

International Institute for Carbon-Neutral Energy Research



Fretting Fatigue in Hydrogen and the Effect of Impurity Addition to Hydrogen on Fretting Fatigue Properties

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Introduction

- Current status of hydrogen in Japan
- Fretting fatigue
- Objectives

Experimental procedure

- Test method
- Material
- Environment

Results of fretting fatigue test and discussion

- *S-N* curves
- Mechanisms that the FF strength in H₂ is reduced
- Effect of oxygen addition to H₂
- Mechanism

Summary

Acknowledgement

1. Introduction

- 2014, commercialization of **FCV**
- Construction of **hydrogen stations** is in progress.

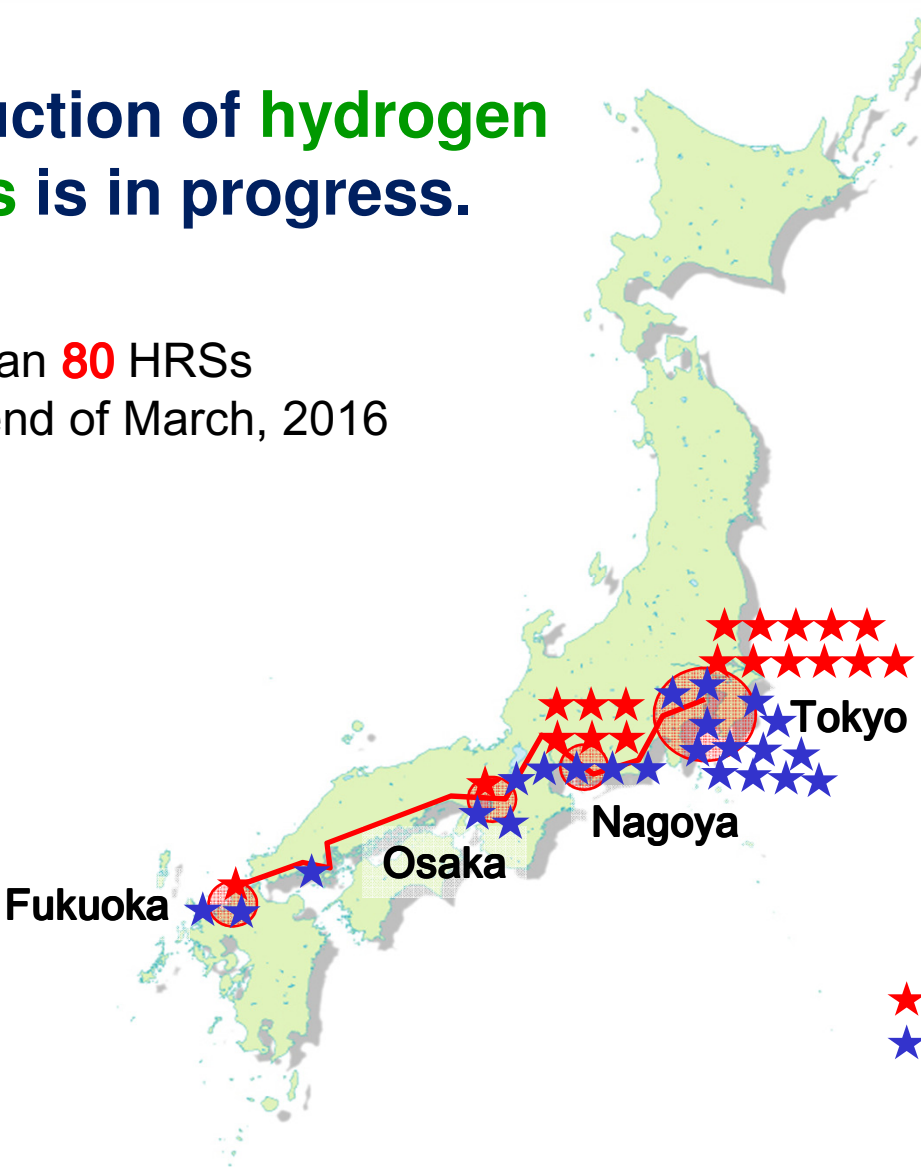


Toyota FCV "MIRAI"
Toyota HP



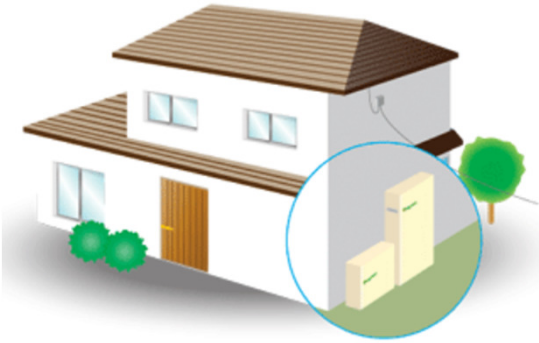
Honda FCV "CLARITY"
autoblog.com HP

More than **80** HRSs
by the end of March, 2016

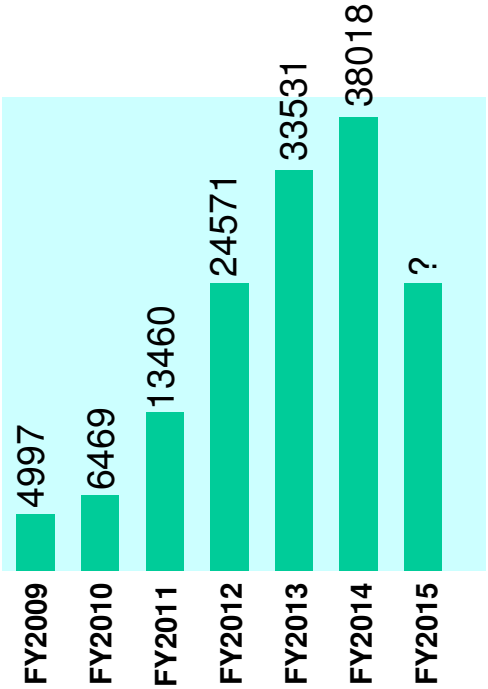
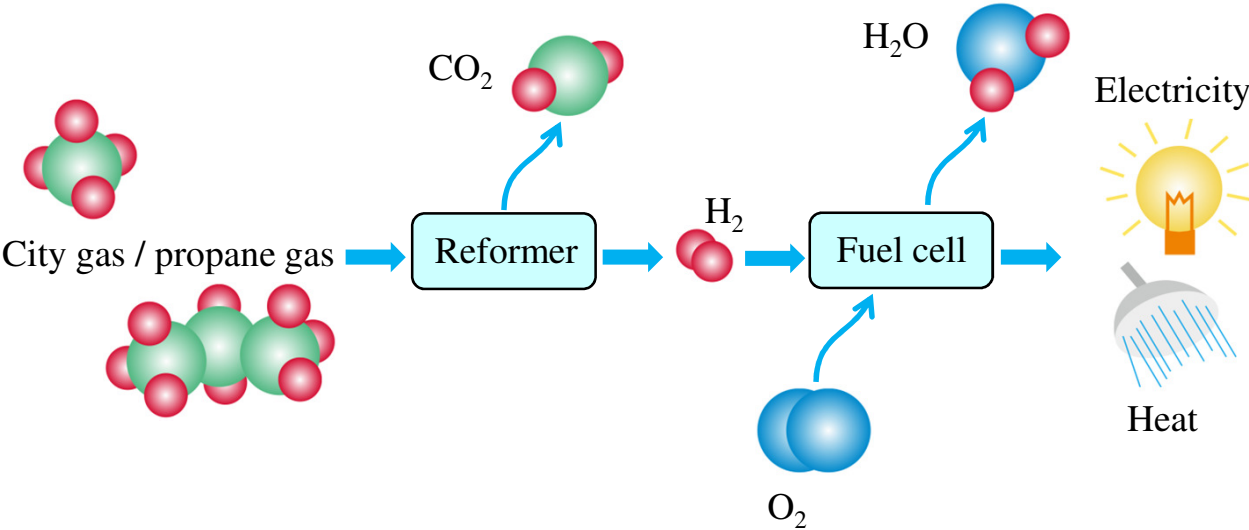


★ 2014
★ 2015

Home fuel cell system



Sales of home FC
More than **130,000**

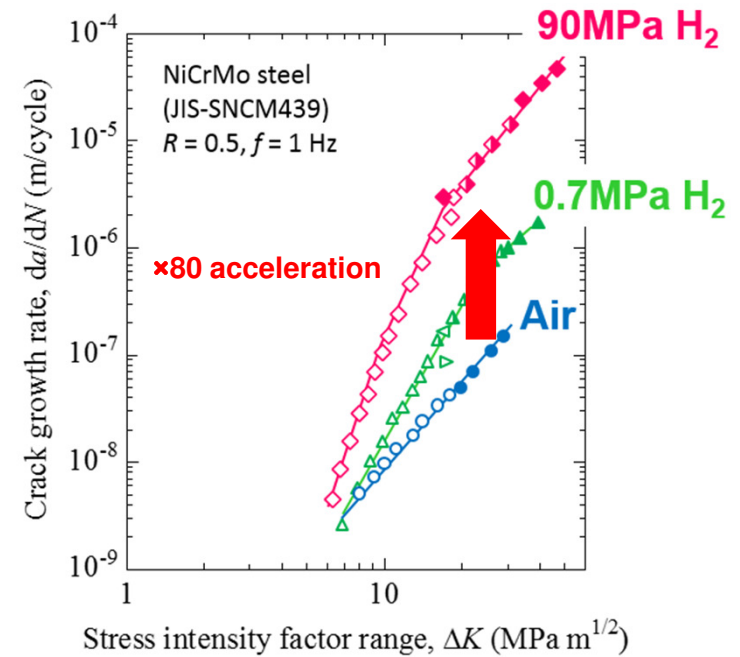


FCV !!



75MPa

Hydrogen deteriorates materials strength.

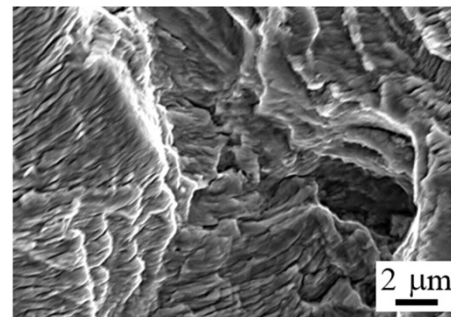


Regular gas cylinder
 15MPa

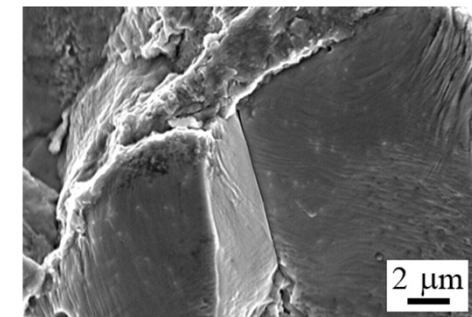


S10C
 $\sigma_a = 206 \text{ MPa}$

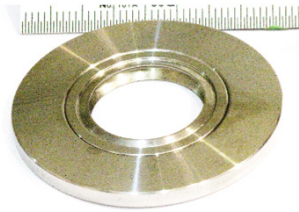
In air ($N_f = 2.06 \times 10^6$)



In H₂ ($N_f = 2.94 \times 10^5$)

