

**8<sup>th</sup> International GD Day on September 15, 2016**  
**Synchrotron SOLEIL L'Orme des Merisiers rond point du Golf de Saint Aubin**  
**91190 Saint Aubin, France**

# **Hydrogen Enhanced Oxidation**

**- Atomic scale simulation and experimental evidences-**  
**-Locality and Causality in Corrosion-**

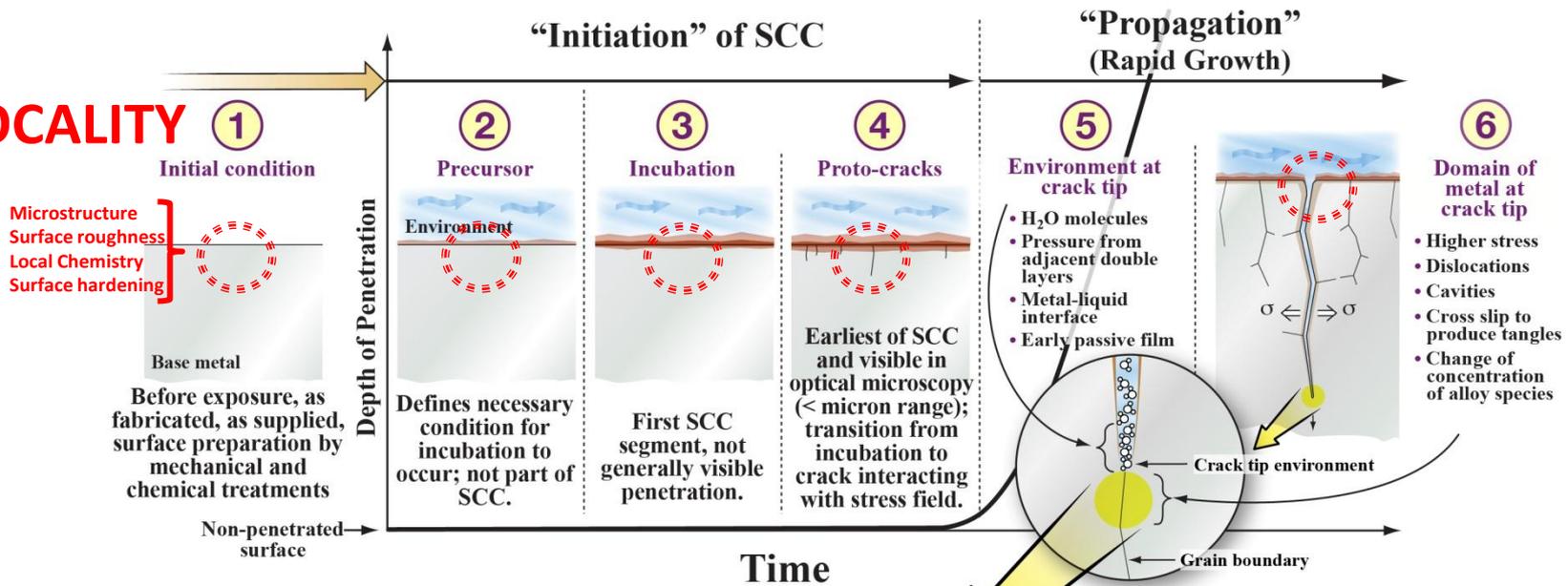
**Sept. 15, 2016**

**Tetsuo Shoji**

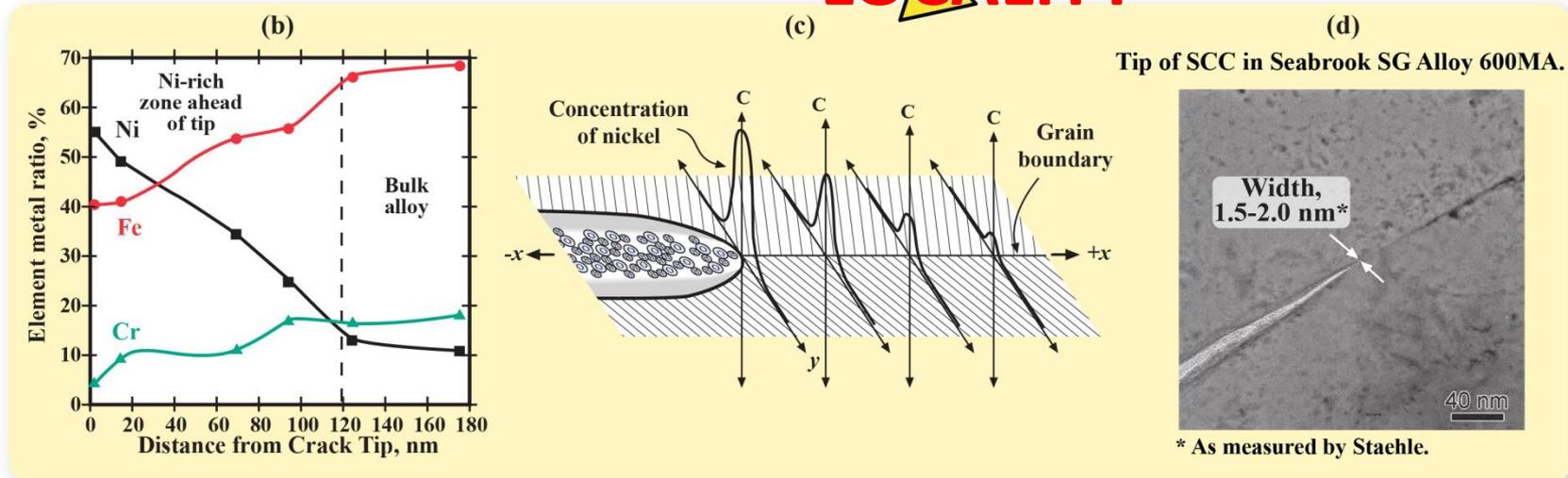
**Tohoku University, Sendai, Japan**  
**University of Science and Technology Beijing, China**

