PHENIICS Fest 2018 May 28-29, 2018

Understanding the first formation stages of (Y, Ti) oxides in Oxide Dispersion Strengthened (ODS) steels

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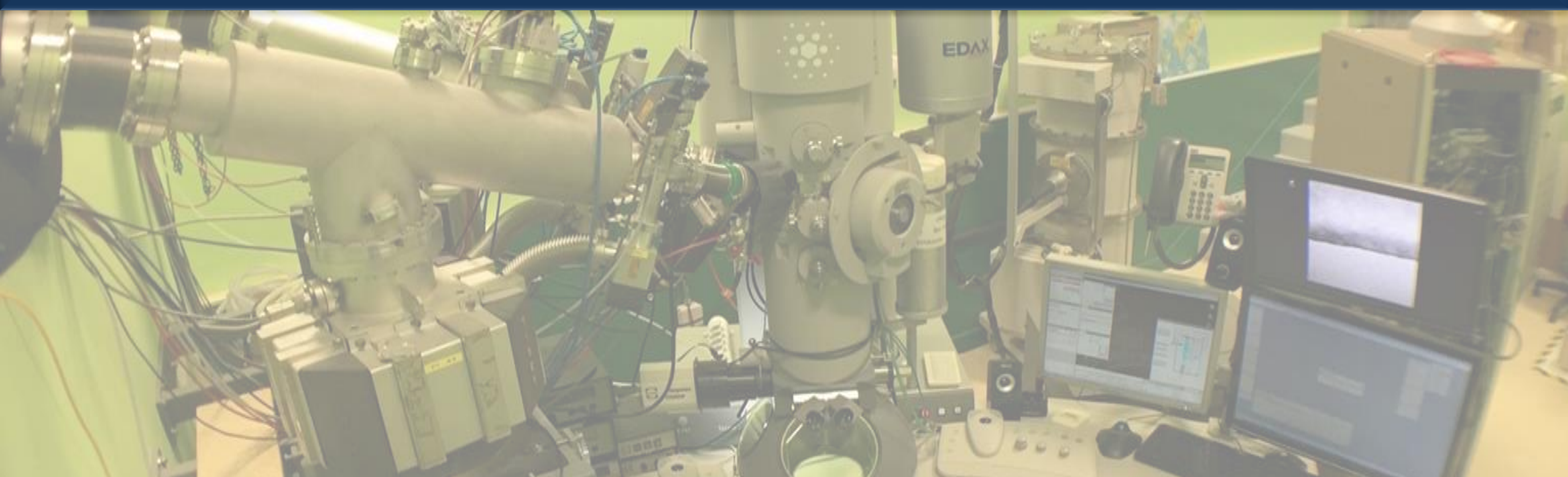
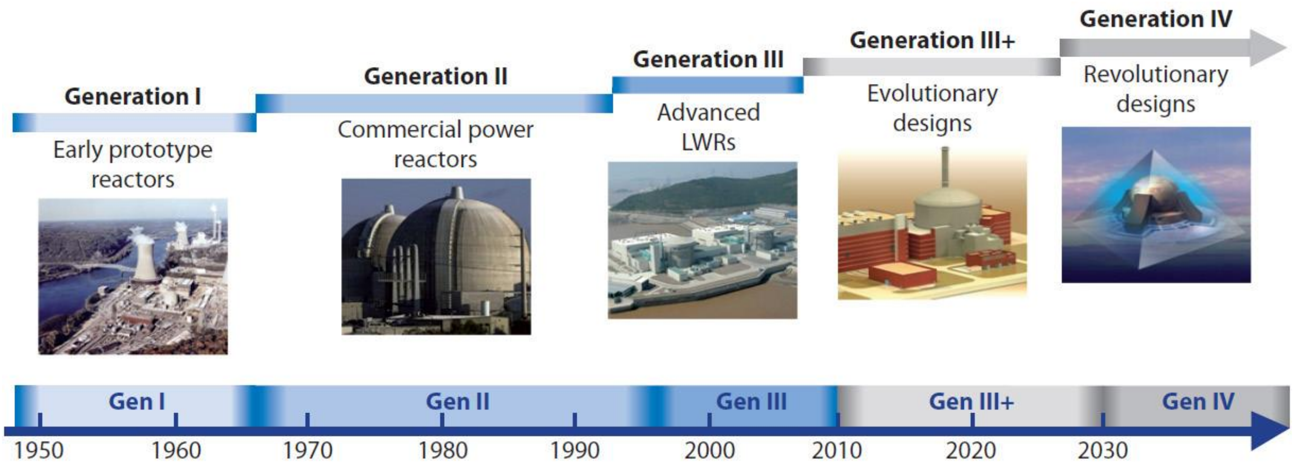


Content

Nuclear Power evolution



Gen IV Forum, 2001

Six technologies:

Sodium Fast Reactor (SFR)

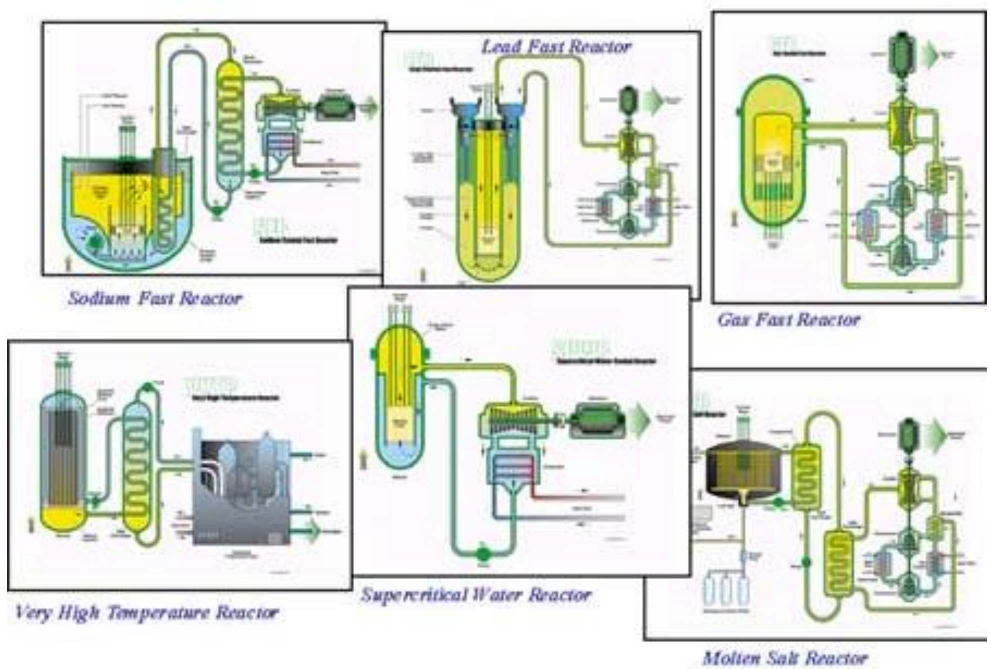
Lead Fast Reactor (LFR)

Gas Fast Reactor (GFR)

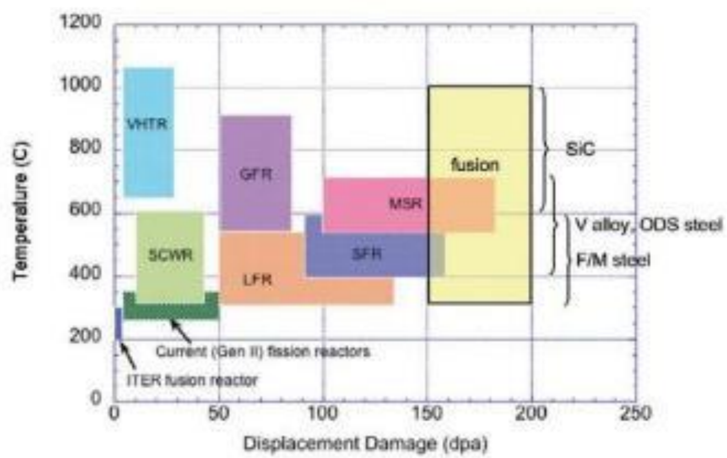
Very High Temperature Reactor (VHTR)

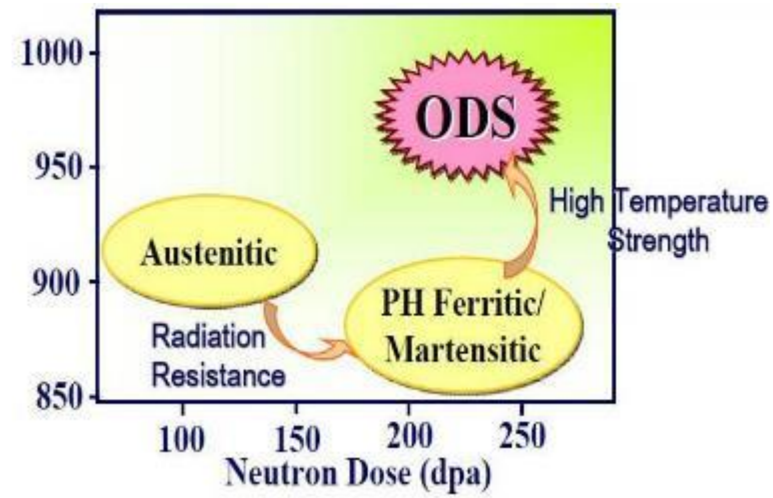
Supercritical Water Reactor (SWR)

Molten Salt Reactor (MSR)



Operating conditions and structural materials of Gen IV





Operating Conditions:

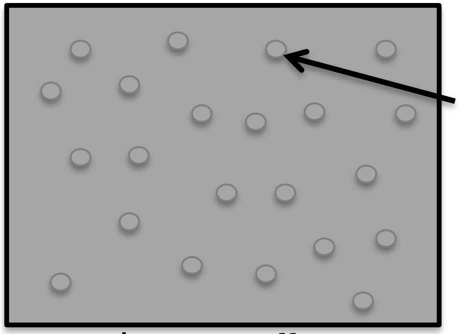
High temperature
(**500 – 1000 °C**)

High Neutron displacement damage
(up to **200 displacements per atom d.p.a.**)

Candidate structural materials:

- Austenitic steels
  - Good high temperature strength ✓
  - Swelling under irradiation ✗
- Ferritic/ Martensitic steels
  - Good irradiation resistance ✓
  - Poor high temperature strength ✗
- **ODS steel**
  - **Improved high temperature strenght ✓**
  - **Good radiation resistance ✓**

Oxide Dispersion Strengthened (ODS) steels

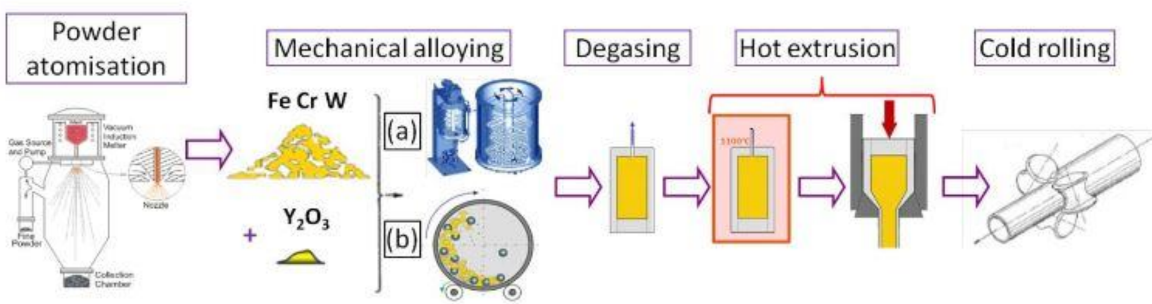


F/M ODS alloy

(Y, Ti, O) nano-particles dispersed in the alloy

Properties of ODS alloys:

- Good mechanical properties at high temperature
- Good irradiation resistance and resistance to corrosion at high temperature
- Better resistance to tension and compression



Mechanical alloying (MA)

- Production of alloying powders (FeCr, Y_2O_3, FeY, etc.) by powder atomisation
- Powder mixing (ball milling)
- Degassing system

