Interaction of high flux plasma with Fe and RAFM steels: experimental and computational assessment

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Outline

- **Part I**
  - Improving high-Cr grades
  - Mechanical data

- **Part II**
  - Exposure of pure Fe (in reference and deformed state)
  - Exposure of E97, T91 and two advanced grades

- **Part III**
  - Atomic-scale assessment of H in Fe
  - Computational model to consider Non-equilibrium trapping and its connection to diffusion limited trapping
Development of RAFM steels with advanced mechanical properties
Standard and improved high-Cr grades for Fusion Appl.

- One principle problem of 9-Cr steels: low temperature embrittlement
- Second one: creep, limiting application up to 650°C
How to reduce DBTT and enhance creep resistance

- Modify precipitate distribution
  - Change ratio MC to MX
  - Modify H-treatment
  - Modify Composition
- V and Nb:
  - Stabilize grains
  - Reduce grain coarsening
  - Increase ductility
- Ta:
  - Carbide former & stabilizer
- 9Cr remains optimum
  - Less Cr – poor corrosion resistance
  - More Cr – hardening ($\alpha'$) and $\delta$-ferrite
### Advanced Thermo-Mechanical Treatment: TMT

<table>
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<th>Pass 3</th>
<th>Pass 4</th>
<th>Pass 5</th>
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*Graph showing temperature and time points:*
- 1050°C 30min.
- 980°C 30min.
- 920°C 30min.
- 880°C 30min.
- 750°C 2hrs

*Diagram with labeled boundaries.*
Effect of Heat Treatment

Effect of Ta content on grain size

- TMT
- TMT+HT

Graph showing the effect of Ta content on grain size.

- 0.09wt%Ta_LFRT
- 0.11wt%Ta_LFRT

Images showing microstructures:
- 0.5 µm
- M23C6

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Role of heat treatment

Main differences after normalizing

880°C $\rightarrow$ dissolution temperature $\text{M}_{23}\text{C}_6$ & restriction prior austenite grain (PAG) growth by untransformed tempered martensite after tempering:

small martensitic blocks with different degree of tempering and relatively large $\text{M}_{23}\text{C}_6$ mainly on packet boundaries

920°C $\rightarrow$ complete transformation to $\gamma$ & homogeneously distributed carbon & hardly no PAG growth & high HAGB density after tempering:

small martensitic blocks with smaller $\text{M}_{23}\text{C}_6$ on block and packet boundaries

980°C $\rightarrow$ dissolution temperature $\text{MX}$ & PAG growth after tempering:

martensitic blocks with $\text{M}_{23}\text{C}_6$ more evenly distributed mainly on the block boundaries

1050°C $\rightarrow$ extended prior austenite grain growth & homogeneously distributed nitrogen & low HAGB density after tempering:

relatively large martensitic blocks with elongated $\text{M}_{23}\text{C}_6$ on block and packet boundaries
Precipitation of Vanadium and Tantalum

Fraction of elements that precipitate at different stages of Q&T treatment

<table>
<thead>
<tr>
<th>Wt%</th>
<th>Cr</th>
<th>Ta</th>
<th>V</th>
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<tbody>
<tr>
<td>0.09Ta</td>
<td>9.3</td>
<td>0.086</td>
<td>0.22</td>
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</table>

wt% V & wt% Ta precipitated

Martensite structure and carbide measurements

<table>
<thead>
<tr>
<th>Annealing temperature [°C]</th>
<th>D_{AV, Eq} [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td>10</td>
</tr>
<tr>
<td>900</td>
<td>20</td>
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<tr>
<td>950</td>
<td>30</td>
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<tr>
<td>1000</td>
<td>40</td>
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<tr>
<td>1050</td>
<td>50</td>
</tr>
<tr>
<td>1100</td>
<td>60</td>
</tr>
</tbody>
</table>

Carbides

Block size

TMT - Anneal - Q&T
Mechanical properties of improved grades

Q&T: 880°C tested at -140°C

Diagram showing EDIAL vs. Test Temperature [°C] with DBTT at -150°C.
Two grades were selected for Plasma exposure

- "196C"
  - 0.11C; 9Cr; 1W; 0.23V; 0.09Ta; 0.0113N; 0.4 Mn; 0.03Si
  - Heat treatment: 880°C 1/2h + water quench + 750°C for 2 hr.
  - Low DBTT (-150C);

- "8Cr"
  - 0.02C; 8Cr; 1W; 0.22V; 0.13Ta; 0.022N (No Mn&Si)
  - Heat treatment: 1050°C 1/4h + water quench + 675°C for 1.5h
  - Fine grain microstructure with; DBTT - 90°C
Part II

- Plasma exposure of pure Fe
- Plasma exposure of advanced RAFM and E97, T91
Depth distribution & sub-surface trapping

[Diagram showing depth distribution and sub-surface trapping with labels for surface, projected range, compressive stress, tensile stress, gas concentration, and regions of H density saturated.]
High heat flux plasma exposures

