Investigation of microstructure changes in EUROFER-ODS after hydrogen loading

O. EMELYANOVA, **Dr. M. GANCHENKOVA**
National Research Nuclear University (MEPhI), Moscow, Russian Federation

E. MALITSKIY ,Dr. Y. YAGODZINSKYY, **Dr. H. HANNINEN**
School of Engineering, Aalto University, FI-00076 Aalto, Finland

Dr. M. KLIMENKOV, Dr. P. VLADIMIROV, R. LINDAU, Dr. A. MOESLANG
Karlsruhe Institute of Technology, Institute of Applied Materials, D-76344
Eggenstein-Leopoldshafen, Germany

V. BORODIN
National Research Centre "Kurchatov Institute"

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Introduction

The oxide dispersion strengthened (ODS) steels are promising materials to fusion blanket applications as well as advanced fission reactor concepts due to suppression of high-temperature creep.

Why hydrogen?

- **Hydrogen production rate for first wall steels is predicted to be about 41 appm/dpa, spallation source (ESS)~33-300appm/dpa, fast breeder (BOR-60) ~0,7 appm/dpa.**

- **Hydrogen induces severe embrittlement and in combination with helium might increase swelling**

Motivation

Investigate microstructure stability of ODS steels in terms accumulation of transmutation gas impurities

Experimental details

Materials

EUROFER-ODS steels were produced by powder metallurgy method and shipped after hot rolling in the form of 6 mm thick plates.

Chemical composition of EUROFER 97 and ODS-EUROFER[a] steels.

Material	C	Si	Mn	Cr	Ni	Mo	Al	W	V	Ti
ODS-EUROFER	0.086	0.03	0.39	9.2	0.02	0.0056	0.003	1.14	0.197	<0.003
EUROFER 97	0.11	0.03	0.55	8.95	0.013	<0.005	0.009	1.06	0.202	<0.003

[a] ODS-EUROFER steel contains about 0.3 wt.% Y_2O_3.

Hydrogen charging and hydrogen uptake measurements

•Electrochemical pre-charging at *RT* from 0.1 N NaOH solution with 20 mg/l of $CS(NH_2)_2$ at controlled electrochemical potential of 1.70 and 1.85 $V_{Hg=Hg2SO4}$ 20-24 h

•TDS apparatus, calibrated UHV chamber equipped with a mass-spectrometer in the temperature range from RT to 850 ºC under controlled heating rate.

Experimental details

Mechanical tesing

CERT tensile tests were performed with 35 kN MTS desk-top machine at strain rate 10^{-4} s^{-1}

Microstructure investigation

Sample preparation for TEM

-As-suppled structures by electropolising in Tenupol 5

-After hydrogen pre-charging and tensile testing by FIB (final ion polishing 3 keV)

Scanning electron microscopy and focus ion beam (FIB)

- Helios 650 Nanolab (Ga ion system)

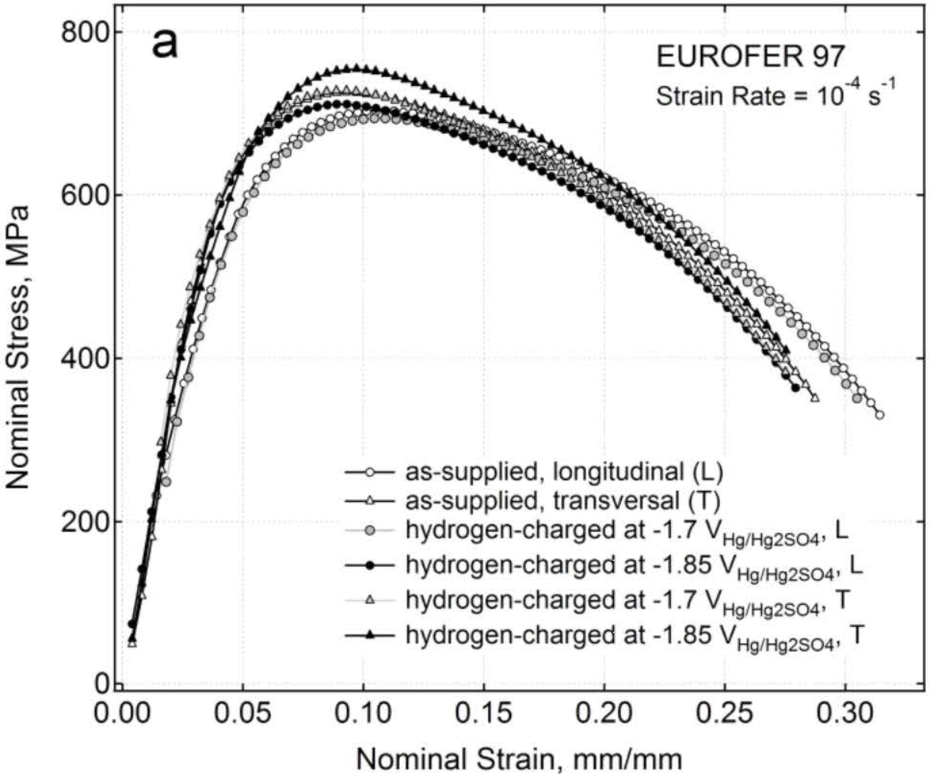
-Quanta 3D FEG (Ga ion system)

