IWSMT13

2016.10. 30 – 11. 4

SIMULATION OF HYDROGEN THERMAL DESORPTION CHARACTERISTICS IN METALS CONTAINING LARGE VOIDS

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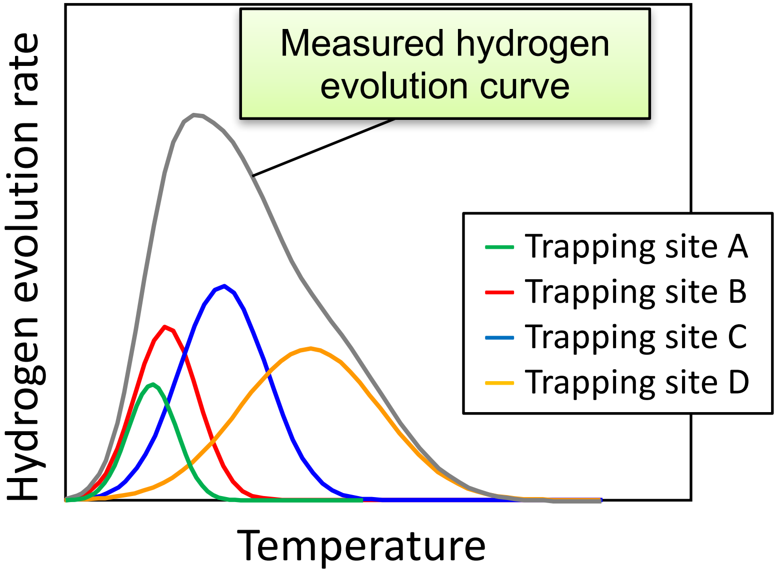
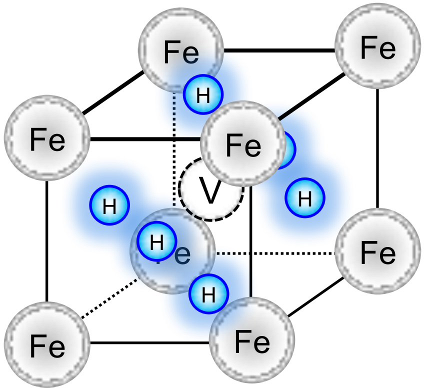
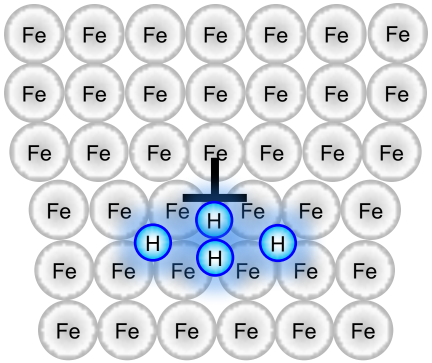
Hydrogen in Steels

- ❖ **It is well known that a large number of hydrogen and helium atoms are formed in the structural materials of the spallation neutron sources. The formed gas causes damage to materials.**
- ❖ **The hydrogen trapped by defects such as vacancies, small vacancy clusters, dislocations, grain boundaries, precipitates, voids/bubbles, etc., can be released from each trap site by heating the material.**
- ❖ **The temperature range of desorption varies according to the kind of trap site, because the binding energy between hydrogen and each trap site is different.**





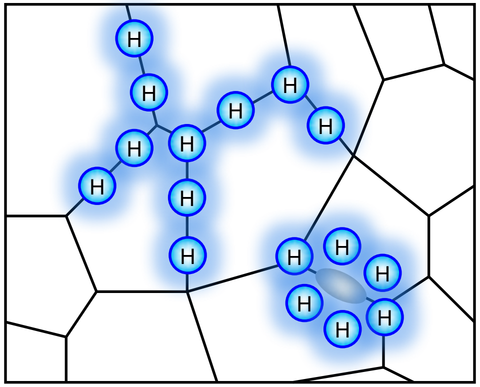
❖ **Vacancy**：40〜50 kJ/mol
❖ **Vacancy cluster**：70 kJ/mol



❖ **Dislocation**

Dislocation core：60 kJ/mol

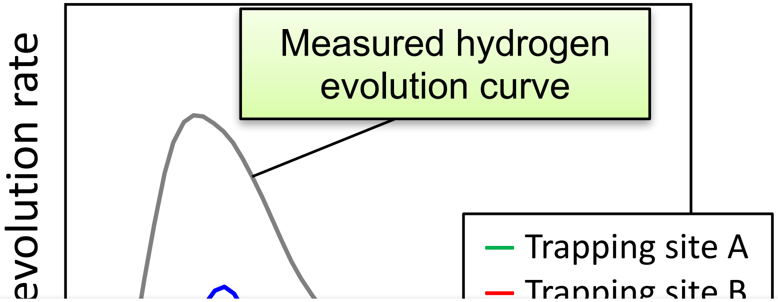
Elastic stress：40〜50 kJ/mol



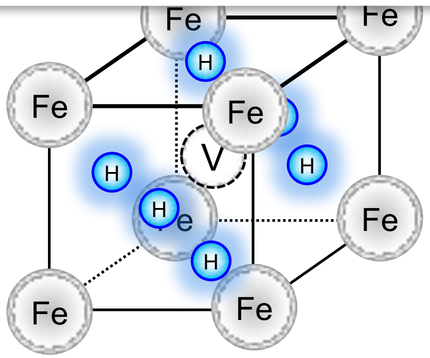
❖ **G.B.**：50〜60 kJ/mol
❖ **Carbides（Fe_3C, TiC）**：80〜100 kJ/mol

Hydrogen in Steels

- ❖ **It is well known that a large number of hydrogen and helium atoms are formed in the structural materials of the spallation neutron sources. The formed gas causes damage to materials.**
- ❖ **The hydrogen trapped by defects such as vacancies, small vacancy clusters, dislocations, grain boundaries, precipitates, voids/bubbles, etc., can be**



In the present study, the most stable structure of hydrogen in a void and vacancy cluster of the pure iron has been investigated by first principle calculations. In addition, the simulation technique for studying the effect of irradiation-induced defects on hydrogen desorption curves has been developed.



❖ **Vacancy**：40〜50 kJ/mol
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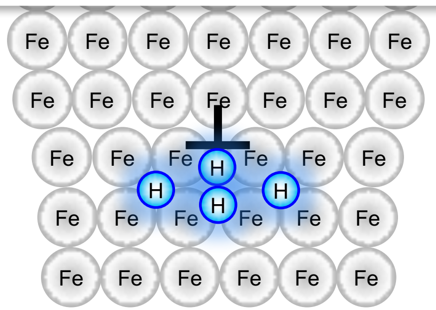

❖ **Dislocation**
Dislocation core：60 kJ/mol
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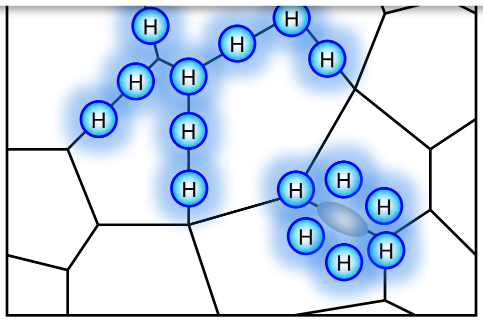


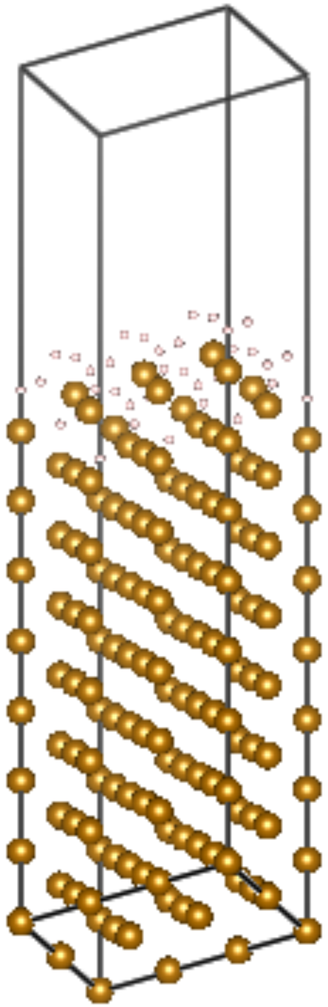
❖ **G.B.**：50〜60 kJ/mol
❖ **Carbides（Fe_3C, TiC）**：80〜100 kJ/mol

The most stable structure of hydrogen in a void and vacancy cluster

First principle calculations condition

The hydrogen was introduced into adsorption site such as 4F,2F of the iron crystal surface（the void surface）.

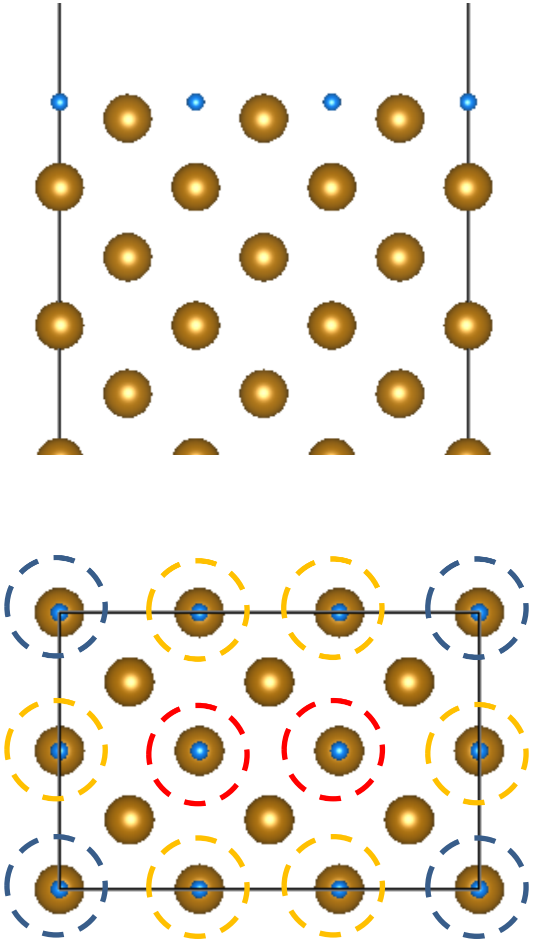
- Program cord
  Vienna Ab Initio Simulation Package (VASP)
- Crystal structure
  BCC unit cell：2×3×8
  Vacuum layer：11.348Å（About four times of lattice constant of BCC）
  Crystal surface ：(100）crystal planes
- Magnetism
  Fe：Ferromagnetics
- Sampling of k point
  Monkhorst-Pack
  6×4×2
- Cut of energy
  348eV
- Relaxation calculation
  Atomic position，Shape of unit cell，Volume
- Convergence condition
  Force applied to atom is less than 0.005eV/Å