# ← CAUSALITY →

## LOCALITY

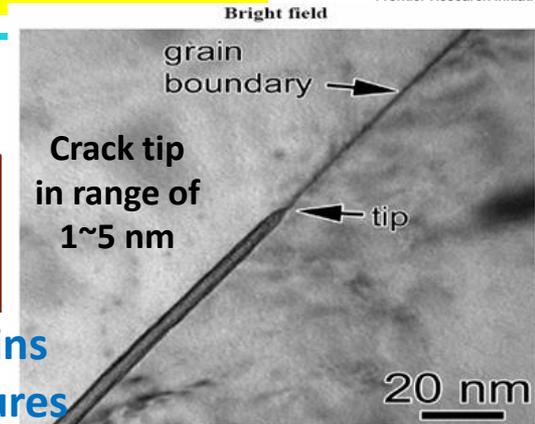
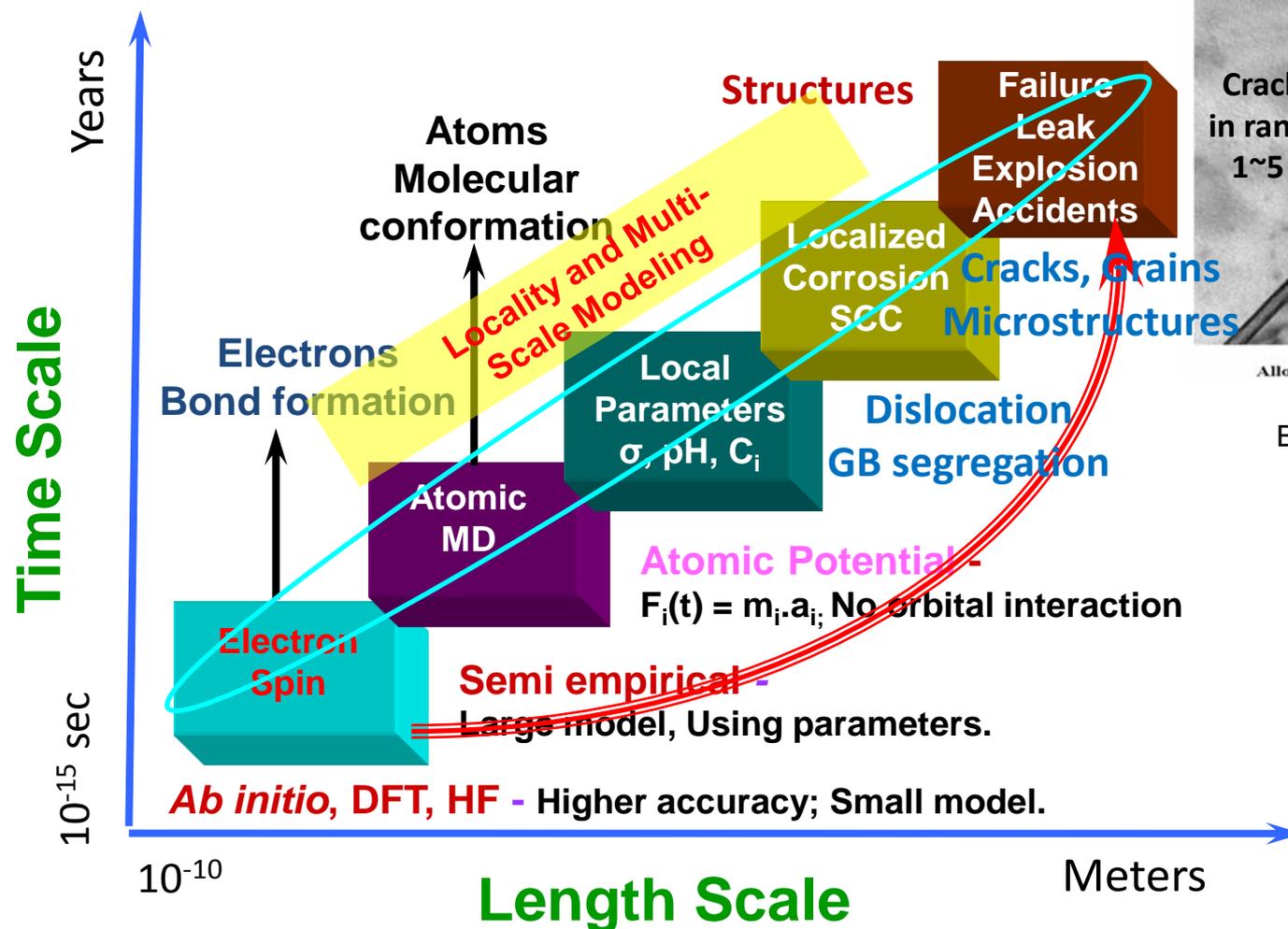


## LOCALITY



**Fig. 1 CAUSALITY and LOCALITY** Modified from the ppt by Koji Arioka, Robert L Tapping and Roger Staehle, Sept. 21, 2015 IMR Symposium, Shenyang, China <sup>2</sup>

# LOCALITY and CAUSALITY in length and time scales



Alloy 600, 320° C PbO experiment

Bruemmer *et al.*, Corrosion

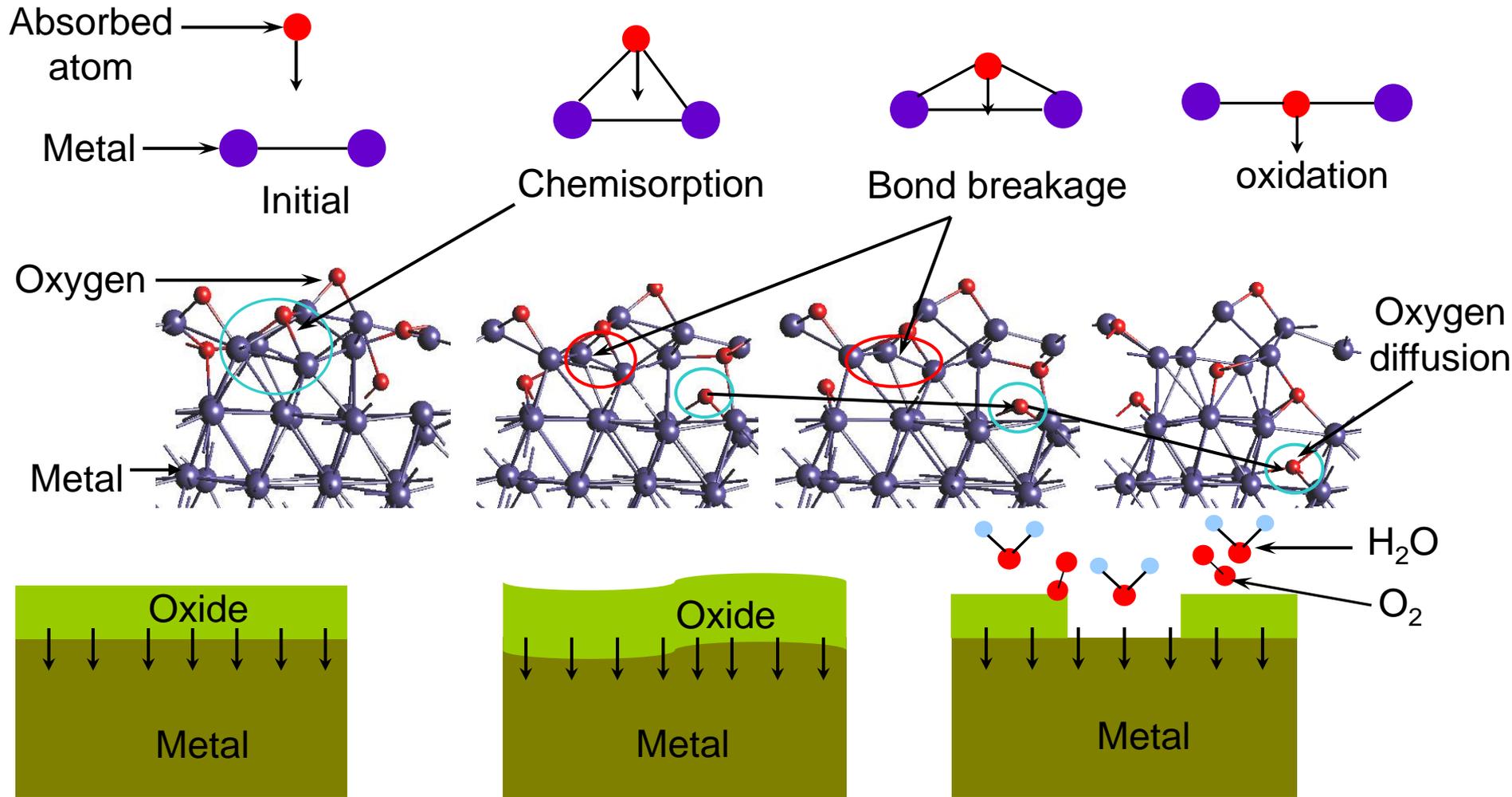
Quantum chemical molecular dynamics and DFT methods are powerful tool to elucidate the oxidation initiation mechanism at atomic scale.

**Fig. 2 LOCALITY and CAUSALITY as a function of length and time scales**

# Simulation, Modeling and Prediction

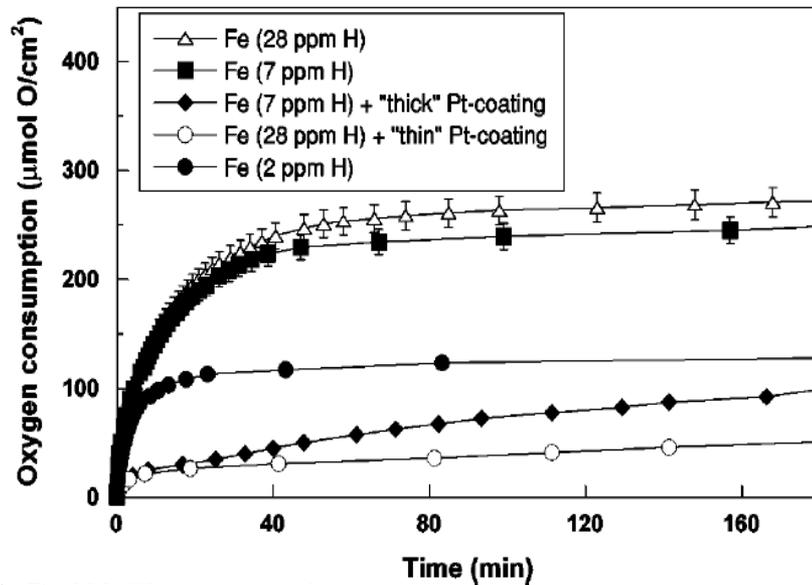
- ▶ **Atomic scale oxidation simulation analysis**
- ▶ **Atomic scale oxidation localization and acceleration**
- ▶ **Role of Hydrogen in metals and oxides, and their interface**
- ▶ **Implication for protection**