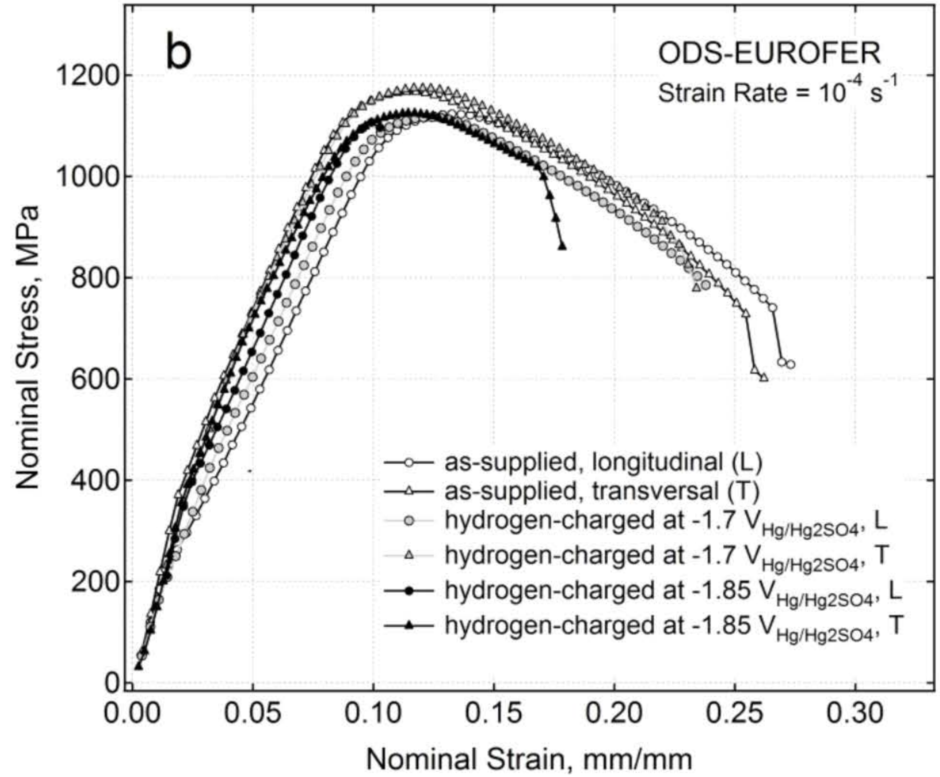
Transmission electron microscopy

-Techai G2 FEI Tecnai G2 20 FEG

- EDX measurment was perfomed with the EDAX EDX using drifft correction

Hydrogen effect on mechanical properties





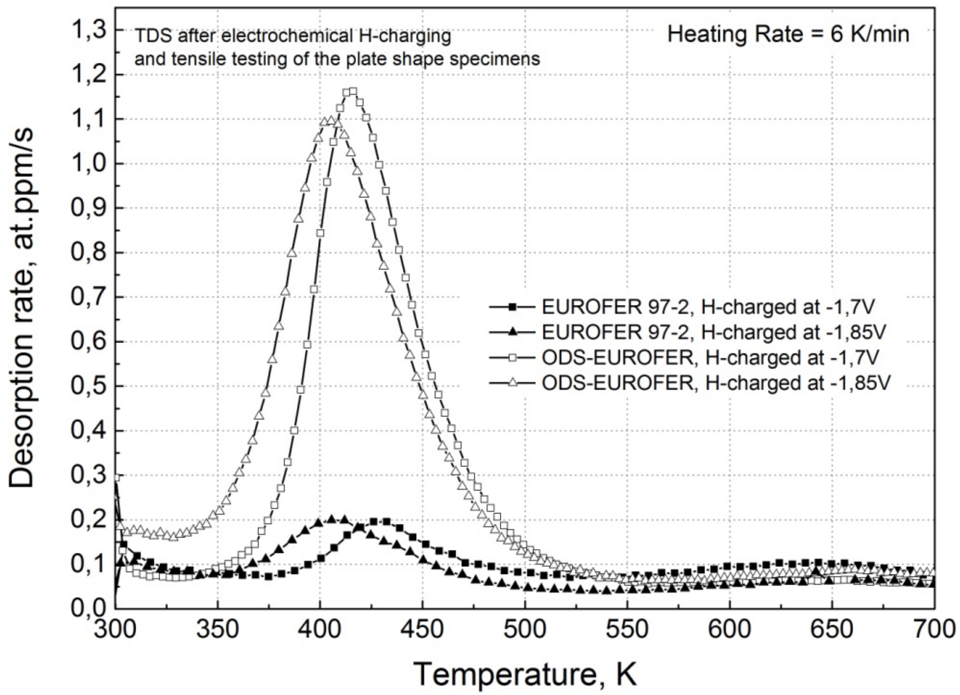
- ✓ EUROFER 97 - Hydrogen has only a minor effect on the tensile properties
- ✓ ODS-EUROFER :

  hydrogen charging at -1.70 $V_{Hg/Hg2SO4}$ - a minor effect on the elongation to fracture

  hydrogen charging at -1.85 $V_{Hg/Hg2SO4}$ - the elongation to fracture of the longitudinal specimens is less than that of the transverse ones.