First principle calculations condition

● : Fe
● : H

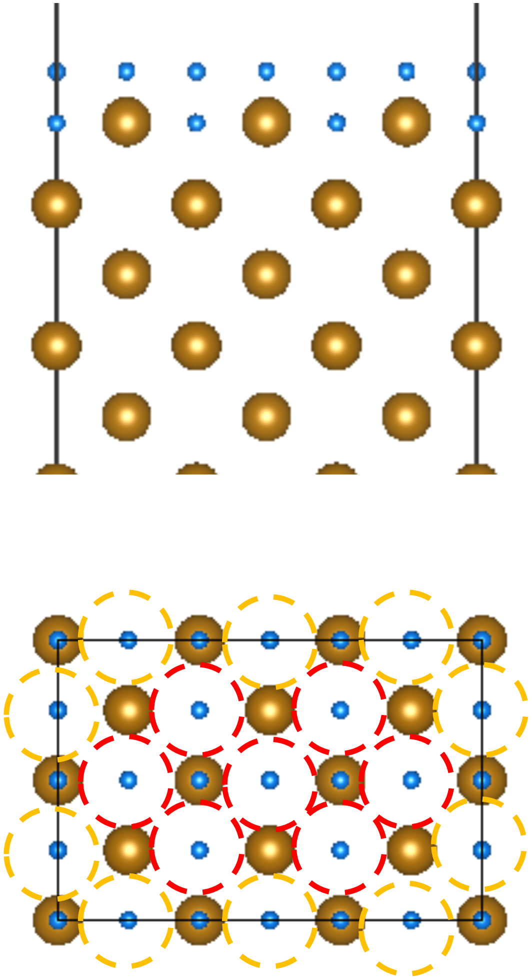
4F



Number of 4F site

$\frac{1}{4}\times4+\frac{1}{2}\times6+1\times2=6$

4F+2F

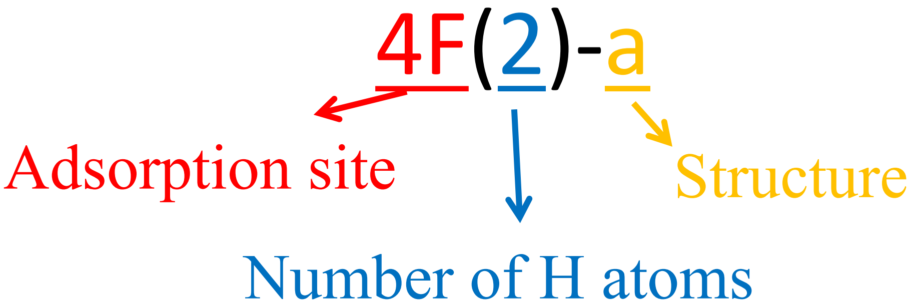


Number of 2F site

$\frac{1}{2}\times10+1\times7=12$

First principle calculations condition

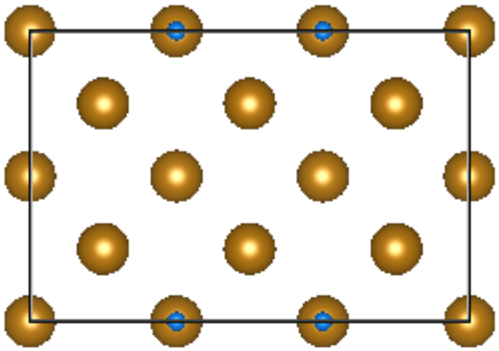
In this model, the structure may be different even if the adsorption hydrogen is the same number. So, when calculation result was written, kind of the structure was written.


4F(2)-a

Adsorption site

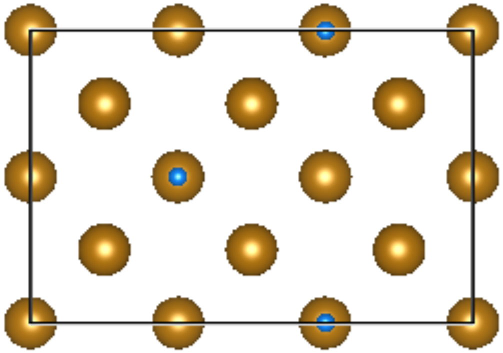
Number of H atoms

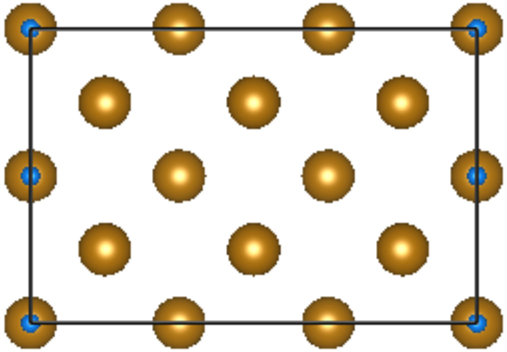
Structure


4F(2)-a

● : Fe

● : H

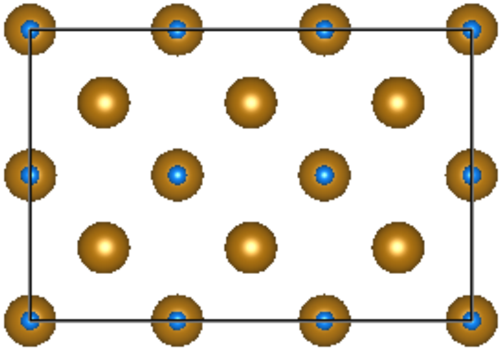

4F(2)-b


4F(2)-c

Determination method of stable structure of hydrogen

In the case of 6 hydrogen atoms, total energy of 6 adsorption hydrogen was compared with sum of total energy of 5 adsorption hydrogen and a half of hydrogen molecules energy of vacuum. Low energy side was stable.

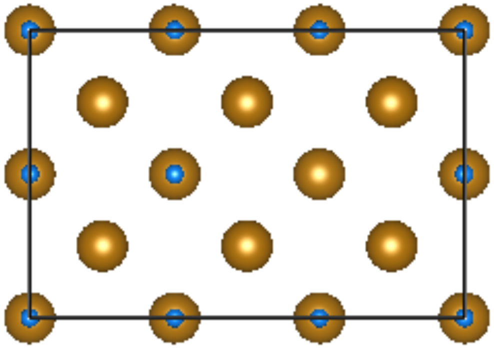
4F(6)



Total energy

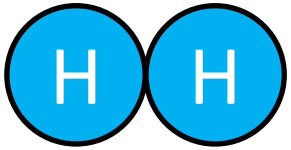
\> or <

4F(5)



Total energy

\+



÷ 2

Hydrogen molecules energy of vacuum/ 2

Result of first principle calculations

		Total energy, ev	Total energy +Hydrogen molecules energy of vacuum/2, ev
4F(0)		−783.274	−786.641
4F(1)		−787.016	−790.383
4F(2)	−a	−790.829	−794.196
	−b	−790.787	−794.154
	−c	−790.807	−794.174
4F(3)	−a	−794.632	−797.999
	−b	−794.549	−797.916
	−c	−794.647	−798.014
4F(4)	−a	−798.416	−801.783
	−b	−798.392	−801.759
	−c	−798.363	−801.729
4F(5)		−802.300	−805.667
4F(6)		−805.932	−809.298
4F(6)2F(1)		−809.489	−812.856
4F(6)2F(2)	−a	−812.542	−815.909
	−b	−812.740	−816.107
	−c	−812.753	−816.120
	−d	−812.855	−816.222

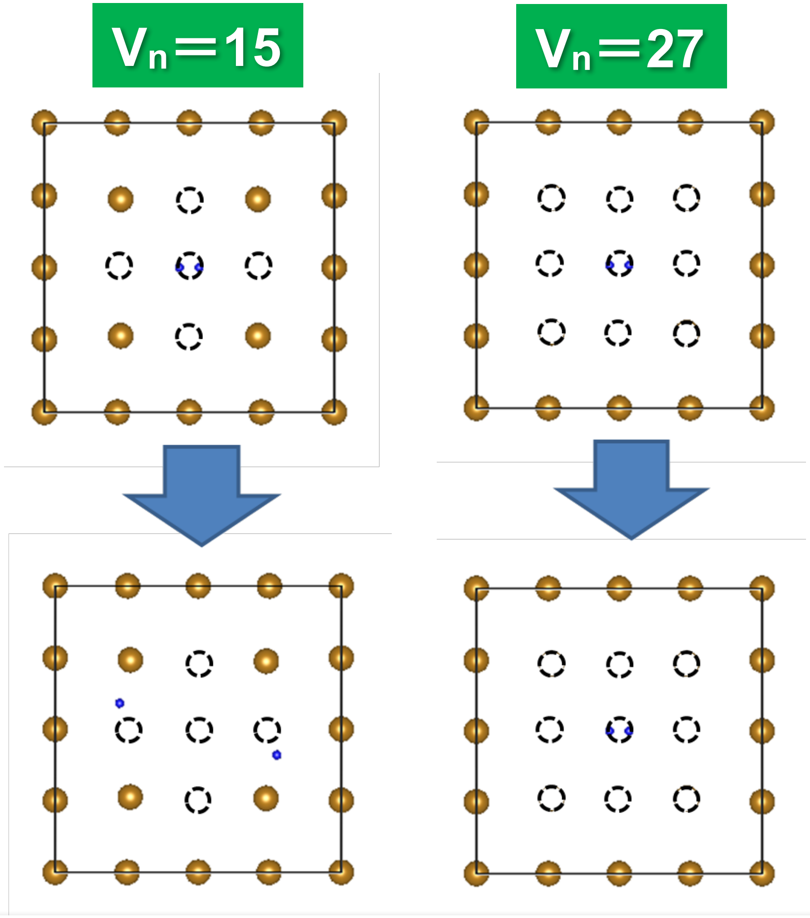
Result of first principle calculations

		Total energy, ev	Total energy +Hydrogen molecules energy of vacuum/2, ev
4F(0)		−783.274	−786.641
4F(1)		−787.016	−790.383
4F(2)	−a	−790.829	−794.196
	−b	−790.787	−794.154
	−c	−790.807	−794.174
4F(4)	b	798.392	801.759
	−c	−798.363	−801.729
4F(5)		−802.300	−805.667
4F(6)		−805.932	−809.298
4F(6)2F(1)		−809.489	−812.856
4F(6)2F(2)	−a	−812.542	−815.909
	−b	−812.740	−816.107
	−c	−812.753	−816.120
	−d	−812.855	−816.222

When all 4F sites was covered and 2F sites was adsorbed by 2 hydrogen, energy became higher than hydrogen molecules exist.
⇒100% of 4F sites and about 8% of 2F sites of the void surface (100) were covered, hydrogen gas was found to be precipitated in the void.

Stable structure of hydrogen in a vacancy cluster

The first principle calculations result that hydrogen molecule was placed in the center of the vacancy cluster.



◌ : Vacancy
● : Fe
● : H

Vacancy cluster consisting of 15 vacancies
⇒Hydrogen molecule separated and adsorbed to surface.

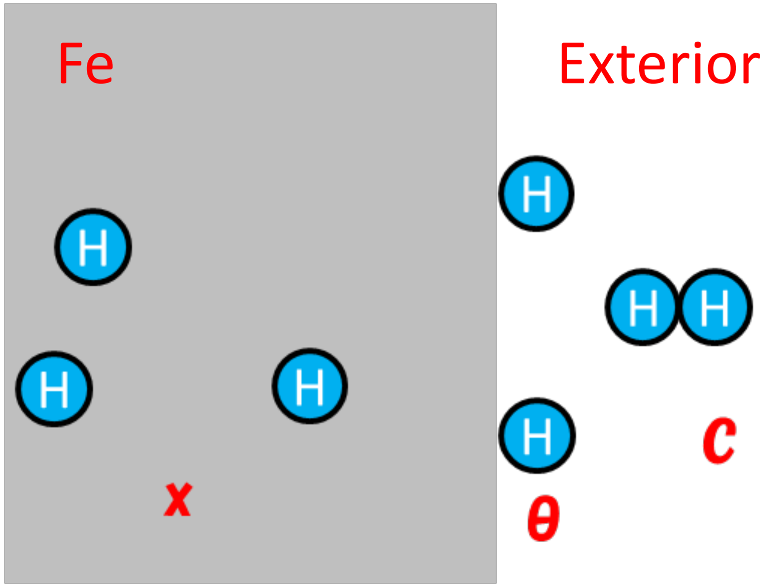
Vacancy cluster consisting of 27 vacancies
⇒Hydrogen molecule did not separate and existed in the center.

The hydrogen gas existed in a vacancy cluster consisting of more than 27 vacancies in the iron.