# A correlation between oxidation and SCC initiation

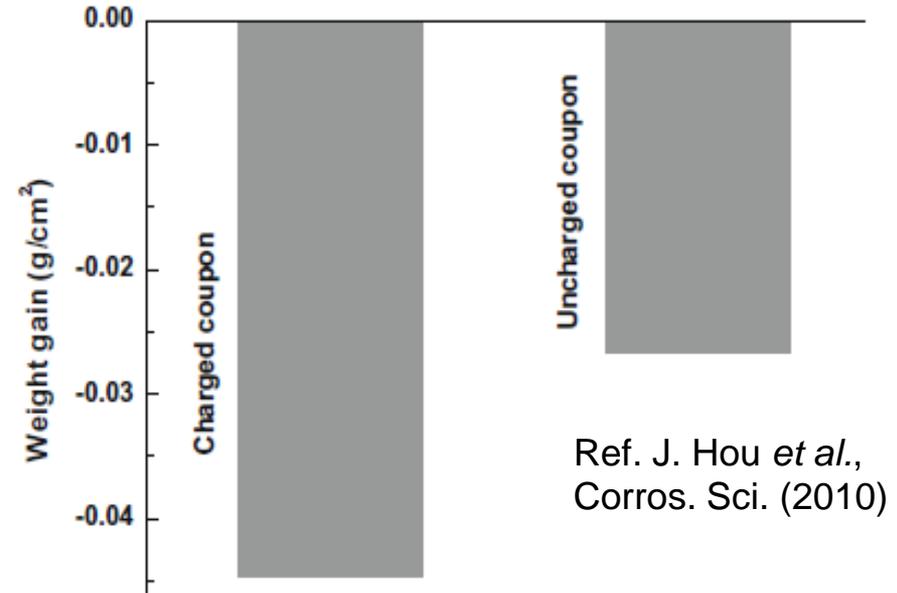


The interaction between alloy and solution is important for oxidation process

# Hydrogen effects on oxidation process



Ref. D. Wallinder *et al.*,  
J. Electrochem. Soc.



The oxidation rate of Fe increases in O<sub>2</sub> (at 500 and 700 °C) with the H charging specimen at different conditions.

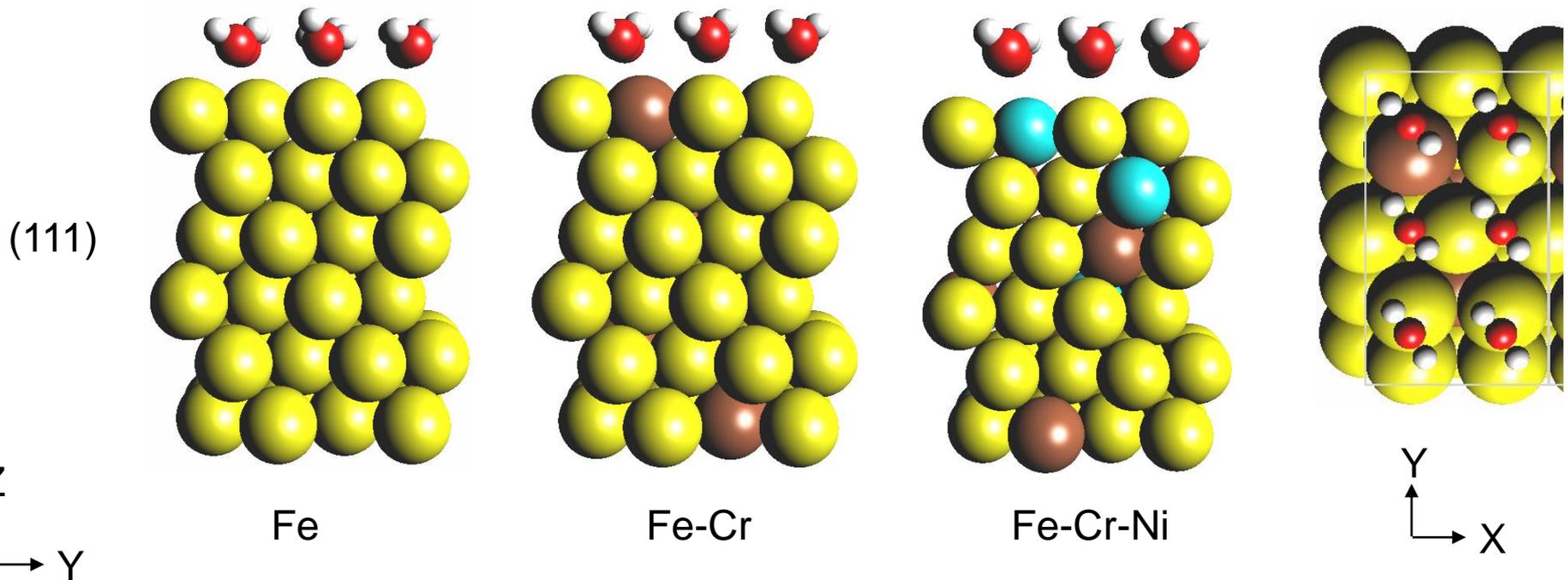
A TEM study has reported that the hydrogen charged coupons formed a thicker oxide film than uncharged coupons

## What is the potential mechanism?

Computational approach might answer this fundamental question because it can deal with atomic scale phenomenon

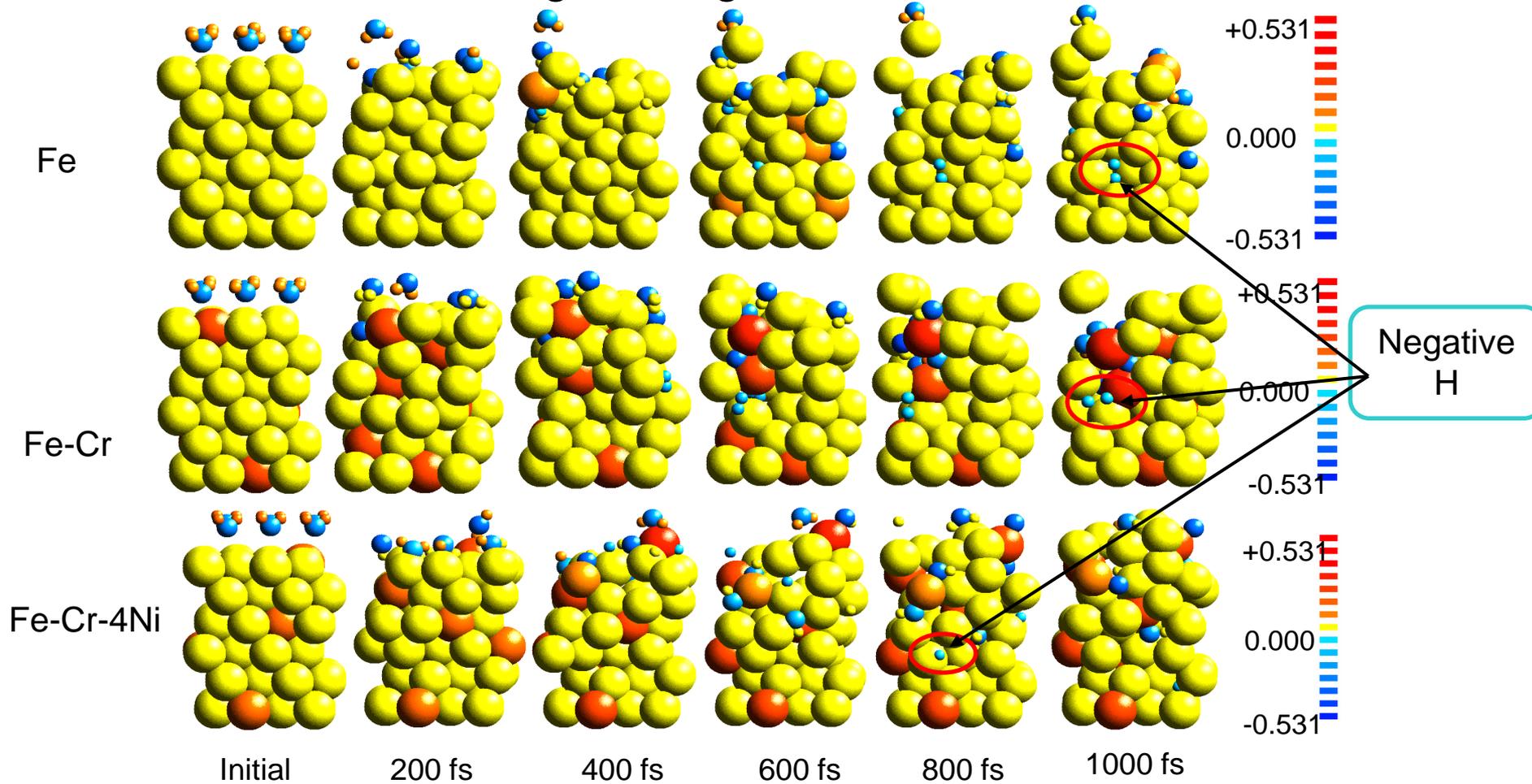
# QCMD model for studying oxidation mechanism