EUROFER vs. EUROFER-ODS (hydrogen uptake)

EUROFER and EUROFER-ODS demonstrate rather different hydrogen uptake at the same electrochemical potential applied for hydrogen charging



H-content

Eurofer 97-2, H-charged at -1,85V

4,2 wt.ppm

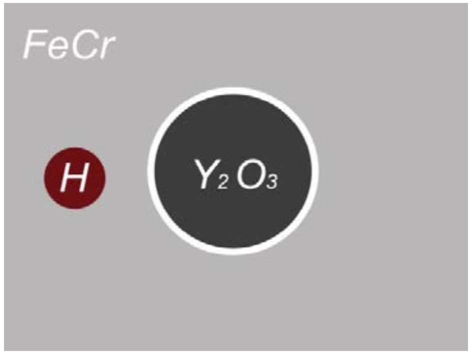
ODS-Eurofer, H-charged at -1,85 V

32,9 wt.ppm

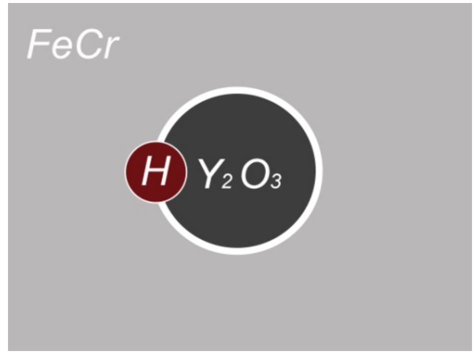
Why does the ODS steel accumulates hydrogen 6 times more intensively in comparison with base material?

Where hydrogen can locate?

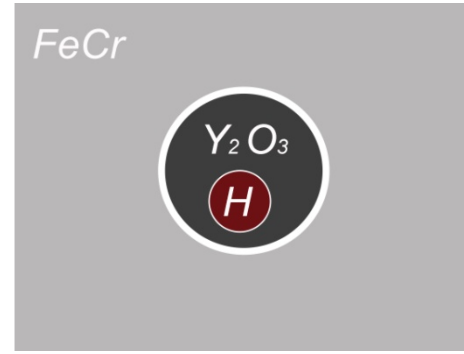
H outside of the particle



H at interface matrix/Y_2O_3



H in Y_2O_3 nanoparticle



If $E_H(Y_2O_3) << E_H(FeCr)$ then there is a driving force for H to be captured by Y_2O_3

Radically different points of view to role of oxide particles in hydrogen accumulation

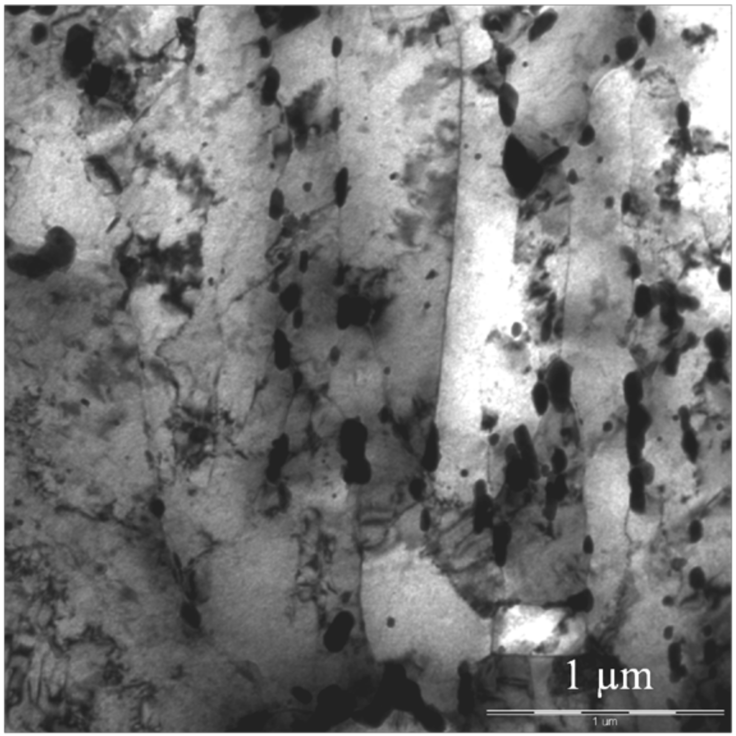
- "the interface of the yttrium particles surface and the martensitic laths of the material have been identified as an additional origin of the H trapping effect"