Simulation of hydrogen desorption

Simulation model of hydrogen desorption and adsorption

The simulation model of Davenport et al（1982）



$$\mathrm{Metal} \underset{f_4}{\overset{f_3}{\leftrightarrows}} \mathrm{Surface} \underset{f_2}{\overset{f_1}{\leftrightarrows}} \mathrm{H_2\ gas}$$

Flux of hydrogen of the metal surface

f_1:Adsorption to the surface

f_2:Desorption from the surface

f_3:Invasions from the adsorption site to the solution site

f_4:Invasions from the solution site to the adsorption site

Changing rate of hydrogen coverage of metal surface

$$\frac{d\theta}{dt} = f_1 - f_2 - f_3 + f_4$$

Changing rate of soluble hydrogen

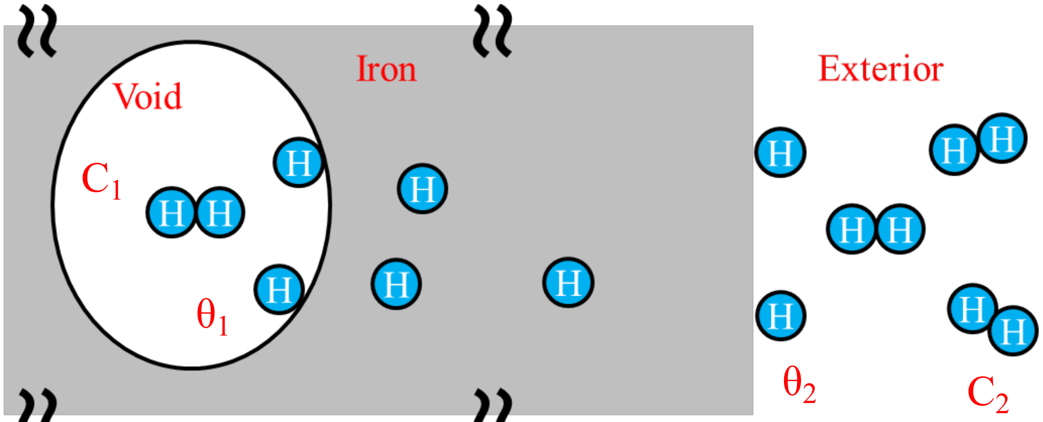
$$\frac{dx}{dt} = \frac{f_3 - f_4}{N}$$

N:Thickness of metal

（Atomicity of metal/Atomicity of surface）

Simulation model of hydrogen desorption

Developed simulation model



$$\text{H}_2\text{ gas} \underset{f_2}{\overset{f_1}{\rightleftarrows}} \text{Surface} \underset{f_4}{\overset{f_3}{\rightleftarrows}} \text{Metal} \underset{f_6}{\overset{f_5}{\rightleftarrows}} \text{Surface} \xrightarrow{f_7} \text{H}_2\text{ gas}$$

Flux of hydrogen of the void surface

f_1:Adsorption to the surface

f_2:Desorption from the surface

f_3:Invasions from the adsorption site to the solution site

f_4:Invasions from the solution site to the adsorption site

Flux of hydrogen of the metal surface

f_5:Invasions from the solution site to the adsorption site

f_6:Invasions from the adsorption site to the solution site

f_7:Desorption from the surface

Changing rate of hydrogen coverage of void surface

$$\frac{d\theta_1}{dt} = f_1 - f_2 - f_3 + f_4$$

Hydrogen desorption rate of void surface

$$\frac{dc_1}{dt} = -f_1 + f_2$$

Changing rate of hydrogen coverage of metal surface

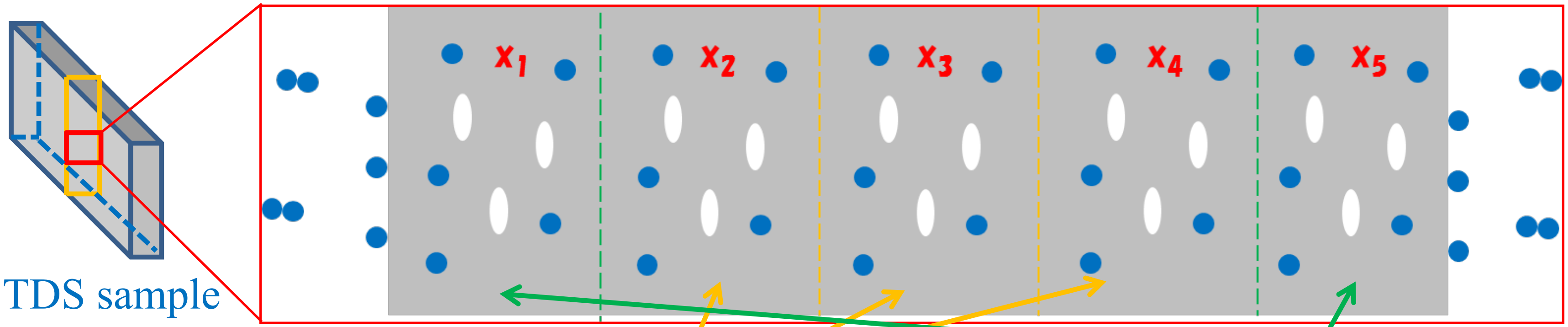
$$\frac{d\theta_2}{dt} = f_5 - f_6 - f_7$$

Hydrogen desorption rate of metal surface

$$\frac{dc_2}{dt} = f_7$$

Simulation model of hydrogen desorption

Developed simulation model



Changing rate of soluble hydrogen

$$\frac{dx_n}{dt} = N_V S\frac{f_3 - f_4}{N_1} + D\frac{x_{n+1} + x_{n-1} - 2x_n}{N^2}$$
$$- N_t(jx_n(1-\varepsilon) - p\varepsilon)$$

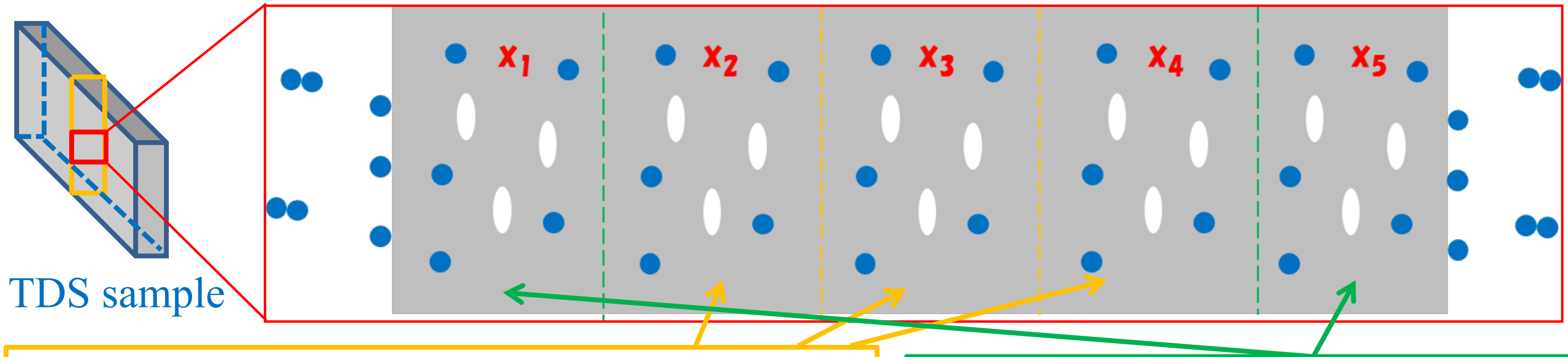
Changing rate of soluble hydrogen

$$\frac{dx}{dt} = \frac{-f_5 + f_6}{N_1} + D\frac{x_{1\ or\ 5} - 2x_n}{N^2}$$
$$+ N_V S\frac{f_3 - f_4}{N_1} - N_t\,(jx_n(1-\varepsilon) - p\varepsilon)$$

These equations are in consideration of trapping and dissociation of hydrogen in the void surface and the trap site in each cell. In addition, hydrogen diffusion of each cell are also calculated according to the diffusion equation.

Simulation model of hydrogen desorption

Developed simulation model



Changing rate of soluble hydrogen

$$\frac{dx_n}{dt} = N_V S \frac{f_3 - f_4}{N_1} + D \frac{x_{n+1} + x_{n-1} - 2x_n}{N^2} - N_t(jx_n(1-\varepsilon) - p\varepsilon)$$

Changing rate of soluble hydrogen

$$\frac{dx}{dt} = \frac{-f_5 + f_6}{N_1} + D \frac{x_{1\ or\ 5} - 2x_n}{N^2} + N_V S \frac{f_3 - f_4}{N_1} - N_t\ (jx_n(1-\varepsilon) - p\varepsilon)$$

N_V : Void number density
S: surface area of metal
N_1: Thickness of metal
N: Thickness of cell
N_t: Trap site density (e. g. dislocation, vacancy)
j: Capturing rate for the trap site
p: Releasing rate for the trap site
ε: Occupation rate of the trapping site by hydrogen

$$D = D_0 \exp\left(\frac{-E_B}{kT}\right)$$

D: Diffusion coefficient of hydrogen
D_0 : Frequency factor of diffusion cofficient
E_B : Diffusion activation energy
k : Boltzmann's constant
T: Temperature

Equation of flux

Adsorption to the surface: f_1

$$\frac{2Ps_0}{N_S\sqrt{4\pi MkT}}\exp(\frac{-2E}{kT})(1-\theta)^2$$

P : Hydrogen pressure in void
= *cRT*/*VN*$_A$
c : Number of hydrogen molecules
R : Gas constant
T : Temperature
V : Void volume
N_A : Avogadro constant
s_0 : Capture coefficient ($\theta = 0$)
N_S : Number of adsorption site
M : Mass of the hydrogen atom
k : Boltzmann's constant
E : Energy of adsorption
of hydrogen molecules
θ : hydrogen coverage rate of surface

Desorption from the surface: f_2 , f_7

$$\nu N_s\exp(\frac{-2E_D}{kT})\theta^2$$

ν : Frequency factor
E_D : Desorption energy from adsorption site

Invasions from the adsorption site to the solution site: f_3 , f_6

$$\nu\exp(\frac{-E_A}{kT})\theta(1-x)$$

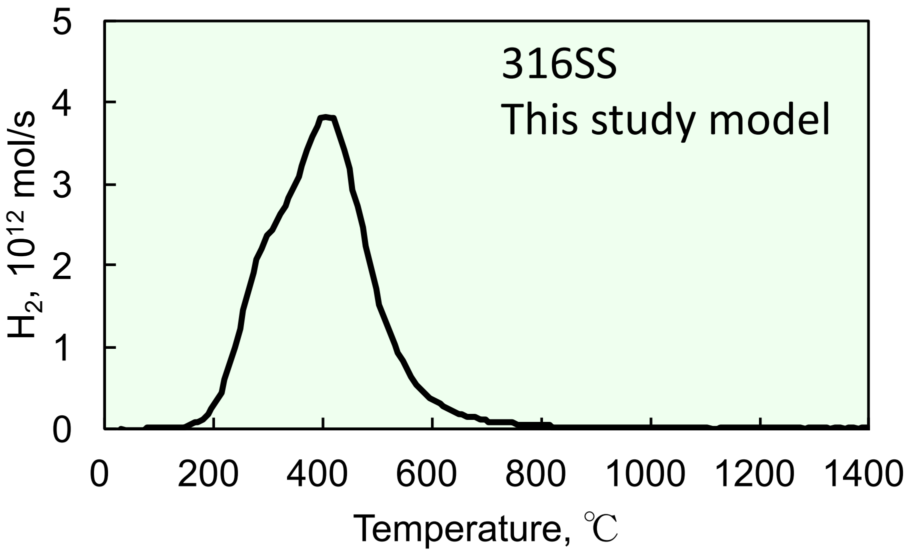
E_A : Activation energy Invasions from the adsorption site to the solution site
x : Occupation ratio of the solution site by hydrogen

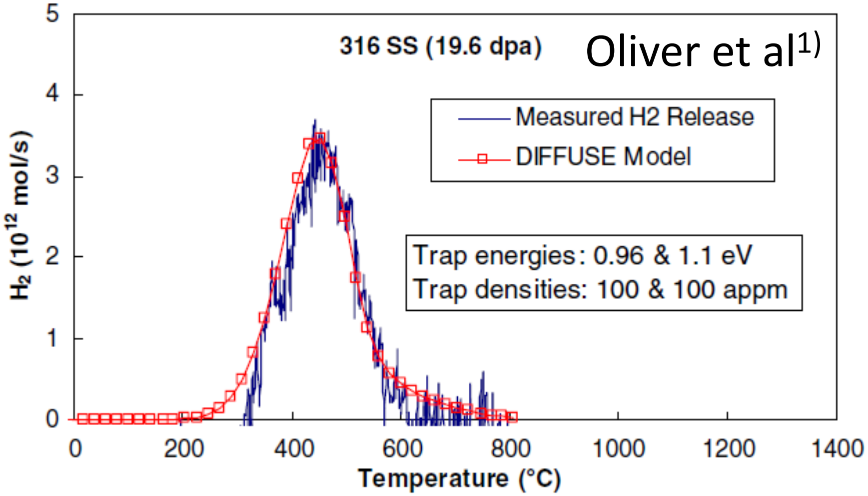
Invasions from the solution site to the adsorption site: f_4 , f_5

$$\nu\exp(\frac{-E_B}{kT})x(1-\theta)$$

E_B : Diffusion activation energy

Validity of model





For the validation test of the this study model, simulated hydrogen desorption curve was compared with the another simulated curve.
⇒Both curve are fitted.
This study model is valid.