Thermal treatment

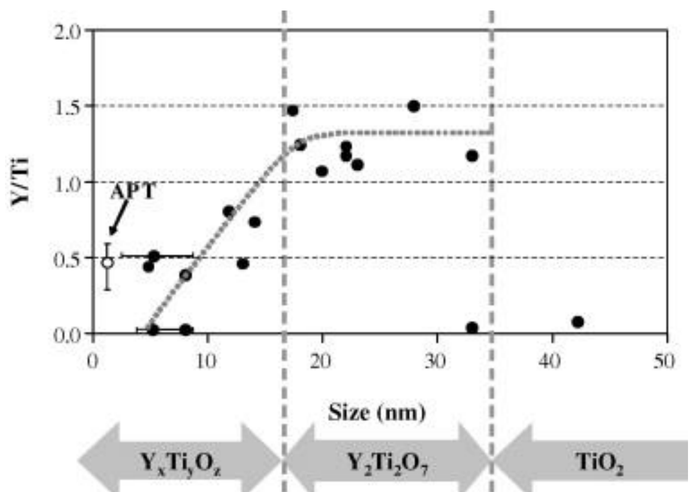
- Consolidation to favour the formation of yttrium oxides
- Cold rolling into required tubes

Nature of the nano-particles -
Y or mixed (Y,Ti) oxide nanoparticles dispersion (MA + Consolidation)

The oxides formed in ODS steels are characterized according to:
size, composition and **structure**

The nature of the particles depend on:
•The composition of the alloy
•The conditions of fabrication

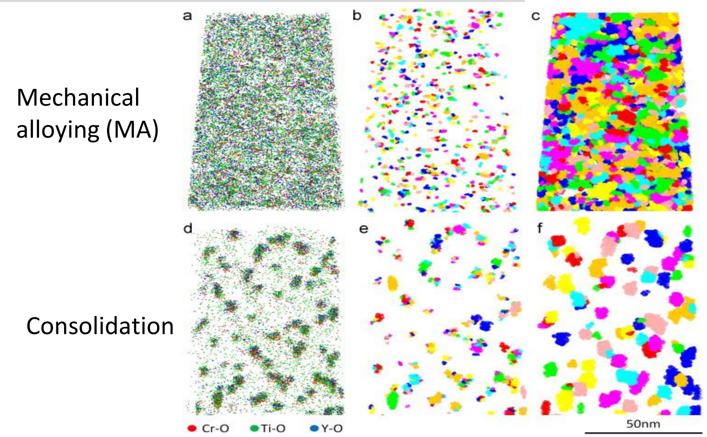
The alloys contain:
Fe, Cr (9-20%), **Y, Ti, O, Al**, Zr, and impurities (W, V, Mn etc.)



Sakasegawa et al., JNM, 2009

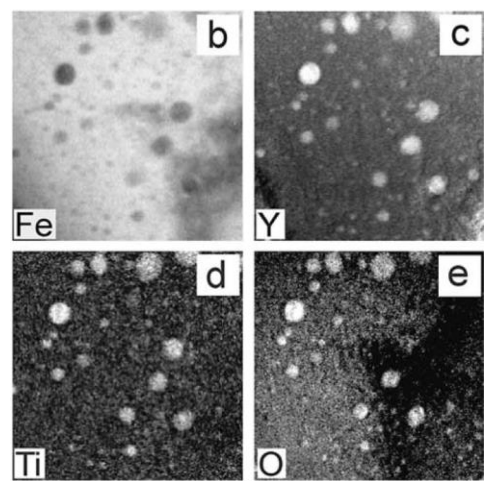
Characterization performed by mainly two main techniques

1. Atom Probe Tomography (APT)



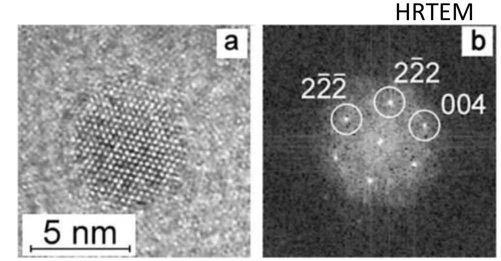
C. Williams et al., Ultramicroscopy, 2013

2. Transmission Electron Microscopy (TEM)



EFTEM

HRTEM



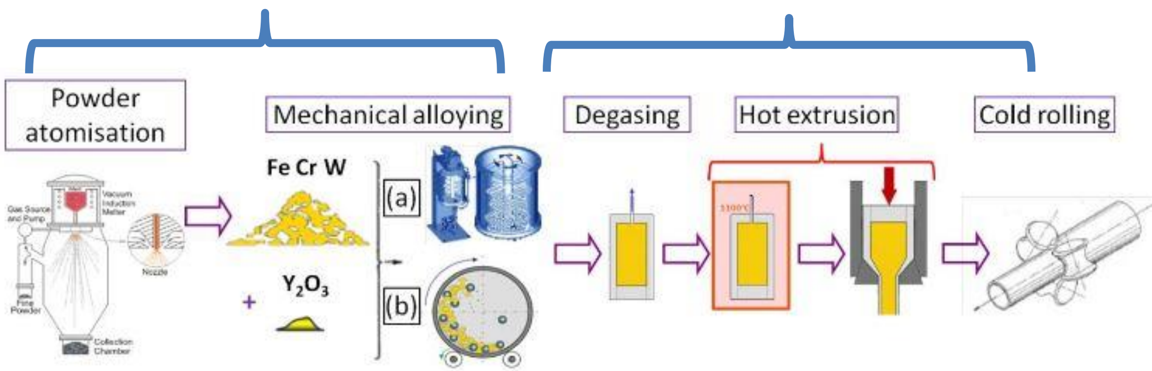
Klimiankov et al., JNM 2004

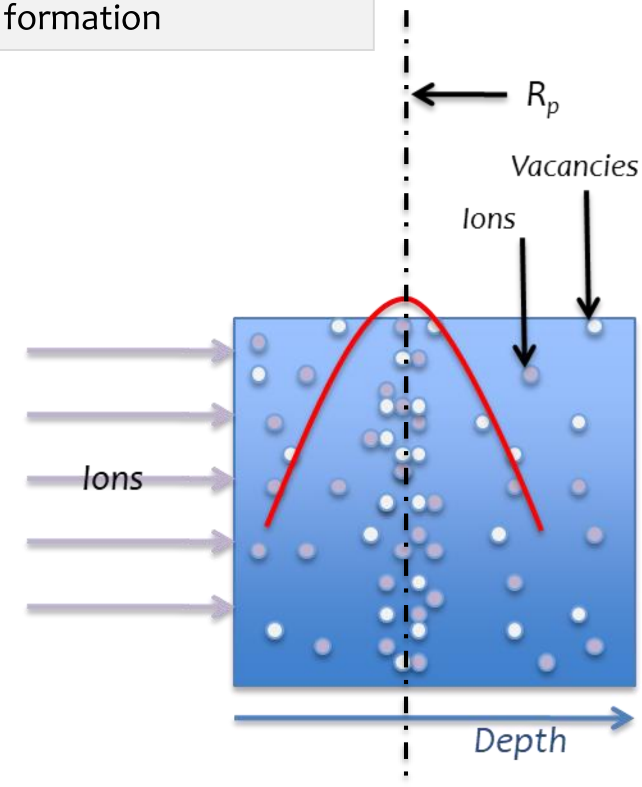
Understanding the mechanisms of formation of (Y, Ti, O) particles in FeCr alloys

- Precise control of the processes of formation via the parameters such as temperature, ion energy, flux, fluence etc.
- Characterization techniques to establish the nano-particle formation

Experimental simulation of the milling process
E.g. ion implantation (Y, Ti, O)
+ creation of vacancies

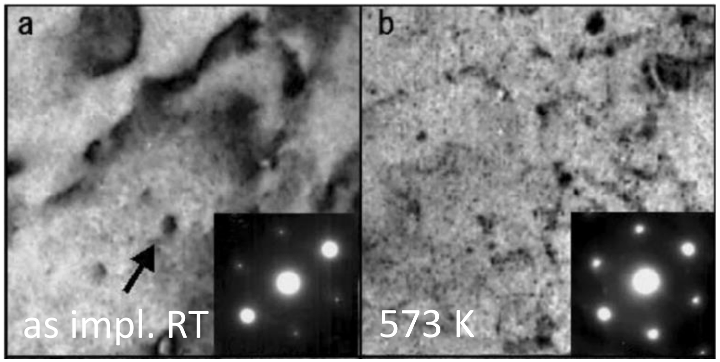
Thermal treatment





Literature review – (1)

D. Sakuma *et al.*, report at ICFRM-11 (Kyoto, Japan, 2003)



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journal of nuclear materials

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Y_2O_3 nano-particle formation in ODS ferritic steels by Y and O dual ion-implantation

D. Sakuma [a], S. Yamashita [b], K. Oka [a], S. Ohnuki [a,*], L.E. Rehn [c], E. Wakai [d]

[a] *Department of Materials Science, Faculty of Engineering, Graduate School of Engineering, Hokkaido University, N-13, W-8, Kita-ku, Sapporo 060-8628, Japan*
[b] *Oarai Engineering Center, JNC, Oarai, Ibaraki 311-1393, Japan*
[c] *Materials Science Division, Argonne national laboratory, Argonne, IL 60439, USA*
[d] *Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan*

Findings:

1. Precipitation starts at the implantation stage (at room temperature)!
2. Precipitates grow after annealing (T > 300°C in TEM foils and > 600°C in bulk samples)
   = direct proof that one can grow precipitates by IBS
3. Oxide particles are <u>bcc</u> according to X-ray analysis (and Y_2O_3 is bixbyite = <u>fcc</u>)
   -> *particles are checked to contain Y, but no proof that they are Y_2O_3 - might be pyrochlore $Y_2Ti_2O_7$*

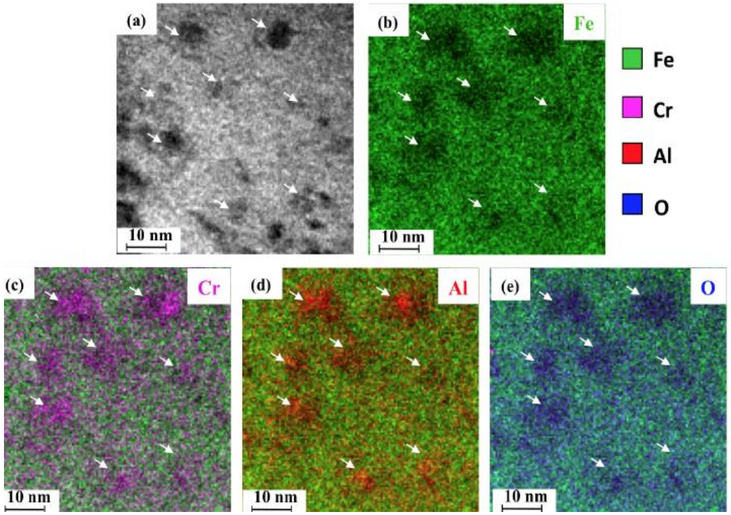
The reason for discrepancy – different matrix composition ?

