高圧水素ガスシール用ゴムの内部き裂発生メカニズムについての破壊力学的検討

第8回ゴムの力学研究分科会
平成23年度研究分科会 (第1回) ～水素高分子材料研究分科会～
2011年7月15日　九州大学伊都キャンパス

九州大学　水素エネルギー国際研究センター　水素安全学研究部門
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Introduction-Types of gas leakage-

・シール材に求められること

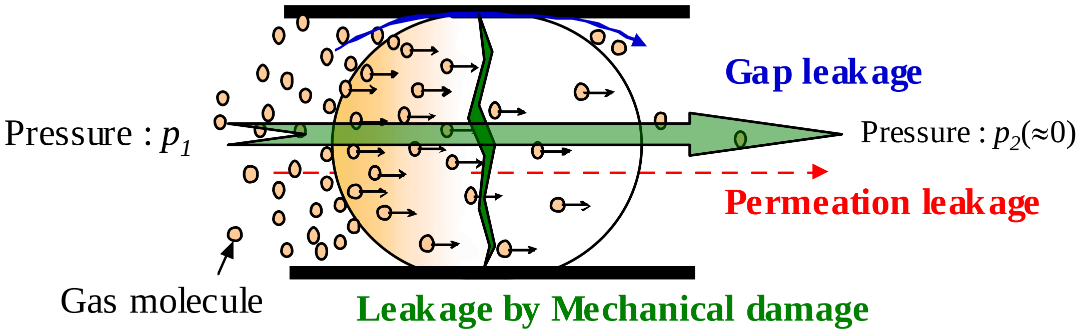
⇒ガスがリークしないようにシールすること．

・ガスリークの種類は3つに分類される．

（1）界面リーク

（2）透過リーク･･･材料のガス透過係数に依存する．

（3）破壊によるリーク･･･高圧ガス環境下で問題となる．



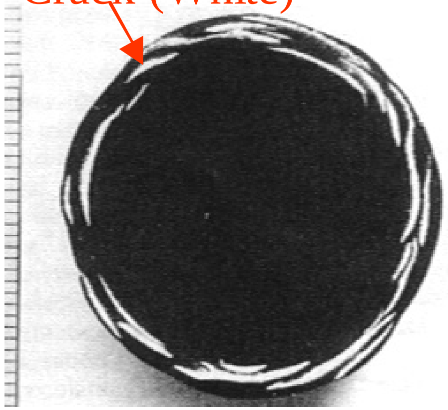
ガス透過係数

$$Q = \frac{ql}{Ap_1 t}$$

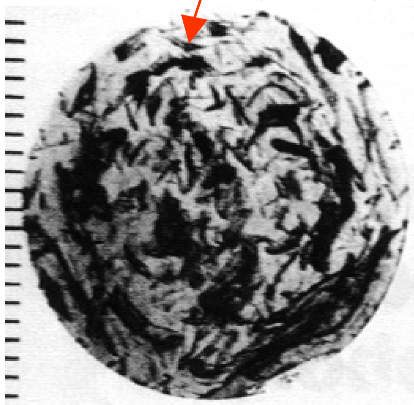
Amount of gas leakage, q
Permeation area, A
Permeation length, l