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1) Oliver et al, Journal of Nuclear Materials, 356, 148(2006)

Material & Creep Specimen

The hydrogen desorption curve of creep ruptured specimen was simulated used our developed simulation model.

❖ Pure Fe

Table Chemical composition of pure Fe (mass%)

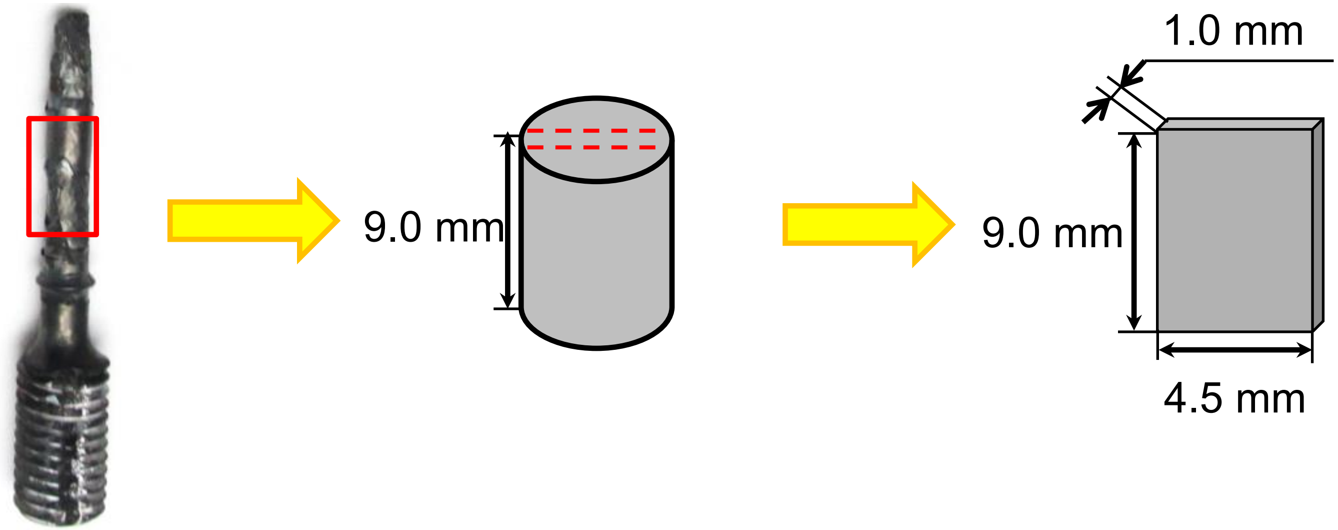
Fe	C	Si	Mn	Cr	Ni	Cu	N	O
99.99	0.001	0.0005	0.0001	0.0001	0.0001	0.0004	0.0006	0.014

❖ Creep specimen

Creep ruptured specimen（Creep damaged ）

Stress, MPa	Temp., ℃	Time, h	Life Fraction, %
10	700	312	100

❖ Rectangular specimen for Hydrogen Thermal Desorption Analysis

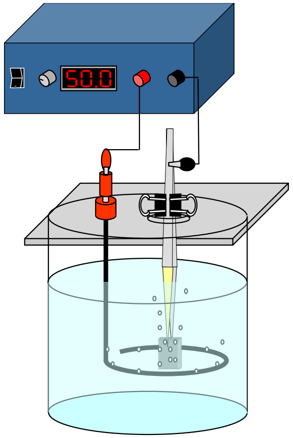


Surface finish:
Emery paper
#2400

Hydrogen Thermal Desorption Analysis

❖ Hydrogen Charging (cathodic electrolysis)

- ✓ Electrolyte: 0.1 mol/L NaOH
  ＋ 0.5mass% NH_4SCN
- ✓ Current density: $5mA/cm^2$
- ✓ Charging time: 72 h
- ✓ Solution Temp.: 30°C



❖ Thermal Desorption Analysis

- ✓ Gas chromatograph
- ✓ Carrier gas: Ar
- ✓ Heating rate: 100°C/h
- ✓ Temperature range: R.T. ~ 270°C
- ✓ Data sampling interval: 5 min.

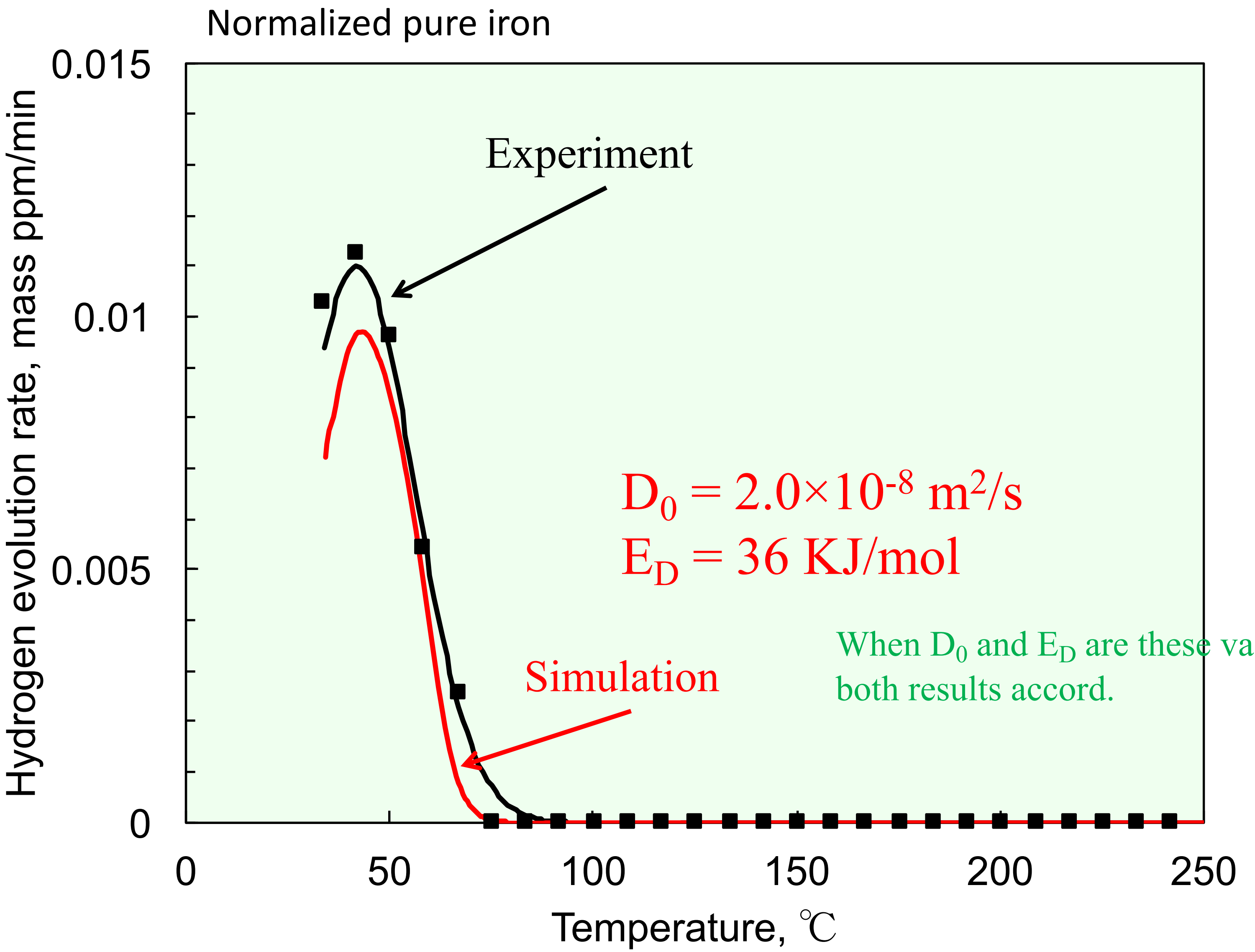
Necessary simulation parameter

	Calculated value	Literature data
D_0 : Frequency factor of diffusion cofficient		1.5×10^{-9}～ 1.6×10^{-7} m^2/s
E_B : Diffusion activation energy		8 kJ/mol
E_D : Desorption energy from adsorption site	32 kJ/mol	50 kJ/mol
P : Hydrogen pressure in void	556KPa	
s_0 : Capture coefficient ($\theta = 0$)		0.03
N_S : Number of adsorption site		1.72×10^{19} /m^2
N_A : Avogadro constant		6.02×10^{23} /mol
M : Mass of the hydrogen atom		1.674×10^{-27} kg
v : Frequency factor		10^{13} /s
R : Gas constant		8.314 J/Kmol
k : Boltzmann's constant		1.38×10^{-23} J/K

D_0 and E_D have a range. So, these value were determined by simulated hydrogen desorption curve of normalized pure iron.

Initial value θ : hydrogen coverage rate of surface 100%
x : Occupation ratio of the solution site by hydrogen 2.42×10^{-7}

Determined parameter



$D_0 = 2.0\times10^{-8}\ m^2/s$

$E_D = 36\ KJ/mol$

When D_0 and E_D are these value, both results accord.

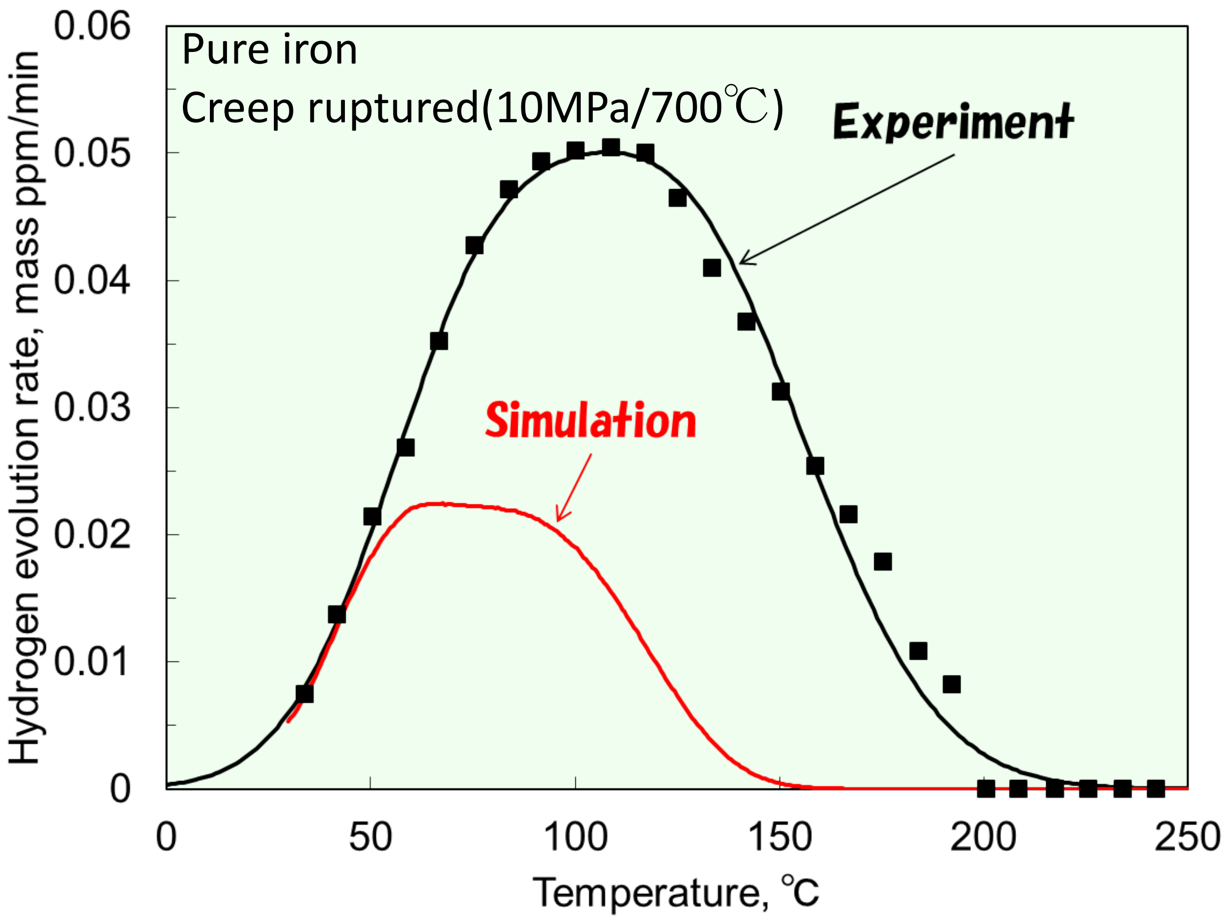
Simulation parameter

	Calculated value	Literature data	Determined value
D_0 : Frequency factor of diffusion coefficient		1.5×10^{-9}～ 1.6×10^{-7} m^2/s	2.0×10^{-8} m^2/s
E_B : Diffusion activation energy		8 kJ/mol	8 kJ/mol
E_D : Desorption energy from adsorption site	32 kJ/mol	50 kJ/mol	36 kJ/mol
P : Hydrogen pressure in void	556KPa		556KPa
s_0 : Capture coefficient ($\theta = 0$)		0.03	0.03
N_S : Number of adsorption site		1.72×10^{19} /m^2	1.72×10^{19} /m^2
N_A : Avogadro constant		6.02×10^{23} /mol	6.02×10^{23} /mol
M : Mass of the hydrogen atom		1.674×10^{-27} kg	1.674×10^{-27} kg
v : Frequency factor		10^{13} /s	10^{13} /s
R : Gas constant		8.314 J/Kmol	8.314 J/Kmol
k : Boltzmann's constant		1.38×10^{-23} J/K	1.38×10^{-23} J/K
Average void radius	1.5 µm		
Void number density	233.7 /mm^2		

These were obtained by scanning electron microscopy.