Exact material composition is not reported, but most probably Fe–(11-13)Cr–3W–0.5Ti (from earlier publications)

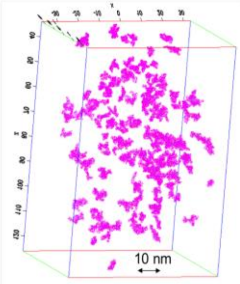
Literature review – (2)

Feasibility proven by C. Zheng *et al.* 2015
In a Fe10Cr alloy of high purity implanted with Al and O at RT

C. Zheng, A. Gentils, J. Ribis et al.
Phil. Mag. 2014, J. Appl. Phys. 2017, PhD thesis 2015, ED PHENIICS, Univ Paris-Sud



EFTEM elemental maps



Result confirmed by APT

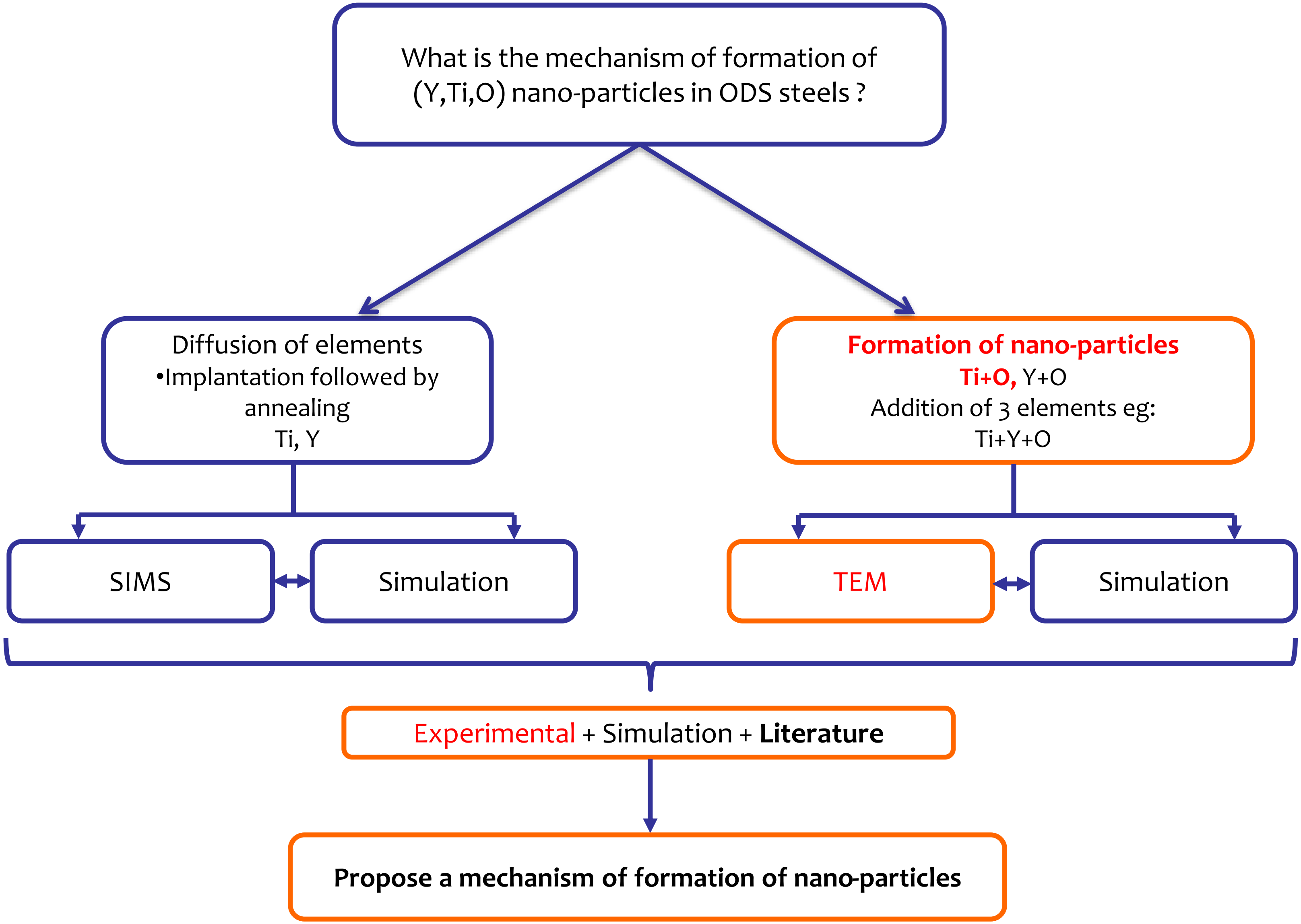
After implantation **at RT**:

Formation of nano-particles

- Average Diameter 4 nm, density = 1 x 10^{22} m^{-3}
- Non-homogeneous distribution
- Chemical composition **(Al,Cr,O)**
- **Face centred cubic structure**

a = 3.7 – 4.2 Å

Experimental Approach



Synthesis and Characterization using ion AcceLerators for Pluridisciplinary research at CSNSM : the SCALP facility

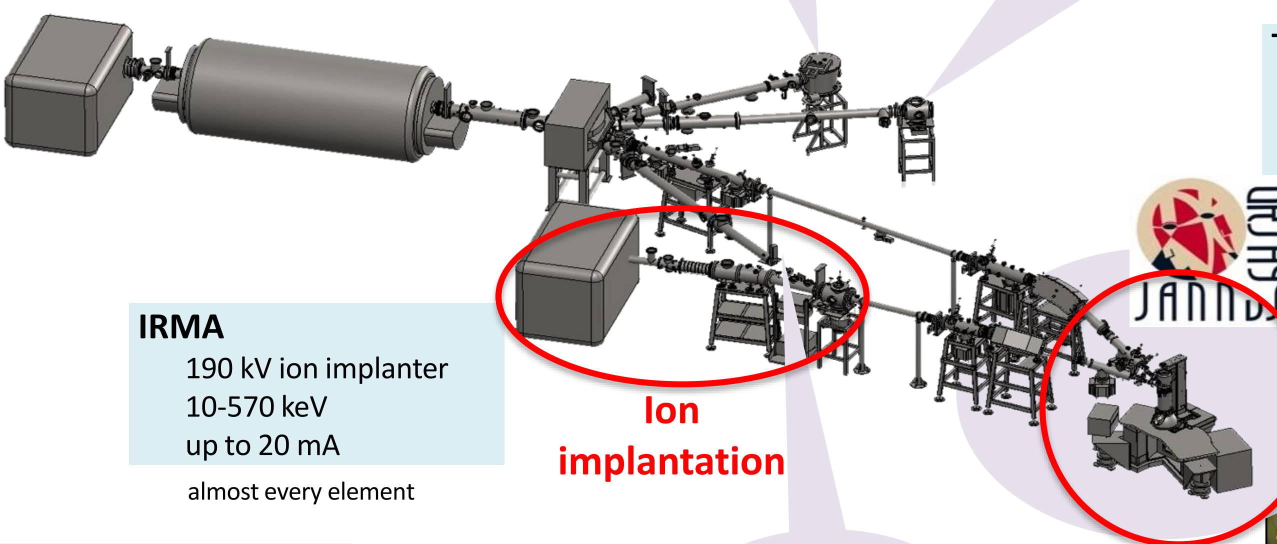
Synthesis & Characterization using ion AcceLerators for Pluridisciplinary research

ARAMIS
2MV Tandem - VdG
0.5 – 11 MeV *
10 nA – 10µA

> 40 elements
* limited to 1 MeV per charge state inside the TEM

Ion Beam Analysis
RBS, RBS/C, ERDA,
PIXE, *µPIXE, PIGE*

implantation / irradiation
LN_2 –> 1000°C



IRMA
190 kV ion implanter
10-570 keV
up to 20 mA

almost every element

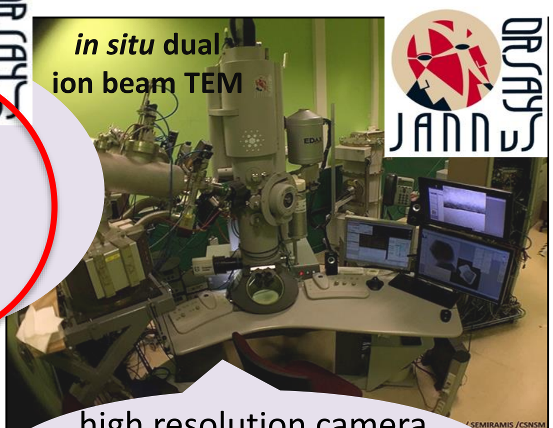
Ion implantation

SIDONIE
50 kV isotope separator
50 eV – 150 keV
up to 20 mA, M/ΔM>1000

in situ RBS/C
and impl.
LN_2 –> 600°C

TEM characterization

TRANSMISSION ELECTRON MICROSCOPE
200 kV *FEI Tecnai G2 F20 Twin*
Resolution: 0.25 nm
Magnification range: 70-700 000



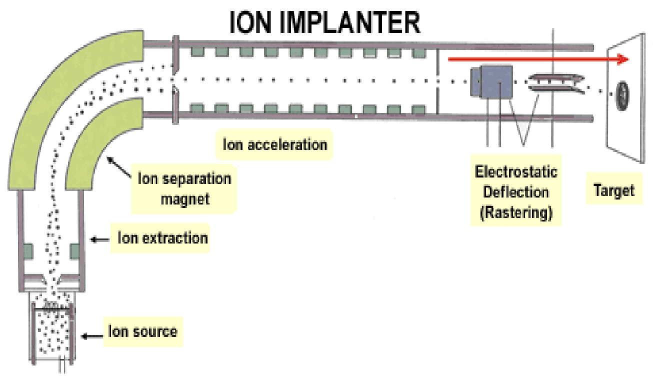
high resolution camera
EDX, GIF (EELS, EFTEM…), STEM
-170°C up to 1300°C

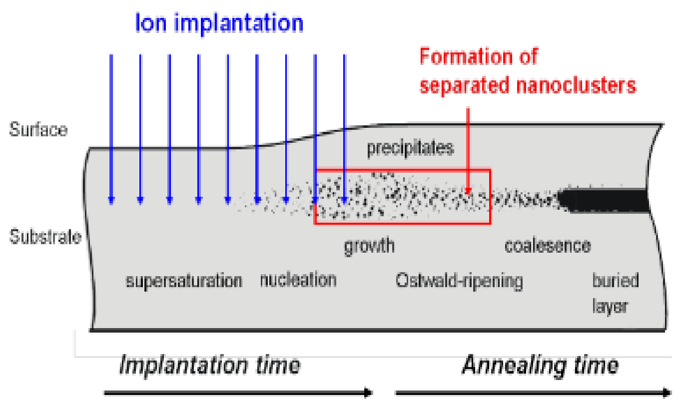
http://www.csnsm.in2p3.fr/SCALP

Member of GIS **JANNuS** (Saclay and Orsay)
Joint **A**ccelerators for **N**anoscience and **Nu**clear **S**imulation
Member of **EMIR** French Accelerators Federation

Ion implantation

Contrary to conventional fabrication routes such as mechanical alloying, ODS steel production by **ion implantation method**

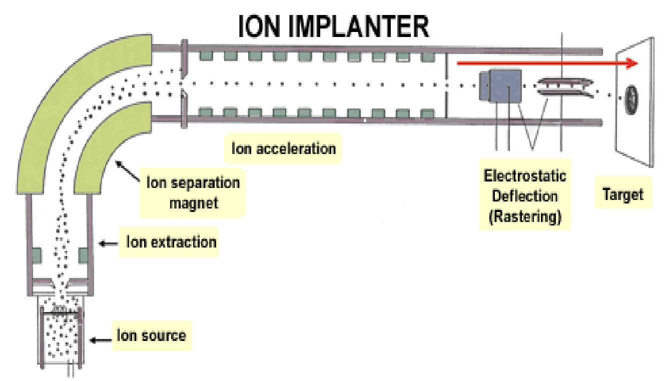




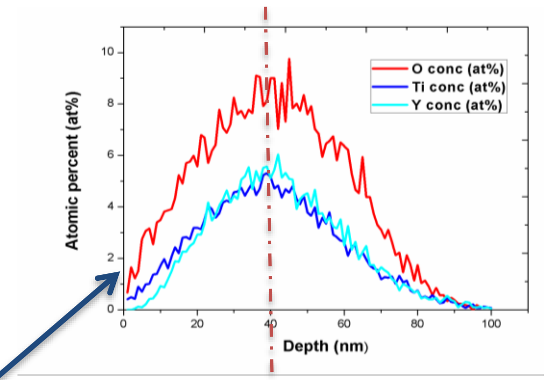
Ion beam synthesis

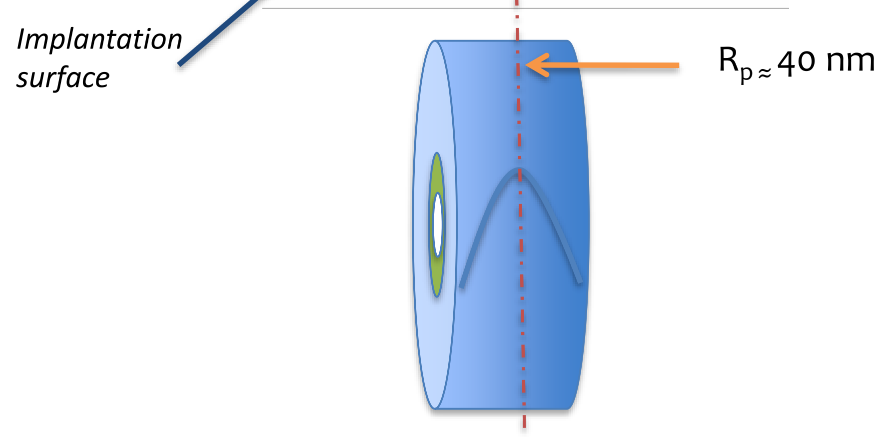
Ion implantation

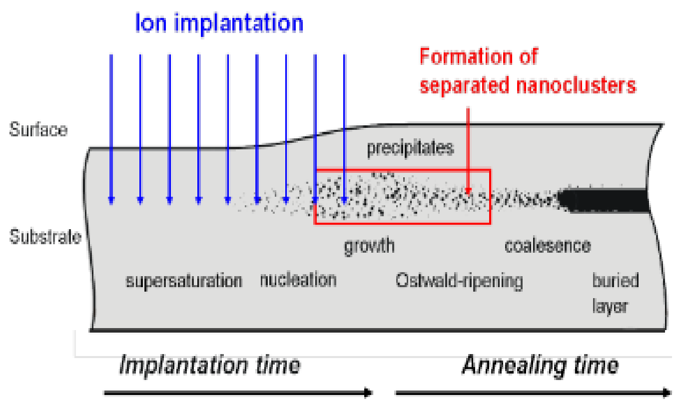
Contrary to conventional fabrication routes such as mechanical alloying, ODS steel production by **ion implantation method**