The Fe, Fe-Cr and Fe-Cr-Ni (111) surface of face-centered cubic structure is used as slab model. The Fe, Fe-Cr and Fe-Cr-Ni/H<sub>2</sub>O interface is modeled by the placement of monolayer six molecules of H<sub>2</sub>O on the (111) surfaces. Temp. is 288 °C.



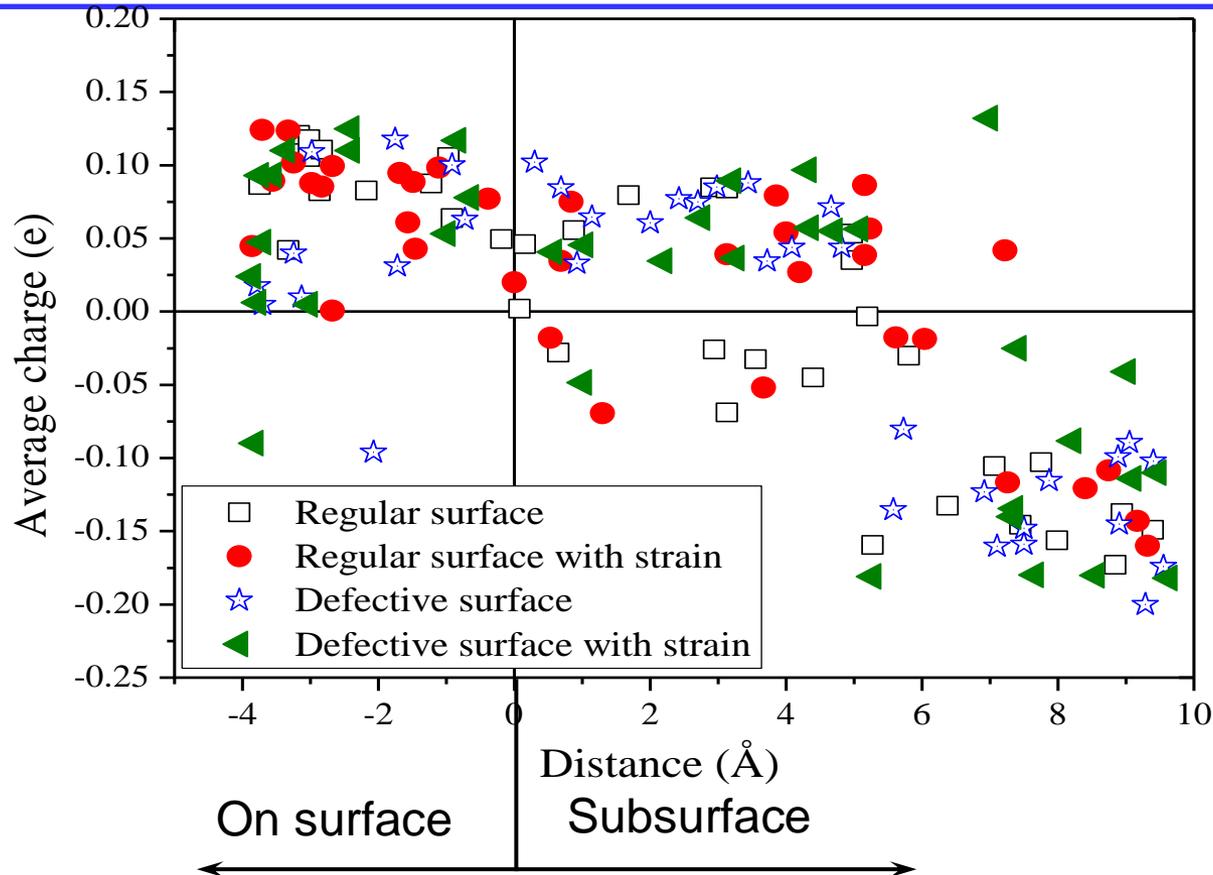
# Atomic charge change with diffusion

Atomic charge change indicates the oxidation



Early dissociated diffused H atoms are negative in charge in the matrix

# Hydrogen atomic av. charge for Fe-Cr-Ni surfaces



Deeply diffused hydrogen atom receives electron from metallic atom leads to weaken the bond strength in order to generate coulombic repulsion consequently the process initiates surface oxidation.

Ref. Das et al., Corro. Sci. 51 (2009),908

# DFT study of Adsorption properties

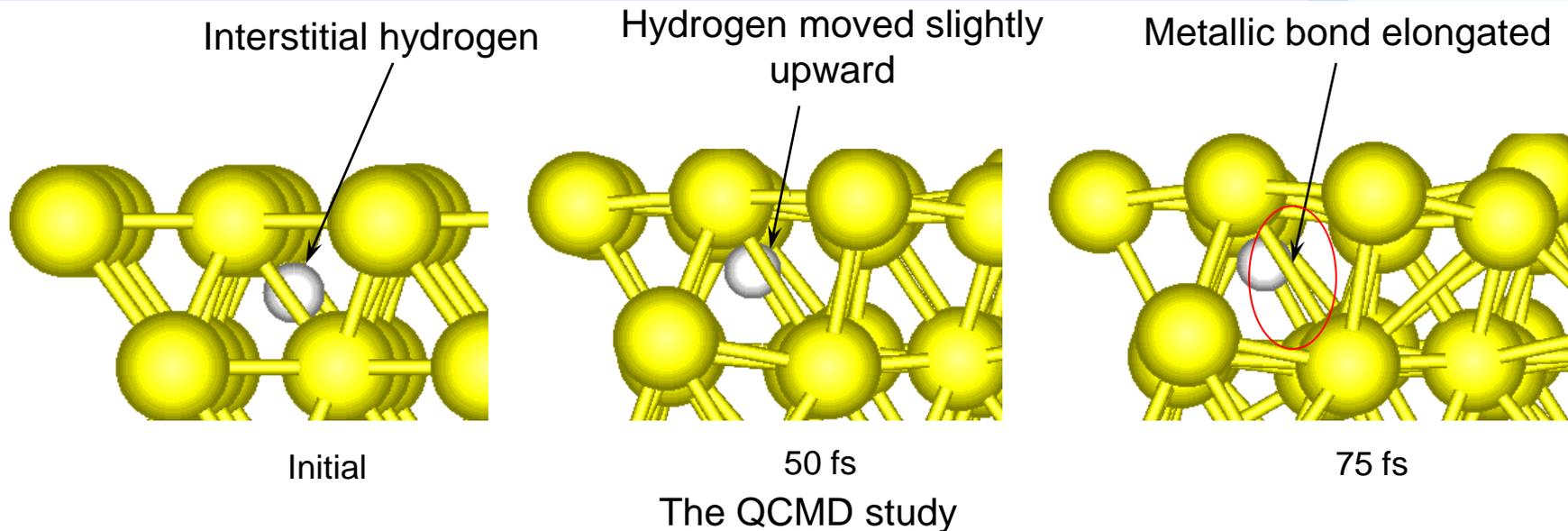
## Adsorption energies

Surfaces	O	OH	H <sub>2</sub> O
Ni (111)	5.48	3.38	0.28
Ni (111) with H	<b>5.25</b>	<b>3.25</b>	0.29
Ni-Cr (111)	6.31	3.76	0.67
Ni-Cr (111) with H	<b>6.20</b>	<b>3.70</b>	0.68

Adsorption energies of O and OH on Ni (111) and Ni-Cr (111) surfaces are decreased by an interstitial H suggesting that the metal-adsorbent bond weakening because of interstitial hydrogen

$E_{ad}$  of H<sub>2</sub>O has not been changed indicating that hydrogen has no effect on molecular adsorption process.