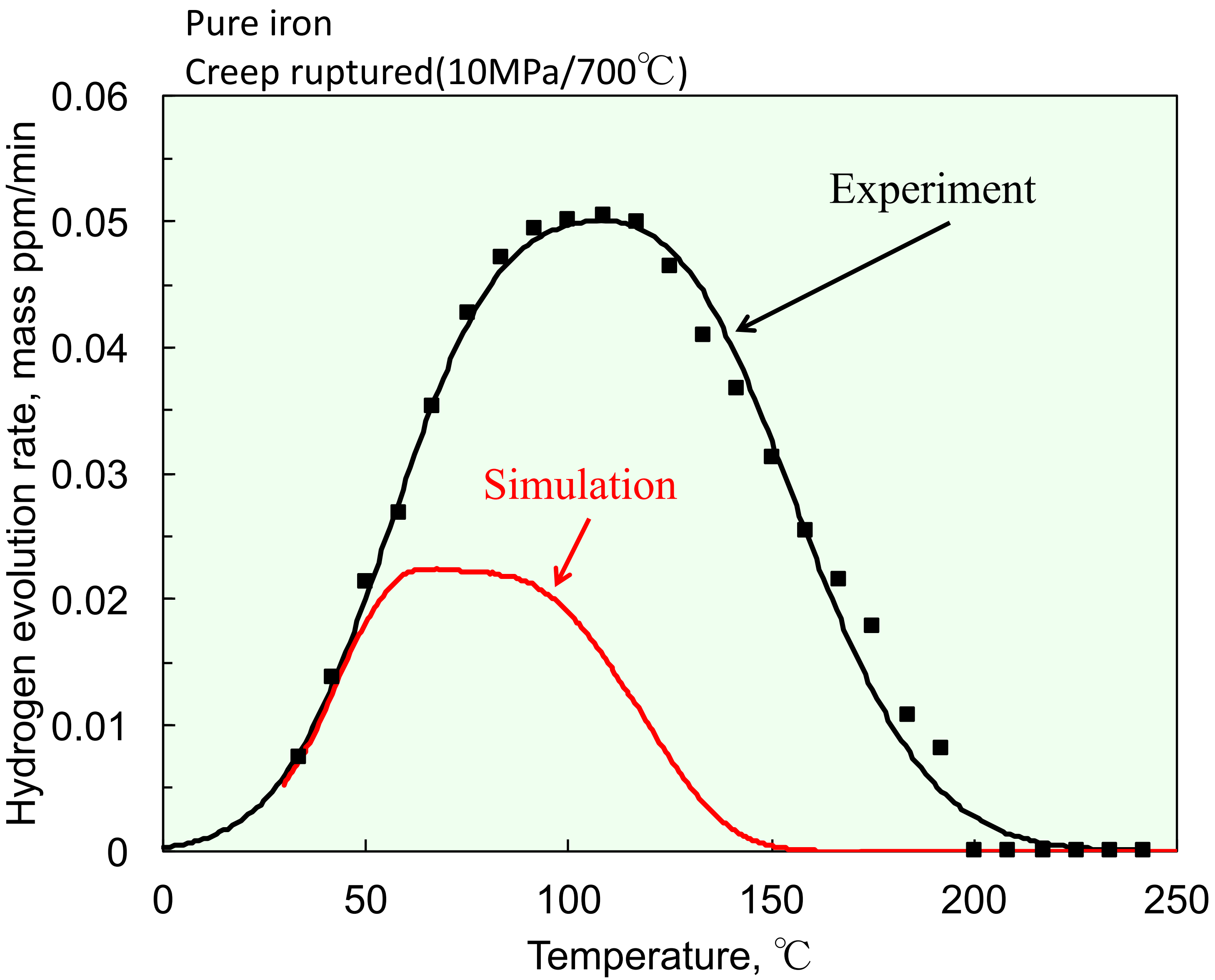
Initial value θ : hydrogen coverage rate of surface 100%
x : Occupation ratio of the solution site by hydrogen 2.42×10^{-7}

Simulation result of hydrogen evolution curve

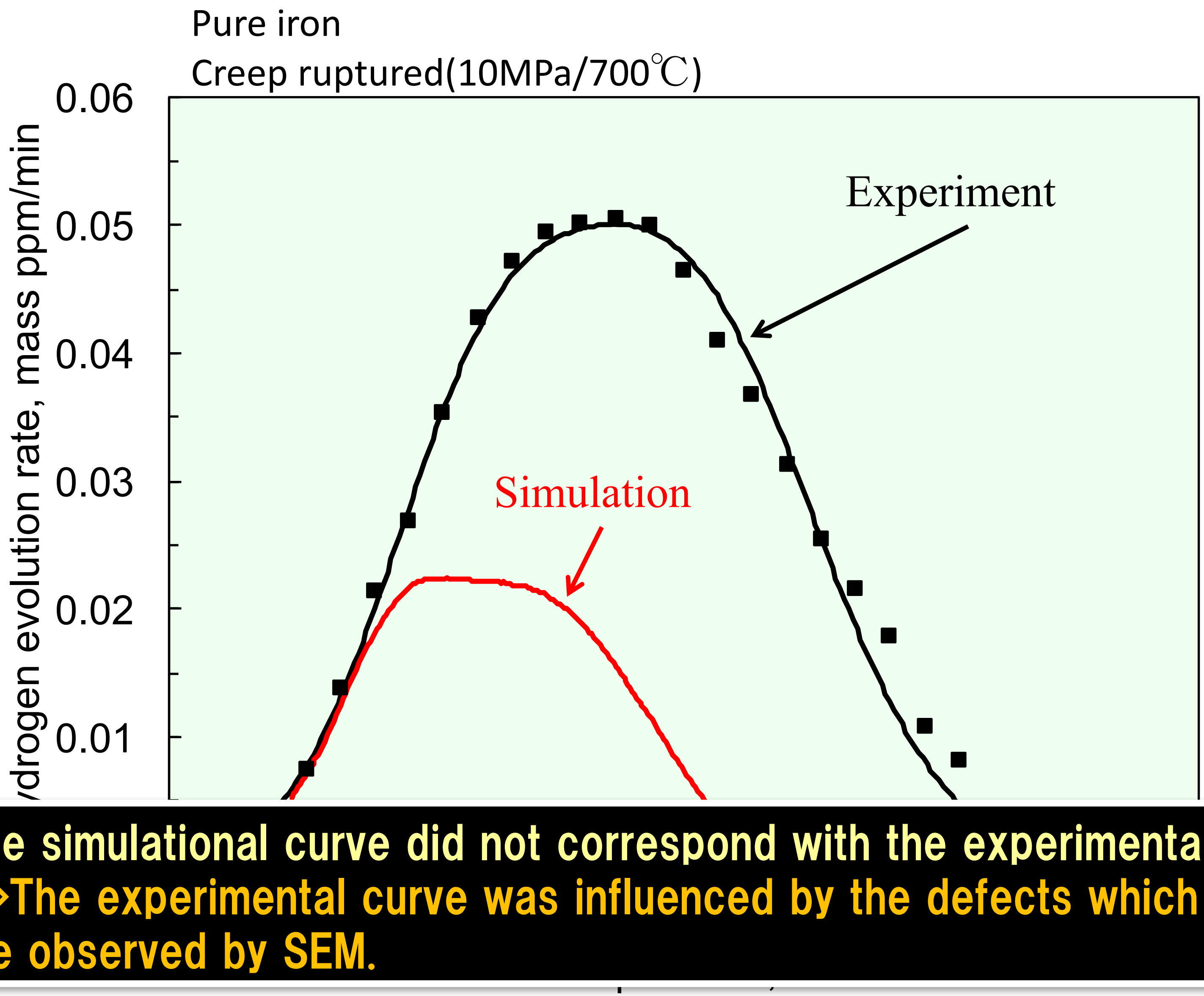


The simulational curve did not correspond with the experimental one.
⇒The experimental curve was influenced by the defects which cannot be observed by SEM.

Simulation result of hydrogen evolution curve



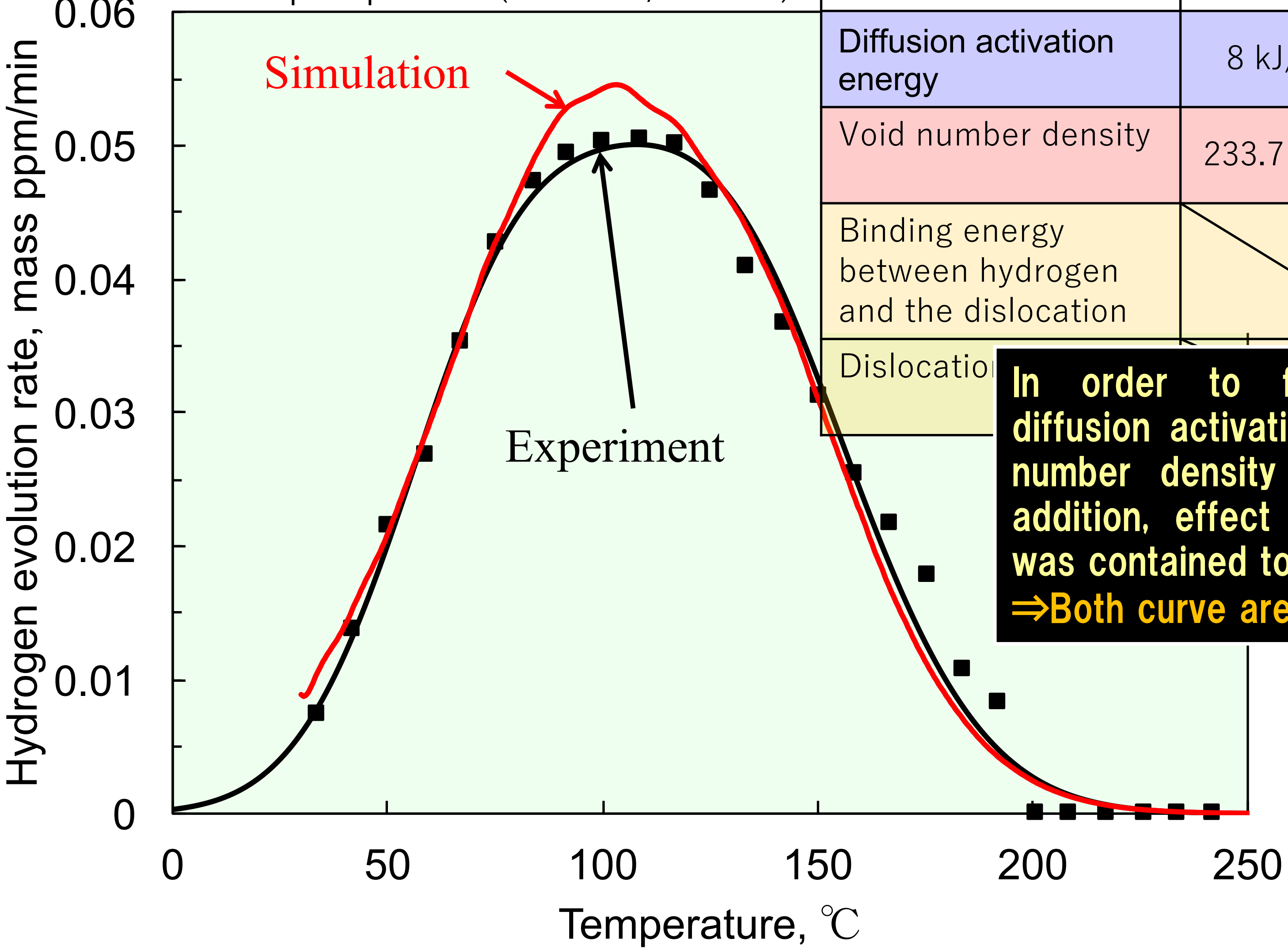
Simulation result of hydrogen evolution curve



the simulational curve did not correspond with the experimental one.
⇒The experimental curve was influenced by the defects which cannot be observed by SEM.