Using SRIM code;
Implantation at RT
R_p = 40 nm
$E_d(Fe)$ = 40 eV







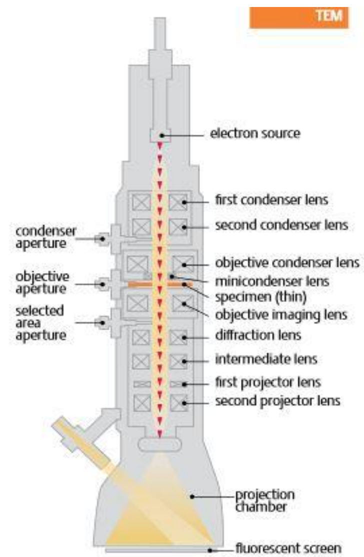
Ion beam synthesis

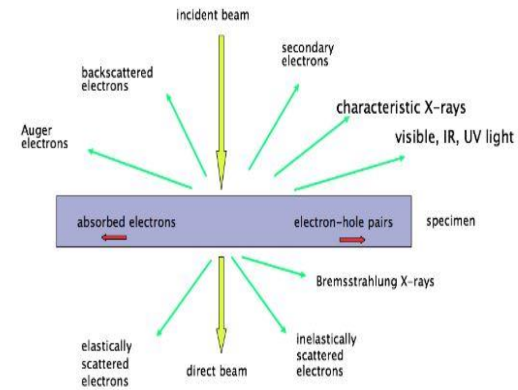
Element	Energy (keV)	Fluence	Max conc (at%)	Max dpa (10-3)
Oxygen	37	$4x10^{16}$ cm^{-2}	9,7	5,5
Titanium	100	$2x10^{16}$ cm^{-2}	5,3	22,4
Yttrium	180	$2x10^{16}$ cm^{-2}	6,0	41,8

Characterization technique:
Transmission Electron Microscopy (TEM)

<u>TEM enables to derive:</u>

- Structure and chemical composition of the material
- Defects (dislocations, grain boundaries etc.)
- Structure and chemical composition of the nanoparticles





FEI Tecnai G² 20 twin
at CSNSM/JANNuS-Orsay

JEOL 2100
at CEA-SRMA, Saclay

200 kV Microscopes

TEM Techniques

Conventional:

- Bright Field (BF)
- Dark Field (DF)
- Diffraction

Analytical (Composition)

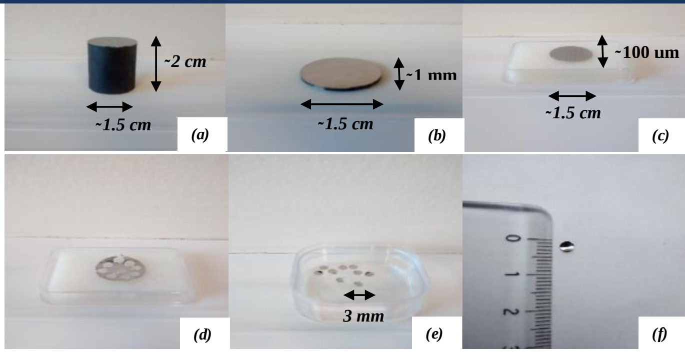
- Energy Dispersive X-ray Spectroscopy (EDX)
- Electron Energy Loss Spectroscopy (EELS)
- Energy Filtered TEM (EFTEM)

Analytical (Structure)

- High Resolution TEM

Sample preparation

Material: High purity **FeCr** alloy fabricated at ENMSE, France
Approx. **9.8wt%Cr**, near to zero impurities



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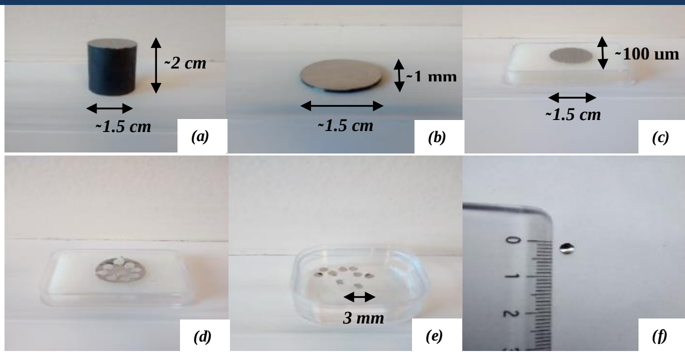


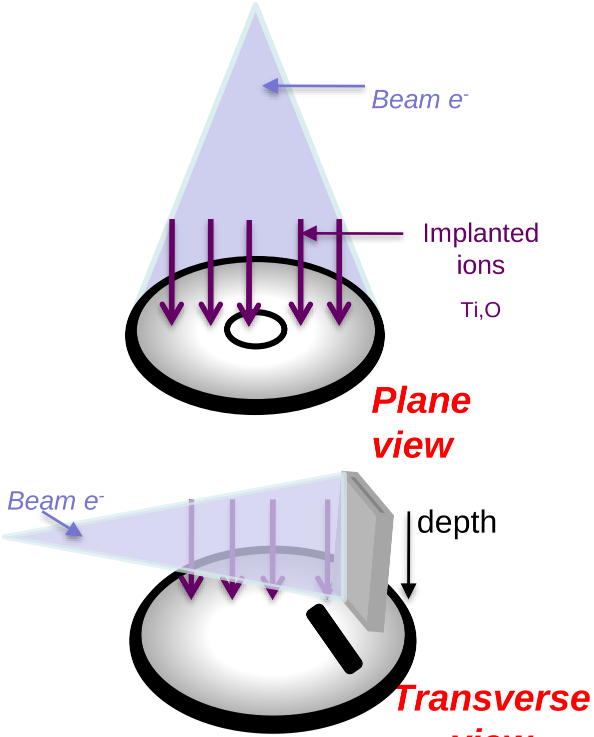
Steps:

- Cutting to obtain ≈ 1 mm slices
- Mechanical polishing to < 100 µm
- Punching of 3 mm discs
- Electropolishing

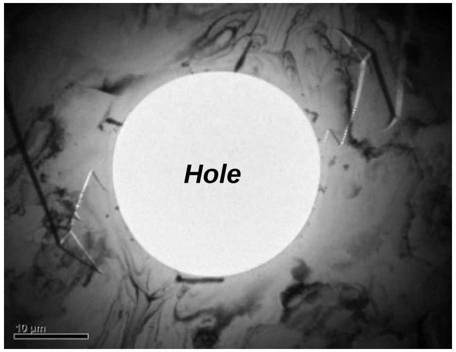
  10% Perchloric acid and 90% ethanol
  Temperature: -20°

Two types of samples:

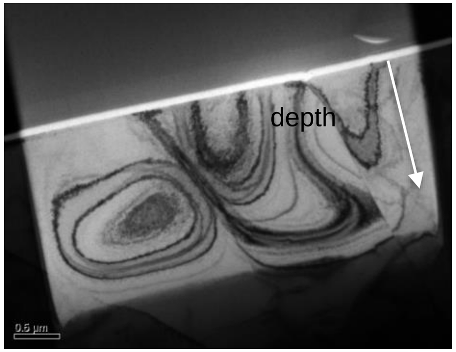
- Thin foils with a hole created by electro-polishing
  Transparent to electrons
- Specimens without hole **by FIB** (Focused Ion Beam)
  Prepared at IEMN, Lille



(i) Thin foil prepared by 'Tenupol'



(ii) Specimen prepared by FIB

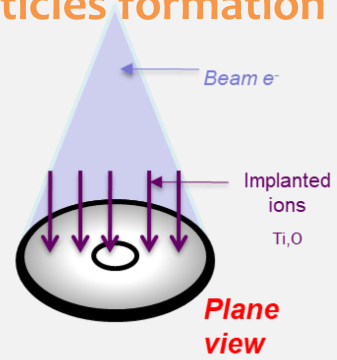


Results

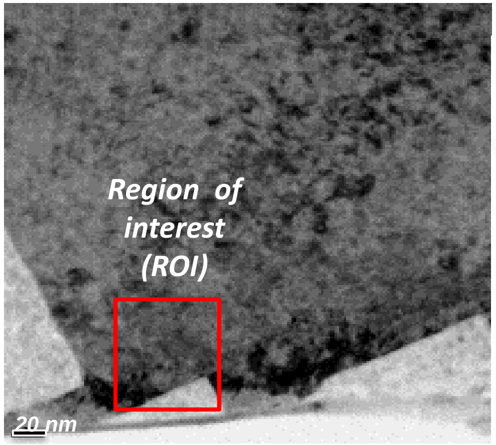
•Nano-particle characterization by TEM of (Ti and O implanted samples)

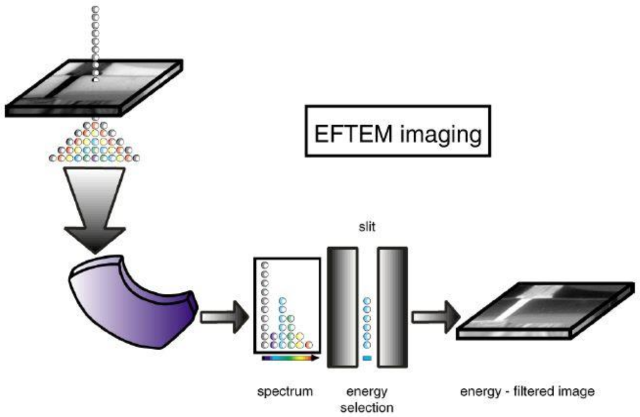
According to the **nature of the particles, chemical composition** and **chrystallographic structure**

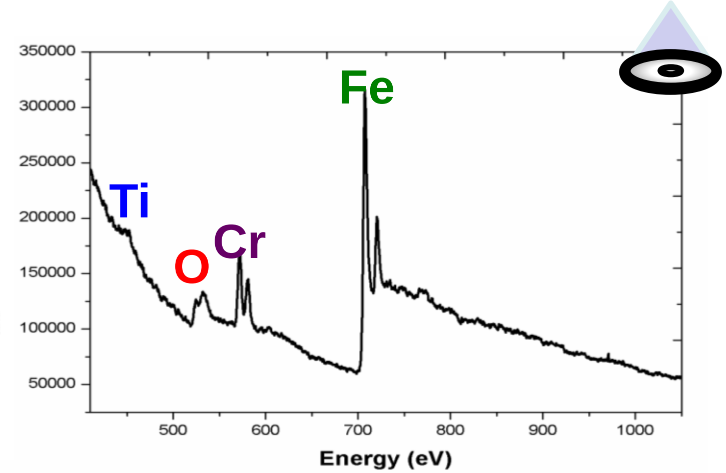
- **As-implanted sample** (no nano-particles formation observed)
- **Annealed thin foils**
  - **500 and 600°C**
  - **800°C**
- Annealed bulk samples
  - 600°C
  - 800°C
  - 1000°C