- PILOT-PSI (NL, DIFFER)
- Stationary Loads & ELM-like pulses
- B field = 0.4-1.6 T; target bias 50 eV
- Water cooling 20 C (passive control of T surface)
- Flux $0.8 \times 10^{24} \text{ D/m}^2/\text{sec}$

Temperature at the centre of sample

Exposure time (sec)

Typical ion flux profile
High flux plasma changes sub-surface

- Compressive stresses in sub-surface region generate:
  - Dense dislocation network
  - Limited within 10-15 μm

- Poly-crystalline (ITER-specification)
High flux plasma changes sub-surface

- Compressive stresses in sub-surface region generate:
  - Dense dislocation network
  - Limited within 10-15 μm

- Poly-crystalline (ITER-specification)
  - Recrystallized at 1600C (1h)
High flux plasma changes sub-surface

- Compressive stresses in sub-surface region generate:
  - Dense dislocation network
  - Limited within 10-15 μm

- Single crystal (110 orientation)
Impact of dislocation networks in pure Fe

- Plastic deformation was applied at RT up to 40%
- Grain size: 50-100 µm
- Dislocation density:
  - Non-deformed: $10^{11}$ m$^{-2}$
  - 20% - $8 \times 10^{12}$ m$^{-2}$; 40% - $3 \times 10^{14}$ m$^{-2}$
Retention in pure Fe

- High Flux D plasma exposure at Pilot PSI (NL)
  - Surface temperature: 430-450 K
  - Flux $0.8 \times 10^{24} \text{ D/m}^2/\text{sec}$
  - Fluence $\sim 5 \times 10^{25} \text{ D/m}^2$

- Detrapping stages
  - Around 470K (1.2 eV)
    Position does change with increase of dislocation density
  - Around 620K (1.6 eV)
    Position shifts with increase of dislocation density

In line with results of Hong and Lee, Acta metall 32 (1984) 1581-1589
Exposure of Eurofer97 and T91

- High Flux D plasma exposure at Pilot PSI (NL)
  - Surface temperature: 430-450K
  - Flux $0.8 \times 10^{24}$ D/m$^2$
  - Fluence $\sim 5 \times 10^{25}$ D/m$^2$
- Reference measurements
  - T91; E97

In line with results of Ogorodnikova et al. Nucl. Fusion 57 (2017) 036011 and in line with Hino et al. JNM 386-388 (2009) 736-739
Surface analysis of Eurofer97

- Exposure at 430-450K: Blisters and individual grains

Size of blisters is about 0.1-2 μm; $3 \times 10^{-15}$ m$^{-2}$; mean spacing 15 μm
Exposure of Eurofer97 vs. two advanced grades

- High Flux D plasma exposure at Pilot PSI (NL)
  - Surface temperature: 430-450K
  - Flux $0.8 \times 10^{24}$ D/m$^2$
  - Fluence $\sim 5 \times 10^{25}$ D/m$^2$

- Release stages
  - 470K – just like in pure Fe
  - In “196C” stage at 740K
Preliminary results

- Exposure at 430-450K: E97 vs. advanced grade

Much smaller surface roughening; lower density of blisters
Amount of plastic deformation induced in “196C” is much smaller than in E97
Summary of experimental data

- Pure Fe: one major release stage at 470K
- Plastically Deformed Fe: major release stage at 470K + emerging stage at 620K. Stage position shifts towards higher temperature with increase of dislocation density
- E97 and T91: spectrum is very similar to pure + minor release above 500K
- Surface microstructure of exposed steels reveals regions with very high dislocation density
- Improved RAFM steels:
  - “Clean Steel” 8Cr + 0.13Ta (no Si, Mn): spectrum same as E97
  - DBTT-optimized (0.09Ta, 880°C quenched): extra release stage at 750K. Same nature as in deformed Fe?
  - Much smaller surface modification (higher toughness)
Part III

- Computational assessment of H in Fe
Atomic-scale description of H in bcc Fe

- H atoms
- He atoms

- Nucleation of stable clusters to occur on lattice defects

(a): Ogorodnikova et al. Nucl. Fusion 57 (2017) 036011
Hypothesis about trapping on dislocations

- Experimental and theoretical ‘facts’:
  - H-H can form clusters, but binding is very weak
    - Binding (H-H)=0.22 eV (A); (H₂-H)=0.08 eV (D), (H₃-H)=0.02 eV (C)
  - Migration energy = 0.09 eV
    - Diffusion of H is controlled by interaction with lattice defects
  - Typical µ-structure of RAFM steels:
    - Dislocations (10¹³-10¹⁴ m⁻²)
    - Ferritic and martensitic grains, precipitates (M-X and M₂₃C₆)
  - Possible mechanism of bubble nucleation without vacancies:
Interaction of Hydrogen with screw dislocation

<111> view: Differential displacements map

\[ \Delta E = -0.27 \text{ eV} \]