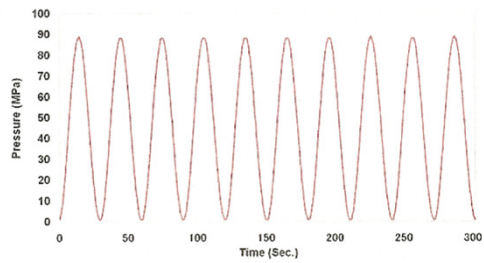


Fretting in 100MPa hydrogen packing

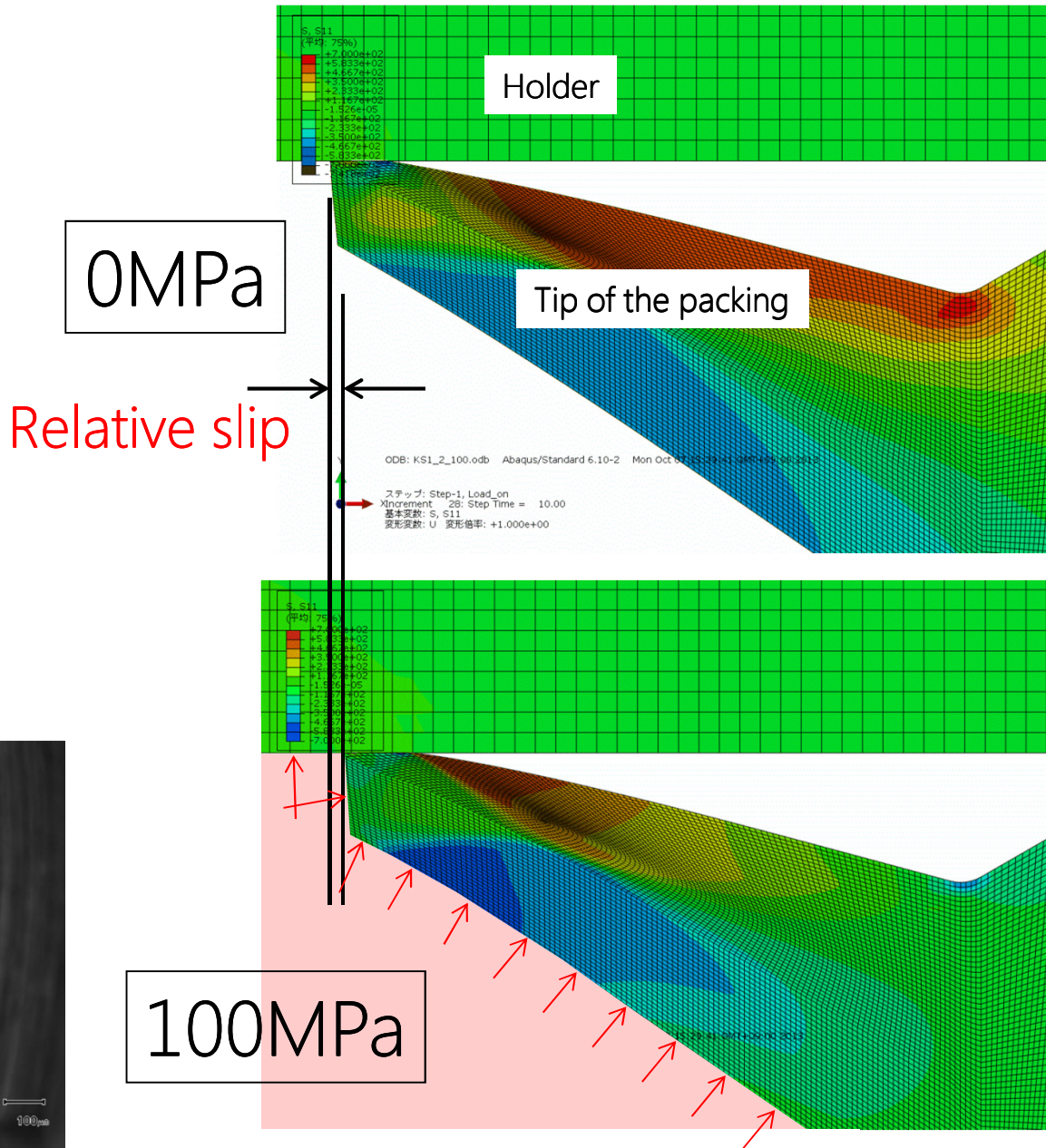


TOKI Engineering Hydroblocker®

H₂ gas pressure cycling test

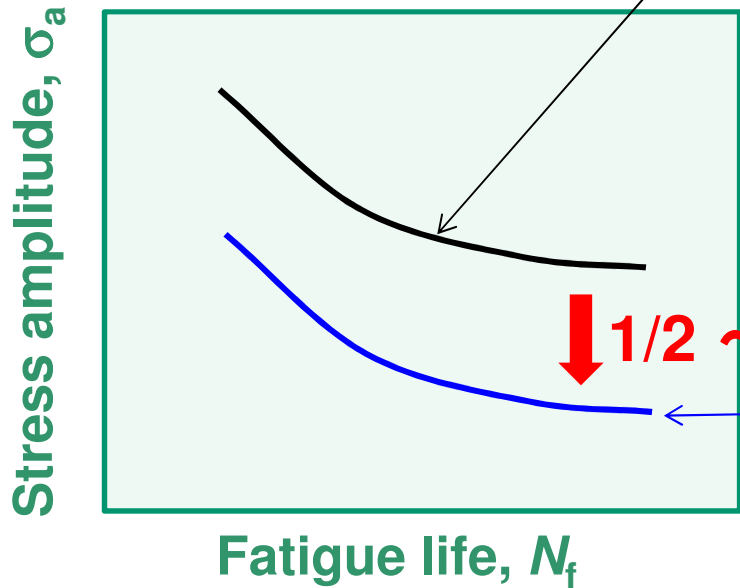


Fretting wear

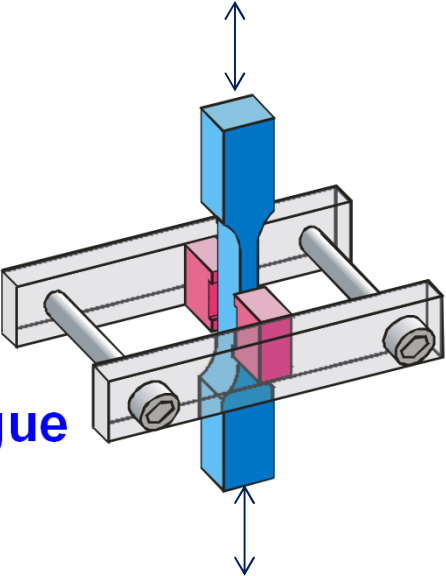
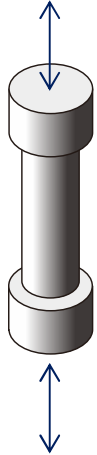


Reduction in fatigue strength due to fretting

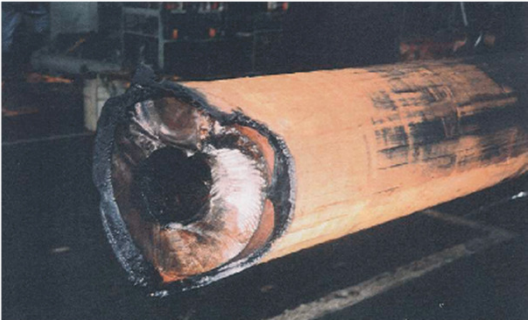
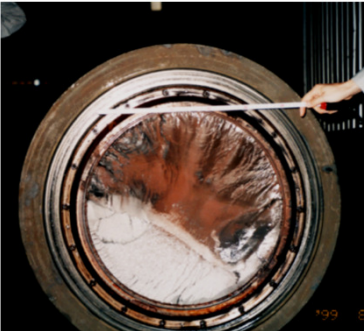
S-N diagram



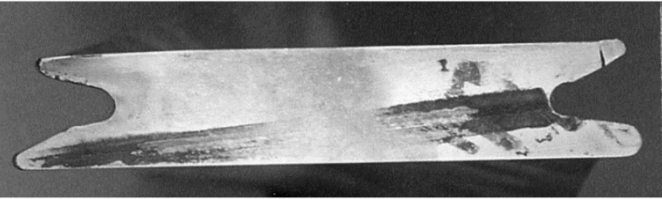
Smooth specimen



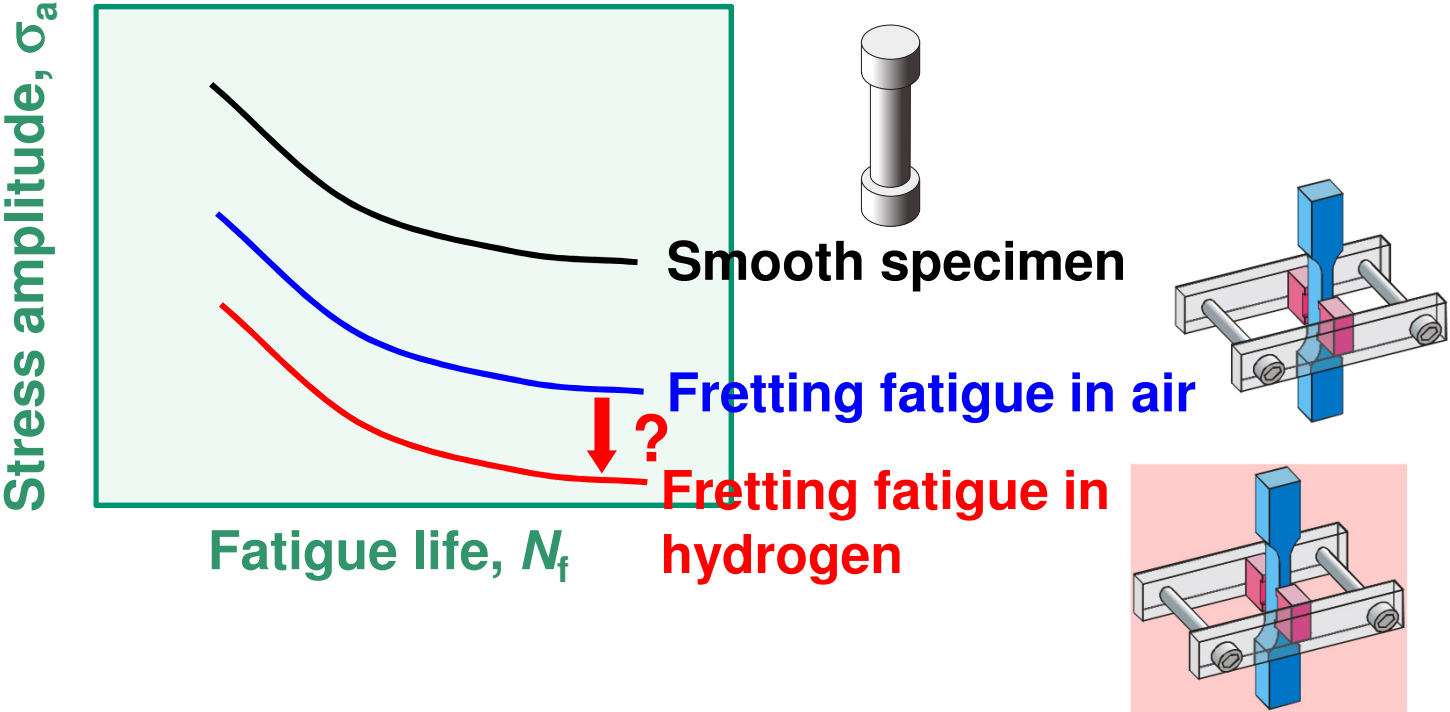
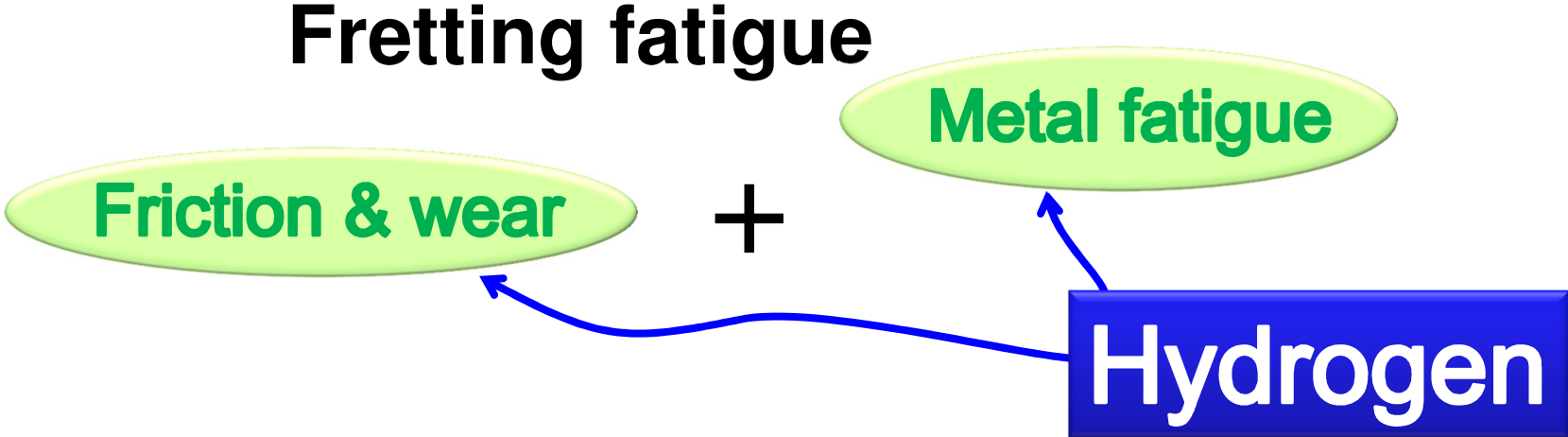
Fretting fatigue



