Close to zero Permeation in Diffusion Barrier Nanoceramic Coatings

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Acknowledgements & ongoing collaborations

Corrosion tests + financial support
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heavy ion irradiations
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Kumar Sridharan

Brillouin spectroscopy
Marco G. Beghi

Nanoindentation + nanoimpact
Luca Ceseracciu
Introduction
Future generation nuclear systems (GIV)

Major bottlenecks for all systems

NEED FOR COATINGS

Tritium management

Corrosion

Radiation damage


J.L. Straalsund – Westinghouse Hanford

S.J. Zinkle and G.S. Was – Acta Materialia - 2013
Future generation nuclear systems aim at:
- Increase efficiency
- Reduce waste generation
- Enhance safety
- Promote non-proliferation

Ultimate goal for LFRs:
- 800 °C
- 150 dpa

Advantages:
- Safety
- Transmutation of minor actinides / fuel breeding

Major issues:
- Corrosion
- Radiation damage
Ni leaching in austenitics (23000 h @ 550°C, 10^{-6} wt.% O)

In-situ passivation is not viable for T > 500°C-550°C

(will be exceeded by fuel cladding)

C. Schroer et al. - Corros. Sci. - 2014

Solubility of Ni in lead is very high
Heavy liquid metal corrosion

Austenitic steels exposed to HLM for 3000 hours at 550°C

V. Gorynin et al. – Metal Science and Heat Treatment - 1999

In-situ passivation is not viable for T > 500°C

(will be exceeded by fuel cladding)
Technology Constraints for ALFRED

Temperature

650
600
550
500
450
400
350
327

V

480

Vessel

400

Internals

400

Cladding

Negligible

few

~ 100

Material embrittlement

Technology gap

Critical Parameter

Technological Limits

O₂ control + aluminization

O₂ control

Low [O] activity

Lead Freezing

Material embrittlement

T, dpa

~ 550

Pumps outlet Core inlet

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DEMO Reactor - Breeding Blanket

- **Eutectic Pb-Li in Breeding Blanket**
  - First wall coolant
  - Neutron moderator/multiplier
  - Tritium breeder through nuclear transmutations on Lithium

**Stability of oxides**

![Graph showing stability of oxides](image)

- $Fe_3O_4$
- $Cr_2O_3$
- $O$ in Pb-15.7Li
- $Al_2O_3$
- $Li_2O$

**Temperature [°C]**

![Section of the Breeding Blanket component](image)
Oxygen Control, fighting with ever narrow operational window!
NANOCERAMICS

Mechanical performance
- Coble creep, twinning, etc.

Corrosion resistance
- Interstitial emission from GBs
  - F. Garcia Ferré et al. – CORROS SCI – 2013

Radiation tolerance
- X.M. Bai et al. – Science - 2010
Aluminium Oxides - Al$_2$O$_3$ films deposited by Pulsed Laser Deposition (PLD)

Acta Materialia 61 (7), 2662-2670, 2013
Corrosion Science 77, 375-378, 2013
Scientific Reports 6, 33478, 2016
Corrosion Science on line, 2017
PLD-grown Al₂O₃ nanoceramic coatings

- high quality coatings
- custom process: bottom-up approach
- process at room temperature
- amorphous films with nanodispersed crystalline domains

<table>
<thead>
<tr>
<th>Property @RT</th>
<th>Sapphire</th>
<th>PLD Al₂O₃</th>
<th>AISI 316L</th>
</tr>
</thead>
<tbody>
<tr>
<td>v</td>
<td>0,24</td>
<td>0,295 ± 0,025</td>
<td>0,3</td>
</tr>
<tr>
<td>E [GPa]</td>
<td>345</td>
<td>193,8 ± 9,9</td>
<td>200</td>
</tr>
<tr>
<td>G [GPa]</td>
<td>175</td>
<td>75,5 ± 3,8</td>
<td>80</td>
</tr>
<tr>
<td>B [GPa]</td>
<td>240</td>
<td>159,2 ± 11,8</td>
<td>140</td>
</tr>
<tr>
<td>H [GPa]</td>
<td>27,8</td>
<td>10,3 ± 1</td>
<td>4</td>
</tr>
<tr>
<td>H/E</td>
<td>0,059</td>
<td>0,049 ± 0,007</td>
<td>0,025</td>
</tr>
</tbody>
</table>

H/E parameter index of wear resistance and fracture toughness
Mechanical behaviour of PLD-grown Al₂O₃

- **Nanoindentation Tests**

  ![Nanoindentation image](image)

  F. Garcia Ferré et al. – ACTA MATER – 2013

  - **Metal-like behavior under plastic strain**

- **Nanoscratch Tests**

  ![Nanoscratch image](image)

  - **Strong interfacial bonding**
Burst test

BEFORE

AFTER

longitudinal cracks

cross shaped cracks

pile-up
STM reveals homogeneous dispersion of Al$_2$O$_3$ nanoparticles (2-5 nm) in amorphous Al$_2$O$_3$ matrix.