Migrations:
- a – in core
- b – in-out
- c – out core

\[ E_m = 0.03 \text{ eV} \]
In-pile migration of H on screw dislocation

- Migration occurs via hops through tetra-sites
- Migration barrier is 0.03 eV
- Saddle point configuration involves modification of the dislocation core structure
- Migration barrier will be strongly impacted by external stress applied
In-pile migration of H on edge dislocation

- Migration occurs via hops between tetra-sites next to the dislocation core
- Migration barrier is 0.1 eV
- Saddle point configuration is distorted octa-site
## Clustering of Hydrogen on screw dislocation

**Binding energy [eV]**

<table>
<thead>
<tr>
<th>Size of H(_N) cluster</th>
<th>SD length = 3b</th>
<th>ED Length = 2.4a(_0)</th>
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</thead>
<tbody>
<tr>
<td>H + SD</td>
<td>0.27</td>
<td>0.47</td>
</tr>
<tr>
<td>H + (H-SD)</td>
<td>0.2</td>
<td>0.51</td>
</tr>
<tr>
<td>H + (H(_2)-SD)</td>
<td>0.18</td>
<td>0.3</td>
</tr>
<tr>
<td>H + (H(_3)-SD)</td>
<td>-0.1</td>
<td>0.18</td>
</tr>
<tr>
<td>H + (H(_4)-SD)</td>
<td>-0.12</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**Charge density maps [e\(^{-}/\text{Å}^3\)]**

- Pure Fe: 0.186
- One H added: 0.152
- Two H added: 0.891
- Three H added: 0.146

**Screw dislocation can trap several hydrogen atoms simultaneously, but incremental binding energy decreases with number of trapped H atoms (from 0.27 eV– down to 0.03 eV).**
Results: Molecular Dynamics Results

Validated two types of potentials EAM and BOP

MD Results:
- Bulk
  - 3D $E_m = 0.11 \text{ eV}$
- 1D edge dislocation
  - 1D $E_m = 0.17 \text{ eV}$

Diffusion coefficient ($m^2/s$)

$$D_n(T) = \frac{R^2}{2n t_{sim}(T)}$$

Migration along the dislocation core simulated by MD reveals $0.17 \text{ eV}$
Hence, formation of stable H cluster must invoke some impurities to reduce the migration, for instance Carbon

$D_n(T) = D_0,ne^{-\frac{E_m}{kT}}$
Nucleation of stable Hydrogen cluster on dislocation

**Loop punching: growth of bubbles due to excess pressure via the emission of dislocation loops**

A: Dislocation + cluster $H_N$

B: dislocation + (Jog$^{-}H_N$) + Jog$^+$

**Classical loop punching mechanism**

No attraction of H in bulk – no way to form critical concentration.

Clustering at dislocation core leads to jog emission at $N_H=8$
Nucleation of stable Hydrogen cluster on dislocation

Because of the negative solution energy, H clusters can not induce jog punching

Jog punching: formation of vacancy jog to accommodate $H_N$ cluster + emission of interstitial jog
Nucleation of stable Hydrogen cluster on dislocation

Jog punching: formation of vacancy jog to accommodate \( H_N \) cluster + emission of interstitial jog

Because of the negative solution energy, H clusters can not induce SIA emission
Summary of atomic-scale data for H in Fe

- H solution energy $-2.33$ (H adds to cohesion of Fe) – tetra-site
- H-H binding in Fe 0.22 eV, and it reduces to 0.02 eV for H$_3$-H cluster
- H-vacancy binding 0.62 eV; one vacancy accepts 5 H atoms and does not growth further by emission of SIAs
- H-dislocation binding 0.27 eV and 0.47 eV (SD & ED); jog-emission is not energetically favourable mechanism
- H migration energy in bulk = 0.09 eV from tetra-to-tetra site;
- H migration energy on screw dislocation = 0.05 eV;
- H migration energy on edge dislocation = 0.1 eV

Formation and growth of H defects resulting in blisters could be related to:
- Nucleation of flake-like H clusters at GB interfaces, Carbide-GB interfaces
- Growth of those defects by loop emission (as availability of H promotes plastic deformation)
Description of the model

H source defined from steady state solution

~ 10-100 μm; time ~ 1000 seconds
 outbreaks

- Complete computational model
  - Assess formation of H clusters at grain boundaries and Carbide-Fe interfaces
  - Assess interaction of H-vacancy-Carbon defects
- Parametric study of the high flux plasma exposure
  - Exposure temperature: 450K – 850K (upper limit for RAFM)
  - Exposure dose: $5 \times 10^{25} – 10^{27}$ D/m$^2$
  - Materials: Fe, Plastically deformed Fe; Eurofer97; “Clean Steel” (no Si & Mn)
Spare slides
Preliminary results

- High Flux D plasma exposure at Pilot PSI (NL)
  - Surface temperature: 950-970 K
  - Flux $\sim 10^{24}$ D/m$^2$
  - Fluence $\sim 5 \times 10^{25}$ D/m$^2$
- Reference measurements
  - E97;