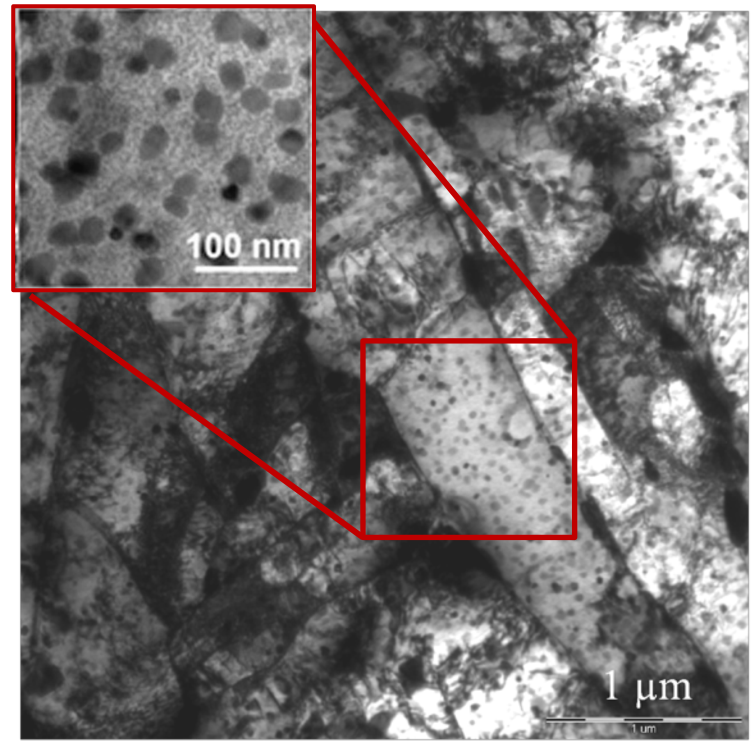
  G.A. Esteban et al. / Fusion Engineering and Design 82 (2007) 2634–2640

- "yttrium oxides and their interfaces are not effective H traps"

  V.V. Sagaradze, V.I. Shalaev, et al., J. Nucl. Mater. 295 (2001) 265–272

EUROFER vs. EUROFER-ODS (as-supplied microstructure)

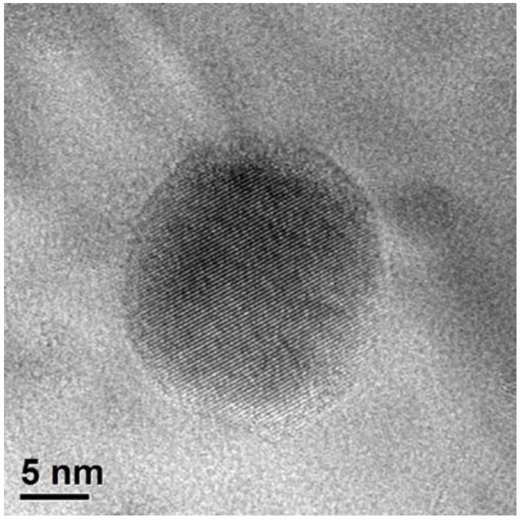




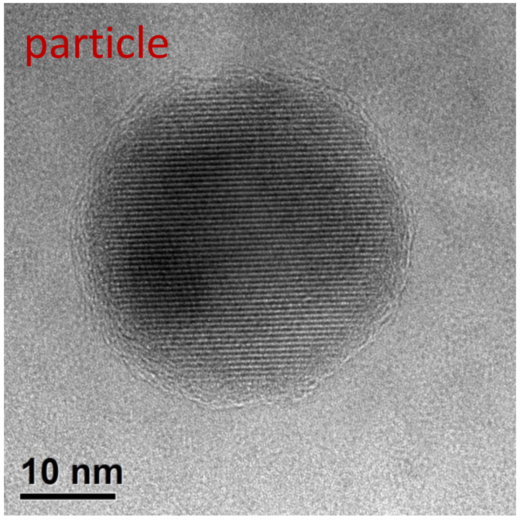
Critical sites to hydrogen accumulation – oxide particle!

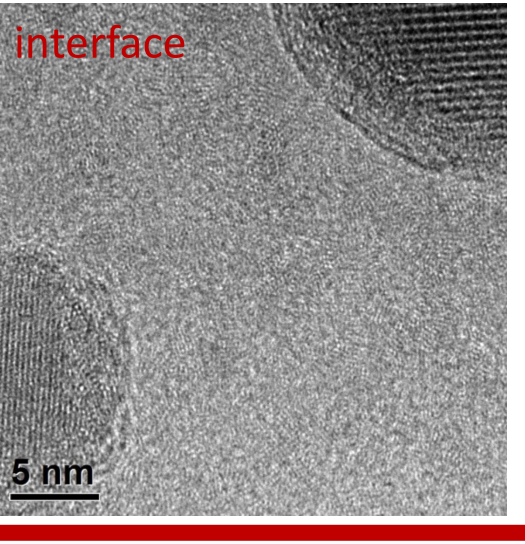
ODS nanoparticle structure before and after hydrogen charging