Introduction-Internal fracture of rubbers by high-pressure gas decompression-

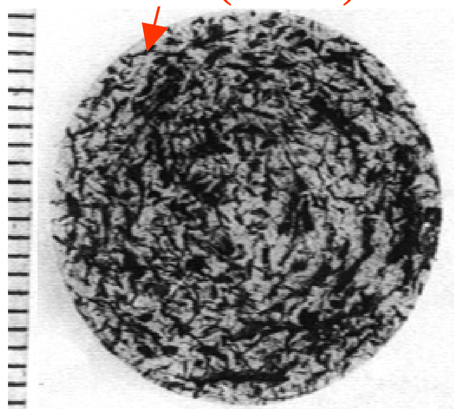
Pressure : about 40 MPa



NBR, CO_2

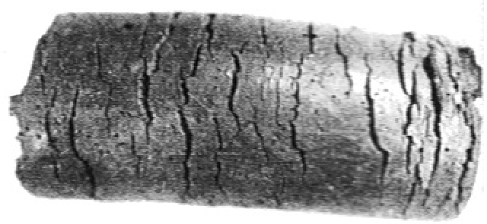


Silicon, CO_2



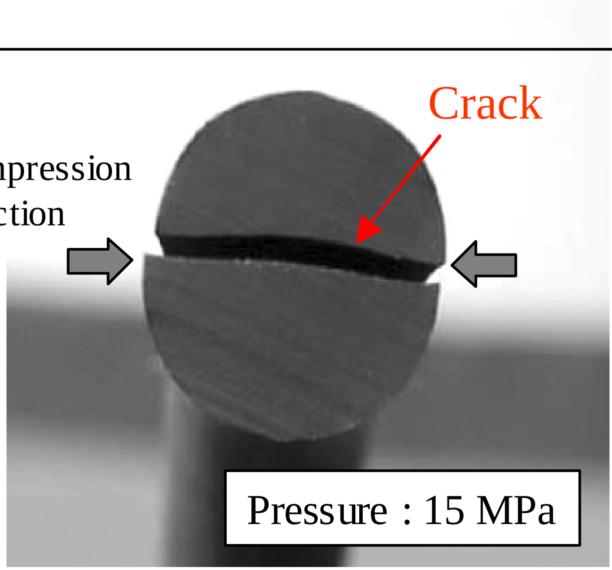
Silicon, N_2

Rapid decompression



Polyurethane, CO_2

S. Zakaria, and B. J. Briscoe, Chemtech, Vol.20, Aug, pp. 492–495 (1990).



Type of material and gas is unknown

P. Embury, Sealing Technology, Vol. 2004, pp. 6–11 (2004).

Type of material and gas is unknown

BHR group, "Elastomeric seals for rapid decompression applications in high–pressure service", HSE books (2006).