Simulation result of hydrogen evolution curve

Pure iron
Creep ruptured(10MPa/700°C)



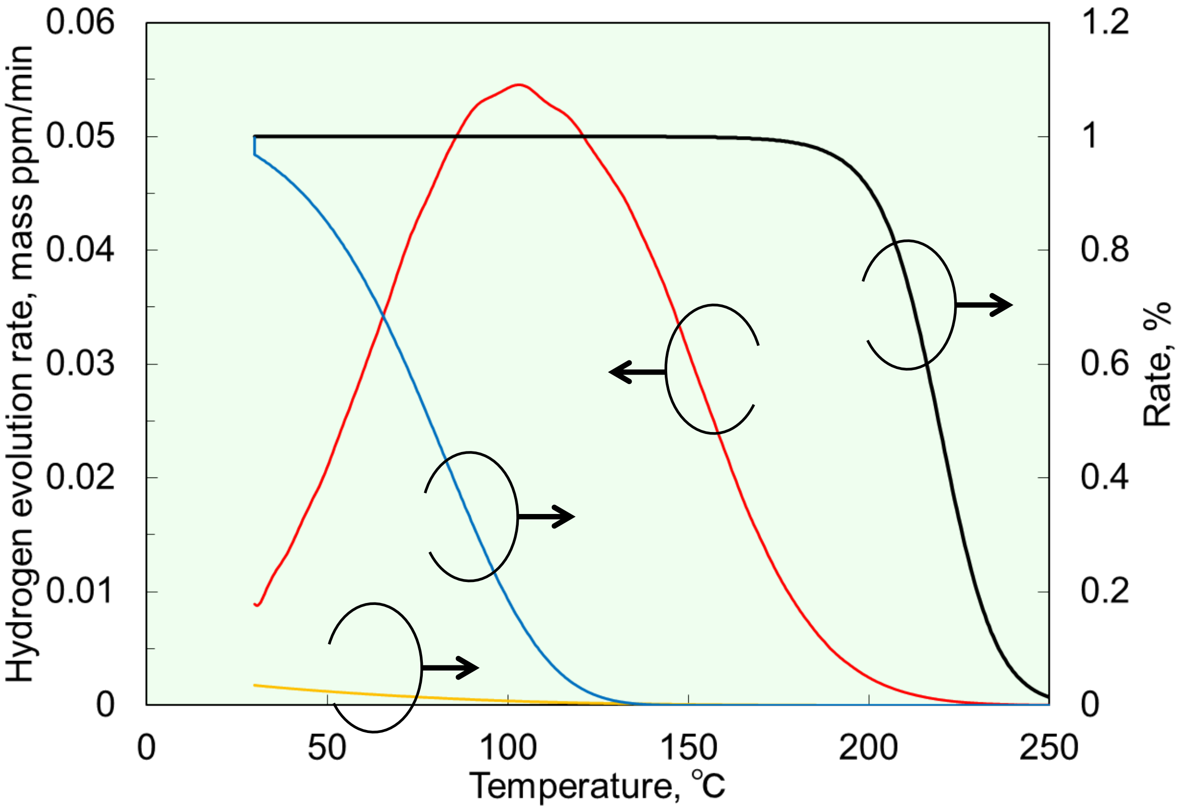
	Before value	Adjust value
Diffusion activation energy	8 kJ/mol	18 kJ/mol
Void number density	233.7 /mm^2	79160.4 /mm^2
Binding energy between hydrogen and the dislocation		37.5 kJ/mol
Dislocatio		

In order to fitted both curve, diffusion activation energy and void number density were adjusted. In addition, effect of dislocation trap was contained to simulation model.
⇒Both curve are fitted.

Simulation result

Pure iron
Creep ruptured(10MPa/700°C)

— Hydrogen evolution curve
— Void coverage rate
— Occupation rate of the dislocation by hydrogen
— Metal surface coverage rate

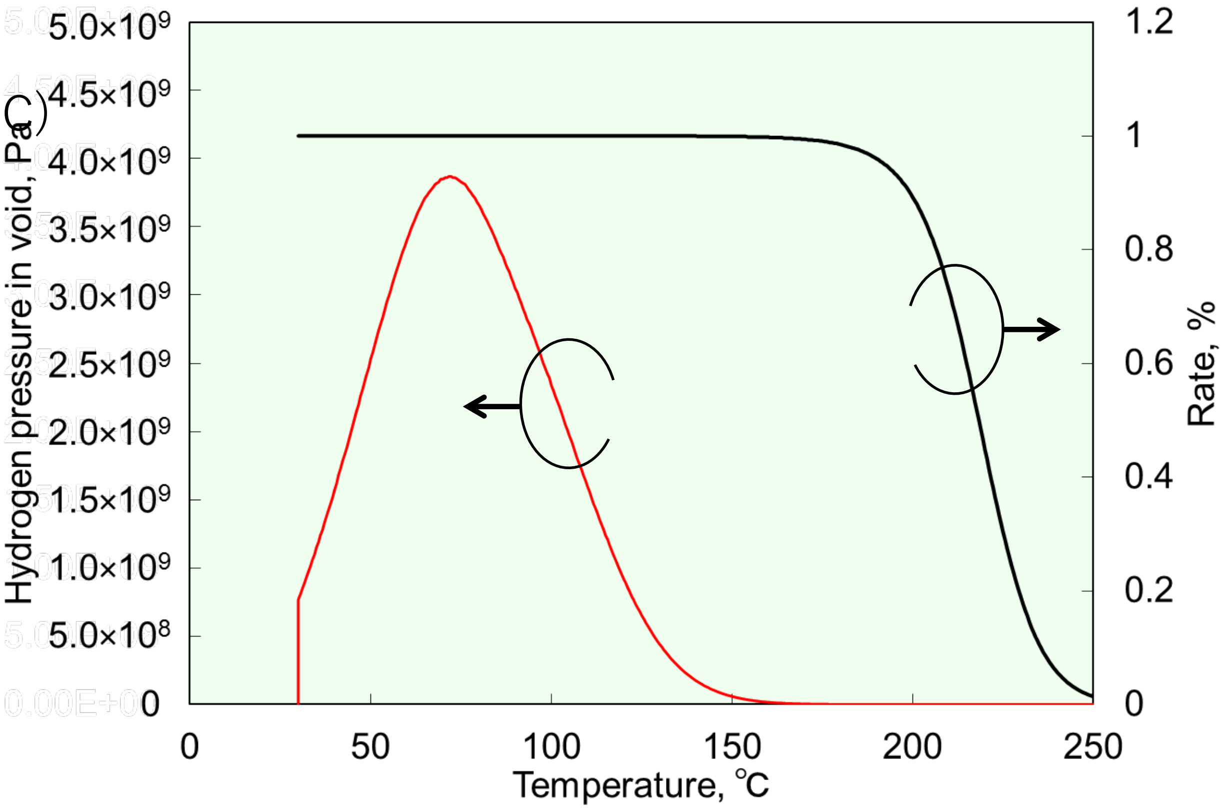


- The metal surface coverage rate is very low from RT. The hydrogen of metal surface is released immediately.
- The occupation rate of the dislocation by hydrogen not be seen from about 130℃.The dislocation affects hydrogen evolution curve until about 130℃.
- Above 130℃, Only the influence of the void is seen.

Simulation result

Pure iron
Creep ruptured(10MPa/700°C)

— Hydrogen pressure in void
—Void coverage rate



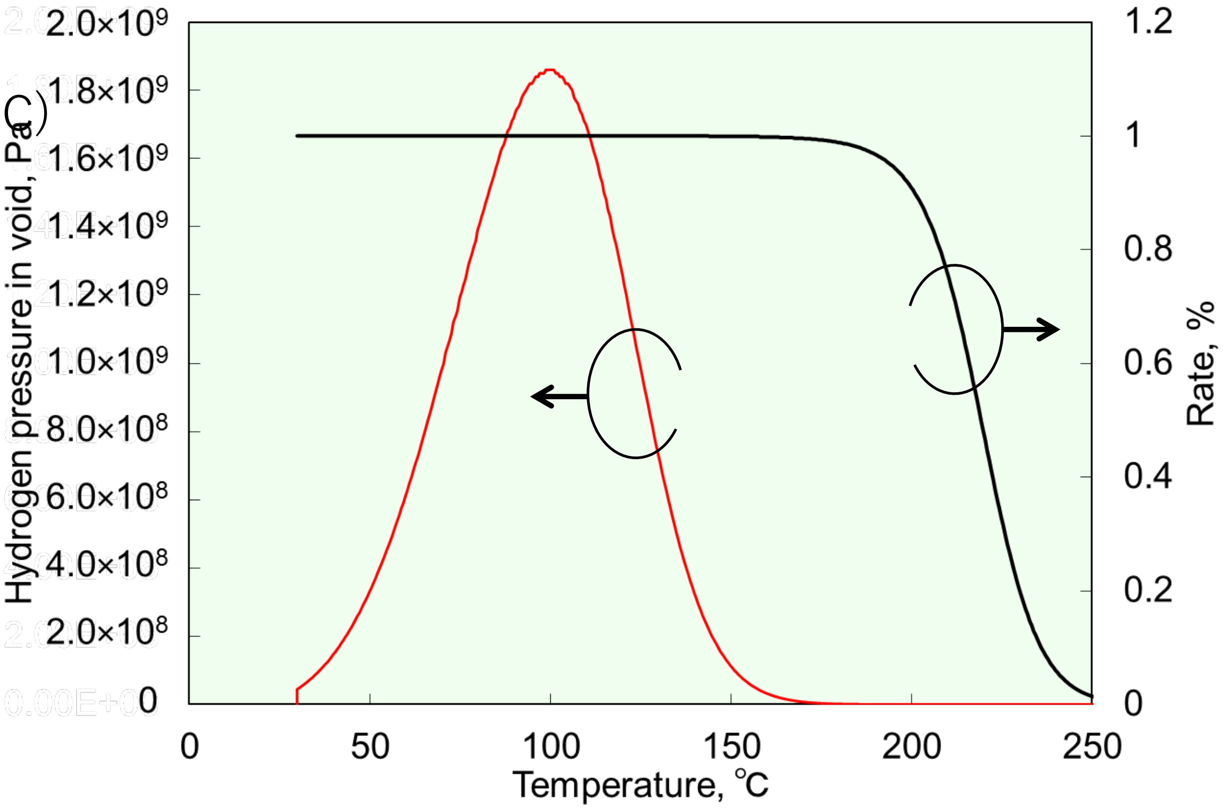
The hydrogen pressure in void disappears about 160℃ and the void coverage rate begins to decrease.