# Localized H effect in alloy surfaces

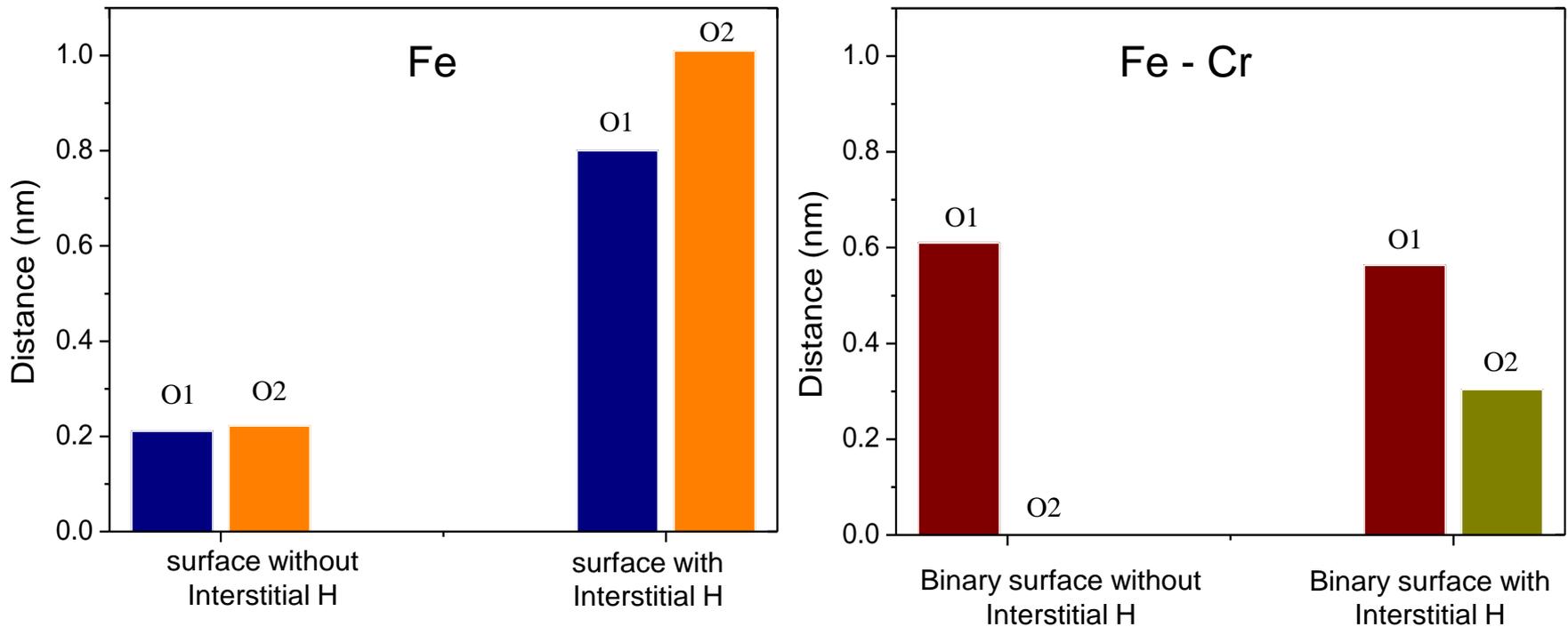


DFT study demonstrates that the top layer metal atomic bonds are further extended about 1 ~ 2% due to oxygen, OH and H<sub>2</sub>O adsorption while interstitial hydrogen atom exists. It reveals that the trapped hydrogen helps to extend local metal atomic bond.

QCMD study has also shown the metal atomic bond elongation during chemisorption process due to interstitial hydrogen

Several studies observe that the hydrogen expands the crystal lattice of host metals. – [Ref. Peisl, Hydrogen in Metals I.]

# Role of H on O diffusivity



Oxygen diffusivity into different surfaces

Diffusivity of oxygen in surface increases along the z-axis due to interstitial hydrogen. Substitution of **Cr** into the surface **decelerates the oxygen diffusivity** due to form strong bond between them.

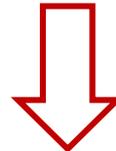
# Hypothesis of hydrogen-accelerated oxidation

Hydrogen is reducing the metal-oxygen adsorption energies

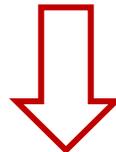


Oxygen mobility is increasing

Hydrogen is taking electron from metal atoms



Increasing the metal atomic bond distance by creating coulombic repulsion between them