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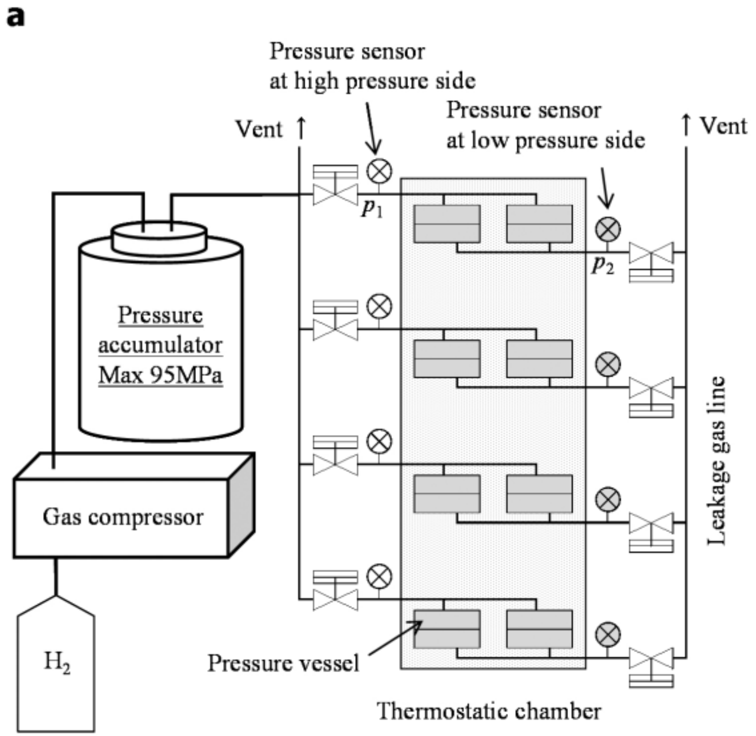
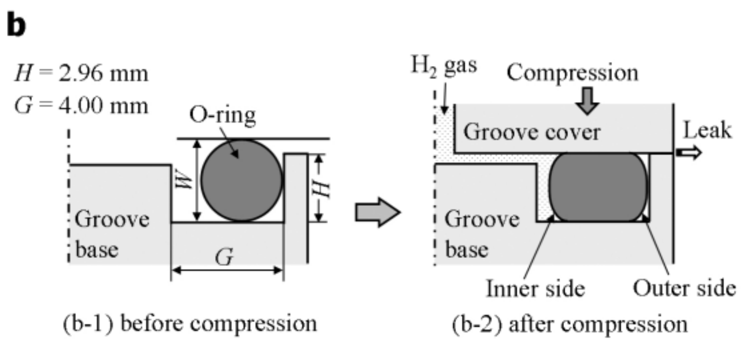
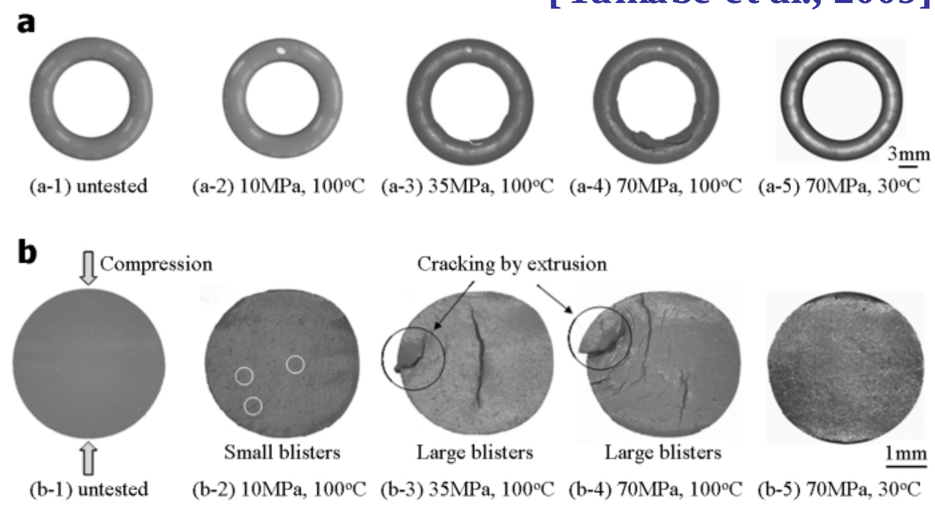
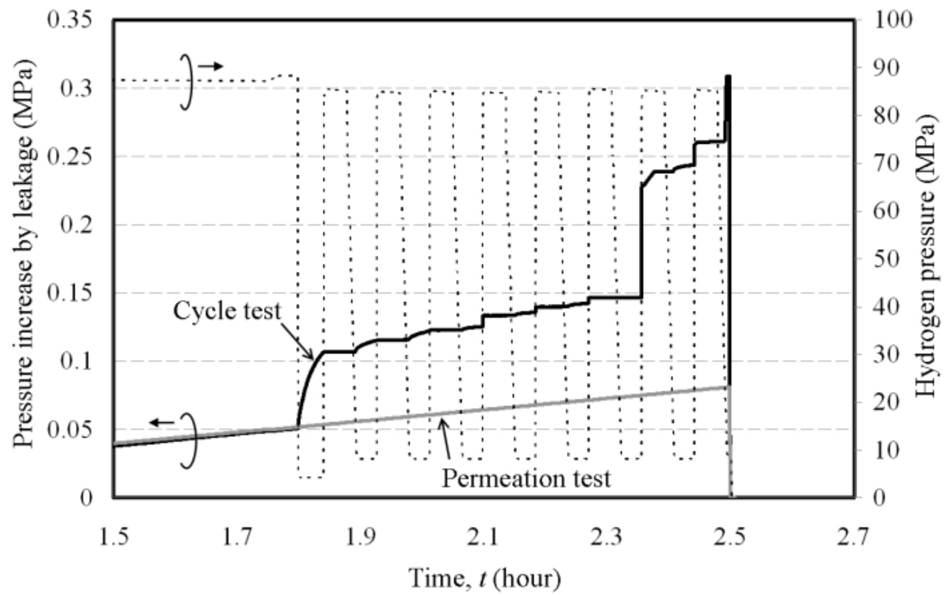
Introduction-Fracture of O-ring under high-pressure hydrogen gas-





[Yamabe et al., 2009]





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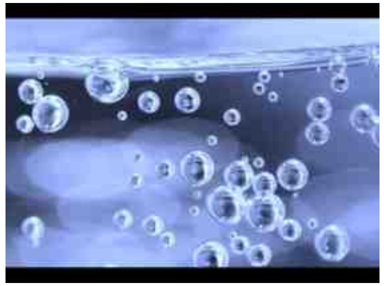
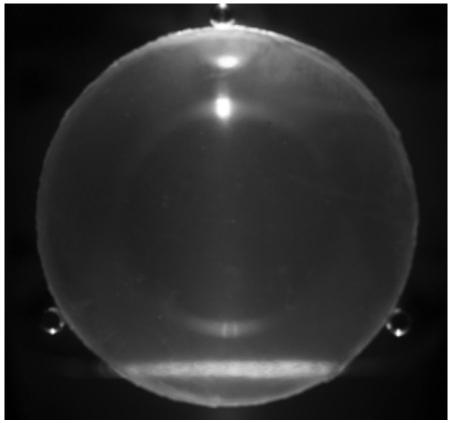
Introduction-Cavitation by high-pressure gas decompression-