Amorphous matrix as “lubricant”
Thermal stability

Thermal stability: in-situ TEM

as-deposited

600°C – 30 min

700°C – 22 min

800°C – 25 min

BF-HRTEM

as-deposited

800°C – 25 min

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H$_2$/D$_2$ permeation tests on Al$_2$O$_3$ films
O₂ permeation barrier

316L steel annealed at 500°C for 2 hrs

316L steel annealed at 1000°C for 2 hrs

316L plate

annealed 2h @ 1000°C in air

coating

oxide scale

coated steel 100 µm
Gas Permeation in solid matter follows the 1° Fick Law

\[ J(t) = \frac{D \cdot K_s \cdot p^2}{d} \left[ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left[ -D \frac{n^2 \pi^2}{d^2} t \right] \right] \]

\[ J = \text{permeating gas flux} \]

\[ J = \frac{DK_s}{d} \left( p_h^{1/2} - p_i^{1/2} \right) \rightarrow J = \frac{P}{d} \cdot p^{1/2} \]

\( P = \text{permeability} \) (permeation coefficient)
High P Section
The section is firstly evacuated and then filled with pure H$_2$ at different pressures (from $10^3$ to $10^4$ Pa)

Meddle Section
A circular sample (usually a steel disk) divides high P and low P sections. The sample is heated from room temperature to 750 °C

Low P section
Pumps system keeps pressure constantly in the range of $10^{-5}$ Pa. A mass quadrupole reads ion current due to permeation of H$_2$
Permeation Reduction Factor (PRF)

... from the Ion Current measurements ...

![Graph showing Ion Current measurements with different barrier thicknesses.]

... to Permeation Reduction Factor ...

PRF increases with the barrier thickness (i.e. the length of the diffusion path) from $\approx 800$ up to $100,000$ @ 650 °C

The growth is typically exponential due to the combination of permeative phenomena
Permeation tests: different film morphologies

... changing the background pressure during depositions (i.e. films morphology) ...
Permeation tests: different film morphologies

Changes in film porosity and compactness
Permeation tests: thermal stability

**Thermal cycling** in order to investigate **barrier stability** and **degradative phenomena**

(50 cycles from 250 to 550 °C)

\[ \text{PRF} \]

**Coatings stability assured** (no delamination at the interface nor cracks)

\[ \text{AS DEPOSITED} \]

\[ \text{ANNEALED} \]

\[ \text{Low decrease in PRFs probably due to substrates degradation (i.e. thermal annealing)} \]
Coated Eurofer97 discs

100nm

250nm

1µm

3µm

5µm
50 cycles from 250°C to 550°C up to 4°C min⁻¹ in fluxed Ar 6.0 and 2hr of dwelling time.
The Activation Energy can be calculated by means of an Arrhenius plot. It is referred to a single bulk material or a tandem system substrate/coating.

\[ P = P_0 \exp\left( -\frac{E_p}{RT} \right) \]

<table>
<thead>
<tr>
<th>Material</th>
<th>Activation Energy [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare steel</td>
<td>11.41</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>5 µm Al₂O₃</td>
<td>56.59</td>
</tr>
</tbody>
</table>

Thin Al₂O₃ films (few hundreds of nm) increase the permeation activation energy 5 times.
Experimental set-up @CIEMAT facilities: RIPER

The diffusion chamber is connected to the beam line of a 2 MeV Van der Graaff electron accelerator (dose rate ≈ $10^2$ Gy/s)

- Low pressure section
- Sample holder
- High pressure section
- Accelerator beam line
Permeation tests: coatings under irradiation

- Permeation tests with Deuterium @ 450 °C for 7 days (one cycle per day)
- **Samples irradiated** with 1,8 MeV electrons

> PRF values confirmed (around $10^3$ @ 450 °C): **no significant degradation under irradiation**

> Absorption/desorption phenomena during heating/cooling ramps
Permeation tests: coatings under irradiation

- Permeation tests with Deuterium @ 450 °C for 7 days (one cycle per day)
  - Samples irradiated with 1,8 MeV electrons

\[
\begin{align*}
\text{Permeation tests with } & \text{Deuterium @ 450 °C for 7 days (one cycle per day)} \\
\text{Samples irradiated with } & 1,8 \text{ MeV electrons}
\end{align*}
\]

\[\text{Deuterium release rate (mbarl/s)}\]

\[\frac{1000}{T} (\text{K})\]