Metallic bond elongation creates some extra spaces into the structure

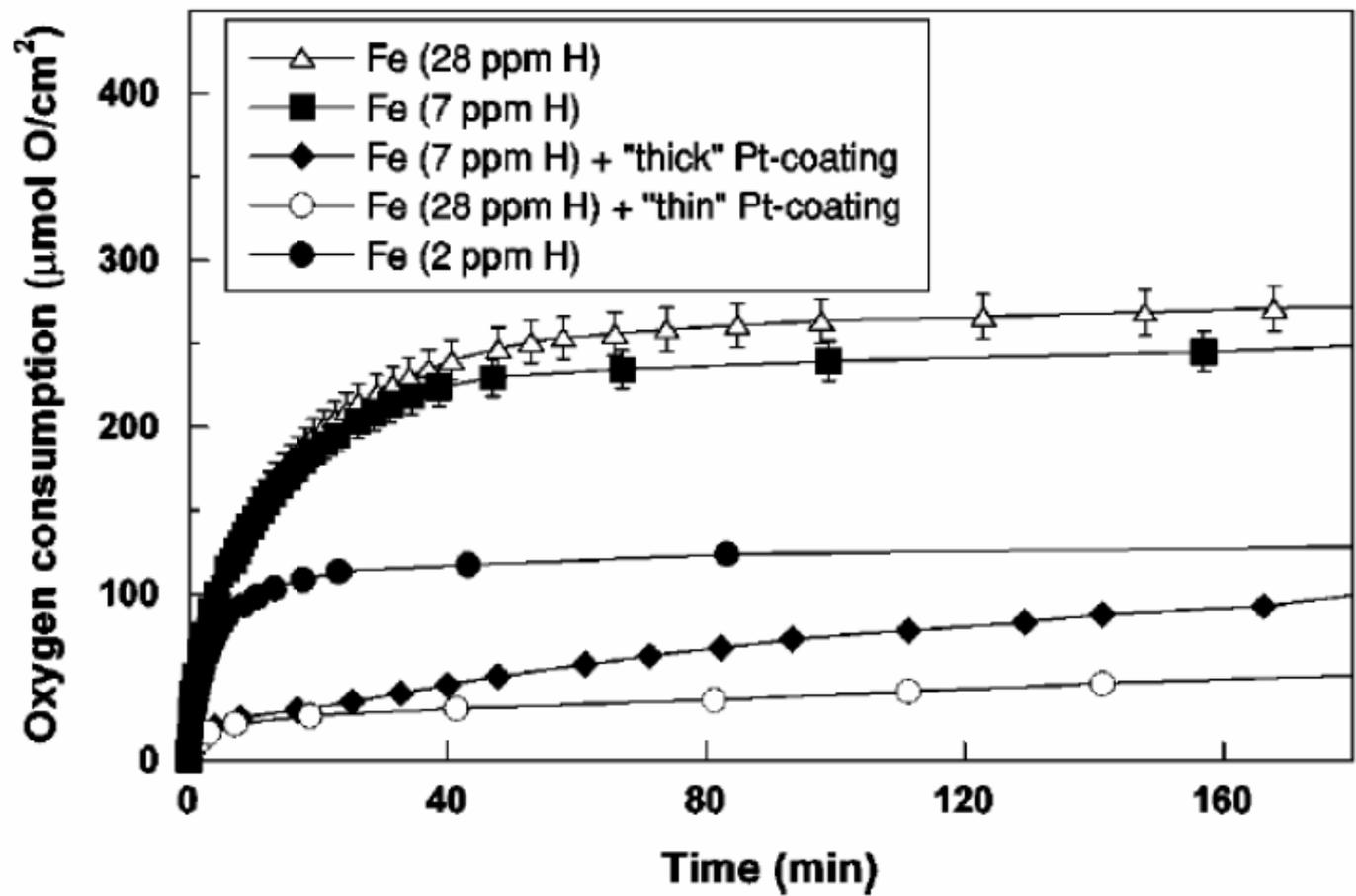


The process might help to accelerates the oxidation process

# Experimental verification of hydrogen accelerated oxidation

- Some experimental evidences support the hydrogen accelerated oxidation
- Larger weight gain was observed in H-charge sample than in non-charged sample
- Thicker oxide formed in H charged samples than in non-charged sample
- Thicker oxide formed when hydrogen permeates to oxidation front during the oxidation tests by use of hydrogen pressurized tube specimens
- Anodic polarization curve shows higher current density in passive state in hydrogen charged specimens

# The oxidation of Fe specimen at 700 °C



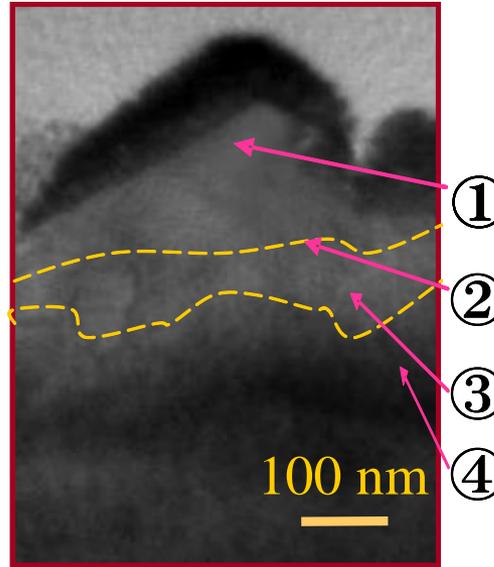
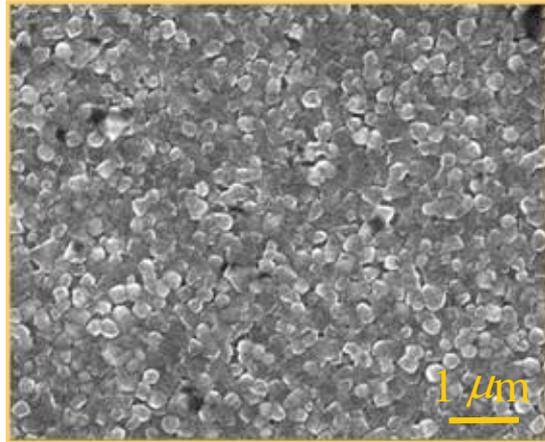
The oxidation rate at 700 °C increased with hydrogen contents specimen.

[D. Wallinder et al., J. Electrochem. Soc.(2002), B393]

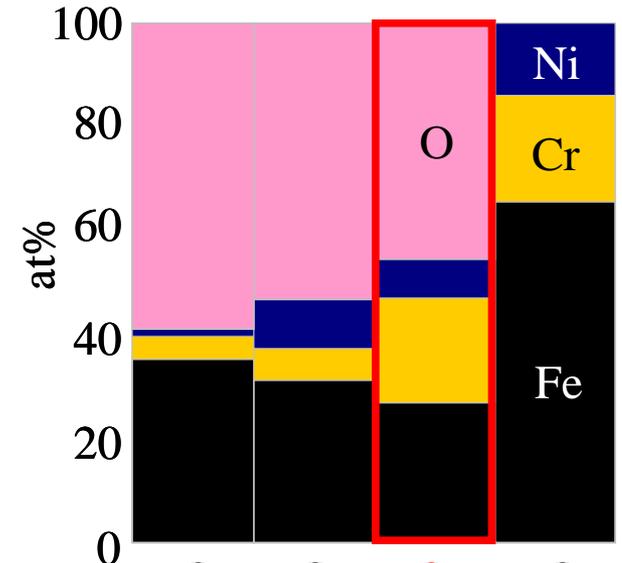
# Hydrogen accelerated oxidation - Experimental evidences

By S. Komazaki,  
Muroran Institute  
of Technology, 2010

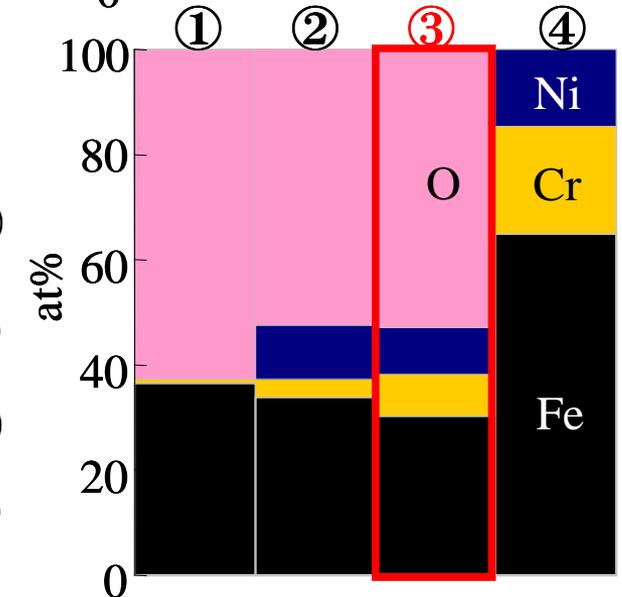
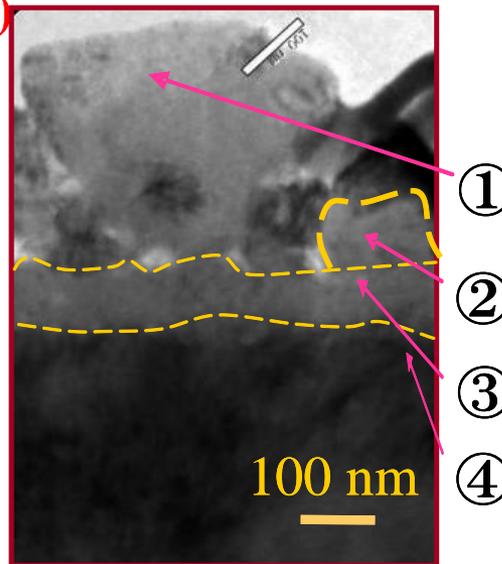
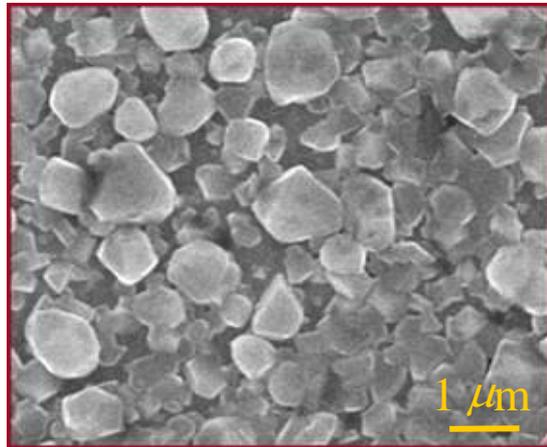
**Non-charged**  
**Exposure time: 887 h**



**evidences**



**H-charged (35 mass ppm)**  
**Exposure time: 887 h**



**Enhanced oxidation on hydrogen charged specimen exposed for 887 hours in simulated BWR environment demonstrating a reduction of Cr content in inner oxide**

# Effect of dissolved hydrogen on oxidation kinetics of Alloy 600, Ni-base alloy

**Objective:** To clarify the mechanism and demonstrate consequences of dissolved hydrogen in metal.

**Material and specimen:** Alloy 600MA coupons of 30mm × 20mm × (0.5-1)mm. Polished using emery papers up to 4000 grit.

**Experiment:** Hydrogen charging:

Condition:  $\text{H}_2\text{SO}_4$  solution of pH=2.5-3.0, 50° C, 1mA/cm<sup>2</sup>.