Simulation result

Pure iron
Creep ruptured(10MPa/700°C)

— Hydrogen pressure in void

—Void coverage rate

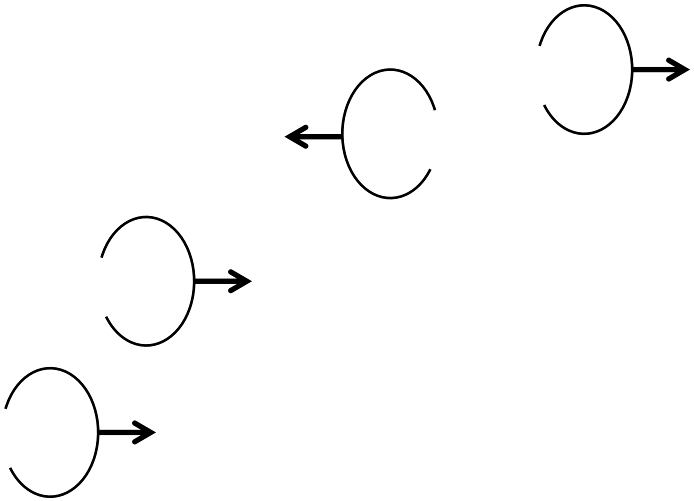


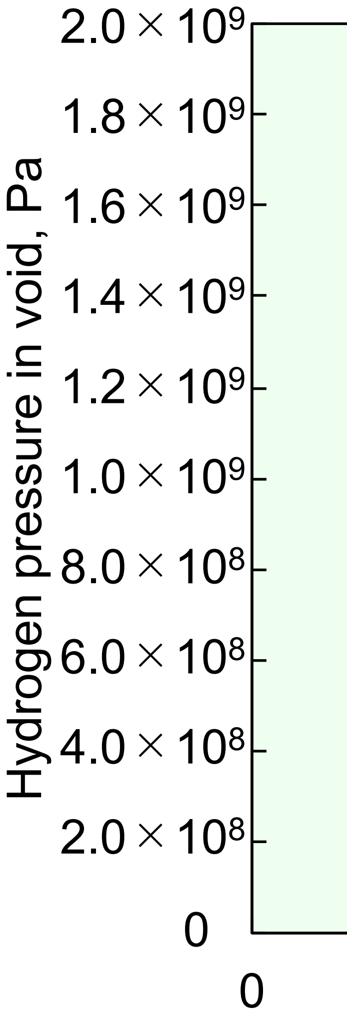
The hydrogen pressure in void disappears about 170℃ and the void coverage rate begins to decrease.

Simulation result of hydrogen evolution curve

Pure iron
Creep ruptured(10MPa/700°C)

— Simulation result of hydrogen evolution curve
—Void coverage rate
— Occupation rate of the dislocation by hydrogen
— Metal surface coverage rate

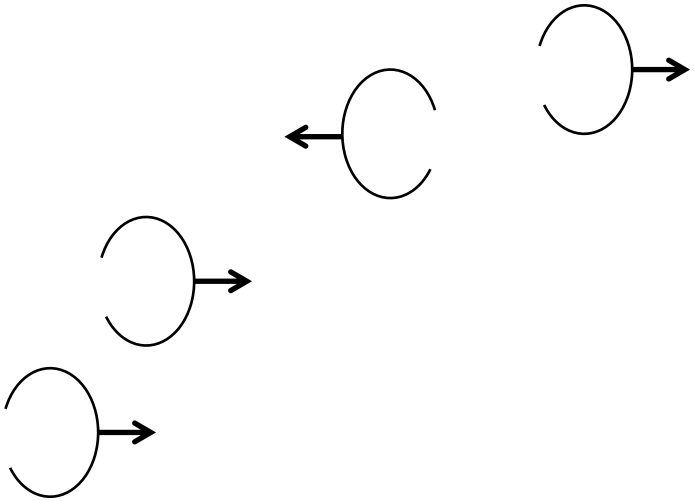


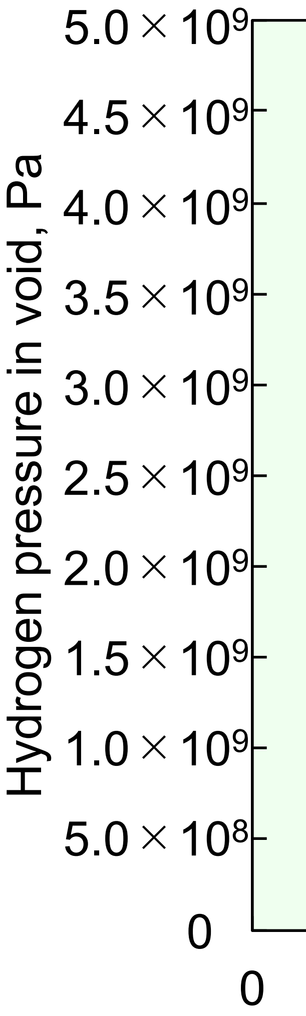


Simulation result of hydrogen evolution curve

Pure iron
Creep ruptured(10MPa/700°C)

— Simulation result of hydrogen evolution curve
—Void coverage rate
— Occupation rate of the dislocation by hydrogen
— Metal surface coverage rate

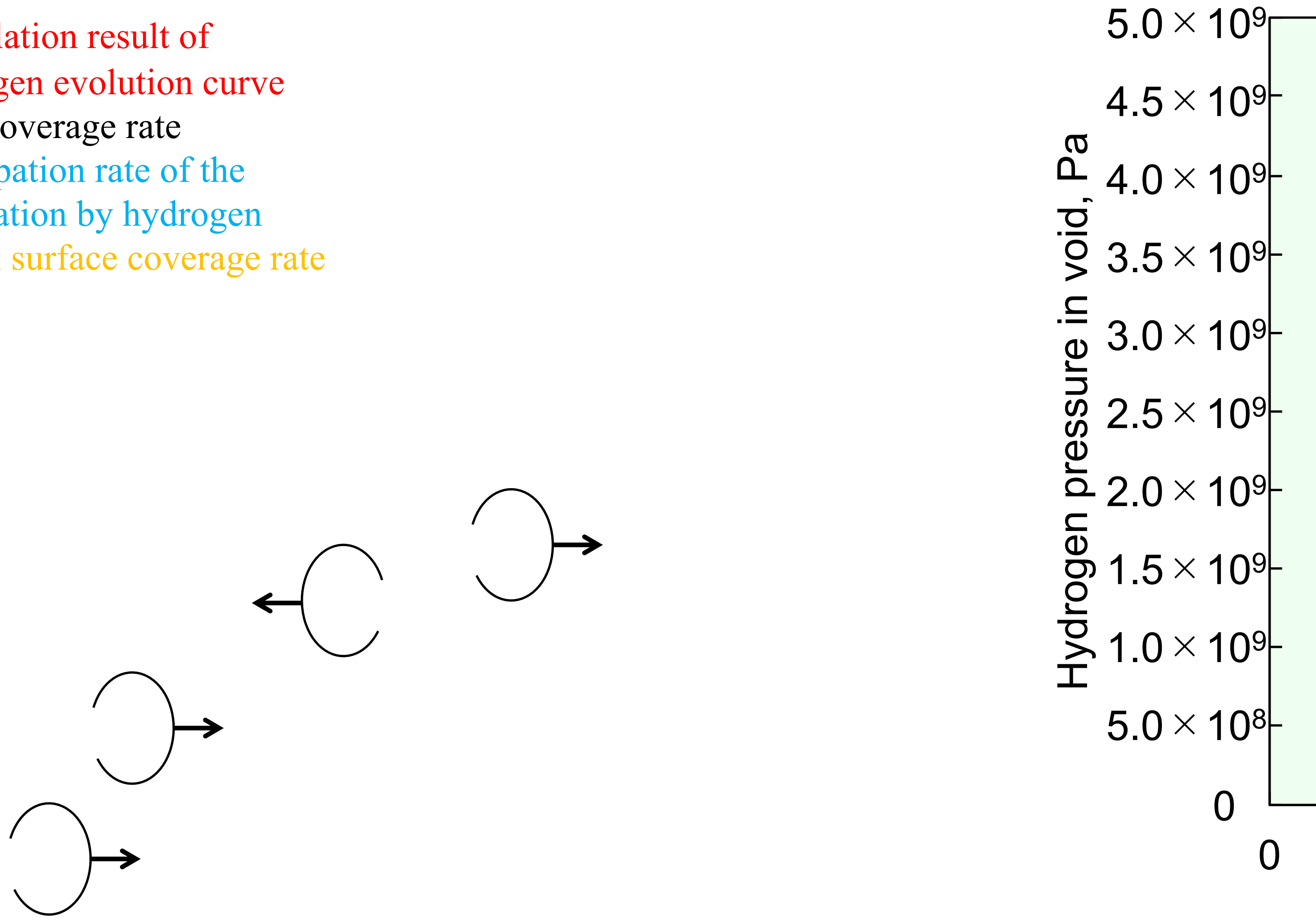




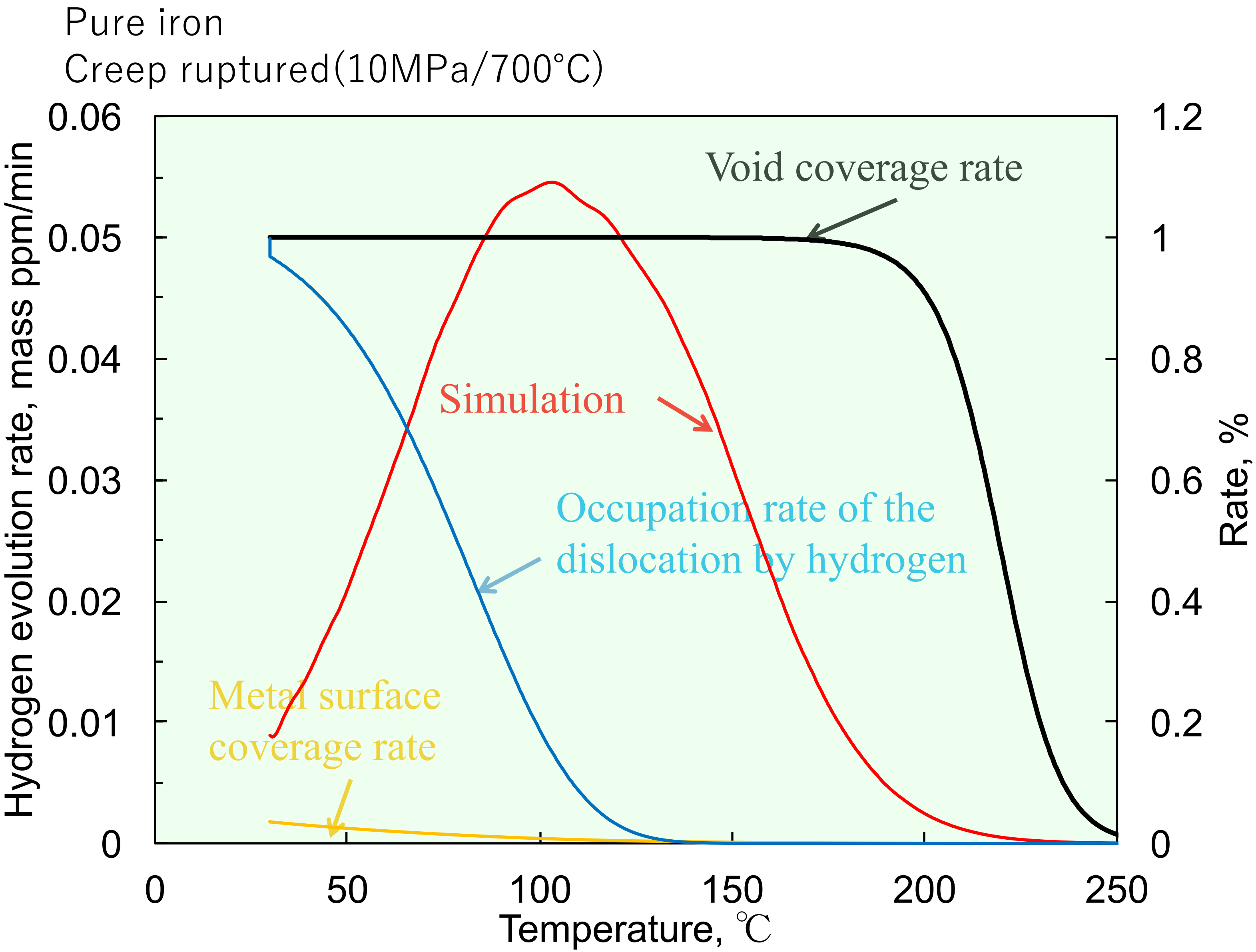
Simulation result of hydrogen evolution curve