Ti + O annealed at 500 and 600°C

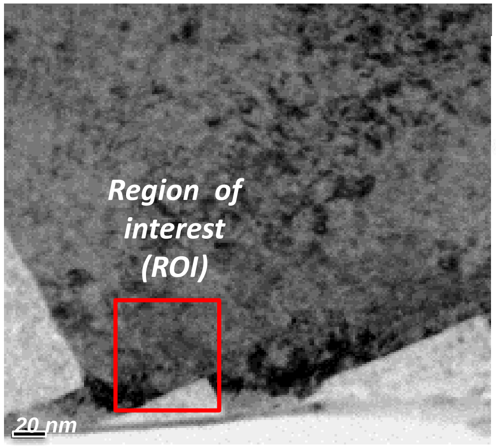


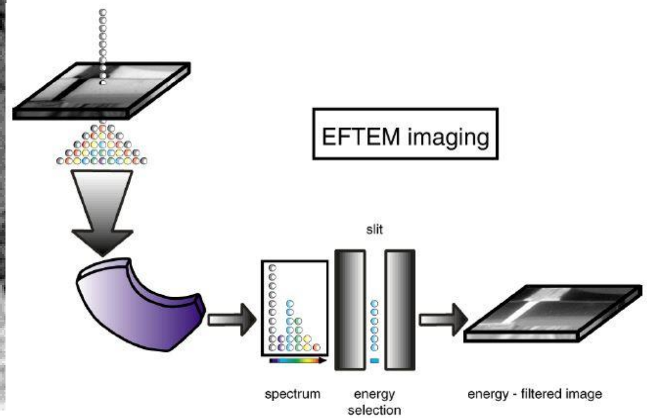


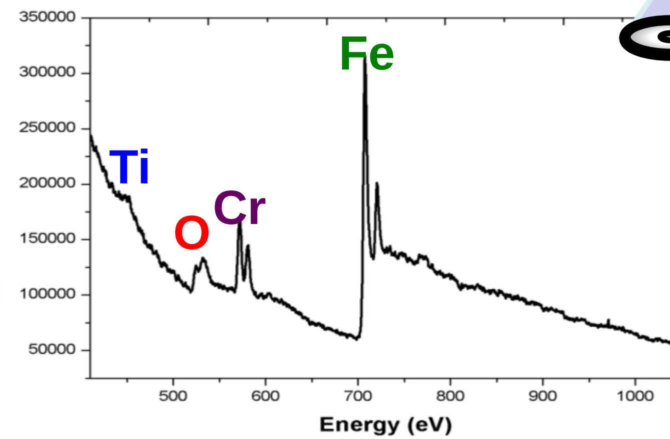


With t<λ 0.4, EFTEM investigation is possible

Ti + O annealed at 500 and 600°C







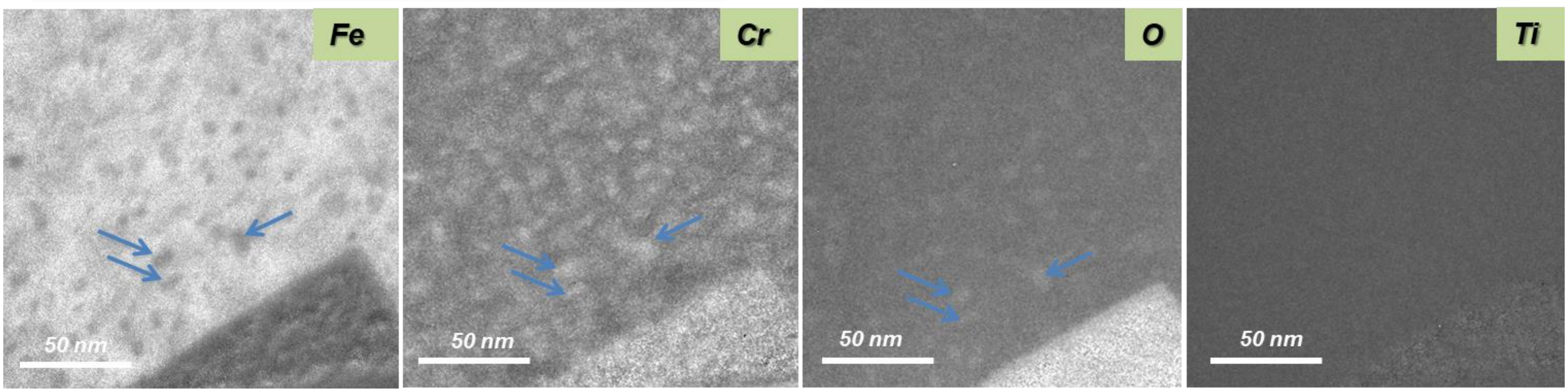
Depletion in Fe
Enrichment in Cr and O

With t<λ 0.4, EFTEM investigation is possible

Formation of Cr,O nano-particle???

White patches → Region of element enrichment

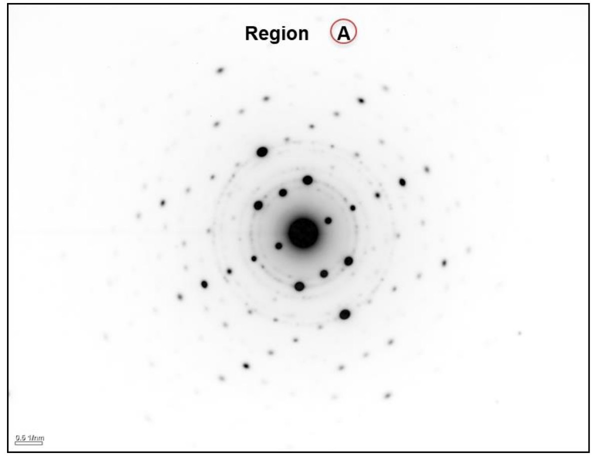
Black patches → Region of element depletion

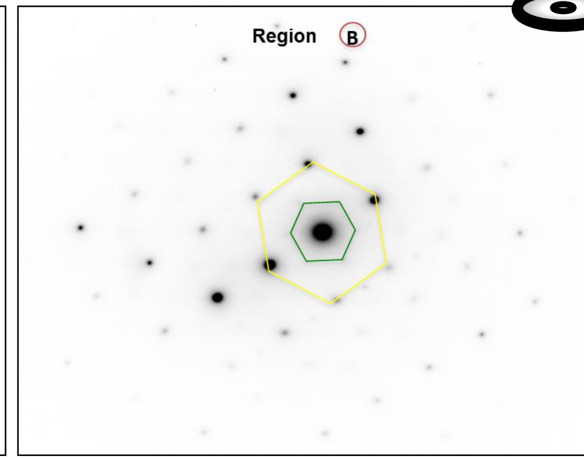


Elemental map by ***EFTEM***

Ti + O annealed at 500 and 600°C

Crystallographic structure

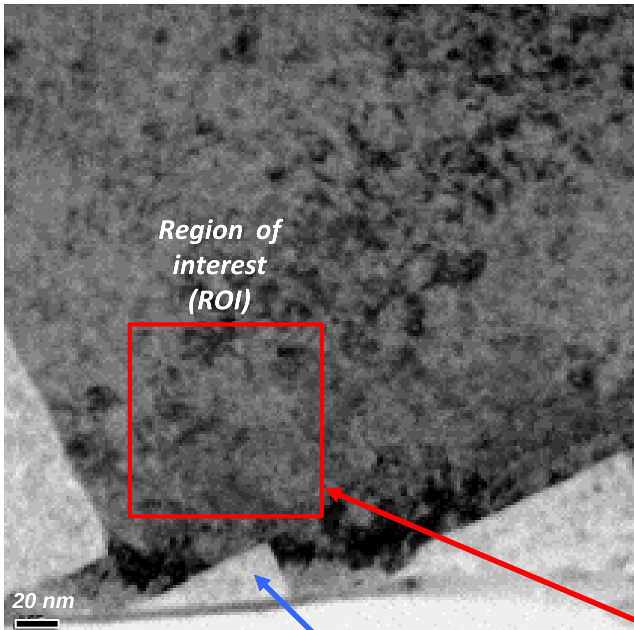




fcc cystal orientation with B = [-112] and a = 0.84 nm which matches Fe_3O_4 or $FeCr_2O_4$

fcc cystal with B = [-112] and a = 0.84 nm as well as bcc with B = [111] which matches the matrix

$FeCr_2O_4$ formation most likely



Quantification by EELS : bord bizarre

Element	Fe	Cr	Ti	O
Conc (at%)	8 - 10	14 - 15	1.5 - 2	70 - 75

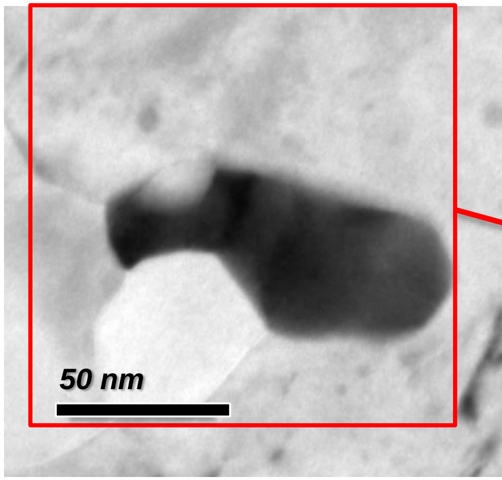
Quantification by EELS : outside of bord bizarre

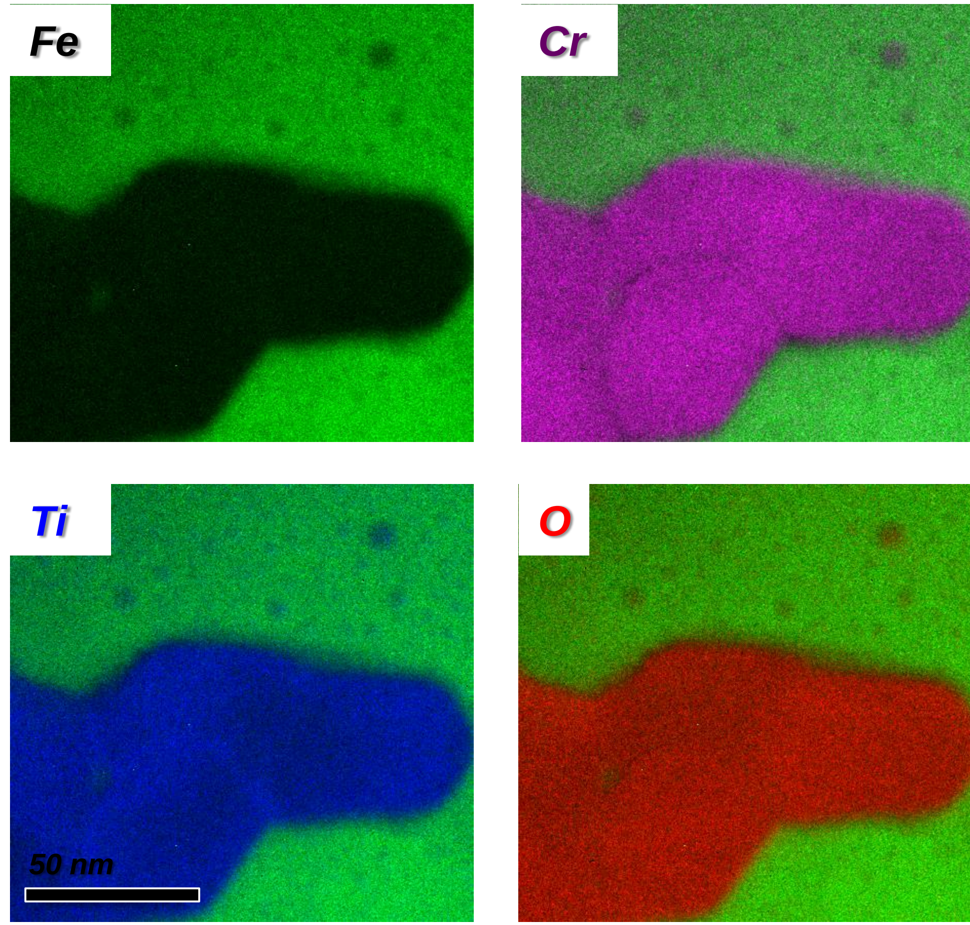
Element	Fe	Cr	Ti	O
Conc (at%)	60 - 65	6 - 7	1.5 - 2	30 - 35