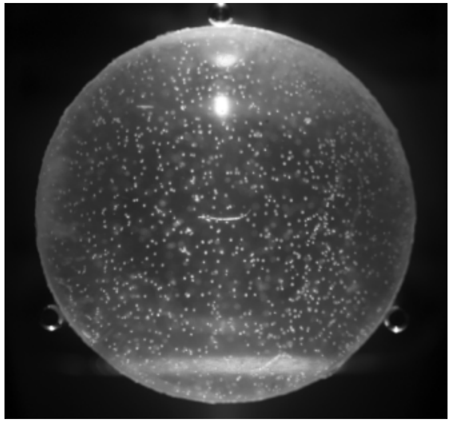
Liquid



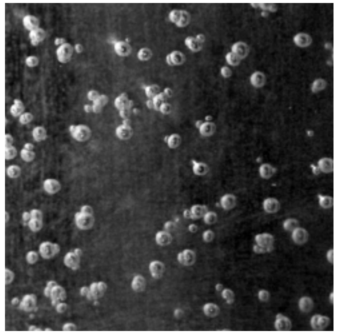
Pressurization — **Decompression**

Rubber





5 mm



5 mm

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Introduction-Process of internal fracture due to high-pressure gas decomperssion-

内部破壊プロセス

・ゴム分子鎖間から気泡が形成される（液体からの気泡形成と同様）．

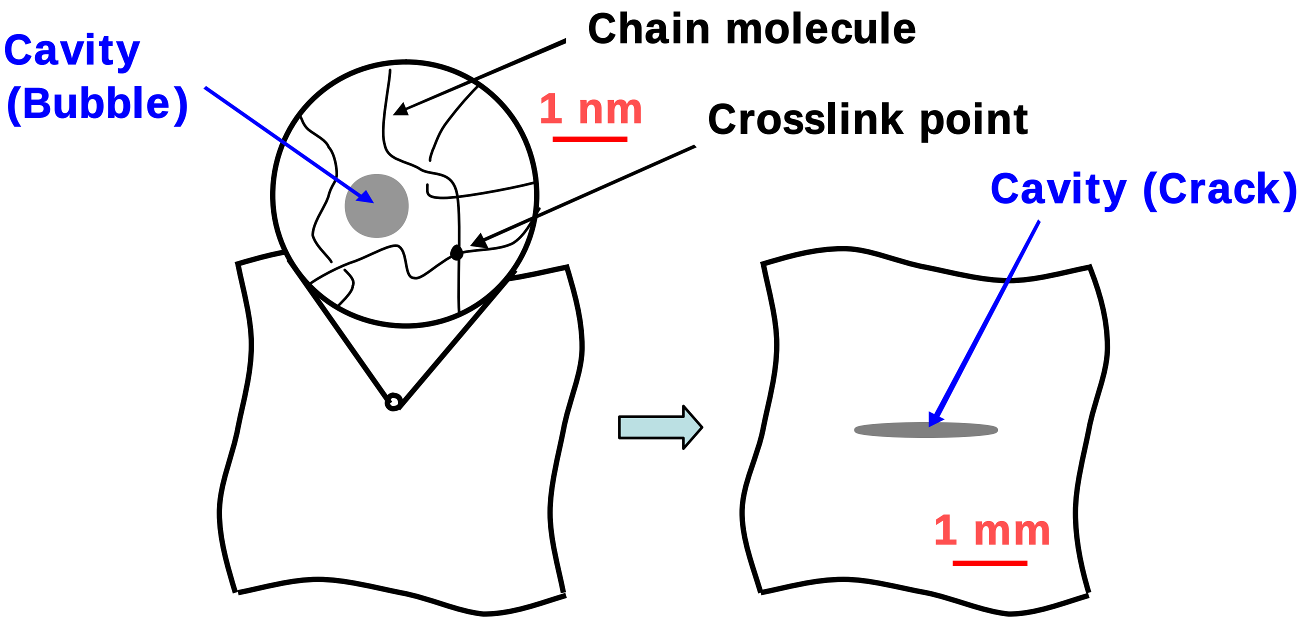
・形成された気泡は分子鎖を破壊し，光学顕微鏡で観察可能なサイズに成長していく．

気泡とき裂の定義

・気泡：分子鎖間に発生した巨視的な分子鎖切断を伴わないキャビティ
（光学顕微鏡で観察困難なミクロンサイズ以下）

・き裂：気泡を起点として発生する巨視的な分子鎖切断を伴うキャビティ
（光学顕微鏡で観察可能なミクロンサイズ以上）