Fretting fatigue
major concerns in the design



Objectives of the research on FF

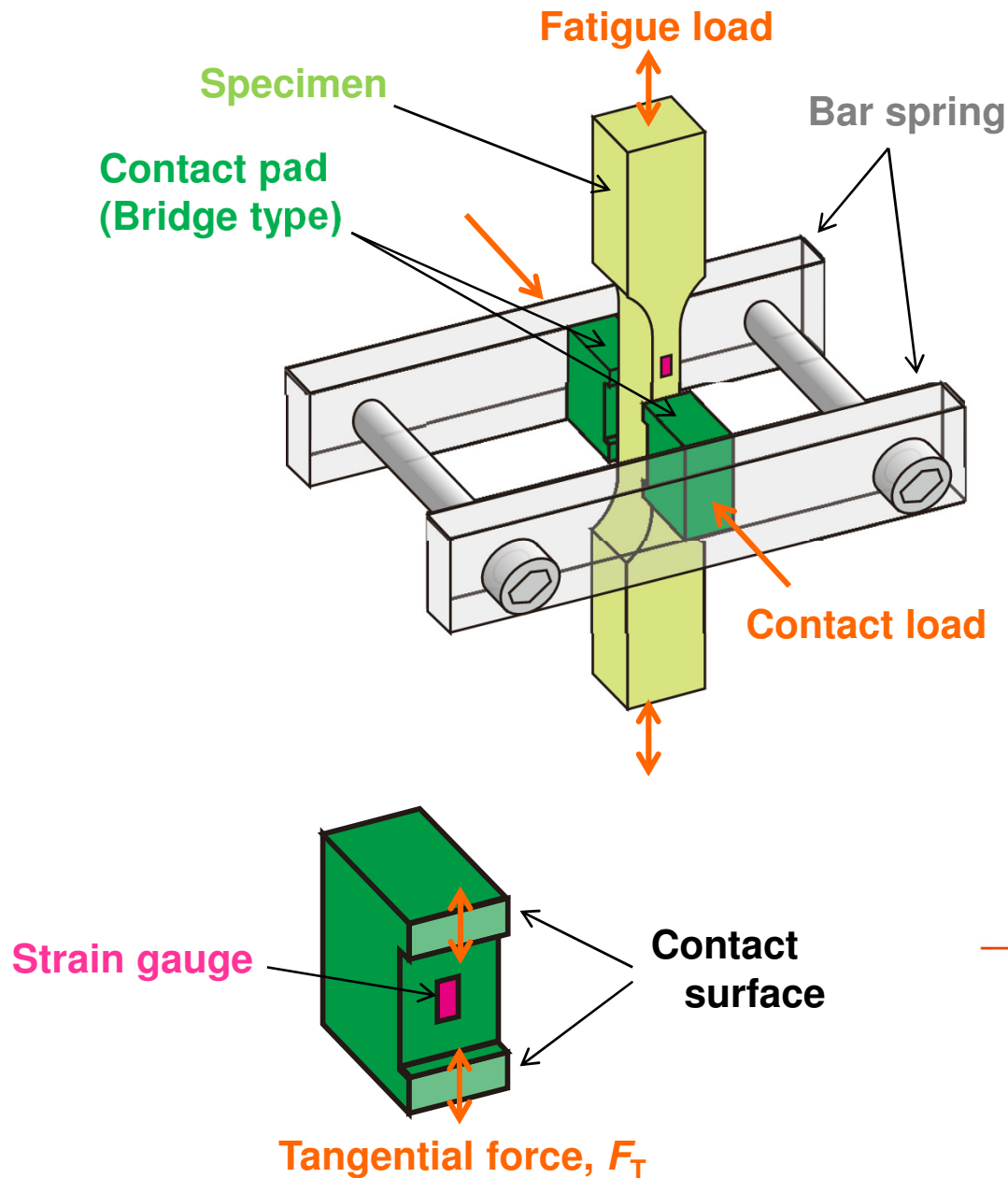


Objectives

- **To characterize the effect of hydrogen on fretting fatigue strength**
- **To elucidate the mechanisms that cause the reduction in the fretting fatigue strength**
- **To clarify the effect of impurities contained in hydrogen.**

2. Experimental procedure

Fretting fatigue test method



Contact pressure:

$$p_c = 100\text{MPa}$$

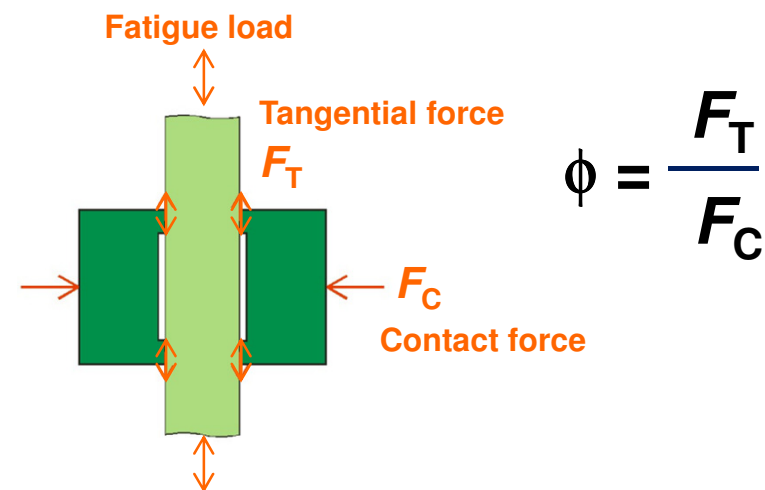
Stress ratio:

$$R = -1$$

Loading frequency:

$$f = 20\text{Hz}$$

Tangential force coefficient



Austenitic stainless steels

Chemical composition (mass %)

Material	C	Si	Mn	P	S	Ni	Cr	Mo	Fe
JIS SUS 304	0.06	0.51	0.92	0.033	0.004	8.08	18.8	-	Bal.
JIS SUS 316	0.05	0.49	1.31	0.030	0.027	10.22	17.0	2.04	Bal.
JIS SUS 316L	0.012	0.19	1.64	0.031	0.012	12.19	16.6	2.22	Bal.

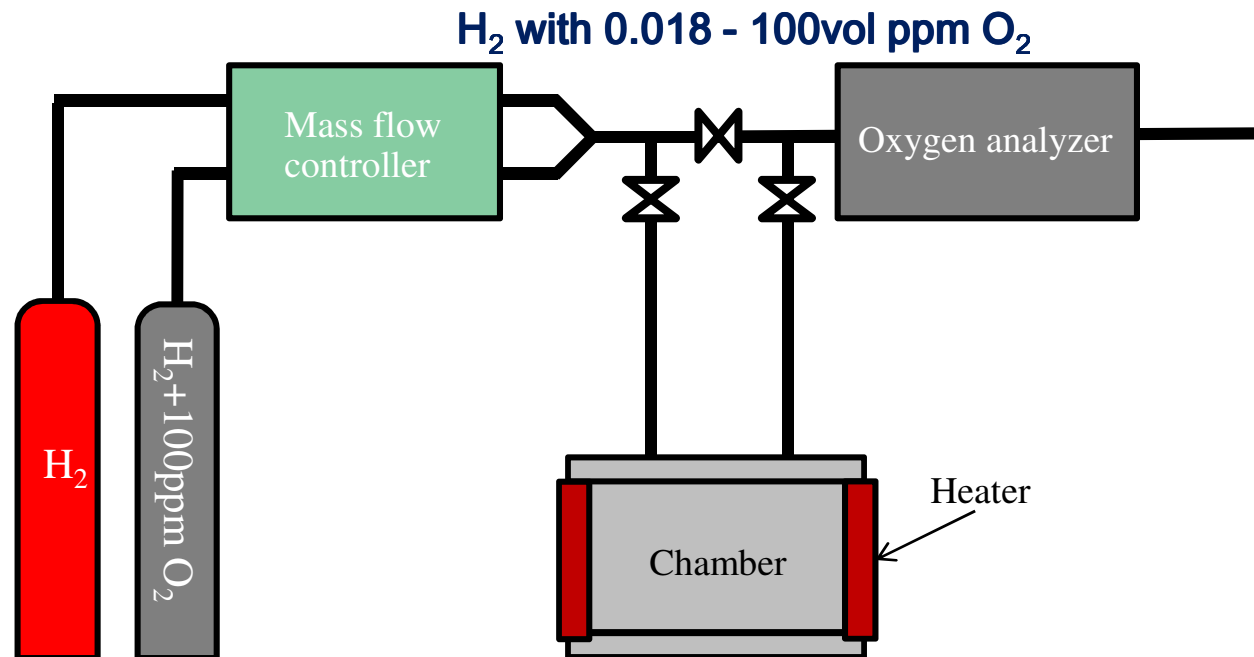
Solution heat treated:

Quenching following heating at 1303K for 3.9ks

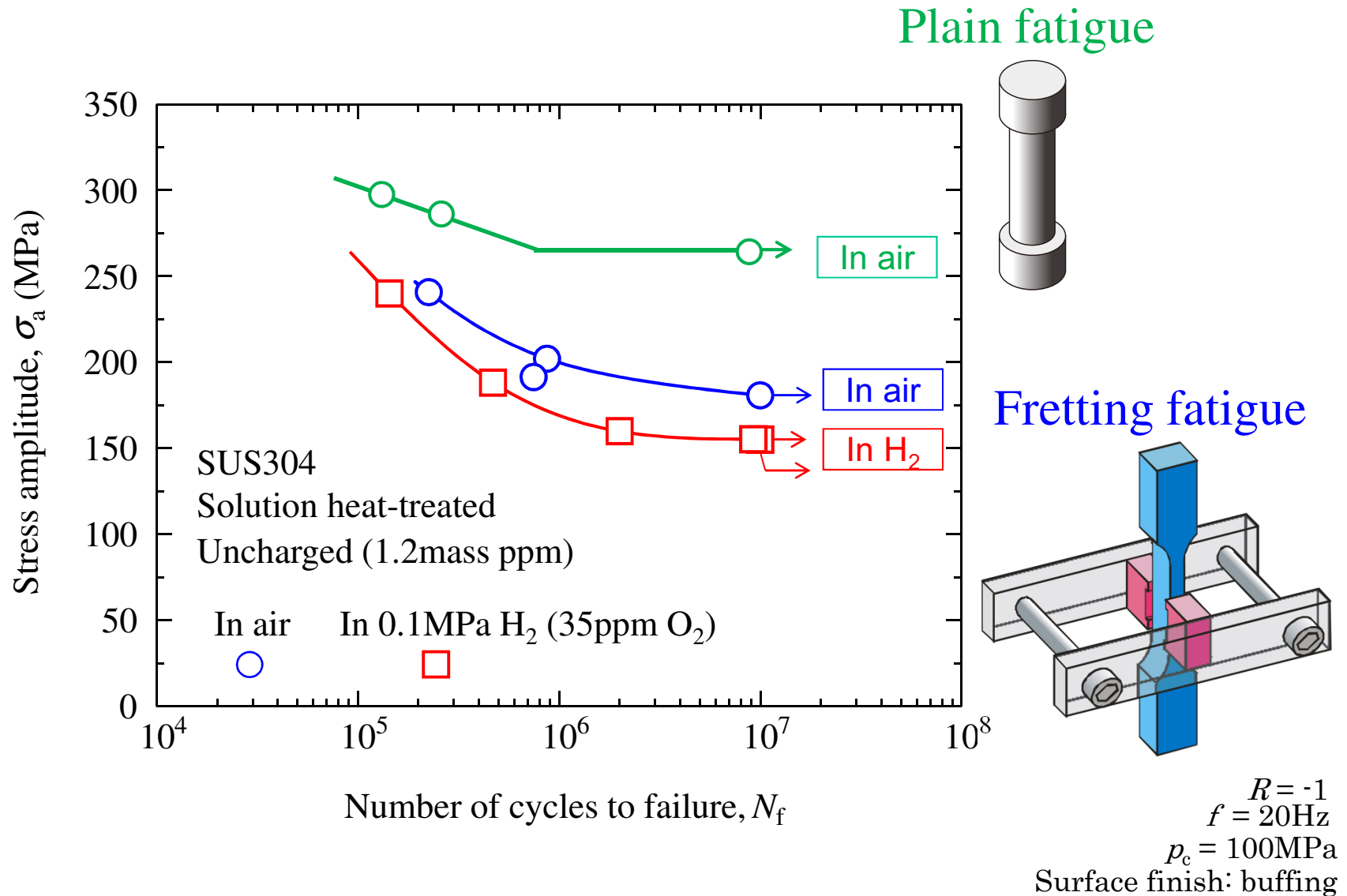
Environment

- **Laboratory air**
- **Hydrogen**
0.018 ppm O₂,
0.1MPa in gauge pressure,
- **Hydrogen – oxygen mixture**
5, 35 and 100 ppm O₂,
0.1MPa in gauge pressure,