- No significant degradation even after seven days of irradiation
- Desorption phenomena increase in time due to Deuterium accumulation in the samples
Permeation tests: coatings under irradiation

- Permeation tests with **Deuterium @ 450 °C** for 7 days (one cycle per day)
  - Samples irradiated with 1,8 MeV electrons

![Graph showing Deuterium release rate vs. temperature and time.](image)

⇒ Deuterium release slightly decreases during irradiation (investigations still undergo)
Pb compatibility of Al$_2$O$_3$ barrier coatings
Corrosion resistance, $O_2$ saturation

SS plates

uncoated sample

heavy liquid metal corrosion

coated sample

protection

Oxidizing stagnant Pb test

F. Garcia Ferré et al. – CORROS SCI – 2013
1515Ti cylinder – 5000 h in stagnant Pb @550°C 10^{-8} \text{wt.}\% \text{oxygen}

1 \mu m \text{Al}_2\text{O}_3 \text{coating}

No solidified lead on the 1515Ti cylinder
NO CORROSION
Corrosion resistance, $O_2$ depletion

**BEFORE**

- 1515Ti
- Pb
- $\text{Al}_2\text{O}_3$
- resin

**AFTER**

- 1515Ti
- Pb
- $\text{Al}_2\text{O}_3$

**NO corrosion**

$100 \mu m$

$15 \mu m$

$2 \mu m$
Corrosion tests in static Pb-16Li

- Preliminary tests on EUROFER 97 SS substrates $\text{Al}_2\text{O}_3$ - coated samples
  - 1,000 hours exposure test @ 550 °C in static Pb-16Li

![Al$_2$O$_3$ - COATED sample](image1)

![UNPROTECTED sample](image2)

![UNPROTECTED sample](image3)
Corrosion tests in static Pb-16Li

- Preliminary tests on EUROFER 97 SS substrates $\text{Al}_2\text{O}_3$ - coated samples
  - 1,000 hours exposure test @ 550 °C in static Pb-16Li
Recent studies have shown the formation of a potential protective layer of LiAlO$_2$ in Pb-Li eutectics at high temperatures (above 500 °C)

- Stable LiAlO$_2$ ternary compound in similar conditions to the ones of DEMO
Heavy Ion Irradiation of Al$_2$O$_3$ barrier coatings

Please, step by M. Vanazzi’s poster!
Model of evolution

**moderate dpa**
- ultra-fine nanoceramic GB-driven deformation
- highest fracture toughness

**high dpa**
- fine nanoceramic GB-driven deformation
- sub-linear grain growth

**pristine**
- bi-phase nanocomposite shear banding
- highest fracture strength

**end-of-life dpa**
- nanoceramic GB-driven deformation
- highest stiffness

**Sublinear grain growth**
Heavy ion irradiation (Au + W): nanoimpact

Impact energy is dissipated more efficiently in irradiated samples.
Heavy ion irradiation (Au + W): nanoimpact – 10 mN
Conclusions
Conclusions

- **Barrier films engineerization at nanoscale level**
  - Strong adhesion substrate/coating with metal-like behavior

- **Irradiation tests with heavy ions (Au + W)**
  - Radiation-induced **crystallization** with enhancement of mechanical properties

- **Chemical compatibility tests in Pb-Li**
  - Preliminary results from **1,000 hours** exposure in static Pb-16Li

- **Permeation tests with H₂/D₂ to simulate the effect of Tritium**
  - PRF evaluation tuning film thickness as well as morphology
  - Maximum PRF value (with PERI set up) close to **100,000** considering DEMO requirements of **15 < PRF < 1,000** @ 550 °C
  - Coatings effectiveness confirmed by secondary measurements
  - **No significant degradation** after thermal cycling and/or irradiation

To do list:

- Complex shape coating
- Scale up of the PLD process
- Neutron irradiation

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Thank You
for your attention!
Radiation damage in polycrystalline sapphire

- high density of small voids and dislocation loops
- anisotropic void swelling along c-axis
- intergranular micro-cracking to accommodate stress
Radiation damage in polycrystalline sapphire

**neutrons**

![Image of neutron damage](image1.png)

- high density of small voids and dislocation loops
- anisotropic void swelling along c-axis
- intergranular micro-cracking to accommodate stress

**ions**

![Image of ion damage](image2.png)

- possible to obtain equivalent microstructural features
- what is the best way to obtain such features?

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