Centre of Excellence for Nuclear Materials

Workshop

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Nuclear Materials Characterization by Tomographic Atom Probe

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Nuclear Materials Characterization by Tomographic Atom Probe

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Nuclear Materials (reactor vessel, internal structures, fuel rod, glass containment...) undergo degradations under neutron irradiation due to particle/matter interaction. These degradations modify their physical, chemical and mechanical properties and are likely to impact the safety or the operation length of the concerned structures. It is thus crucial to anticipate and quantify these effects in order to ensure an efficient use of present or future nuclear reactors. The phenomena controlling materials behavior under irradiation are on an atomic scale.

Understanding the phenomena on this scale is thus essential for the development of a predictive simulation and understanding of the ageing and safety of materials. This atomic scale is the first floor of the multi scale approach necessary for modeling and prediction, as illustrated in figure 1. The major technique in this field is the Tomographic Atom Probe, nanoanalytical technique with atomic resolution.

Fig. 1: Development of numerical tools and experiments for a multiscale approach.

Atom Probe Tomography (APT) is an extension in 3D of the atom-probe field ion microscope (APFIM), an instrument designed in the late sixties by E.W. Müller [1]. APT is the only approach able to map out the 3D distribution of chemical species in a material at the atomic-scale. The principle of APT [2,3] is based on the field evaporation of surface atoms of the specimen (a sharply pointed needle, $R \sim 50$ nm) and the chemical identification of field evaporated ions by time-of-flight mass spectrometry. The position of atoms at the sample surface is derived from the impact position of ions striking the detector. A major advantage of APT is its quantitativity. The local composition in a small selected region of the analyzed volume is simply derived from the number of atoms of each observed species. This is a big advantage compared to number of other instruments. No calibration is required. The in-depth resolution, independent of technologic details of these instruments, reaches 10 picometers. Atomic planes can therefore be imaged and the chemical order can be both exhibited and characterised. The lateral resolution is close to 0.5 nm. This makes it possible the quantitative analysis of small precipitates in alloys or the study of solute segregation to crystal defects (as illustrated in figure 2 [4]).

The last few years have been the witness of a major breakthrough in the development of APT. Formerly limited to metals or good conductors, the implementation of ultra-fast pulsed laser to the instrument opened APT to semi-conductors or oxides [5, 6]. Laser pulses give rise to very rapid thermal pulses that promote the field evaporation of surface atoms.

Fig. 2: Tomographic Atom Probe experiment in a RPV steel. Each dot represents an atom (Si or P here). Irradiation induced clusters and segregation on dislocation lines are visible.

In addition, a wider field of view is achieved so that larger area of analysis are obtained ($\sim 100 \times 100 \text{ nm}^2$) improving therefore statistics together with shortening the number of analyses required to get the relevant information. This technique brings key information for the understanding of the evolution of the microstructure of nuclear reactor steels under neutron irradiation, evolution responsible for their hardening and embrittlement. The basic principles of the technique, the sample preparation and some examples of applications in the field of “Metals under Irradiation” [7,8,9] will be presented and discussed.

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Nuclear materials characterization by Tomographic Atom Probe

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Understanding the behavior of nuclear materials

Need to explore each scale and to link them
Need to explore more and more at small scale

To understand
Physical properties
Reliability
Ageing

No technique
is multi-scale

Contents

□ Basic Principles

- ✓ Field evaporation
- ✓ Time of flight mass spectrometry
- ✓ 3D reconstruction

□ Sample preparation

- ✓ Electropolishing
- ✓ Focused Ion Beam

□ Application to nuclear materials

- ✓ RPV steels
- ✓ Internal structures
- ✓ FeCr alloys

Prof. E. W. Müller

FIM (1955)