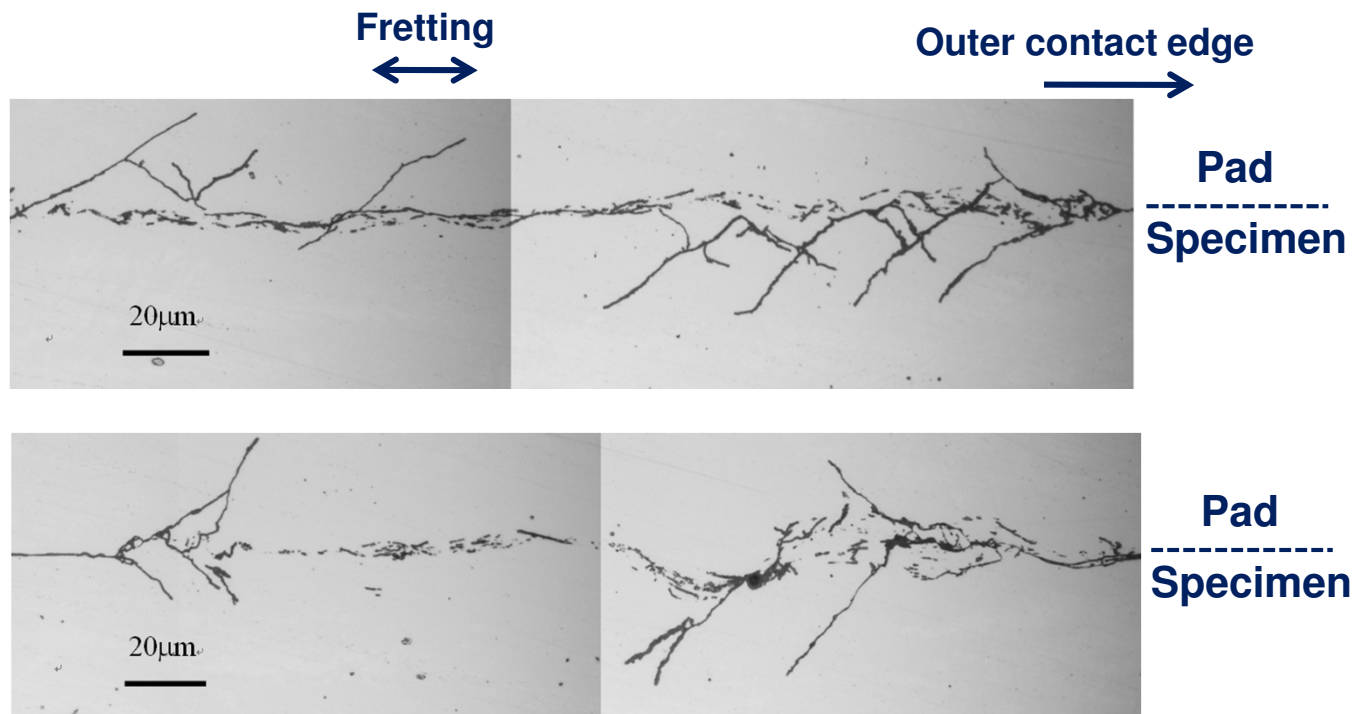
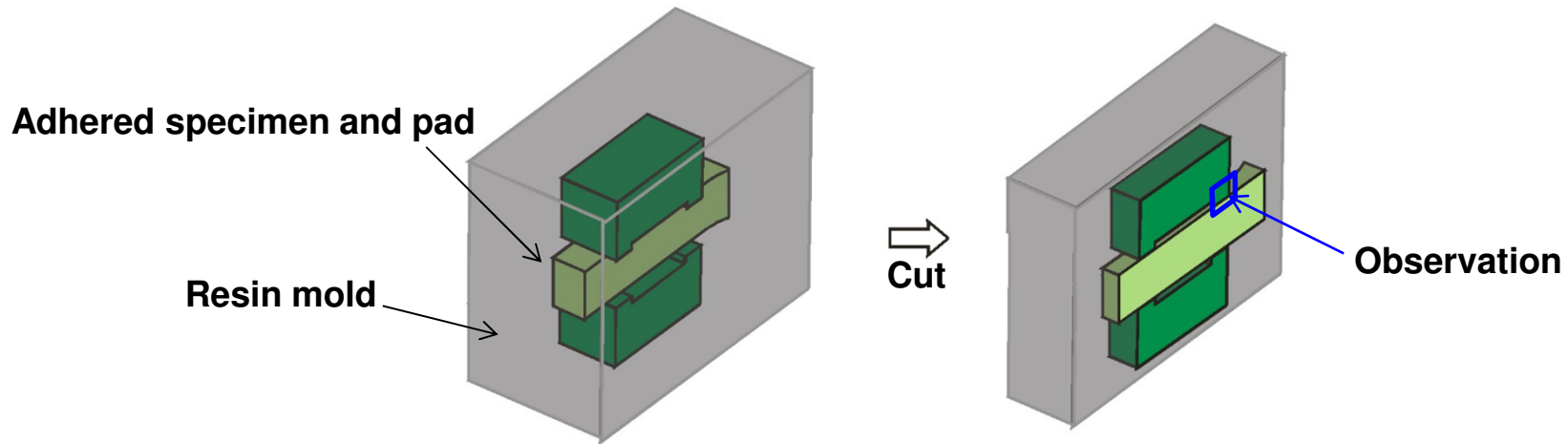
Ambient temperature



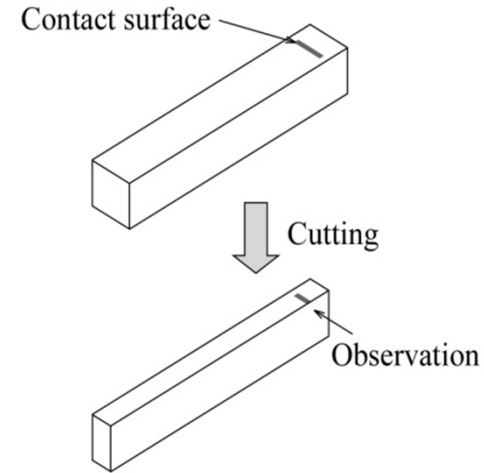
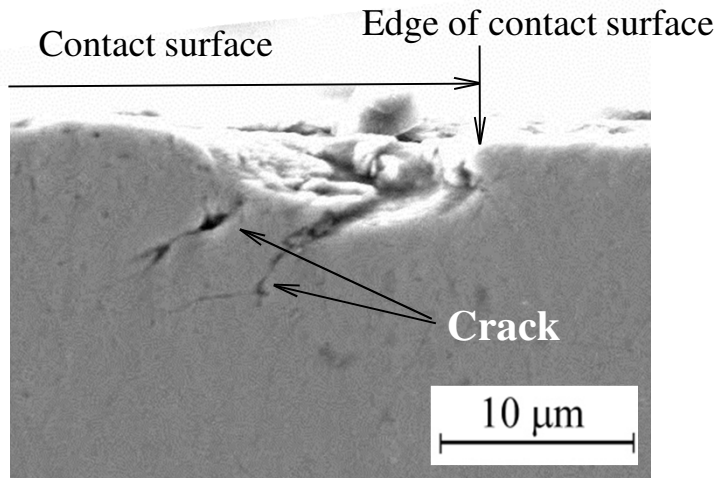
3. Result and discussion



Local adhesion and small cracks during FF in H₂



Critical stress to crack initiation



Result of identification of small fretting crack initiation (At $N = 10^5$ cycles)

In air

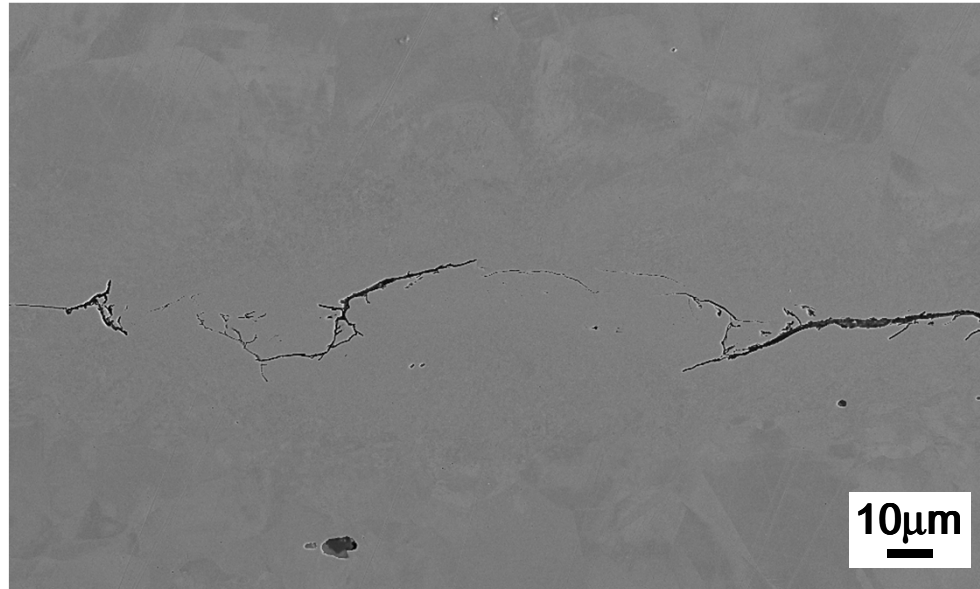
SUS304		Contact pressure, p_c (MPa)		
		25	50	100
Tangential force coefficient, ϕ	0.3	No	No	No
	0.5	No	No	No
	0.7	No	No	No

In H₂

SUS304		Contact pressure, p_c (MPa)		
		25	50	100
Tangential force coefficient, ϕ	0.3	No	No	Crack
	0.5	No	No	Crack
	0.7	Crack	Crack	Crack

Grain refinement during FF in H₂

SUS316L
H-charged,
In H₂,
 $Ra = 0.008\text{mm}$,
 $\sigma_a = 182\text{MPa}$,
 $N_f = 1.0 \times 10^6$