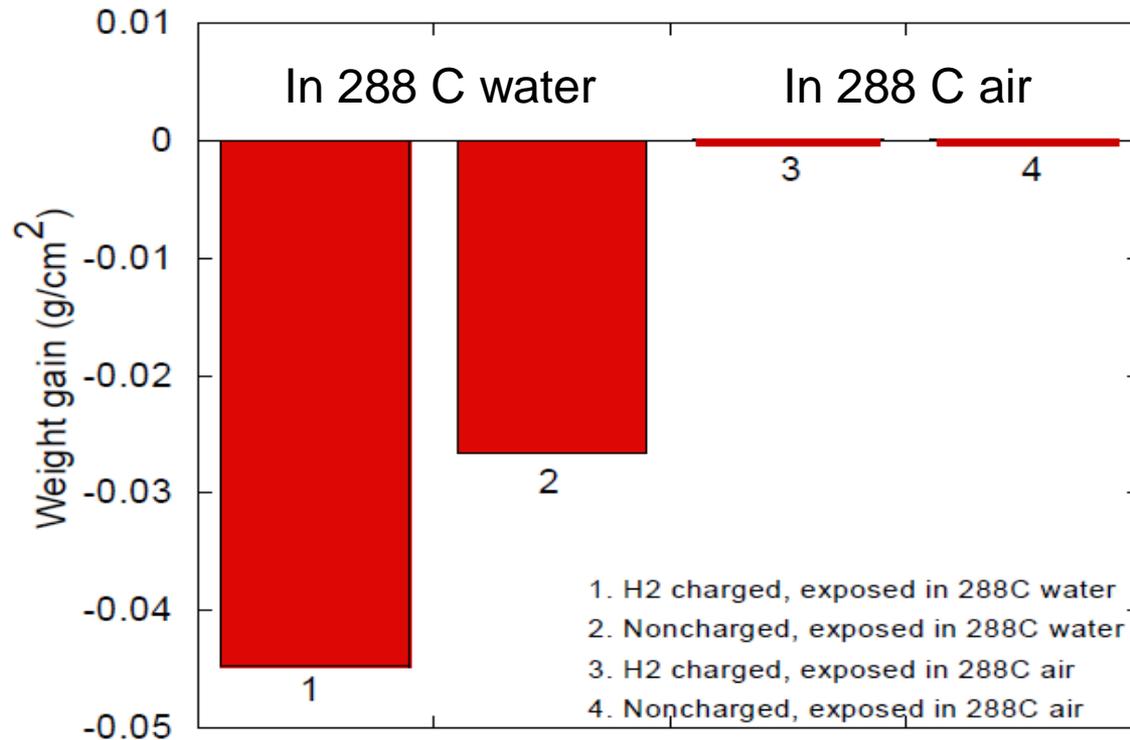
Charging time: ~1678hrs.

Polish again the charged coupons using #4000 emery paper.

**Exposure tests:** 288° C, pure water at DO=8ppm for 100 hours

**Analysis methods:** Weight gain measurement; SEM observation, XPS and TEM analyses.

# Effects of H and water on oxidation

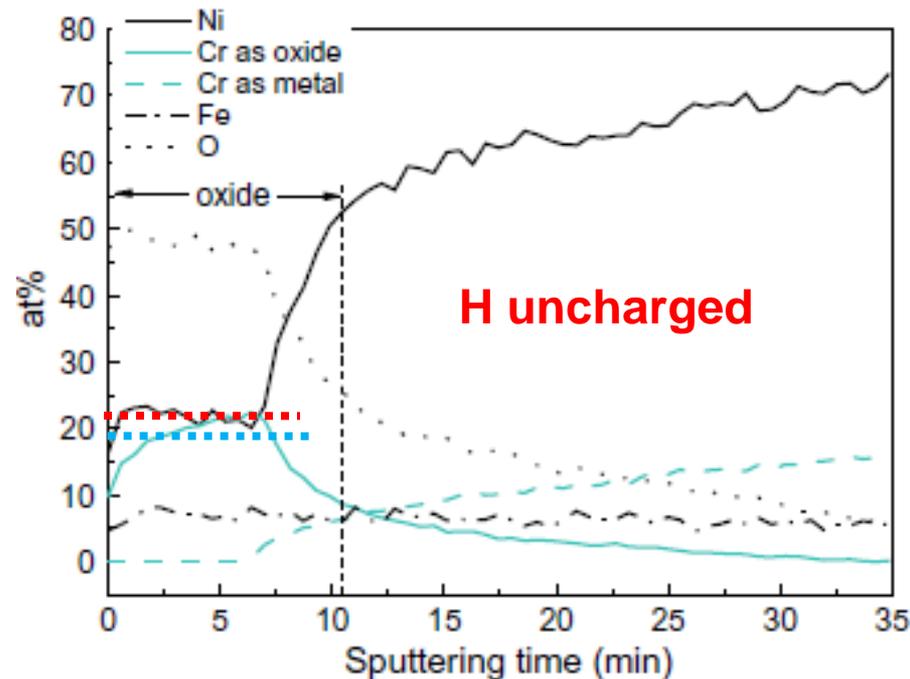
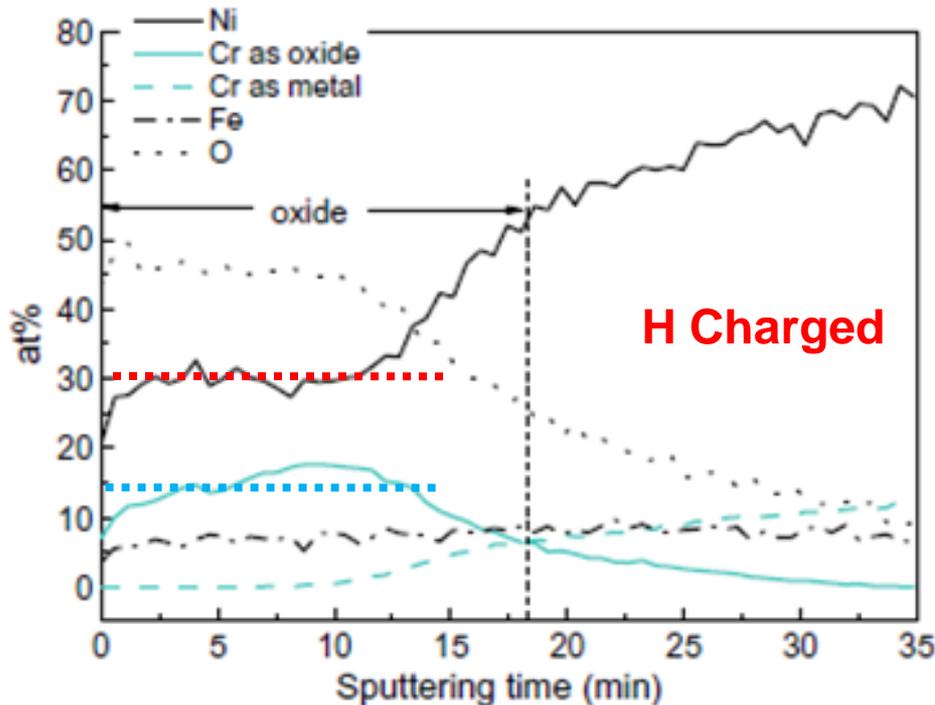


Weight change of the coupons after exposure tests in 288° C water and air.

After exposure in water, weight loss of hydrogen charged coupon is ~1.7 times larger than those of uncharged coupon.