Pure iron
Creep ruptured(10MPa/700°C)

— Simulation result of hydrogen evolution curve
—Void coverage rate
— Occupation rate of the dislocation by hydrogen
— Metal surface coverage rate

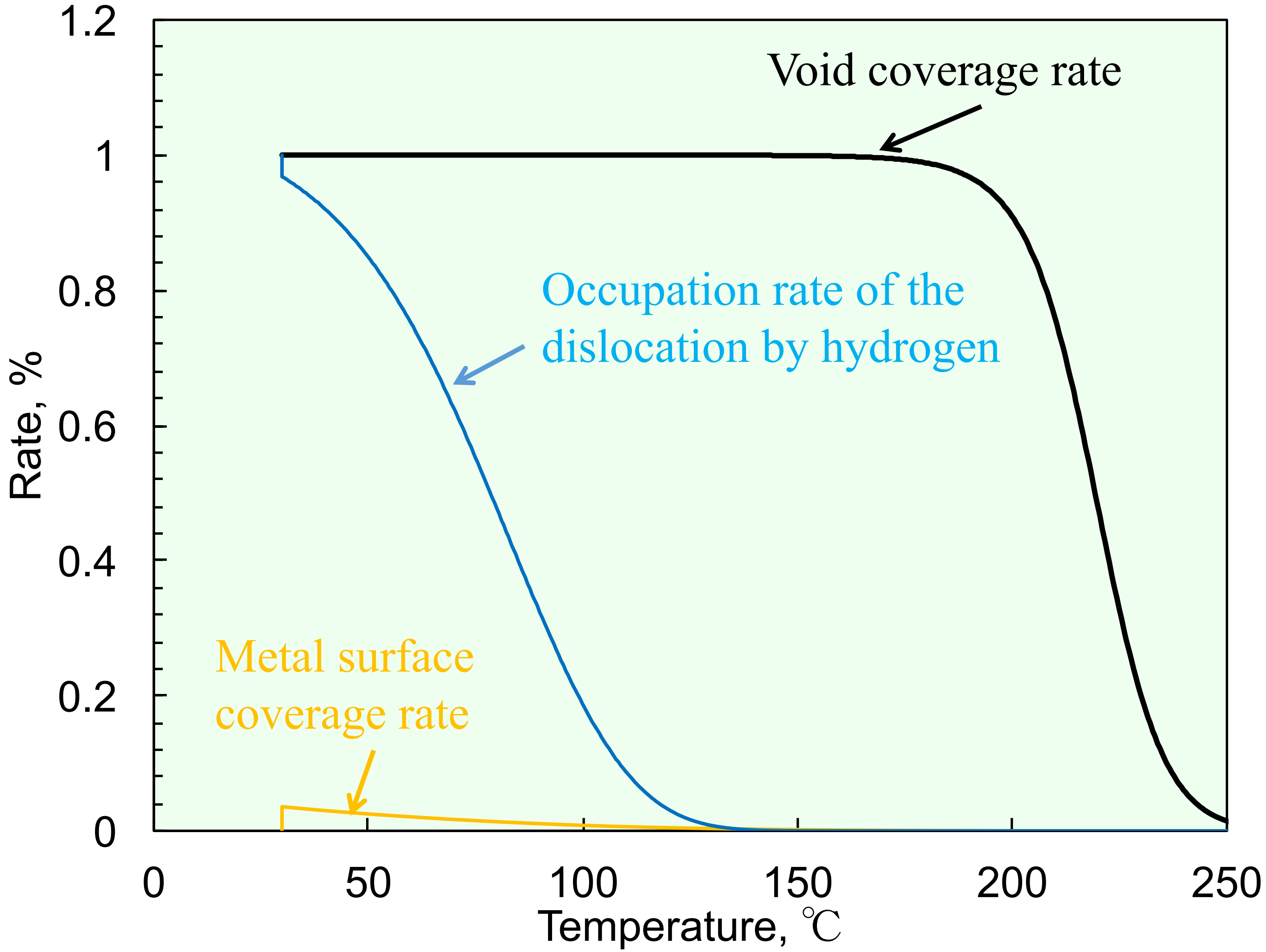


Simulation result of hydrogen evolution curve

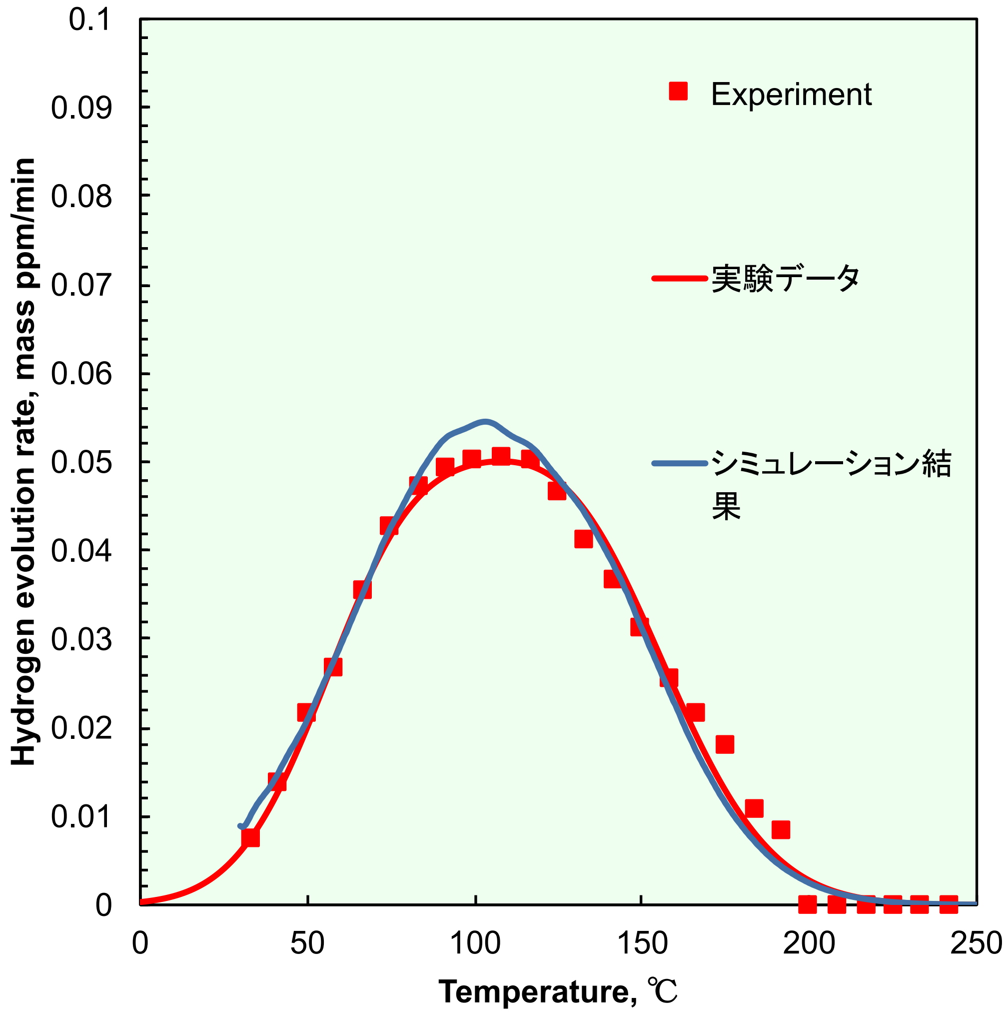


Simulation result of hydrogen evolution curve

Pure iron
Creep ruptured(10MPa/700°C)



水素の移動の活性化エネルギーを変化させた時のフィッティング結果



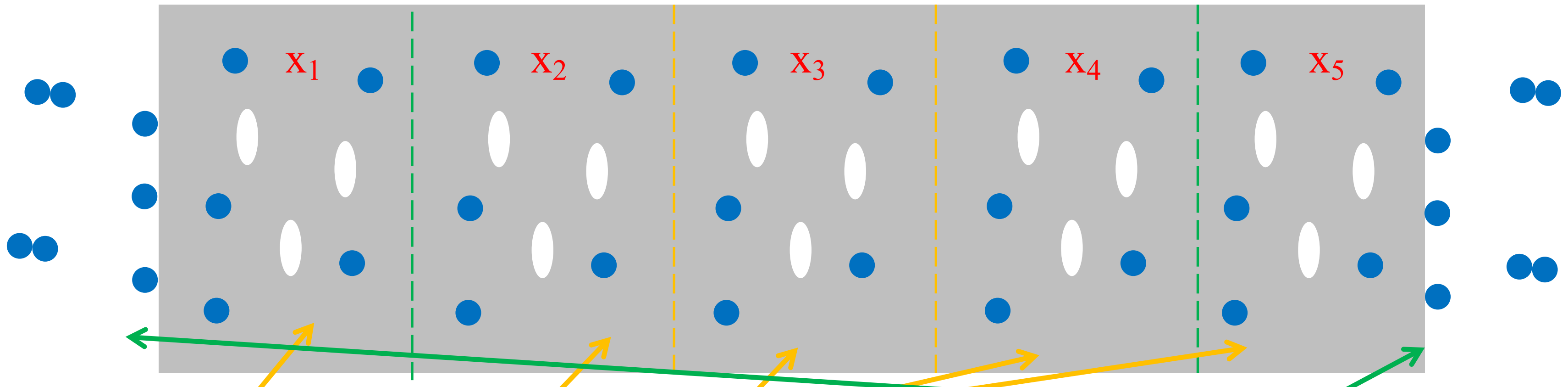
シミュレーション結果1の条件（トラップサイト1つ＋キャビティ）

拡散の頻度因子：D_0=1.5×$10^{-8}[m^2/s]$
トラップサイト濃度：2.59128×10^{-4}
キャビティ濃度：1.295×10^{-8}
水素の活性化エネルギー：18$[kJ/mol]$
トラップサイトの結合エネルギー：37.5$[kJ/mol]$
吸着サイトから固溶サイトへ侵入の
活性化エネルギーEA：77$[kJ/mol]$
固溶サイトから吸着サイトへ逆戻りするための
活性化エネルギーEB：32$[kJ/mol]$
溶解熱ES：27$[kJ/mol]$

Summary

1. In the iron, 100% of 4F sites and about 8% of 2F sites of the void surface (100) were covered, hydrogen gas was found to be precipitated in the void.
2. The hydrogen gas existed in a vacancy cluster consisting of more than 27 vacancies in the iron.
3. The simulation model was developed to consider the void.
4. In creep ruptured pure iron, the simulational curve did not correspond with the experimental one. The experimental curve was influenced by the defects which cannot be observed by SEM.
5. The hydrogen of metal surface was released immediately.
6. The dislocation affected hydrogen evolution curve until about 130℃.
7. Above 130℃, Only the influence of the void was seen.
8. The hydrogen pressure in void disappeared about 160℃ and the void coverage rate began to decrease.

水素放出シミュレーションモデル



固溶水素濃度変化速度

$$\frac{dx_n}{dt} = N_t S \frac{f_3 - f_4}{N_1} + D\frac{x_{n+1} + x_{n-1} - 2x_n}{N^2}$$

$$D = D_0 \exp(\frac{-E_B}{kT})$$

N_tキャビティ数密度
S 試料表面積
D 水素拡散係数 D_0拡散係数の頻度因子
E_B: 拡散の活性化エネルギー
k : ボルツマン定数
N_1, N 試料厚さ

N_1（全原子数/キャビティ表面原子数）

N（セルの厚さ）

固溶水素濃度変化速度

$$\frac{dx}{dt} = \frac{-f_5 + f_6}{N_2} + D\frac{x_{1\ or\ 5} - 2x_n}{N^2}$$

N_2:試料厚さ

N_2（全原子数/試料表面原子数）

キャビティ表面の水素のフラックス

$f_{3:}$:吸着サイトから固溶サイトへの侵入

$f_{4:}$:固溶サイトから吸着サイトへ侵入

試料表面の水素のフラックス

$f_{5:}$:固溶サイトから吸着サイトへ侵入

$f_{6:}$:吸着サイトから固溶サイトへの侵入