Normal SEM

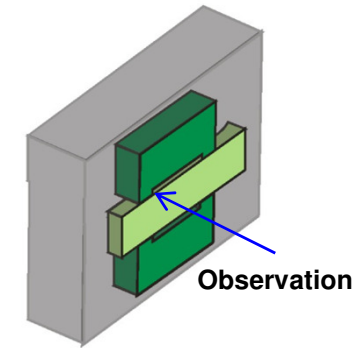
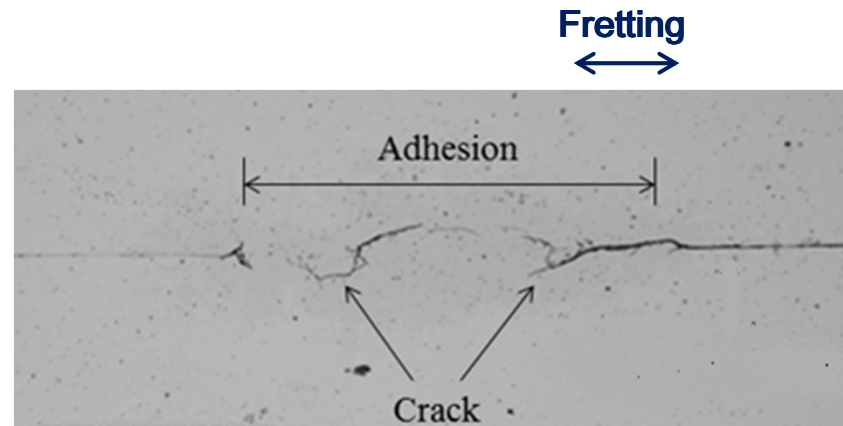


High contrast SEM

Transformation from austenite to strain-induced martensite

EBSD (Electron BackScatter Diffraction image)

SUS316L
 H-charged,
 In H₂,
 $Ra = 0.008\text{mm}$,
 $\sigma_a = 182\text{MPa}$,
 $N_f = 1.0 \times 10^6$

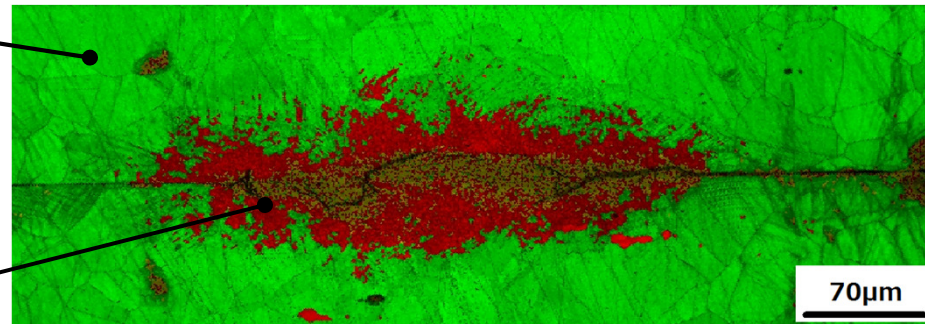


Pad

Specimen

Austenite

Strain-induced
 martensite

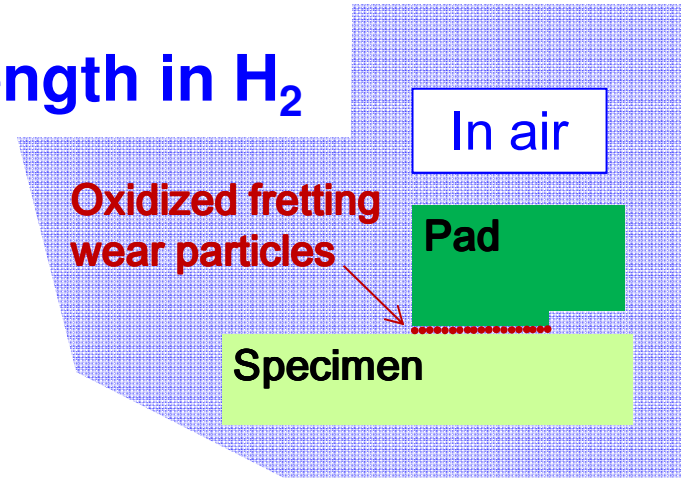


γ -iron

α -iron

Phase map

Role of adhesion in the reduced FF strength in H₂



Adhesion

Localized cyclic plastic strain

Mechanical reason

Crystalline structure change

Crack initiation

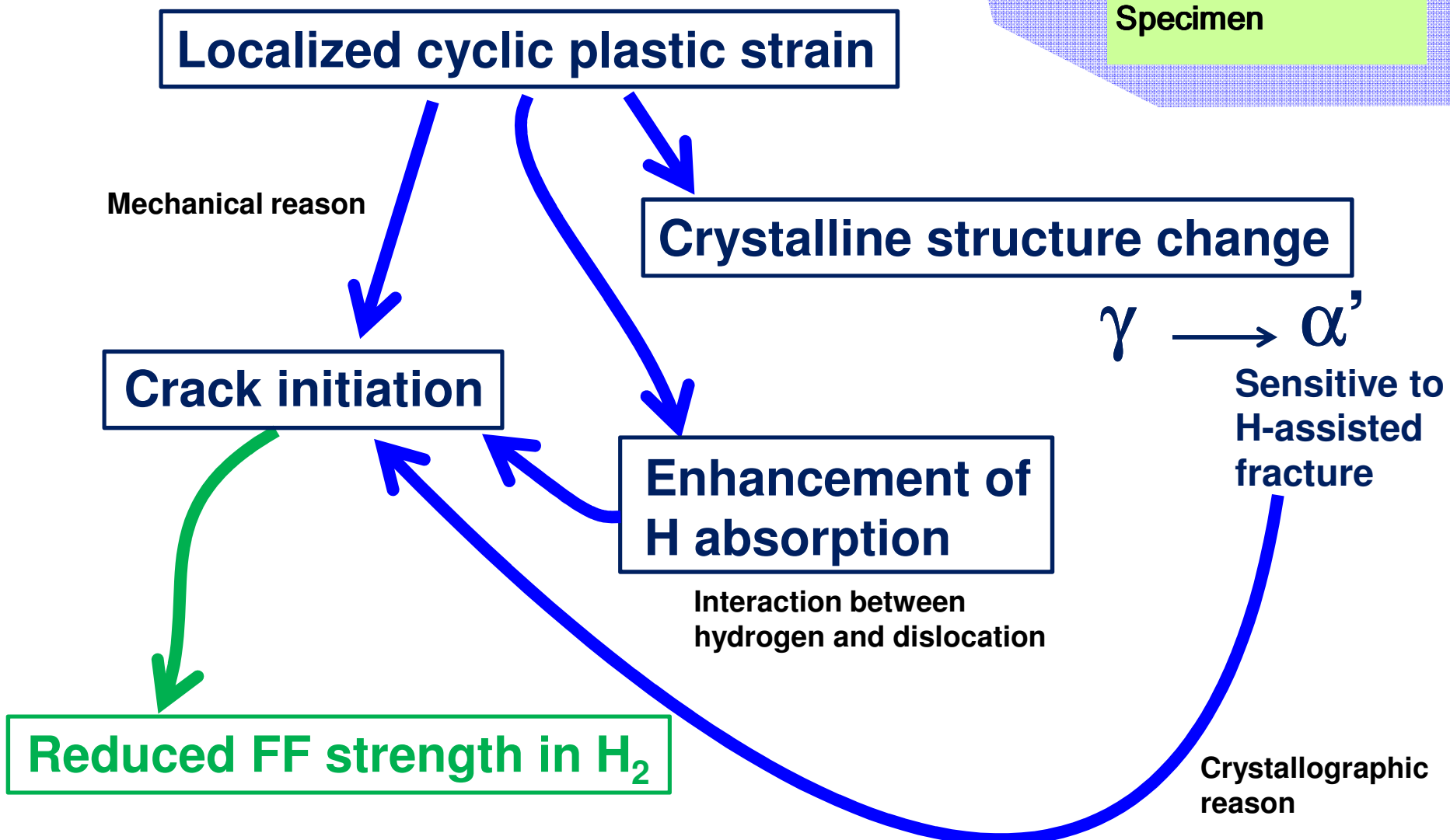
Enhancement of H absorption

Interaction between hydrogen and dislocation

$\gamma \longrightarrow \alpha'$
Sensitive to H-assisted fracture

Reduced FF strength in H₂

Crystallographic reason



Purity of hydrogen for FC

Hydrogen fuel – Product specification -

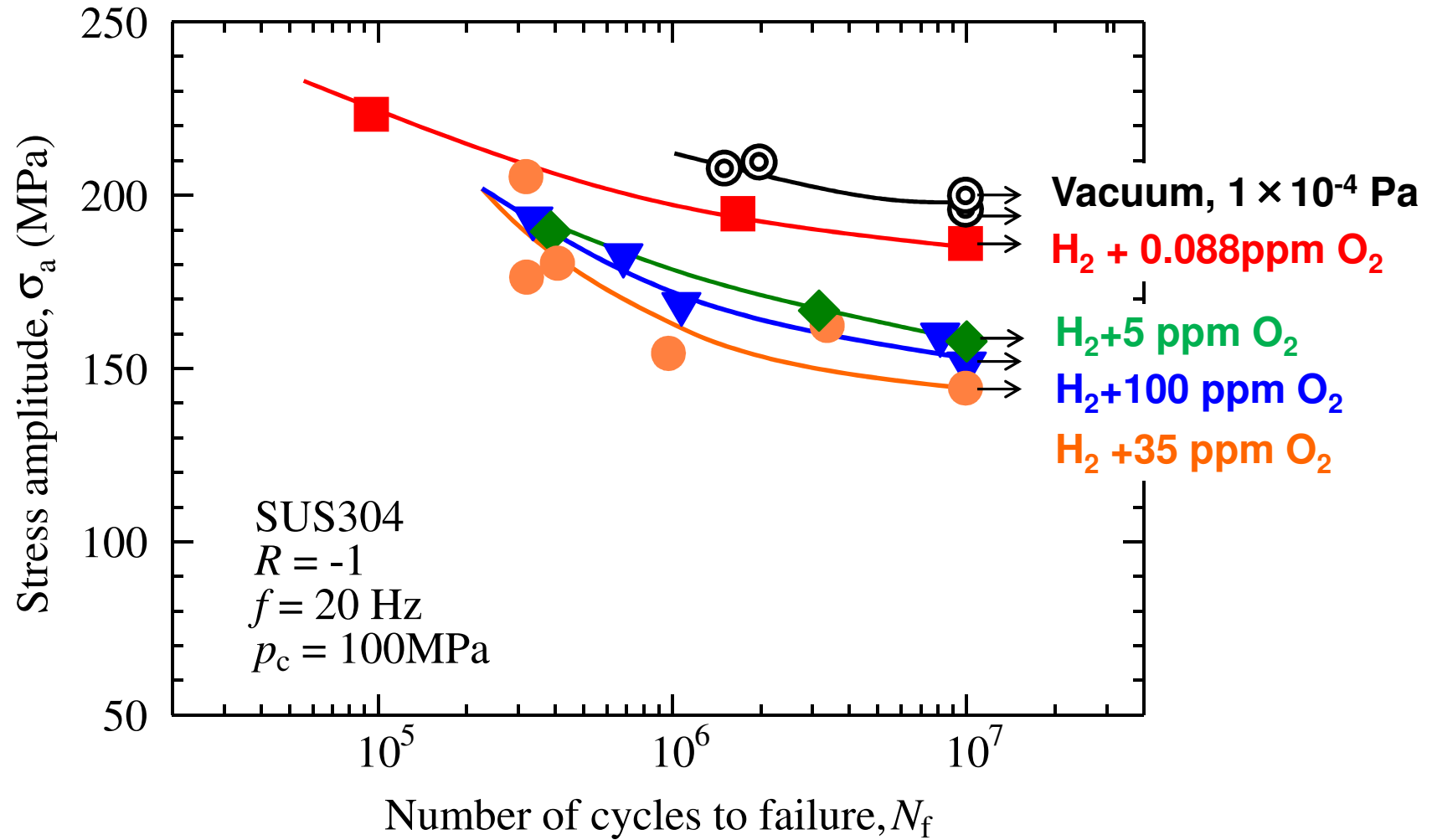
ISO 14687-2: 2012

Species	Allowable value
Hydrocarbon	< 2 ppm
H ₂ O	< 5 ppm
O ₂	< 5 ppm
He	< 300 ppm
Ar, N ₂	< 100 ppm
CO ₂	< 2 ppm
CO	< 0.2 ppm
S	< 0.004 ppm
HCHO	< 0.01 ppm
HCOOH	< 0.2 ppm
NH ₃	< 0.1 ppm
Halide	< 0.05 ppm
Particle	< 1 mg/kg

(1) Hydrogen contains impurities.