As-supplied



H-charged at 1, 85 V

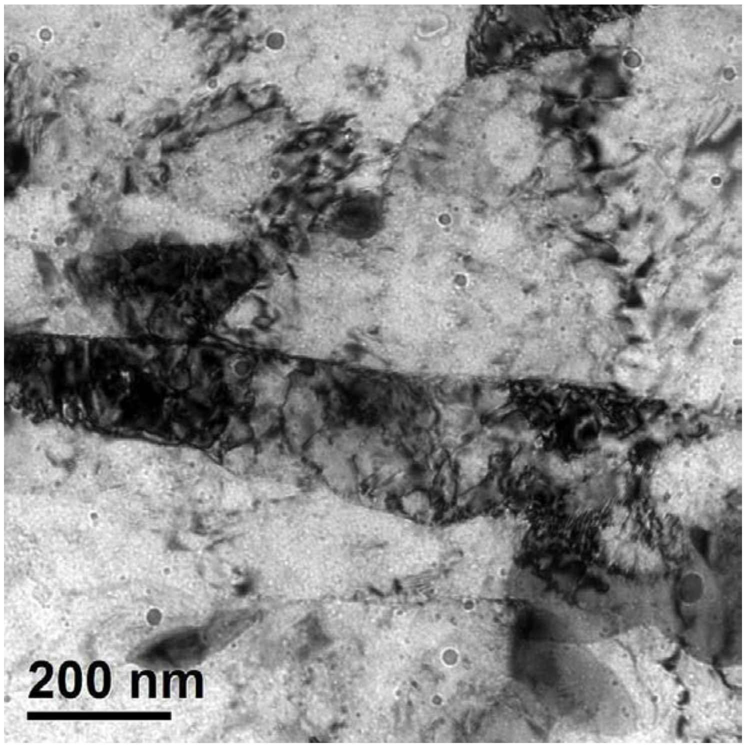




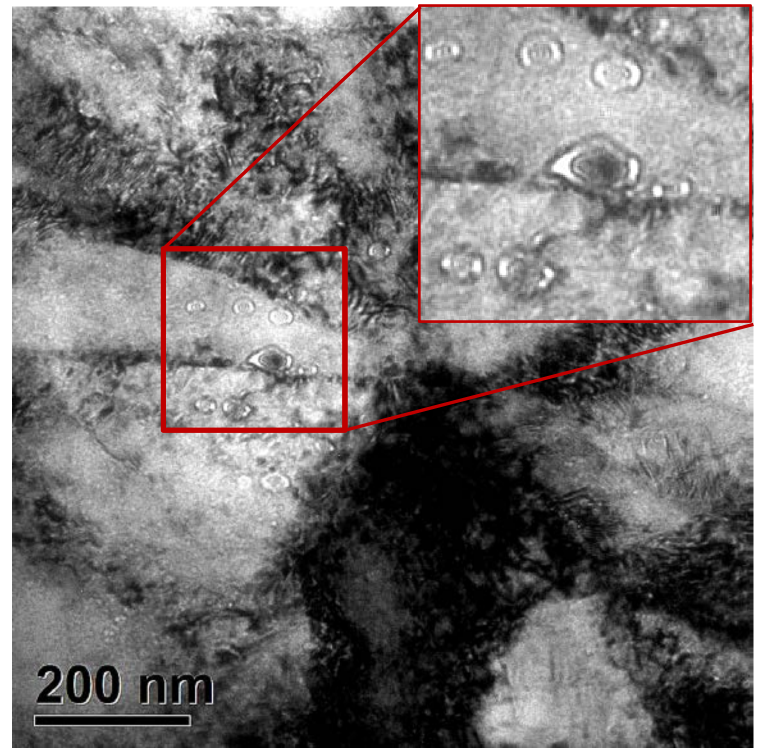
✓no changes both in the structure of the particle and at the interface