Ti + O annealed at 800°C

<u>*Elemental maps by **EFTEM**;*</u>

Thickness ≈ 30nm





Two types of particles observed:

•Larger particles of the order of 100 nm

•Smaller particles of a few nm

Both particles with similar contrast

Depletion in Fe
Enrichment in Cr, Ti, O

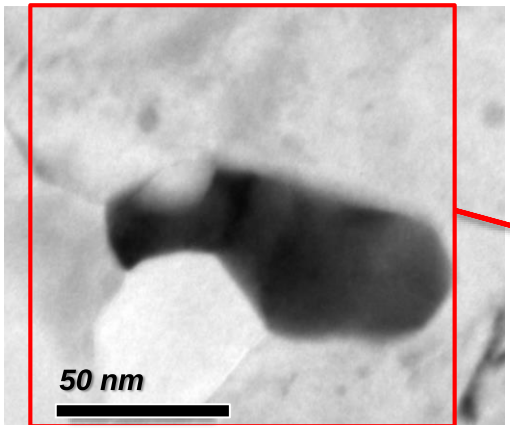
Suggesting →

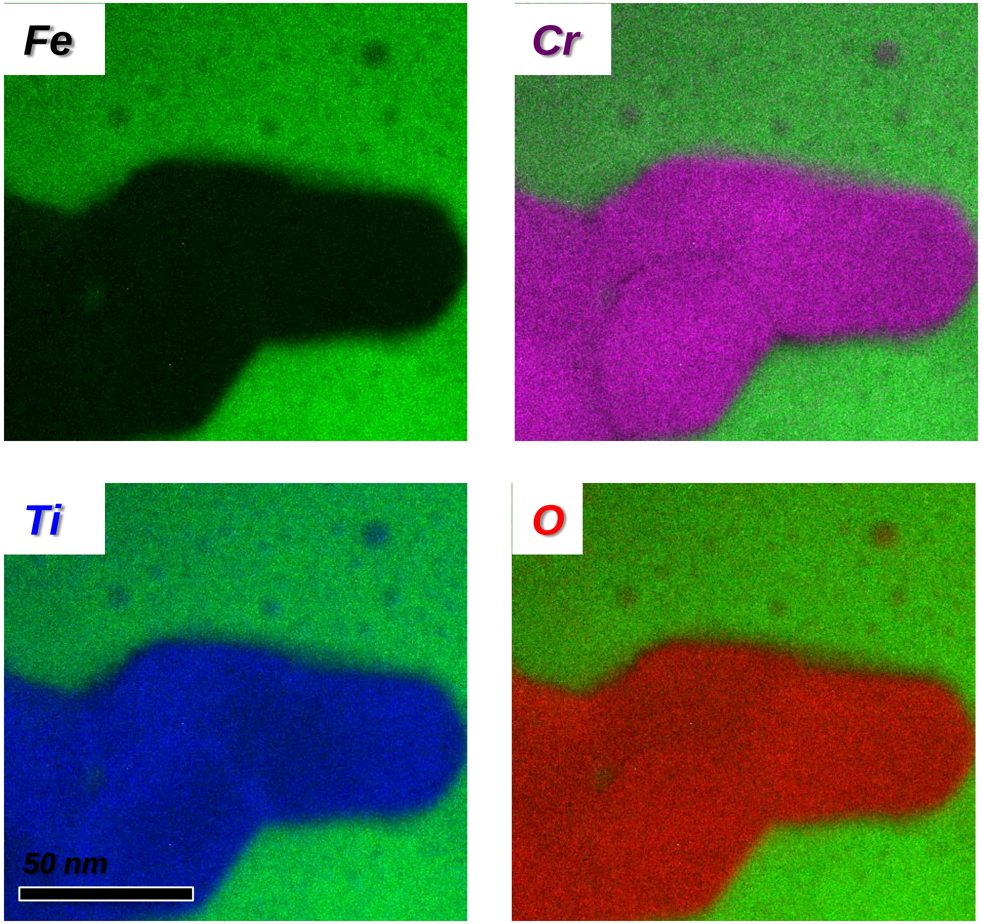
Oxide of Ti and Cr formation

Ti + O annealed at 800°C

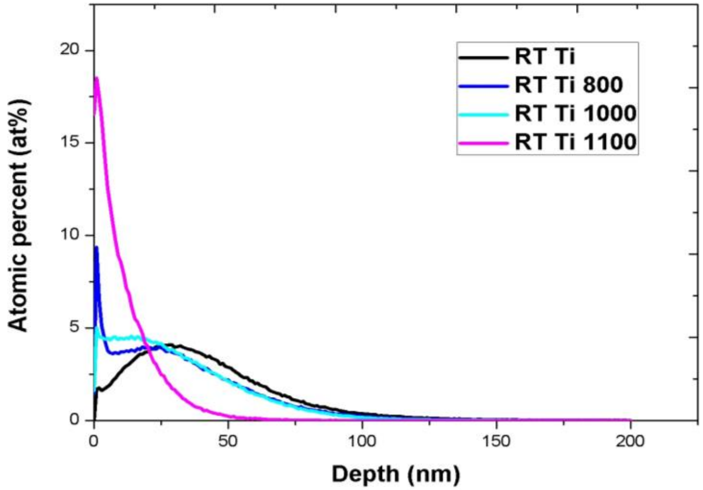
Elemental maps by ***EFTEM;***

Thickness ≈ 30nm





Secondary Ion Mass Spectroscopy (SIMS)

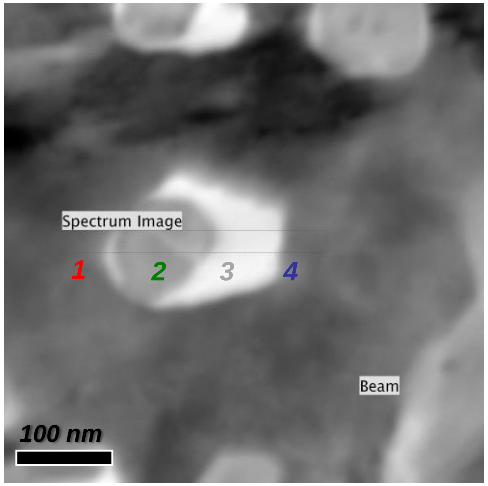


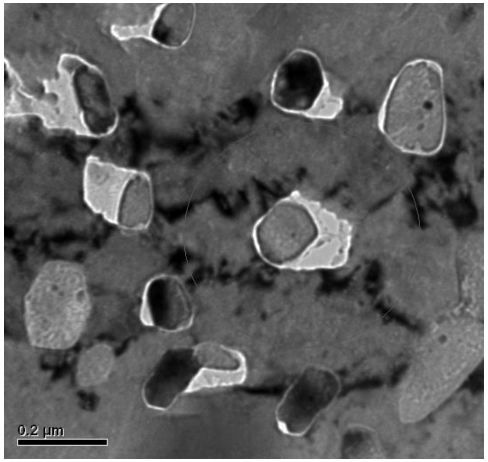
Depletion in Fe
Enrichment in Cr, Ti, O

Suggesting → **Oxide of Ti and Cr formation**

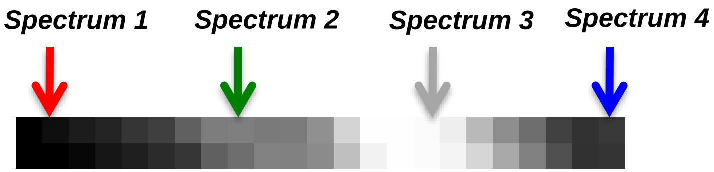
Ti + O annealed at 800°C

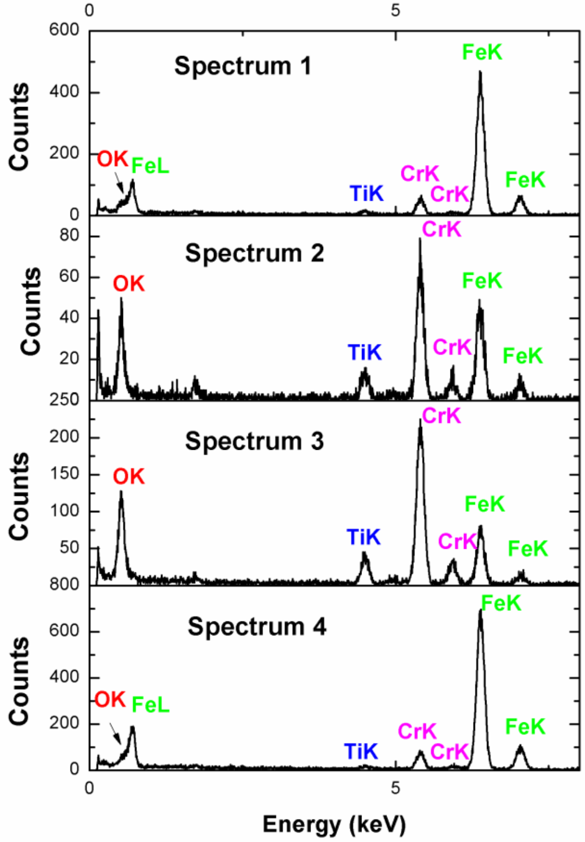
Characterization of particle by ***STEM EDX***





Zones of spectra

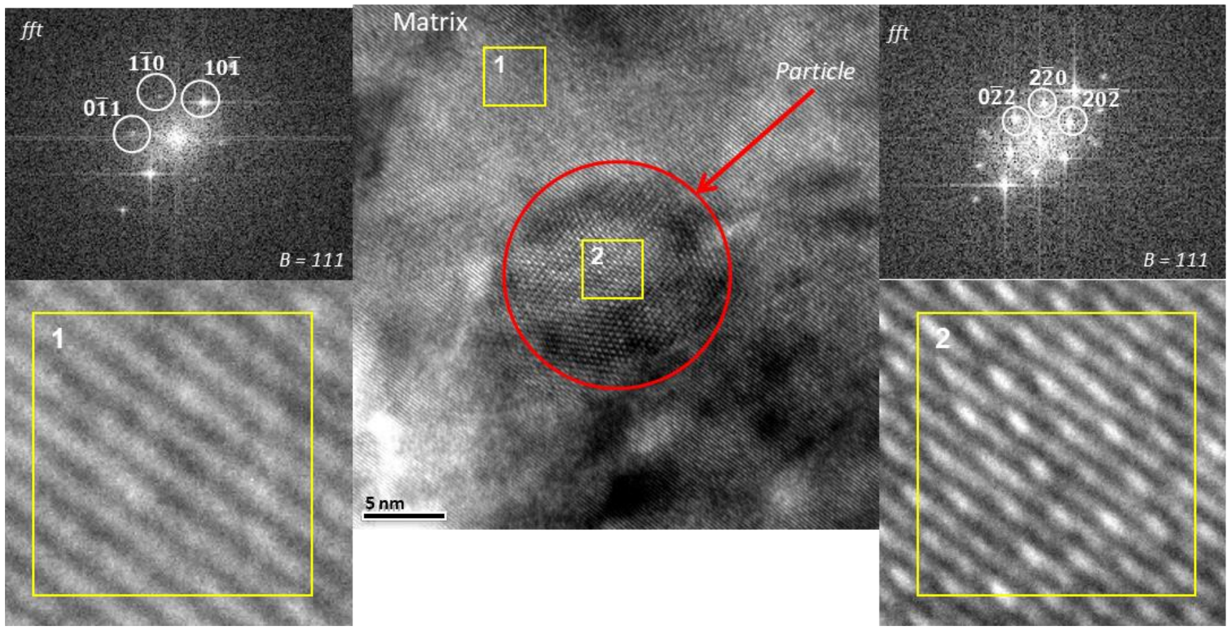




High Resolution TEM (HRTEM) of thin foil annealed at 800°C

(HRTEM) imaging of particle

Size of particle: ≈ ***12 nm***



Zone axis B = 111
a_{exp} = 0,269 nm

Zone axis B = 111
a_{exp} = 0,863 nm

Matrix corresponding to the face centred cubic structure of **FeCr** **(a_{th} = 0,286 nm)**