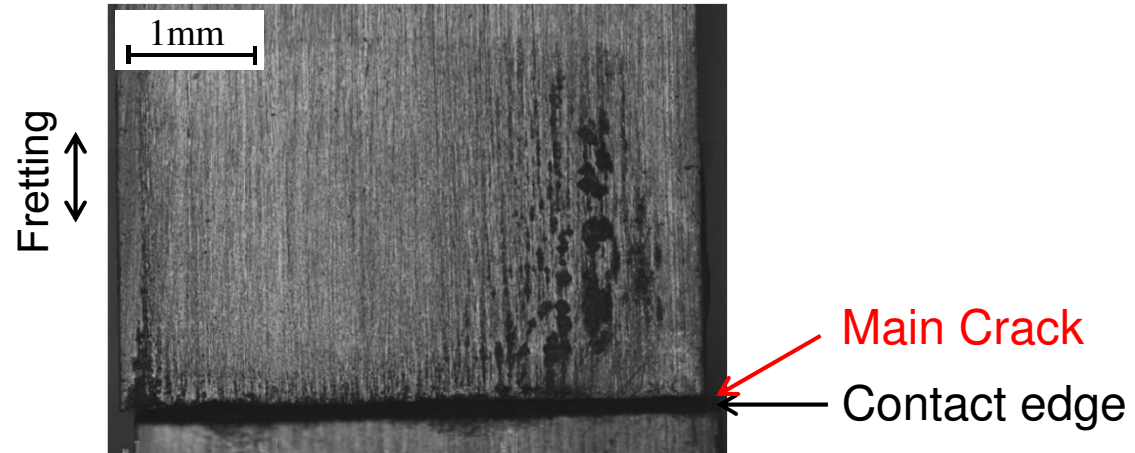
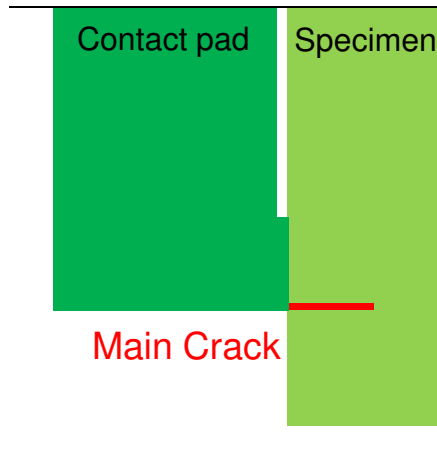
(2) Adhesion is sensitive to impurities.

Effect of O₂ addition on FF strength in H₂



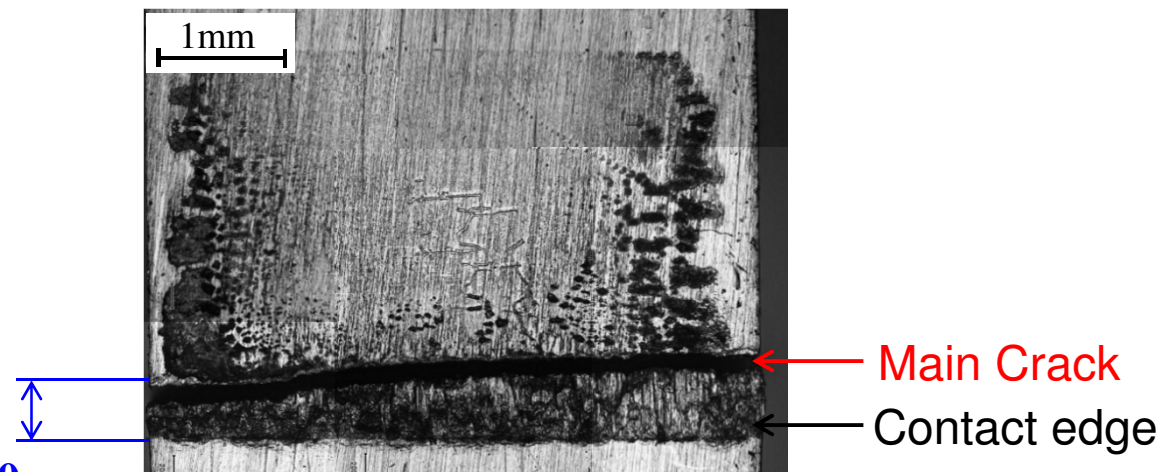
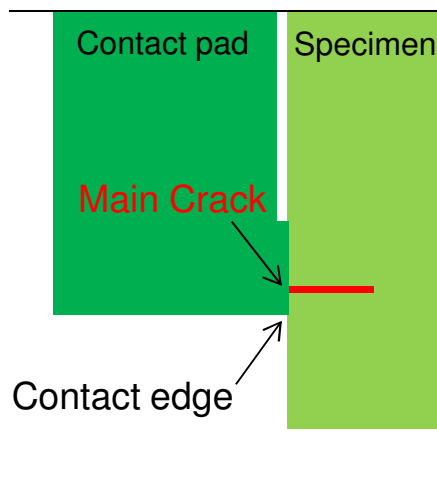
Shift of crack initiation site by the addition of O₂

H₂ + 0.088ppm O₂



$\sigma_a = 194\text{MPa}$, $\phi = 0.478$, $N_f = 1.6 \times 10^6$

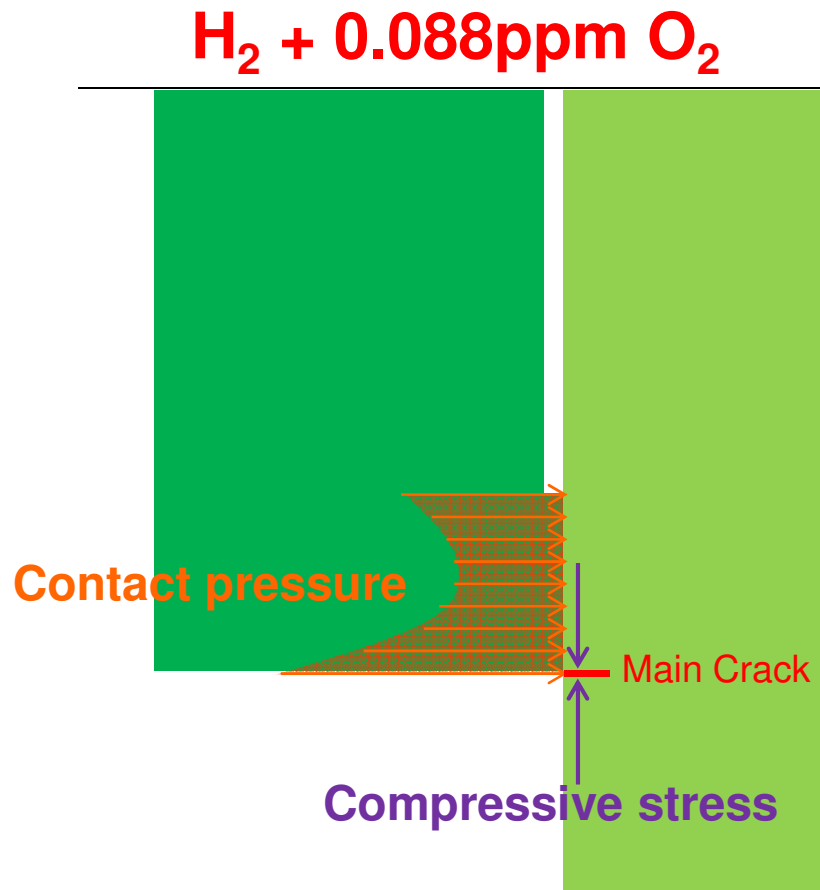
H₂+5 ppm O₂



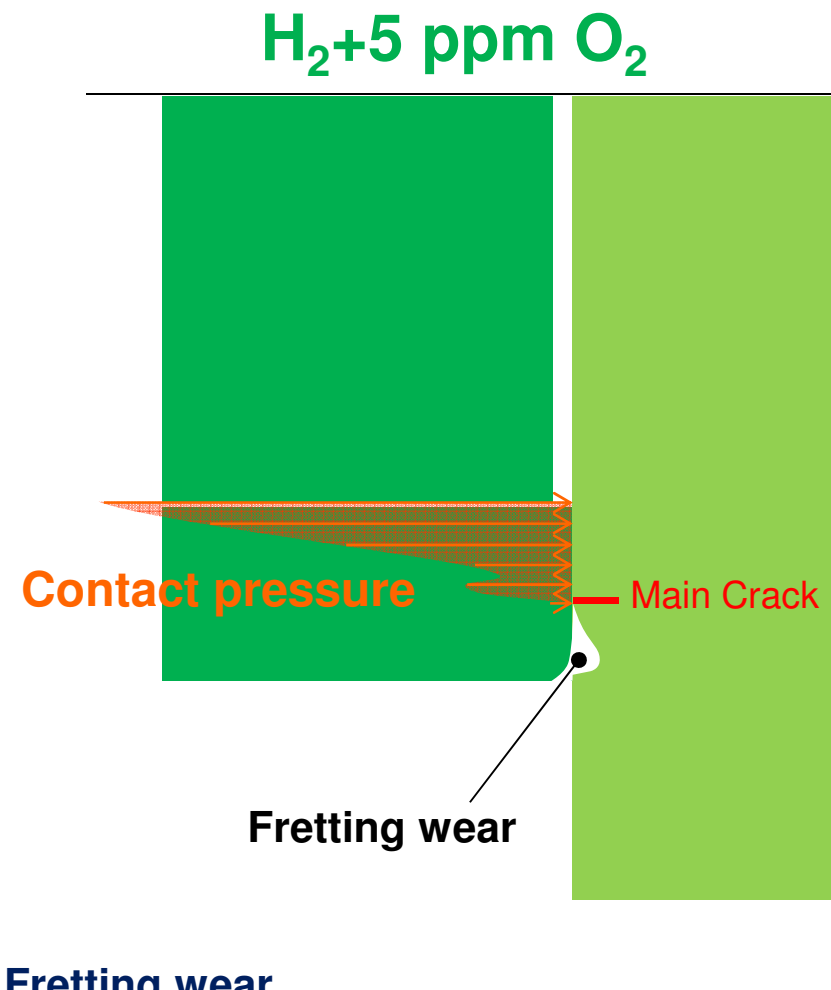
$d_c = 490\mu\text{m}$

$\sigma_a = 189\text{MPa}$, $\phi = 0.492$, $N_f = 3.9 \times 10^5$

Mechanism that O₂ addition reduces FF strength



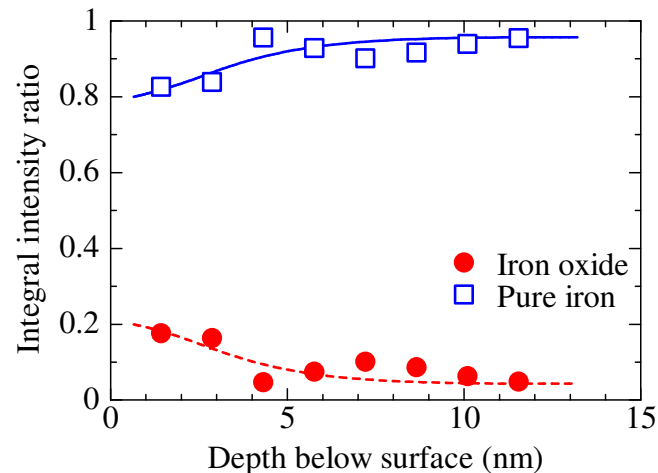
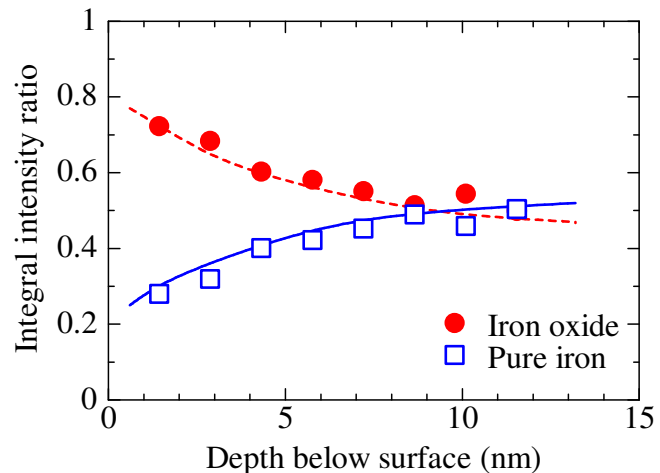
Concentration of the contact pressure
Compressive stress field
Prevention of crack growth
Higher FF strength