Synergetic effect of tensile and hydrogen

H-free



H pre-charged at 1,85 V

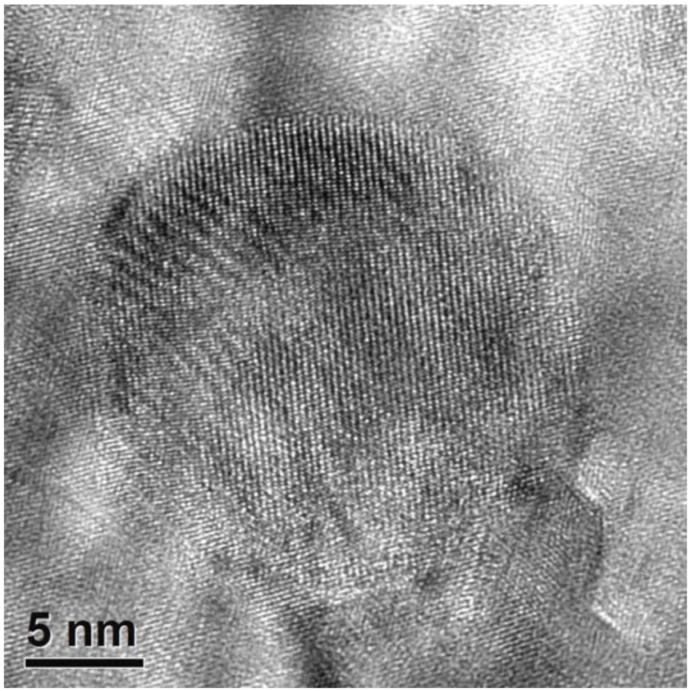


Loading direction

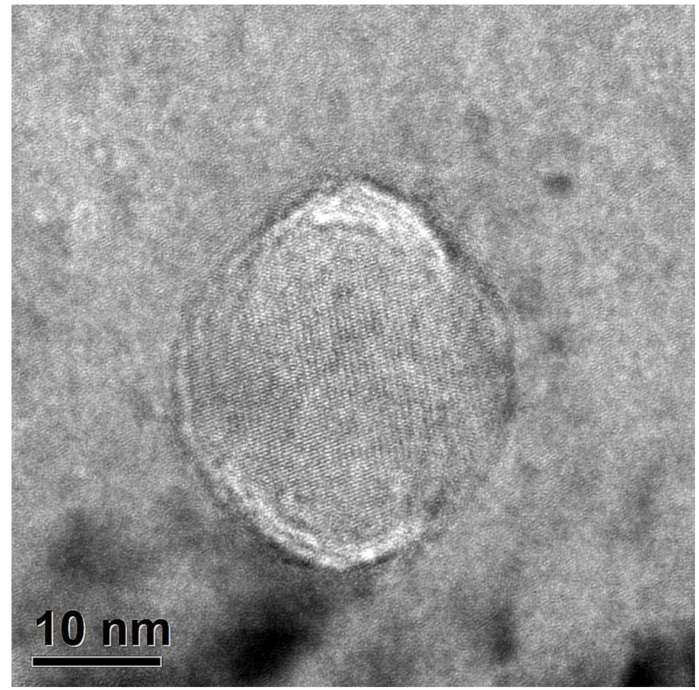
Synergetic effect of deformation and hydrogen on the microstructure of EUROFER-ODS

Loading direction

H-free



H pre-charged at 1,85 V



decohesion effect was observed on ~ 80% yttrium particles after H-charging!

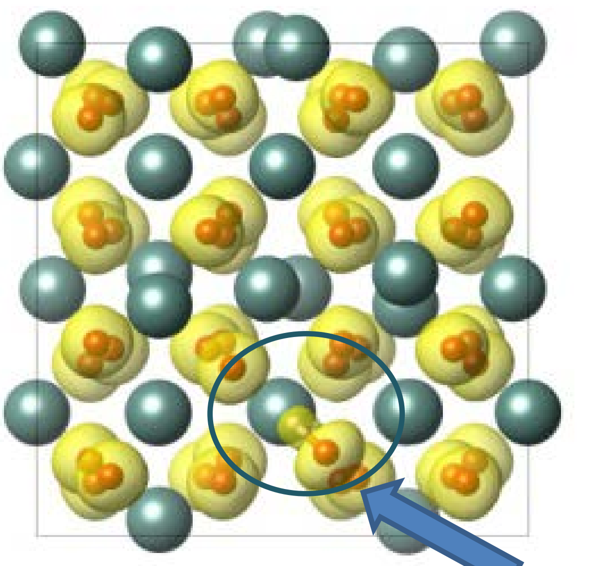
Ab Initio calculations of interaction between hydrogen and Y_2O_3

How it was studied:

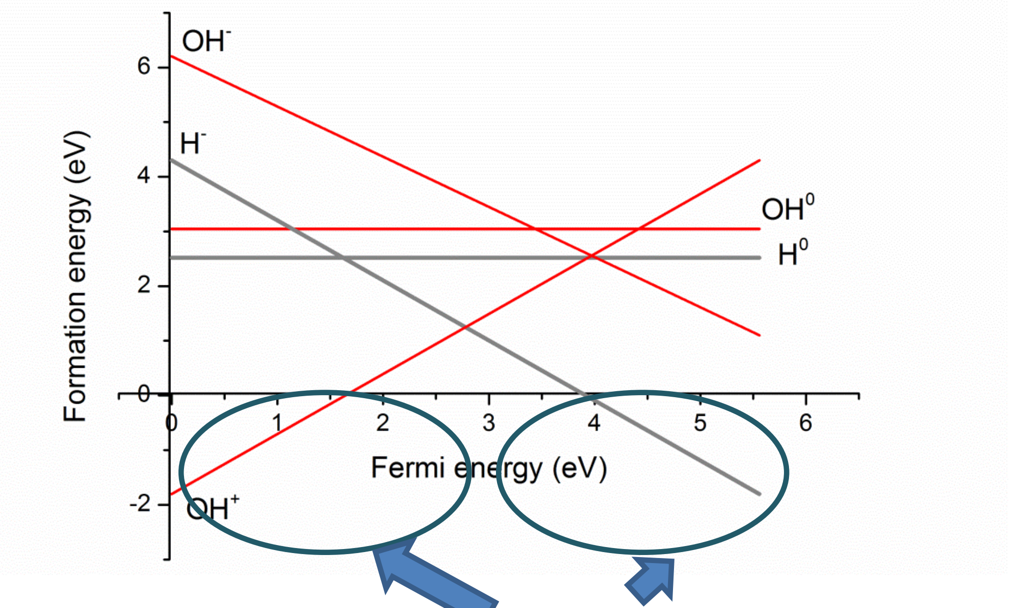
- VASP
- Molecular statics
- GGA
- PBE (Perdew Burke Ernzerhof)
- 80 atom supercell (SC)
- 2x2x2 Monkhorst-Pack k-points mesh