Basic Principle: Field Evaporation

Sample

Field Ionisation and Field Evaporation

Field Ion
Microscopy

3D Reconstruction

Basic Principle: How to obtain High Elec. Field

$$V = \frac{q}{4\pi\epsilon_0} \frac{1}{R}$$

$$E = \frac{q}{4\pi\epsilon_0} \frac{1}{R^2} = \frac{V}{R}$$

$$\Rightarrow \begin{aligned} R &\sim 100\text{nm} \\ V &\sim 1000\text{V} \end{aligned} \quad E \sim 10\text{V.nm}^{-1}$$

Thin needle shaped samples

Courtesy: E. Cadel

$$\begin{aligned} R &= 20-50 \text{ nm} \\ V &= 1 - 15 \text{ kV} \\ \beta &= 3 - 8 \\ E &= \frac{V}{\beta R} > 10\text{V.nm}^{-1} \end{aligned}$$

Field Ion Microscope = Field Ionisation of gas atoms at the surface of a metallic needle

Dislocations

Basic Principle: ToF mass spectrometry

Principle scheme of an AP

Energy conservation

$$n \cdot e \cdot V = \frac{1}{2} m \cdot \left(\frac{L_f}{t_f} \right)^2$$

Potential energy

Kinetic energy

Mass over charge ratio

$$\frac{m}{n} = 2e \cdot V \cdot \left(\frac{t_f}{L_f} \right)^2$$

Chemical nature of ions

Basic Principle: TOF and 3D reconstruction

3D Atom Probe, a projection microscope

Courtesy G. Da Costa -

Basic Principle: Mass spectrum

Mass spectrum

- Mass resolution $\left(\frac{M}{\Delta M}\right)_{\%}$
- Isotopic overlap Ex: $^{58}\text{Fe}^{2+} / ^{58}\text{Ni}^{2+}$
- Analyse conditions (Preferential evaporation)

Chemical composition

$$C_i = C_i^{mes} \pm 2\sigma$$

with

$$C_i^{mes} = \frac{N_i}{\sum_i N_i}$$

$$\sigma = \sqrt{\frac{C_i^{mes}(100 - C_i^{mes})}{N}}$$

Basic Principle: 3D reconstruction

Reconstruction of the depth

Position and chemical nature of each atom at the surface

Magnification

$$G = \frac{L}{(m+1)R}$$

$$G \sim 10^6 - 10^7$$

30x30x100 nm³

Performance and limitations

Detection efficiency

position on mass spectrum
number of isotopes
mass resolution
noise level

→ down to 10 at. ppm in most favorable cases

Lateral resolution

Magnification
Ion mass
Magnification
Temperature
Laser or electrical pulses

→ few Å

Depth resolution

Penetration depth of electrical field
($<$ reticular distance in metals)

→ d_{hkl}

Specimen preparation : Electropolishing

The most common method for metallic sample preparation

Double layer method

Micro Loop

Specimen preparation: Focused Ion beam

Principle: sputtering of sample atoms by Ga ions

Sample preparation in :

- Poor conductor, insulating materials
- material with geometry not adapted for electro polishing
- specific sites

Specimen preparation: Focused Ion beam

Annular milling

ODS model powder

- Iron and iron oxydes
- Yttrium and yttrium oxydes

Specimen preparation: Focused Ion beam

Lift-out method

- GB analysis
- Ion irradiated samples
- poor conductors

...

A. Etienne et al (2010)

$70 \times 67 \times 330 \text{ nm}^3$

Phase MAXTi₃SiC

Atomic planes Si/Ti $\rightarrow$ (0110)

C. Hatzoglou

Application of APT to RPV steels (1/3)

Exemple: French RPV steel (low Cu <0.08%)

16MND5 (A508-cl3)

Neutron irradiation

$T \sim 290^\circ\text{C}$

$\phi \sim 0.7 \times 10^{15} \text{ m}^{-2} \cdot \text{s}^{-1}$

hardening

embrittlement

Application of APT to RPV steels

Cluster identification algorithm

P Si Mn Ni Cu Fe

Solute cluster

P Si Mn Ni Cu

52×52×135 nm³

Objects	Cluster (M)	Cluster (D)	Dislocation
P	0,11 ± 0,06	0,76 ± 0,14	0,53 ± 0,12
Si	8,84 ± 0,54	6,92 ± 0,41	6,10 ± 0,40
Mn	5,60 ± 0,44	8,10 ± 0,45	5,85 ± 0,40
Ni	10,76 ± 0,59	9,69 ± 0,48	7,20 ± 0,40
Cu	0,34 ± 0,11	0,40 ± 0,10	0,27 ± 0,08
Radius	1,4	1,5	-
Density (m ⁻³)	9.2 ± 1.3		-