・このような内部き裂は，一般的にブリスタと呼ばれる．



Experimental-Material-

- Since cracks initiated from the interior, a transparent rubber material was employed.
- Filler is not added.

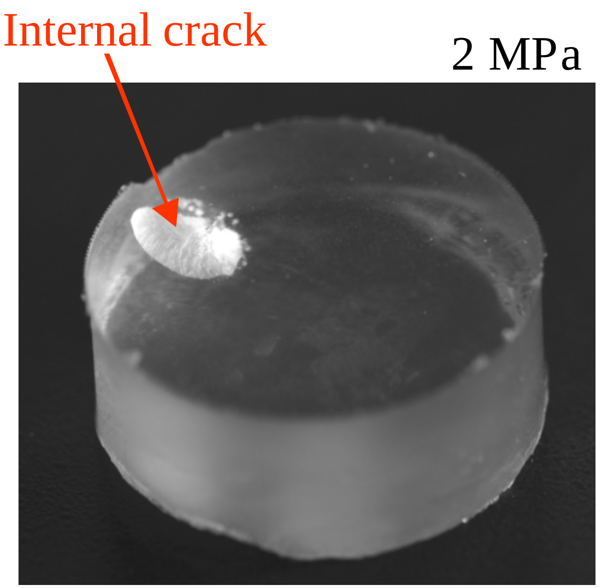
Material compound (phr)

EPDM	100
Dicumyl peroxide	1.6
Stearic acid	0.5

(phr: parts per hundred rubber)

Density and hardness

Density (g/cm^3)	0.873
Hardness	A 51



Cylindrical specimen
(ϕ 29.0 mm × 12.5 mm)

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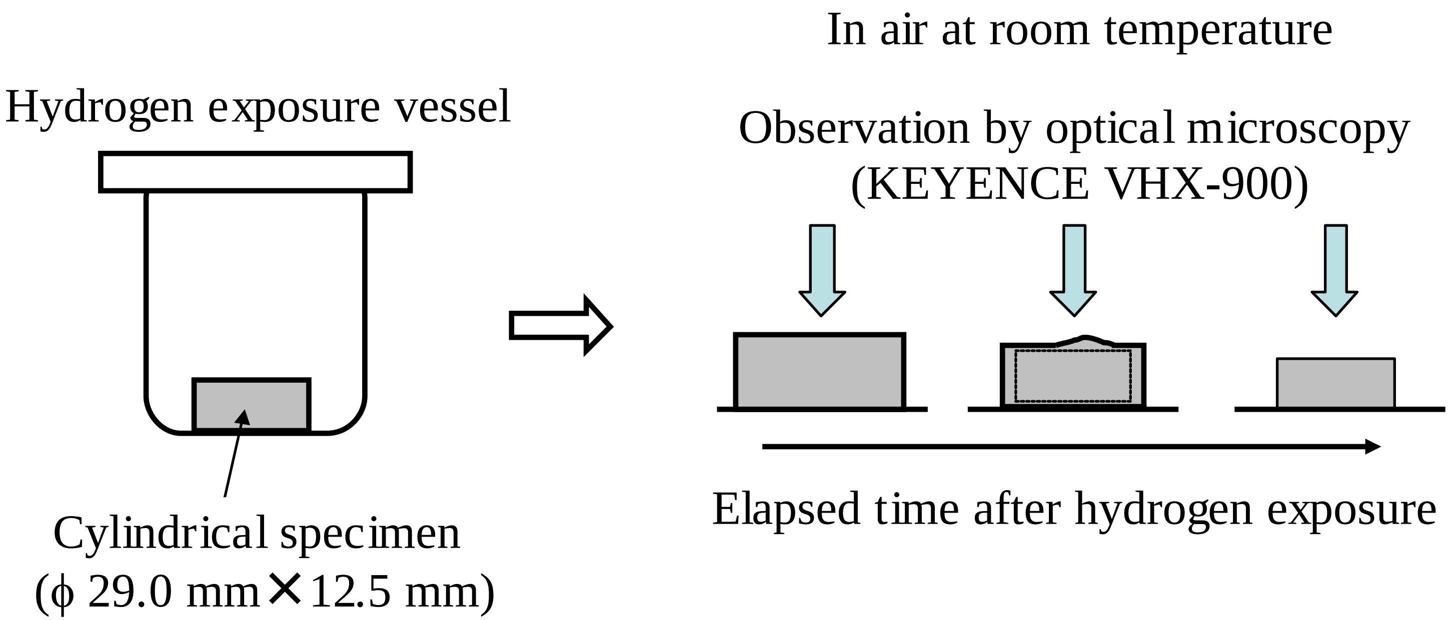
Experimental-Hydrogen exposure and observation of crack-