No obvious weight change is observed for both charged and uncharged coupons after exposure in air, suggesting a higher temperature water is needed for this oxidation.

# Elemental distribution by XPS

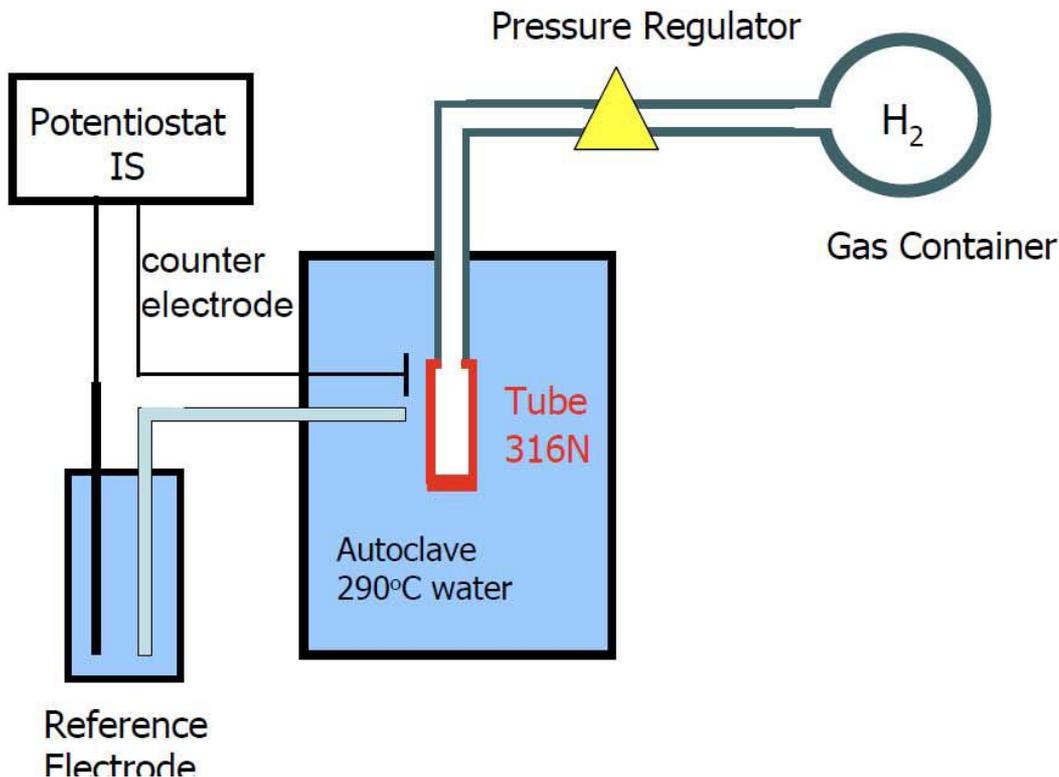


Depth profile analysis of oxide by XPS

The thickness of the oxide film estimated by the half height of oxygen is about **70 nm** on charged coupon and **40 nm** on uncharged coupon.

The oxide film on charged coupon has a **higher Ni** concentration but **lower Cr** concentration throughout the film than the oxide film on uncharged coupon

# Effect of hydrogen on oxidation of 316NG stainless steel



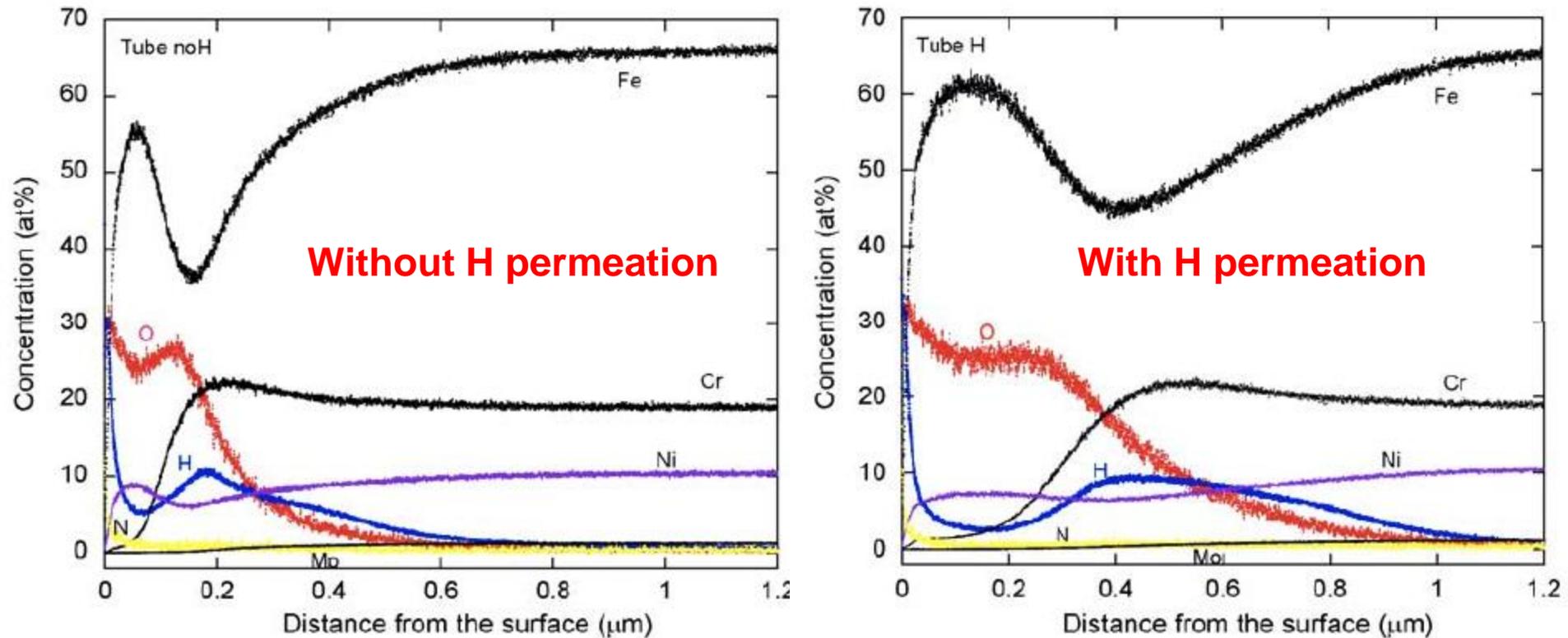
- Testing condition
- Dissolved H in water; 30cc/kg (3.74 atm)

Two tube samples exposed under the same water condition

- Internal H: 4.2 atm
- Vacuum: <-1 atm

Corrosion Condition: 290 °C water with dissolved hydrogen (DH) of 30cc/kg H<sub>2</sub>O and tube specimens with & without internally pressurized hydrogen. Oxidation and hydrogen distribution analyzed by GD-OES

# Oxide film analysis by GD-OES



The GD-OES analysis has shown the deeper oxidation behavior under the internally pressurized hydrogen associated with more extensively hydrogenated zone.

# Summary-1

- Demonstrate the importance of LOCALITY and CAUSALITY in corrosion for better understanding of fundamental processes of CAUSALITY.
- Adsorption energies of O and OH on Ni and Cr-doped Ni surfaces are decreased by interstitial.
- H remains closer to Ni which indicates the preferential bond formation.
- Interstitial H increases the metal atomic bonds about 1~2% when O, OH and H<sub>2</sub>O adsorb on Ni and Cr-doped Ni surfaces.
- H 1s orbital make bond with Ni 3d and 4s orbitals while Ni 3p orbitals are contributing very small.
- Interstitial H accelerates oxygen diffusivity in metal surface.
- Diffused negatively charged H weakens metallic bond by taking electrons.

# Summary-2

- QCMD study applied to understand the fundamental mechanism of the early stage of oxidation where we found that the deeply diffused hydrogen is accelerating the oxidation process.
- Experimental study suggested that comparatively thick oxide film formed on the hydrogen charged coupon specimen suggesting H played some role in it.
- GD-OES results confirmed the hydrogen accumulation at oxide/metal interface and can enhance atom diffusivity such as SAV model.
- Need further study to bridge the approaches by the continuum and by the atomic scale with a special emphasis on the role of HYDROGEN.

# Acknowledgements

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