Application of APT to internals

Exemple: 316 Austenitic stainless steels

Bolt (316)

Cavities / gas bubbles

Dislocation loops

Segregation at grain boundaries

Formation of new phases under irradiation

TEM studies:

- γ' phase
- G phase
- Carbides
- Unknown phases

- Chemical composition
- Atomic scale description
- Solute distribution

Application of APT to internals

Irradiation effect on inter and intra granular solute redistribution in ASS?

Fe^{5+} (10MeV) irradiation of bulk ^{316}SS

Dose (ions.m ⁻²)	Dose (dpa)	Dose rate (dpa.s ⁻¹)	T (°C)
4.7×10^{20}	10	5.3×10^{-4}	350

Lift-out method

A. Etienne et al, JNM 406 (2010)

Application of APT to internals (4/5)

3D reconstruction of irradiated GB

Concentration profile through GB

Average composition of grain boundaries

Si	Cr	Ni
6.3 ± 0.1	9.4 ± 0.2	26.6 ± 0.2

Inter-granular segregation at the atomic scale

Application of APT to internals

Radiation damage into grains

$62 \times 58 \times 230 \text{ nm}^3$

Si
Ni
P

Cluster identification

- (1) Rounded / lenticular clusters
- (2) Torus shaped clusters
- (3) Segregation along Dislocation lines

	Density	Si	Cr	Ni
(1)	$1.0 \times 10^{22} \text{ m}^{-3}$	12.3 ± 0.5	10.2 ± 0.5	28.2 ± 0.7
(2)	$0.6 \times 10^{22} \text{ m}^{-3}$	7.6 ± 0.5	10.7 ± 0.6	25.6 ± 0.7
(3)	$\sim 5 \times 10^{14} \text{ m}^{-2}$	9.8 ± 0.5	10.4 ± 0.5	26.1 ± 0.8

Intra-granular segregation and precipitation in some neutron irradiated Fe-Cr alloys

Fe-Cr alloys with different Cr content:

☞ Fe - 2.5 at.% Cr

☞ Fe - 4.9 at.%Cr

☞ Fe - 8.9 at.%Cr

☞ Fe - 12.3 at%Cr

Dose : 0.6 dpa

Neutron flux: $9 \cdot 10^{13} \text{ n}/(\text{cm}^2 \text{ s})$

Temperature: 300°C

BR2 reactor (SCK-CEN) –

MIRE-Cr irradiation program

Low purity:

As measured with Atom-Probe Tomography (APT) – in at.%

Fe	Bal.	Fe	Bal.	Fe	Bal.	Fe	Bal.
Cr	2.21 ± 0.01	Cr	4.61 ± 0.02	Cr	9.16 ± 0.04	Cr	11.2 ± 0.04
Si	0.020 ± 0.001	Si	0.059 ± 0.002	Si	0.065 ± 0.003	Si	0.18 ± 0.01
Ni	0.040 ± 0.001	Ni	0.034 ± 0.002	Ni	0.057 ± 0.003	Ni	0.07 ± 0.01
P	0.0090 ± 0.0005	P	0.013 ± 0.001	P	0.013 ± 0.001	P	0.025 ± 0.002

Two independent families of clusters are revealed

Summary

Echantillon sous forme d'une pointe
pour faire de la tomographie
Image STEM-HAADF (alliage
d'aluminium AlZrSc)

Zoom sur le bout de la pointe
Image STEM-BF (alliage
d'aluminium AlZrSc)

APT
SEM
TEM