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

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• Introduction
  o Context of study
  o Motivation
• Experimental approach
  o Characterization techniques
  o Implantation, parameters and conditions
• Results
  o In-situ annealing
  o Bulk sample annealing
    According to the nature, chemical composition and crystallographic structure
• Summary
• Perspectives
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 strength ✓
  - Good radiation resistance ✓
Oxide Dispersion Strengthened (ODS) steels

(Y, Ti, O) nanoparticles dispersed in the alloy

**F/M ODS 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, Y₂O₃, 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
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.)

Characterization performed by mainly two main techniques:

1. **Atom Probe Tomography (APT)**
2. **Transmission Electron Microscopy (TEM)**

Sakasegawa et al., JNM, 2009

C. Williams et al., Ultramicroscopy, 2013

Klimiankov et al., JNM, 2004

S. Owusu-Mensah, PHENIICS Fest, May 29, 2018
Objective

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

- Powder atomisation
- Mechanical alloying
- Degasing
- Hot extrusion
- Cold rolling

Depth
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 bcc according to X-ray analysis (and Y₂O₃ is bixbyite = fcc)
   -> particles are checked to contain Y, but no proof that they are Y₂O₃ - might be pyrochlore Y₂Ti₂O₇

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.

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

EFTEM elemental maps

Result confirmed by APT
What is the mechanism of formation of (Y,Ti,O) nano-particles in ODS steels?

- Diffusion of elements
  - Implantation followed by annealing Ti, Y

- Formation of nano-particles
  - Ti+O, Y+O
  - Addition of 3 elements eg: Ti+Y+O

SIMS, Simulation, TEM, Simulation

Experimental + Simulation + Literature

Propose a mechanism of formation of nano-particles
Synthesis and Characterization using ion Accelerators for Pluridisciplinary research at CSNSM: the SCALP facility

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

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

**IRMA**
190 kV ion implanter
10-570 keV
up to 20 mA
almost every element

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

**TRANSmission ELECTron MICROscope**
200 kV FEI Tecnai G2 F20 Twin
Resolution: 0.25 nm
Magnification range: 70-700 000

**in situ dual ion beam TEM**
high resolution camera
EDX, GIF (EELS, EFTEM...), STEM -170°C up to 1300°C

**implantation / irradiation**
LN₂ → 1000°C

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

**Ion implantation**
in situ RBS/C and impl.
LN₂ → 600°C

**characterization**

**Member of GIS JANNuS (Saclay and Orsay)**
Joint Accelerators for Nanoscience and Nuclear Simulation
Member of EMIR French Accelerators Federation

http://www.cnsns.in2p3.fr/SCALP
Contrary to conventional fabrication routes such as mechanical alloying, ODS steel production by ion implantation method.
Contrary to conventional fabrication routes such as mechanical alloying, ODS steel production by ion implantation method

Using SRIM code;
Implantation at RT

\[ R_p = 40 \, \text{nm} \]

\[ E_d(\text{Fe}) = 40 \, \text{eV} \]

<table>
<thead>
<tr>
<th>Element</th>
<th>Energy (keV)</th>
<th>Fluence</th>
<th>Max conc (at%)</th>
<th>Max dpa (10^-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>37</td>
<td>(4 \times 10^{16} , \text{cm}^{-2})</td>
<td>9,7</td>
<td>5,5</td>
</tr>
<tr>
<td>Titanium</td>
<td>100</td>
<td>(2 \times 10^{16} , \text{cm}^{-2})</td>
<td>5,3</td>
<td>22,4</td>
</tr>
<tr>
<td>Yttrium</td>
<td>180</td>
<td>(2 \times 10^{16} , \text{cm}^{-2})</td>
<td>6,0</td>
<td>41,8</td>
</tr>
</tbody>
</table>
Characterization technique: Transmission Electron Microscopy (TEM)

TEM enables to derive:
- Structure and chemical composition of the material
- Defects (dislocations, grain boundaries etc.)
- Structure and chemical composition of the nanoparticles

FEI Tecnai G³ 20 twin at CSNSM/JANNuS-Orsay

JEOL 2100 at CEA-SRMA, Saclay

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

200 kV Microscopes
Sample preparation

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

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

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°C

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

According to the nature of the particles, chemical composition and crystallographic 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

Region of interest (ROI)

With \( t \ll \lambda \), EFTEM investigation is possible
Ti + O annealed at 500 and 600°C

Depletion in Fe
Enrichment in Cr and O

Formation of Cr,O nano-particle??