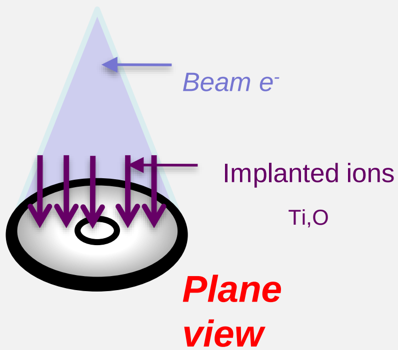
Particle corresponding to the ***face centred cubic*** structure of the type **$FeCr_2O_4$ (a_{th} = 0,850 nm)**

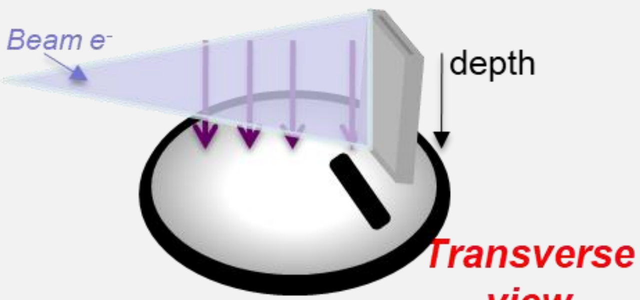
Results

•Nano-particle characterization by TEM of (Ti and O implanted samples)

According to the **nature of the particles, chemical composition** and **chrystallographic structure**

- As-implanted sample
- Annealed thin foils
  - 500 and 600°C
  - 800°C
- **Annealed bulk samples**
  - **600°C**
  - **800°C**
  - **1000°C**

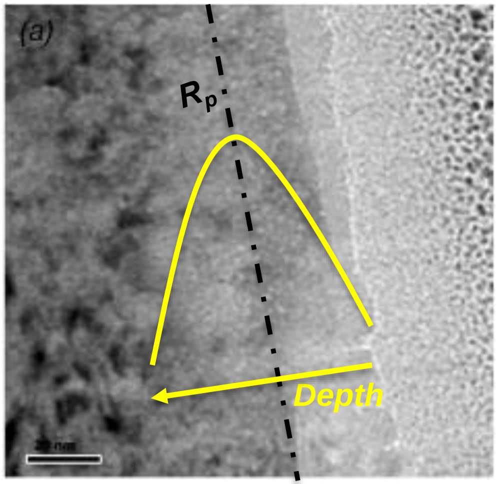


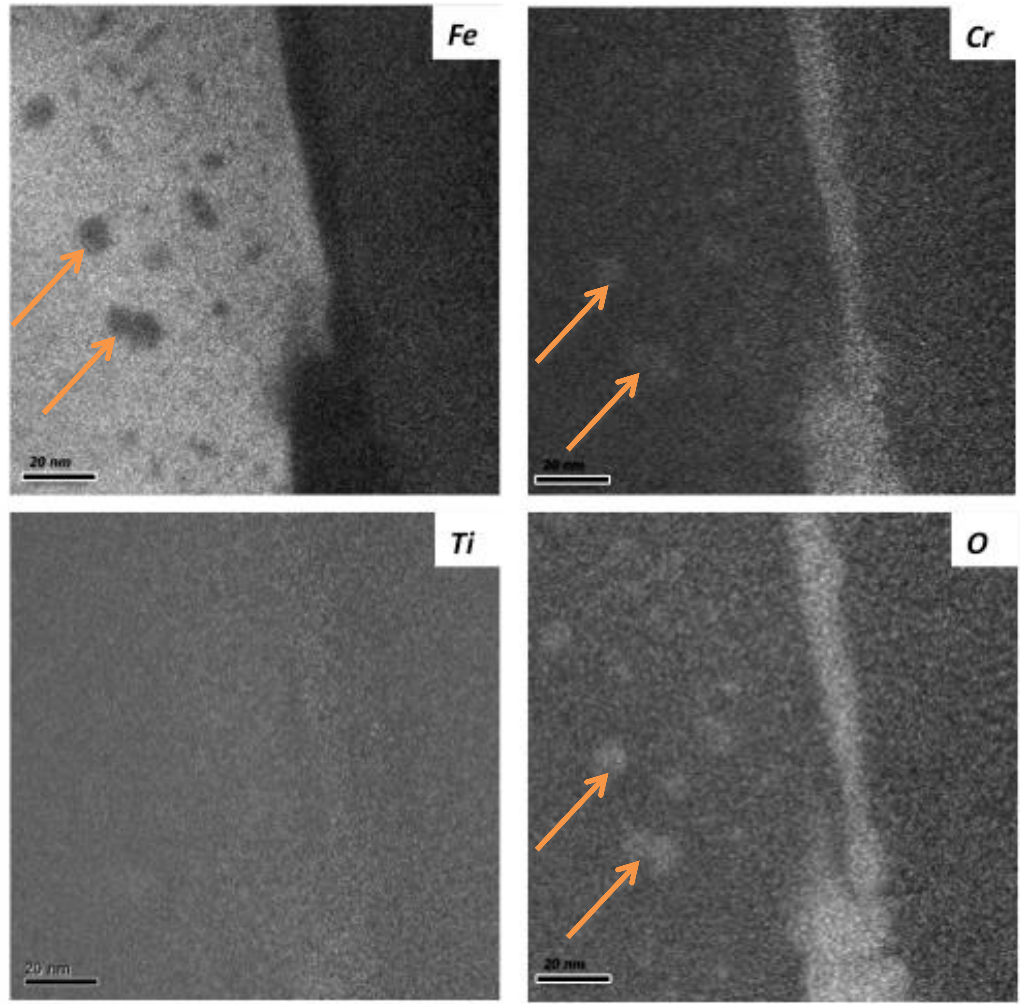


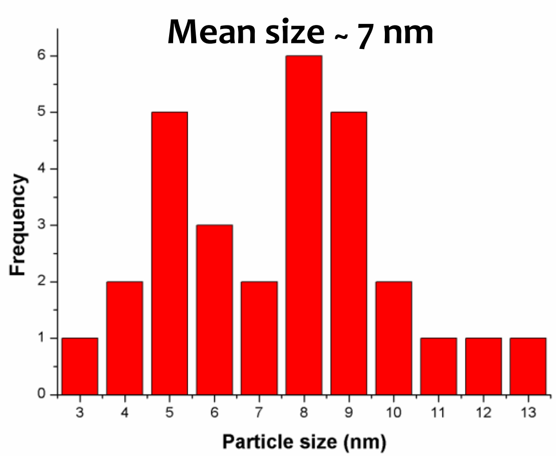
Ti + O annealed at 600ºC - bulk

*Elemental maps by **EFTEM;***

Thickness ≈ 35 nm







Depletion in Fe
Enrichment in Cr, O

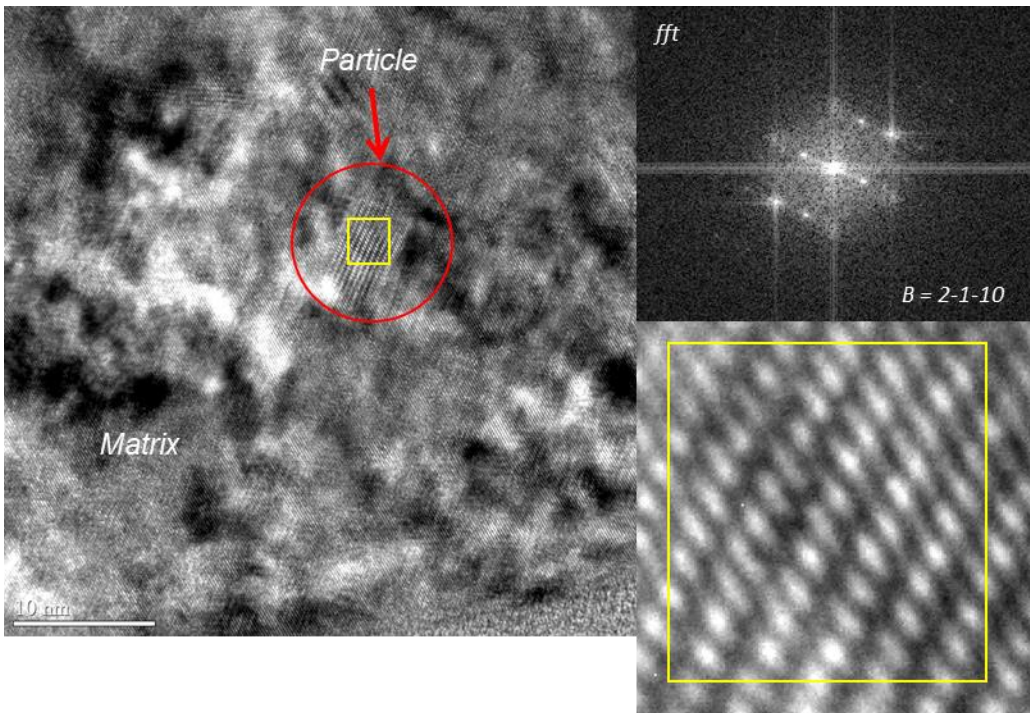
Suggesting →

Oxide of Cr formation

High Resolution TEM (HRTEM) of bulk specimen annealed at 600°C

(HRTEM) imaging of particle

Size of particle: ≈ ***12 nm***



Zone axis B = 111

a_{exp} = 0.51 nm and c_{exp} = 1.34 nm

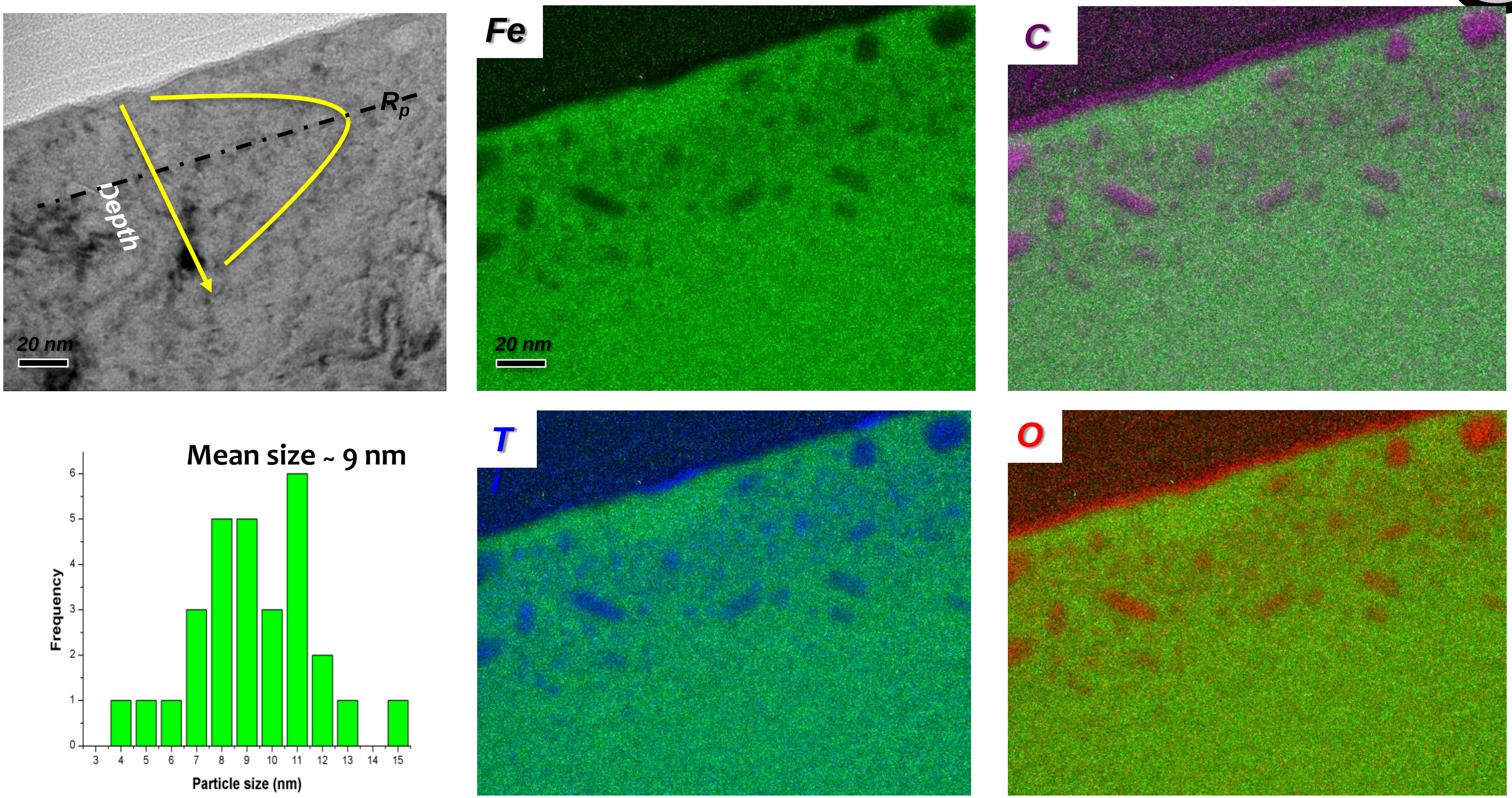
Particles with the structure
corundum hexagonal of the type Cr_2O_3