Fretting wear
Relieve concentration of the contact pressure
No compressive stress field
Lower FF strength

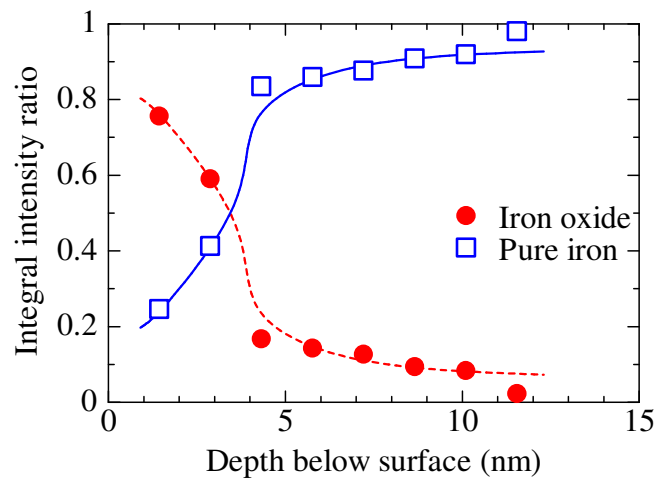
XPS analysis of fretted surface

Abundance ratios of iron & iron oxide



Unfretted surface

H₂ + 0.088ppm O₂



H₂+5 ppm O₂

4. Conclusion

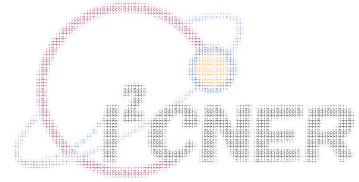
Fretting fatigue strength in H₂ and the effect of O₂ addition was studied.

- (1) The FF strength in H₂ is significantly lower than that in air.
- (2) Adhesion between the contacting surfaces occurred during FF in H₂. The adhesion causes localized severe cyclic plastic strain and transformation of crystalline structure. All these phenomena are responsible for the reduced FF strength in H₂.
- (3) The addition of ppm-level O₂ drastically changed the FF strength in H₂.
- (4) The addition of O₂ changed fretting wear behavior. It resulted change in the stress conditions at the contact edge. As the result, the FF strength in H₂ was reduced.

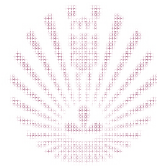
Acknowledgement

Most part of this study was carried out in collaboration with Air Liquide, France and Air Liquide Japan.

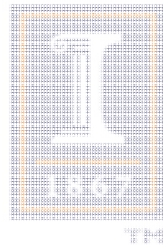




Thank you for your attention.

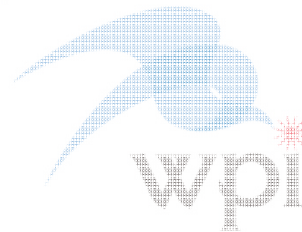


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World Premier International
Research Center Initiative



Creative Oxygen

Hydrogen campus of Kyushu University



Professor Petros Sofronis,
Director

WPI-I2CNER



SOFC + MGT
Power generation
250kW



NEXT-FC



Establish sustainable society

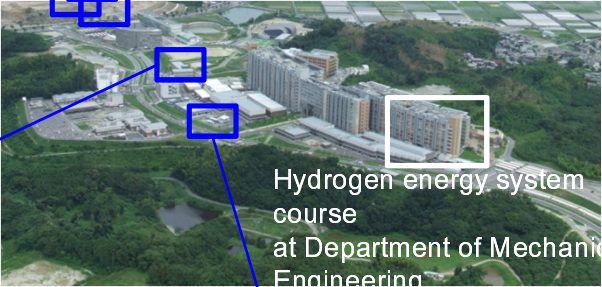
CO2 reduction, H2 production, Fuel cell, CCS, Hydrogen embrittlement, etc.

HYDROGENIUS



Accelerate transition to hydrogen economy

Reduce regulation, Help R&D, etc.



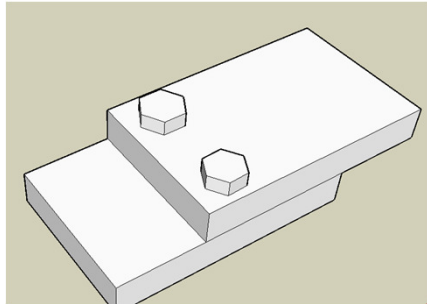
Hydrogen energy system course
at Department of Mechanical Engineering



Hydrogen station

Field test
Advertising of hydrogen energy
Foster public acceptance

Typical components suffering from fretting fatigue



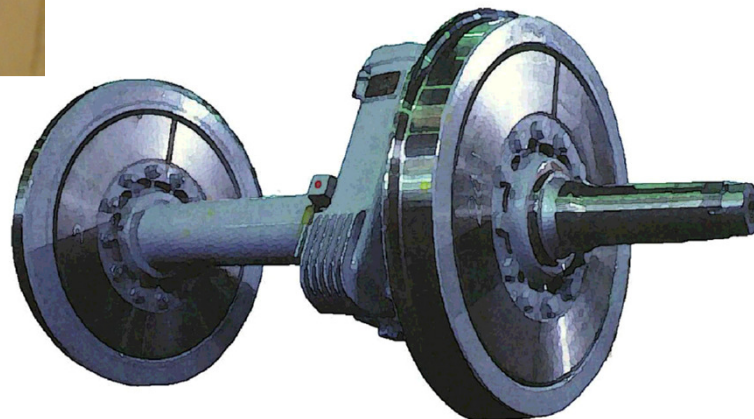
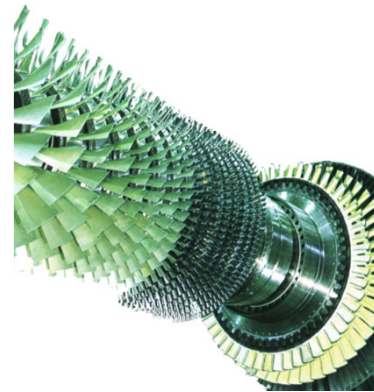
Bolted joint



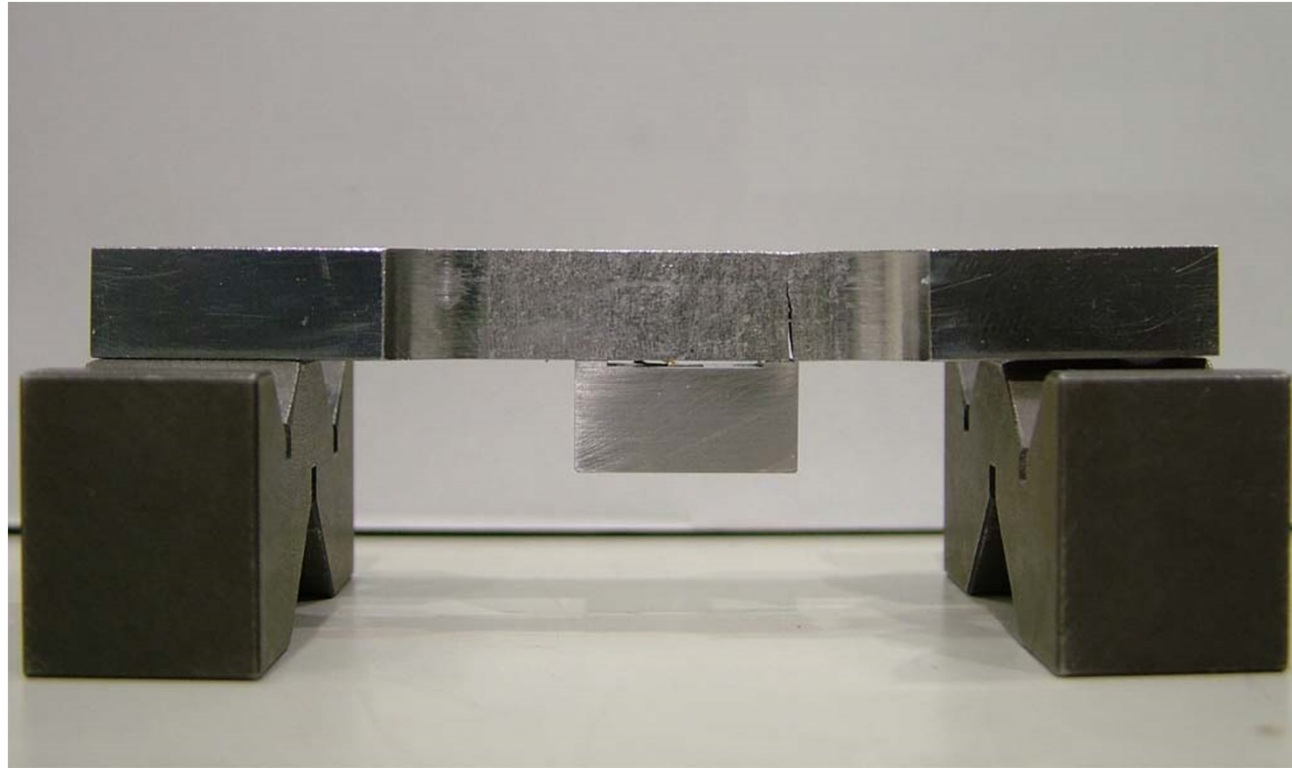
Clamp



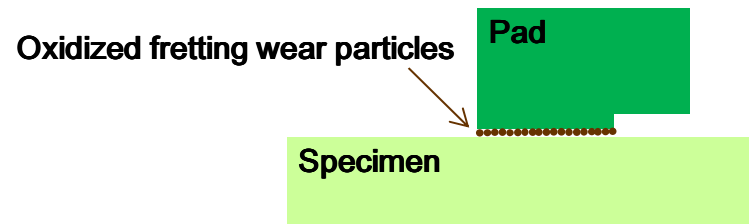
Interference fitting
(Press fit, Shrink fit)



