED PARTICLES
(B) WIDTH AND LENGTH VERSUS FAST FLUENCE

- Almost circular at 1 cycle, they elongated at longer irradiation time.
- The size rises rapidly from 0 to 4 cycles (8x10^{25} n/m^2) and then remains constant.
- T-XRD measurements give rather similar values.
III. 2.- RADIATION-ENHANCED PARTICLES (C) NUMBER DENSITY AND VOLUME FRACTION

- The number density of « needle-like » particles remains constant all along the irradiation and close to $1.5 \times 10^{22} \text{ m}^{-3}$.

- The volume fraction increases to about 0.2% at $8 \times 10^{25} \text{ n/m}^2$ and then levels out.

- No impact of iron content in the range of 100 to 650 ppm.
III. 2.- RADIATION-ENHANCED PARTICLES (A+B+C) Nb TAKEN OUT OF THE MATRIX

- Based on the volume fraction by TEM and the Nb content of the « needles » thanks to T-XRD we can evaluate the total Nb taken out from the matrix by these particles.

- Total Nb content of needles rises very rapidly until 4 cycles (8x10^{25} n/m^2) and then remains content.

- More than 0.1% Nb is taken out from the matrix.
III. 3.- *<c>*-COMPONENT LOOPS

**COMPARISON M5™ AND Zr1%NbO_B ALLOYS WITH RXA Zy-4**

- **M5™**
  - \( \approx 9 \times 10^{25} \, \text{n/m}^2 \)

- **Zr1%NbO_B**
  - \( \approx 20 \times 10^{25} \, \text{n/m}^2 \)

- **RXA Zy-4**

- *<c>*-component loops much more numerous in RXA Zy-4 than in M5™ and in Zr1%NbO_B alloy for the same fluence levels.
III. 3.- <c>-COMPONENT LOOPS
LINEAR DENSITY VERSUS FLUENCE

- For M5™ and Zr1%NbO alloys, the linear density of <c>-component loops is rising slowly up to a fluence of $20 \times 10^{25}$ n/m$^2$ with a fluence threshold (for occurrence) of about $3 \times 10^{25}$ n/m$^2$.

- No influence of the iron content in the range of 100 to 650 ppm

- There is a ratio of 5 between M5™ cladding tubes and RXA Zy-4
III. 3.- \(<c>\)-COMPONENT LOOPS
LINEAR DENSITY AND GROWTH BREAKAWAY REGIME

- For RXA Zy-4 alloys irradiated in PWR conditions (at ~320°C) a fluence level of about 10x10^{25} n/m^2 appeared to correspond already to the growth breakaway regime (S. Doriot et al., ASTM STP 1467, pp 175-201). For this fluence the \(<c>\)-loop linear density was measured in our study as high as 10x10^{13} m/m^3.

- It was previously shown that no growth breakaway occurs for M5™ cladding tubes for very high doses in PWRs (Mardon et al. Proceeding of LWR Fuel Performance Meeting TopFuel/WRFPM, 2010 and V. Chabretou et al., ASTM STP 1529). This is consistent with \(<c>\)-component loop linear density much lower than 10x10^{13} m/m^3 in our study.
CONCLUSION

- **T-XRD**
  - allowed to measure for the first time the composition and the lattice parameters of radiation-enhanced nanometric needle-like precipitates: they are $\beta$Nb particles with $\sim 60\%$Nb.
  - confirms the “equilibrium” Nb content of native $\beta$Nb under irradiation of $\sim 60\%$.

- **ATEM** allowed to assess the evolution of microstructural features such as $<c>$-component loops, native and radiation-enhanced particles as a function of irradiation fluence level up to $20\times10^{25}$ n/m$^2$.

- **These two complementary techniques** permitted to propose an evaluation of the niobium content in the matrix during irradiation.

- **M5™ exhibits:**
  - no further evolution in size, number density and niobium content of the particles after a fluence of $8\times10^{25}$ n/m$^2$.
  - moderate linear density of $<c>$-component loops for cladding-tubes compared to RXA Zy-4.
  - noticeable decrease in Nb content in the matrix of more than 0.1%.

- The iron content in M5™, Zr1%NbO$_A$ and Zr1%NbO$_B$ alloys has no influence either on $<c>$-component loop linear density, or on “needle-like” particle size or density, in the range of **100 to 650 ppm**.
THANK YOU FOR YOUR ATTENTION