Ab Initio calculations of interaction between hydrogen and Y_2O_3

- ✓ H^+ shifts towards O **forming OH group**.
- ✓ transformation of H^0 and H^- to OH requires **overcoming an activation barrier.**



Charge Density map for OH^+ in Y_2O_3

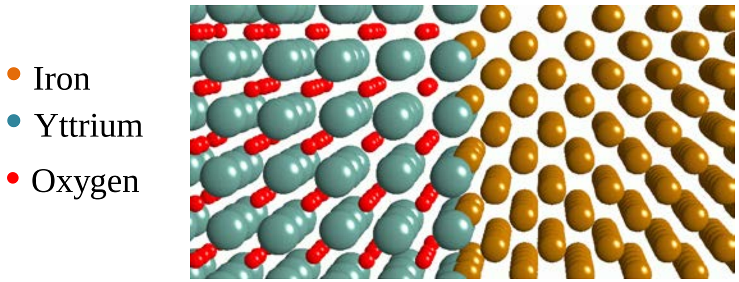


$E_H(Y_2O_3) < E_H(FeCr) = 0.12eV$

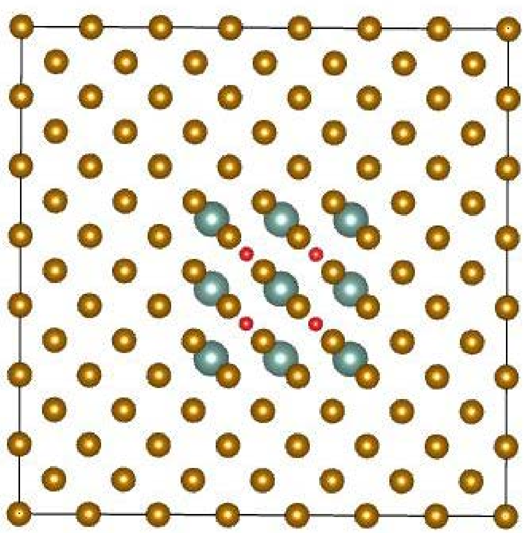
Formation energy dependence from Fermi level position for H and OH in Y_2O_3

DFT MD experiments of interaction between hydrogen and particle/matrix interface

(100) Fe-Y



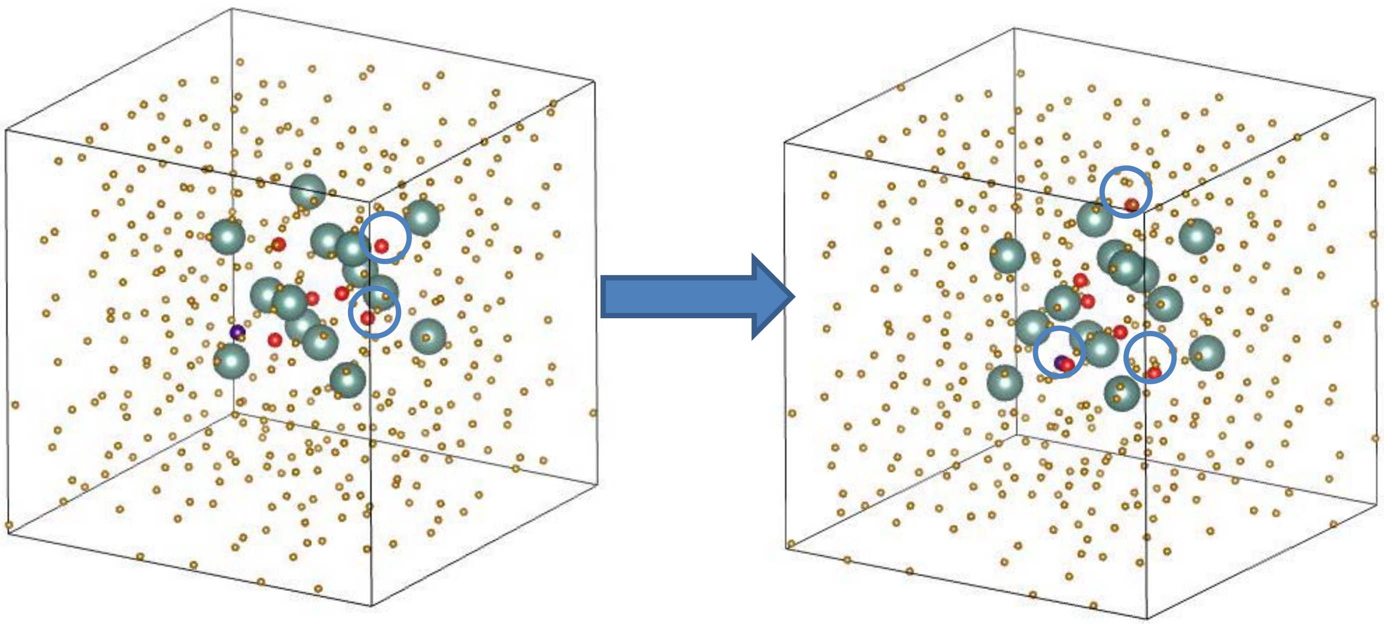
modified 'simple' interface



Model of simple interface by Brodrick, D.J. Hepburn, G.J. Ackland, J.Nucl.Mat. 8 (2013)