**With $t<\lambda 0.4$, EFTEM investigation is possible**

**White patches** $\rightarrow$ **Region of element enrichment**

**Black patches** $\rightarrow$ **Region of element depletion**
Ti + O annealed at 500 and 600°C

### Crystallographic structure

- **Region of interest (ROI)**
- **Quantification by EELS: bord bizarre**
  - Fe: 8 - 10, Cr: 14 - 15, Ti: 1.5 - 2, O: 70 - 75
- **Quantification by EELS: outside of bord bizarre**
  - Fe: 60 - 65, Cr: 6 - 7, Ti: 1.5 - 2, O: 30 - 35

fcc crystal orientation with $B = [-112]$ and $a = 0.84$ nm which matches $\text{Fe}_3\text{O}_4$ or $\text{FeCr}_2\text{O}_4$

$\text{FeCr}_2\text{O}_4$ formation most likely

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

Crystallographic structure M.

Owusu-Mensah Ι PHENIICS Fest Ι May 29, 2018
Elemental maps by EFTEM;

Thickness $\approx 30\text{nm}$

Two types of particles observed:

• Larger particles of the order of $100\text{ nm}$
• 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
Characterization of particle by STEM EDX

Zones of spectra

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

(HRTEM) imaging of particle

Size of particle: ≈ 12 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 crystallographic 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 600°C - bulk

Elemental maps by EFTEM:

Depletion in Fe

Enrichment in Cr, O

Suggesting Oxide of Cr formation

Mean size ~ 7 nm

Thickness ≈ 35 nm
High Resolution TEM (HRTEM) of bulk specimen annealed at 600°C

(HRTEM) imaging of particle

Size of particle: ≈ 12 nm

Particles with the structure corundum hexagonal of the type Cr$_2$O$_3$

$a_{th}$ (Cr$_2$O$_3$) = 0.49 nm and $c_{th}$ (Cr$_2$O$_3$) = 1.36 nm

Zone axis B = 111

$a_{exp}$ = 0.51 nm and $c_{exp}$ = 1.34 nm
Ti + O annealed at 800°C - bulk

Elemental maps by EFTEM;

Thickness ≈ 30 nm

Mean size ~ 9 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: \( \approx 20 \text{ nm} \)

Size of particle: \( \approx 18 \text{ nm} \)

Particles with the structure corundum hexagonal of the type \( \text{Cr}_2\text{O}_3 \)

\[ a_{\text{th}} (\text{Cr}_2\text{O}_3) = 0.49 \text{ nm} \] and \[ c_{\text{th}} (\text{Cr}_2\text{O}_3) = 1.36 \text{ nm} \]

\( \Rightarrow \) Nanoparticles \( \text{Cr}_x\text{Ti}_y\text{O}_z \) of structure corundum hexagonal
Elemental maps by EFTEM;

Depletion in Fe  
Enrichment in Cr, Ti, O  
Suggesting Oxide of Ti and Cr formation
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 $\text{FeCr}_2\text{O}_4$ formed with avg length of 5 nm
- Formation of $\text{Cr}_2\text{O}_3$ nano-particles with a corundum hexagonal structure within the implanted region with avg length of 7 nm

**Annealing at 800°C**
- Ti begins to diffuse
- Surface oxide $\text{FeCr}_2\text{O}_4$ enriched in Ti
- $\text{Cr}_2\text{O}_3$ nano-particles enriched in Ti to form $(\text{CrTi})_2\text{O}_3$ with avg length of 9 nm

**Annealing at 1000°C**
- Surface oxide presence
- $(\text{CrTi})_2\text{O}_3$ nano-particles grow significantly to an avg length of 20 nm
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
  \[ Y, \, Ti, \, O \text{ and } Ti, \, Y, \, O \]

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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