a_{th} (Cr_2O_3) = 0,49 nm and c_{th} (Cr_2O_3) = 1,36 nm

Ti + O annealed at 800ºC - bulk

*Elemental maps by **EFTEM**;*

Thickness ≈ 30 nm



Depletion in Fe
Enrichment in Cr, Ti, O

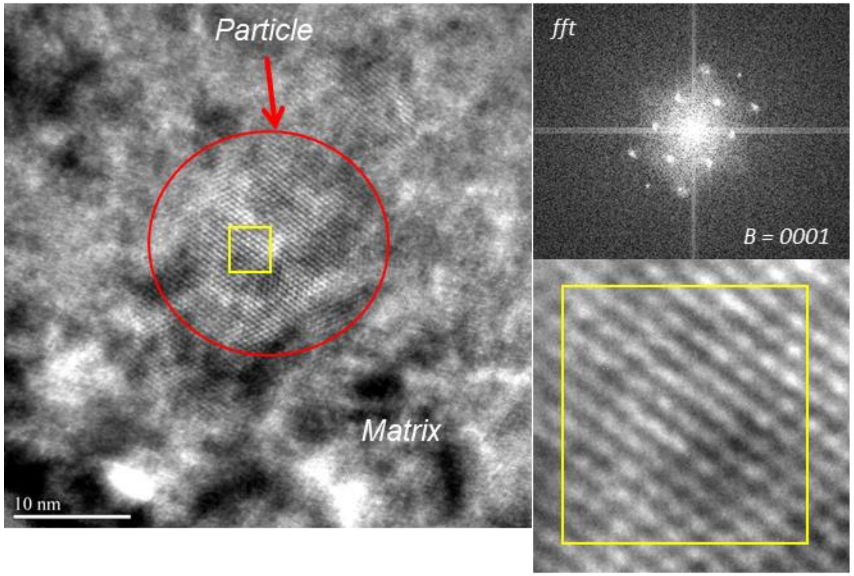
Suggesting

Oxide of Ti and Cr formation

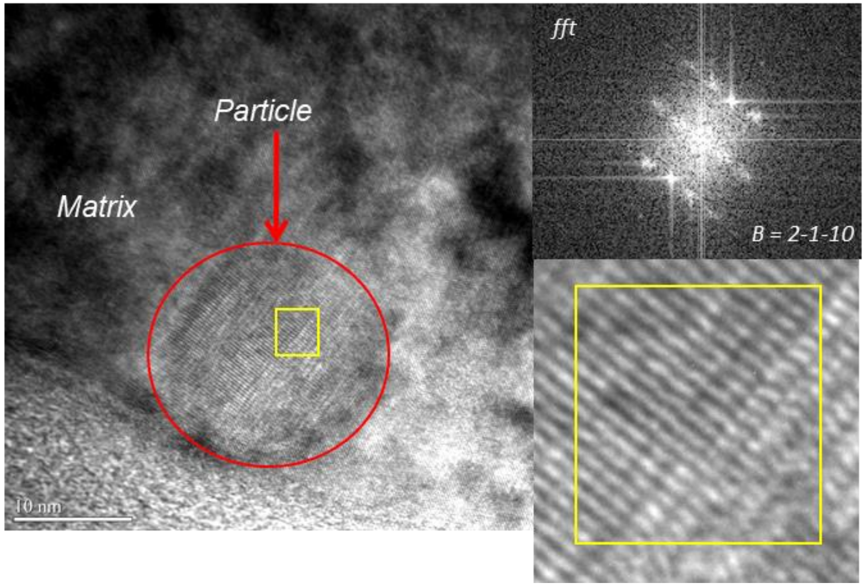
High Resolution TEM (HRTEM) of bulk specimen annealed at 800°C

(HRTEM) imaging of particle

Size of particle: ***≈20 nm***



Size of particle: ***≈18 nm***



Zone axis B = 001 or 0001
a = 0,53 c = 1,31

Zone axis B = 2-1-10
a = 0,52 c = 1,33

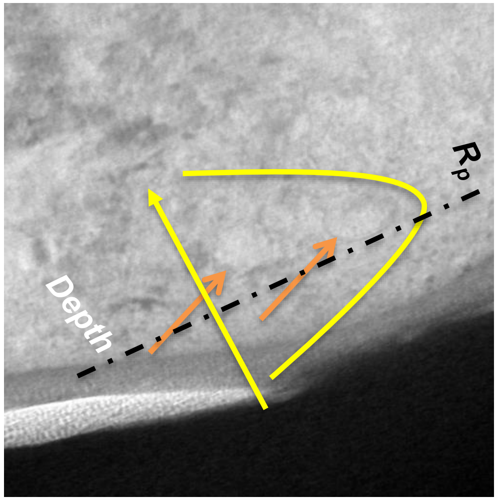
Particles with the structure
corundum hexagonal of the type Cr_2O_3

a_{th} (Cr_2O_3) = 0,49 nm and c_{th} (Cr_2O_3) = 1,36 nm

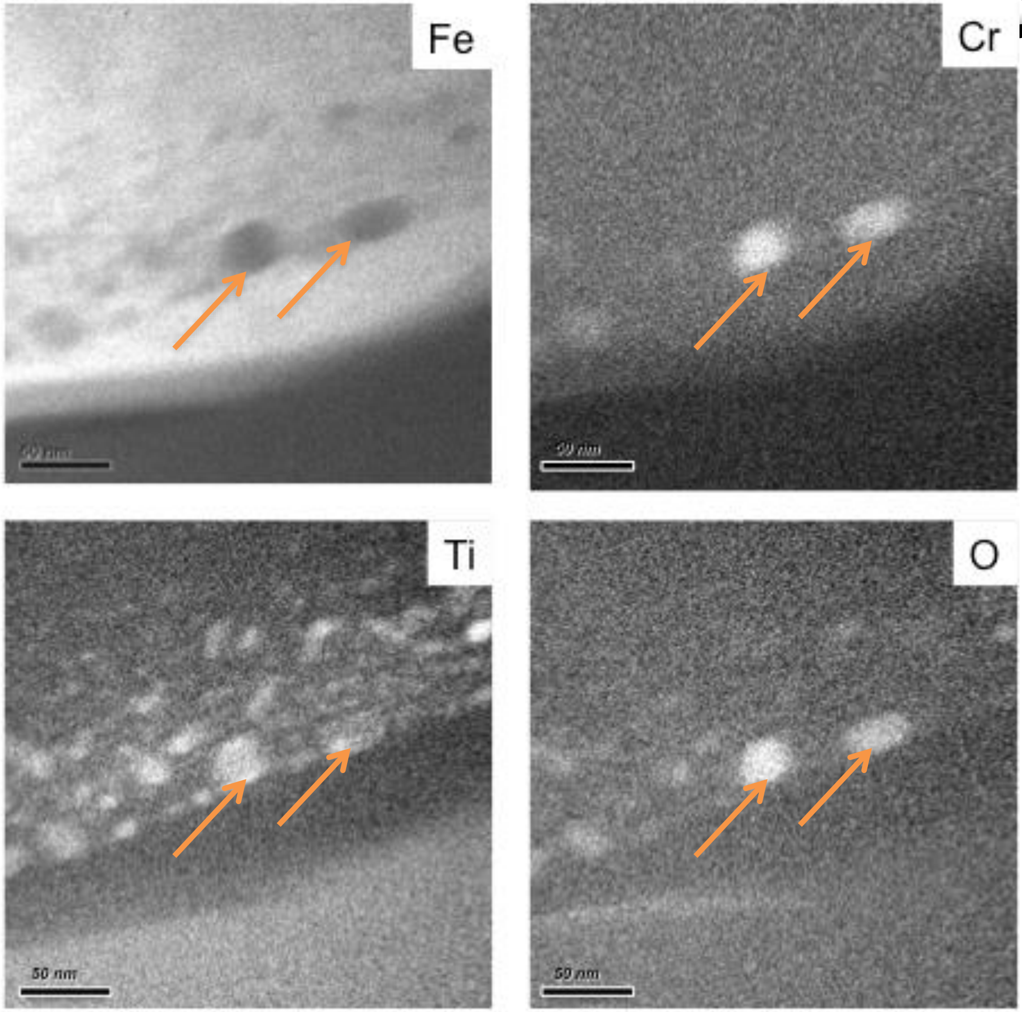
→ Nanoparticles $Cr_xTi_yO_z$ of structure corundum hexagonal

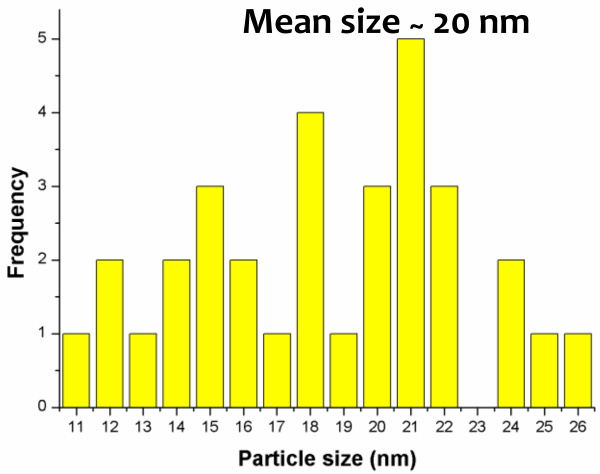
Ti + O annealed at 1000°C – bulk (preliminary)

*Elemental maps by **EFTEM;***



Thickness ≈ 35 nm





Depletion in Fe
Enrichment in Cr, Ti, O

Suggesting

Oxide of Ti and Cr formation

Summary

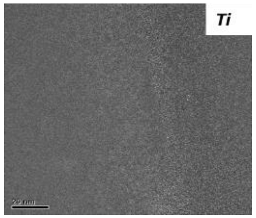
The synthesis of oxides of Ti in Fe10%Cr alloy after room temperature implantation and subsequent annealing of Ti and O is as follows:

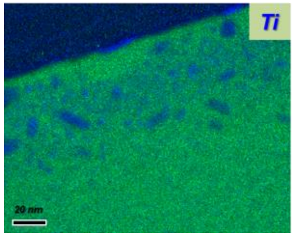
Room temperature implantation

- **Creation of vacancies**
- **No nano-particles are formed**

Annealing at 500 and 600°C

- **Surface oxide $FeCr_2O_4$ formed with avg length of 5 nm**
- **Formation of Cr_2O_3 nano-particles with a corundum hexagonal structure within the impanted region with avg length of 7 nm**





Annealing at 800°C

- **Ti begins to diffuse**
- **Surface oxide $FeCr_2O_4$ enriched in Ti**
- **Cr_2O_3 nano-particles enriched in Ti to form $(CrTi)_2O_3$ with avg length of 9 nm**

Annealing at 1000°C

- **Surface oxide presence**
- **$(CrTi)_2O_3$ nano-particles grow significantly to an avg length of 20 nm**

Perspectives

Nano-particle formation:

•Implantation of a **high purity Fe without Cr** sample with Ti and O as a comparison with the high purity FeCr sample

•Implantation at RT followed by annealing or implantation at high temperature
Y, Ti, O and Ti, Y, O

Diffusion and mobility of elements:

- Determination of the diffusion coefficient of elements
- Extraction of activation energy and other possible parameters
- Experimental simulation using a lattice diffusion Monte Carlo code called CASINO to;
  Determine the SIMS depth profile for elements
  Possible cluster formation at annealing temperatures

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Thank you for listening