- ✓ The model of a modified 'simple' interface
- ✓ The coherent interface, the interface does not induce much stress to the matrix
- ✓ The interface is terminated with Y atoms
- ✓ The model was constructed for 427 and 660 atom Super Cell

DFT MD experiments of interaction between hydrogen and particle/matrix interface



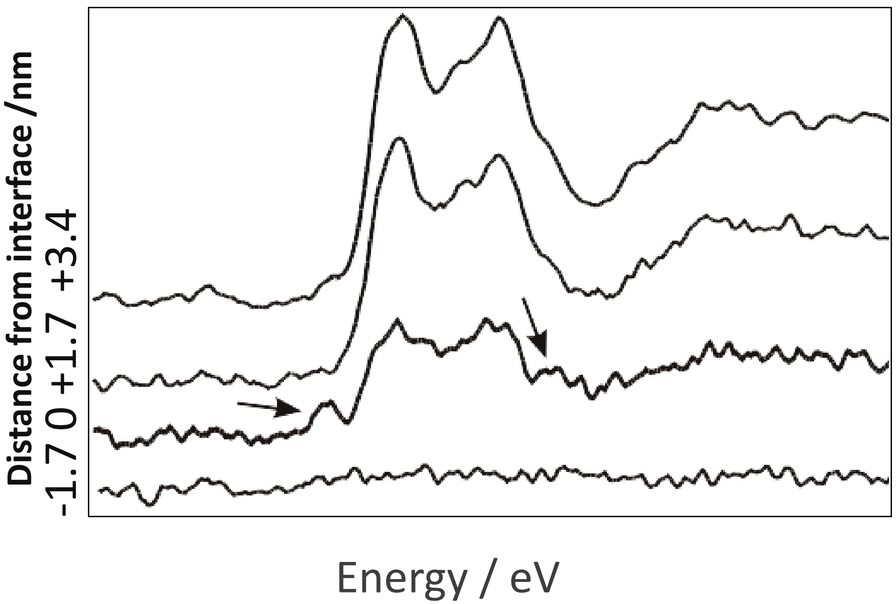
✓OH-group can be really formed

✓the tendency of oxygen to move to the surface – oxygen terminated interface

The cell contains: Fe=396, Y=14, O=6 + 1 H

About oxygen terminated interface….

M. Klimenkov, A. Moeslang, and R. Lindau **EELS analysis of complex precipitates in PM 2000 steel.** Eur. Phys. J. Appl. Phys. **42, 293–303 (2008)**



<u>**ELNES of the O-K edge obtained from ODS particle**</u>

Evidence of presence
Y-O-Me bond
(can be Ti, V, Cr,Fe)

Summing up

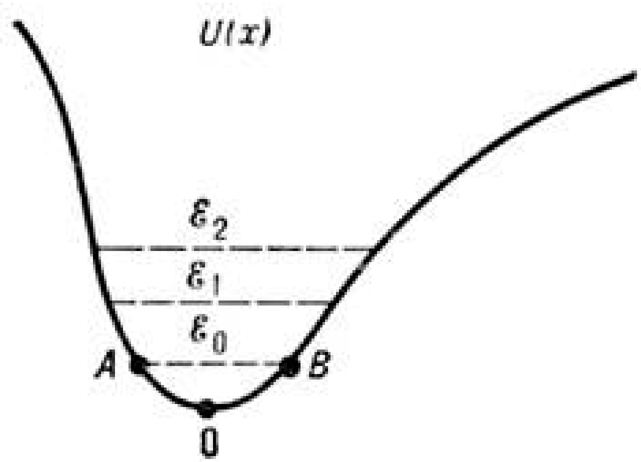
- ✓ presence of yttrium oxide particles leads to notable increase in hydrogen uptake
- ✓ hydrogen promotes the effect of decohesion at the interface oxide particle / matrix under mechanical loading
- ✓ we can tentatively assume that formation of the -OH groups at the nanoparticle surface leads to weakening the Fe-O-Y bonds and facilitates the process of decohesion on the interface of the Y_2O_3 nanoparticle and the Fe matrix

Thank you for your attention!

In addition

➢ **Hydrogen solution energies are calculated as**

$$E_f = E_{tot}^{H} - E_{tot}^{bulk} - \frac{1}{2}\mu_{H_2} + ZPV + q(E_v + \mu_e)$$



ZPV does not introduce significant correction!

where $\frac{1}{2}\mu_{H_2}$ is the hydrogen chemical potential in the hydrogen molecular gas, E_{tot}^{H} is the total energy of the supercell with and E_{tot}^{bulk} without hydrogen atom in the interstitial site.

ZPV is the contribution from the zero-point hydrogen vibrations:

$$ZPV = \frac{1}{2}\sum_{i=1}^{3} \hbar\, \omega_i$$

The defect can be charged!

In addition – Cr shell

M. Klimenkov et al. / Journal of Nuclear Materials 409 (2011) 65–71