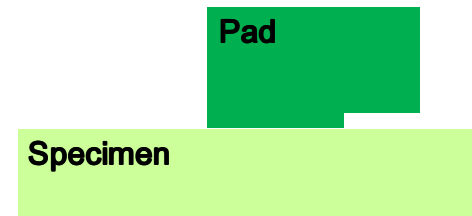
Adhesion during FF in H₂



In air

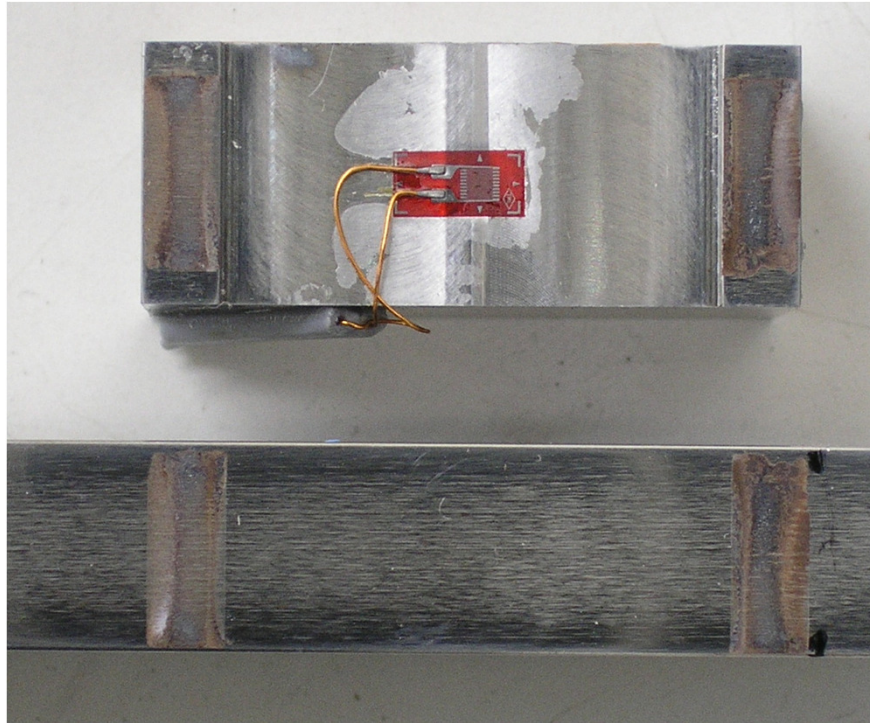


In H₂



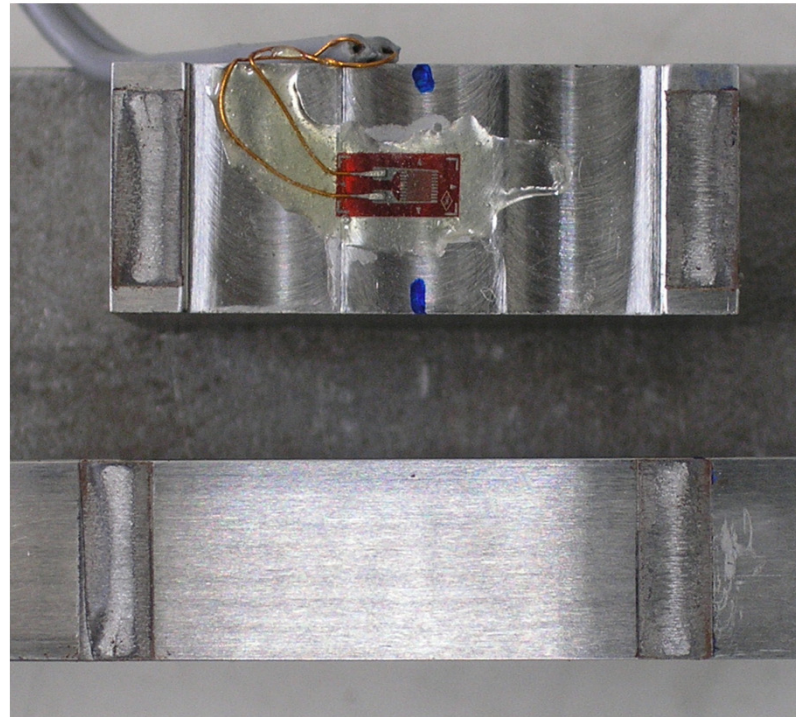
Fretted surface

In air



3mm

In H₂

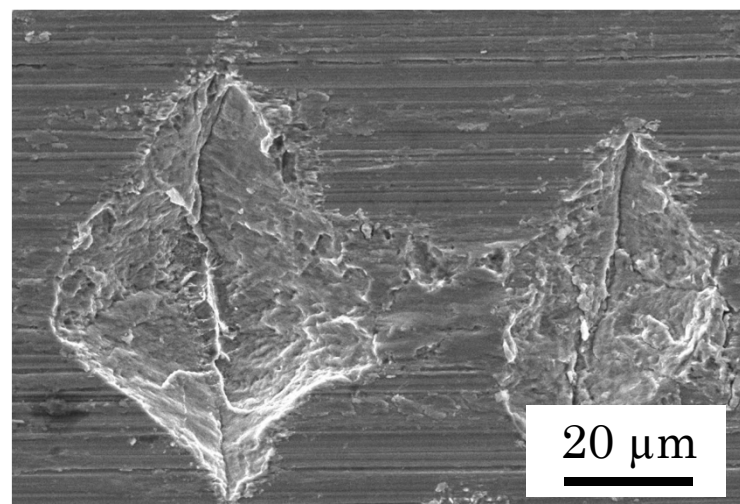
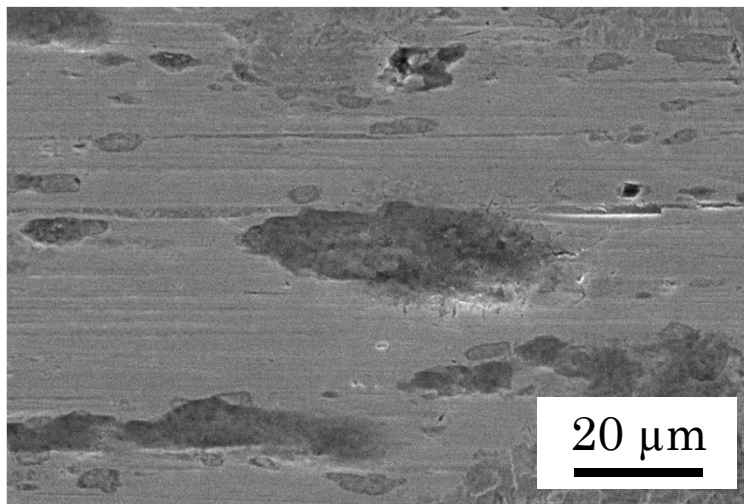
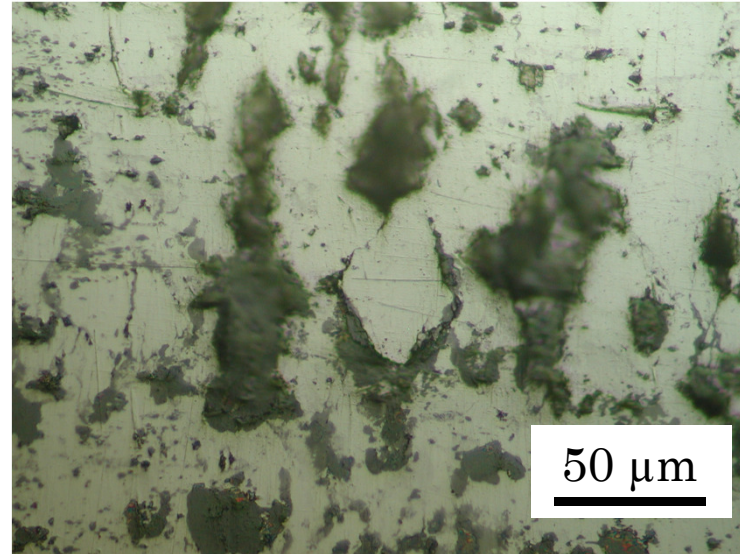
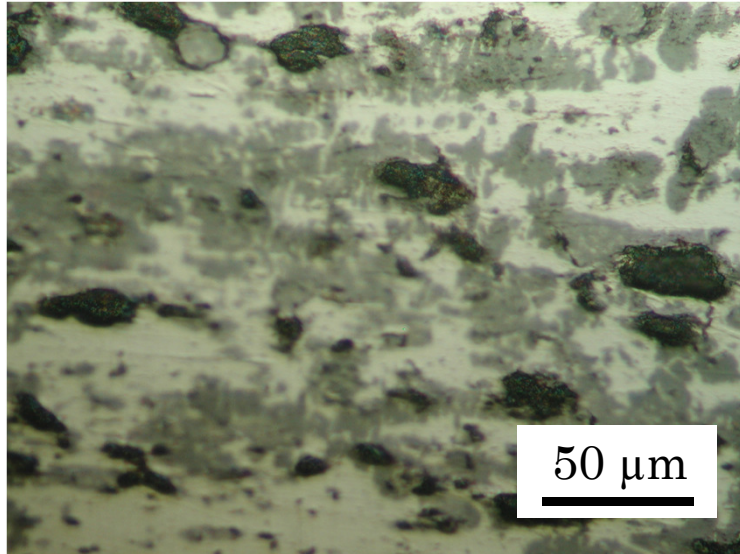


Fretting damage

In air

Fretting
↔

In H₂



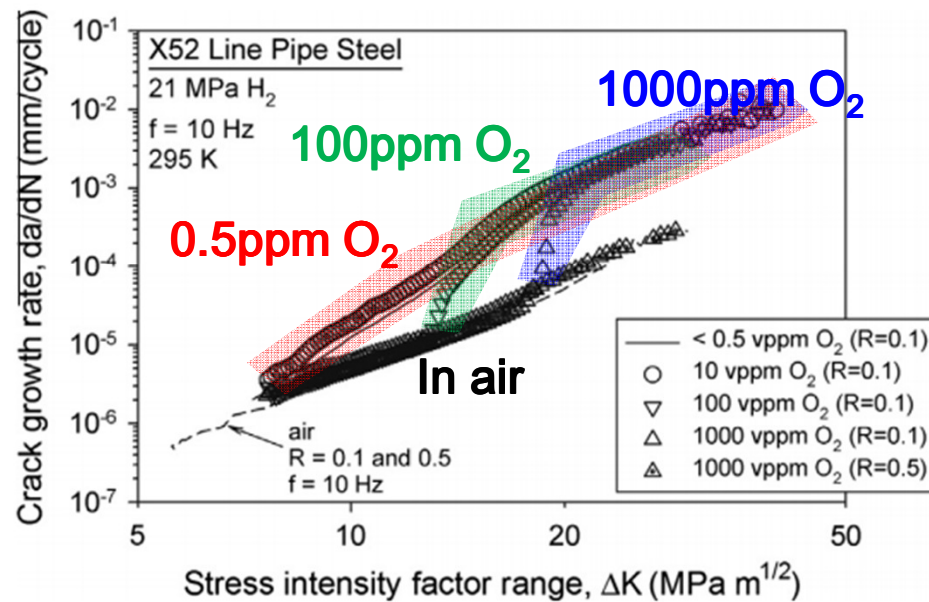
$\sigma_a = 183 \text{ MPa}$, $N_f = 2.96 \times 10^6$

$\sigma_a = 188 \text{ MPa}$, $N_f = 2.23 \times 10^6$

Effect of oxygen addition to H₂

Fatigue crack growth behavior

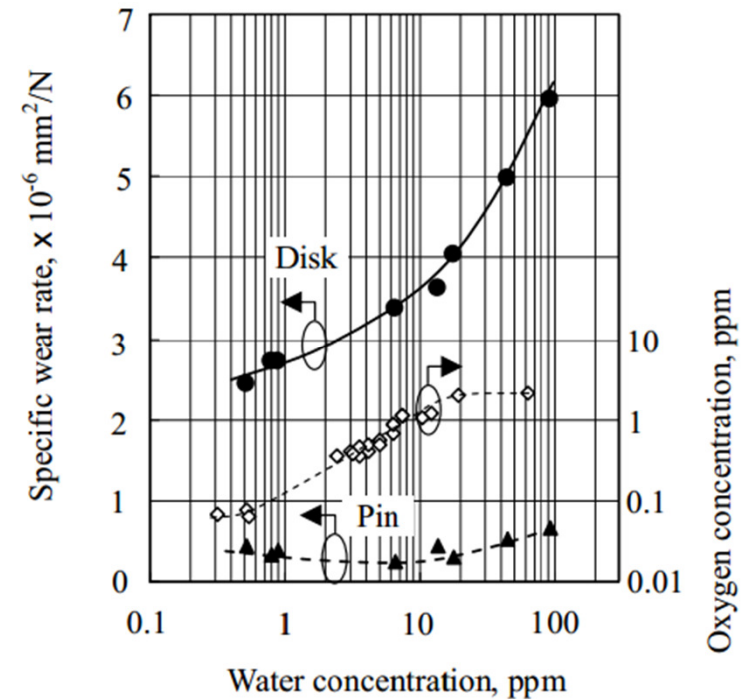
H₂ + 0.5 – 1000ppm O₂



Somerday BP, Sofronis P, Nibur KA, San Marchi C, Kirchheim R. Elucidation the variables affecting accelerated fatigue crack growth of steel in hydrogen gas with low oxygen concentrations. Acta Materialia 2013;61(16):6153-6170.

Wear behavior

H₂ + 0.01 - 10ppm O₂
 H₂ + 0.5 – 100ppm H₂O



K.Fukuda, Y.Kurono, N.Izumi and J.Sugimura, Influence of Trace Water and Oxygen in a Hydrogen Environment on Pure Fe Friction and Wear, Tribology Online, 5, 87(2010).

Shift of crack initiation site by the addition of O₂