- Cylindrical specimen (ϕ 29.0 mm × 12.5 mm) was employed.
- Hydrogen exposure was conducted by using 10 MPa hydrogen vessel at 30 ^{o}C.
- After decompression, crack initiation behavior was observed by using optical microscopy in air at room temperature.



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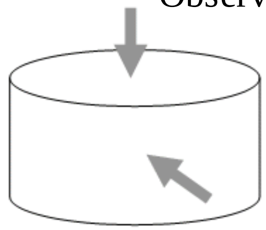
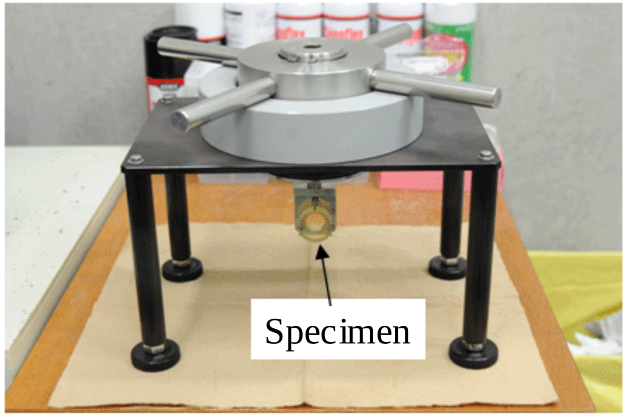
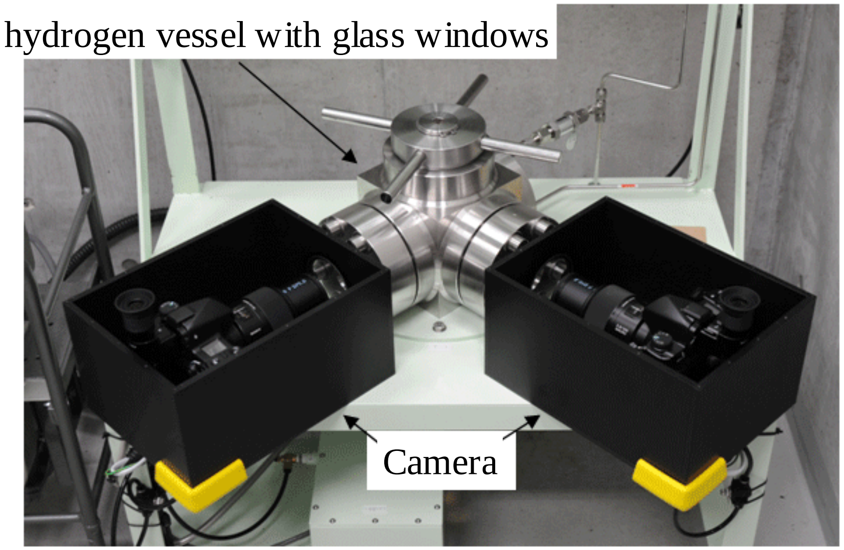
Experimental-Hydrogen exposure and observation of crack-

- Hydrogen vessel with glass windows was employed; then, crack initiation behavior of the rubber during pressurization was also observed.







Camera: SONY α900 DSLR–A900, SAL100M28

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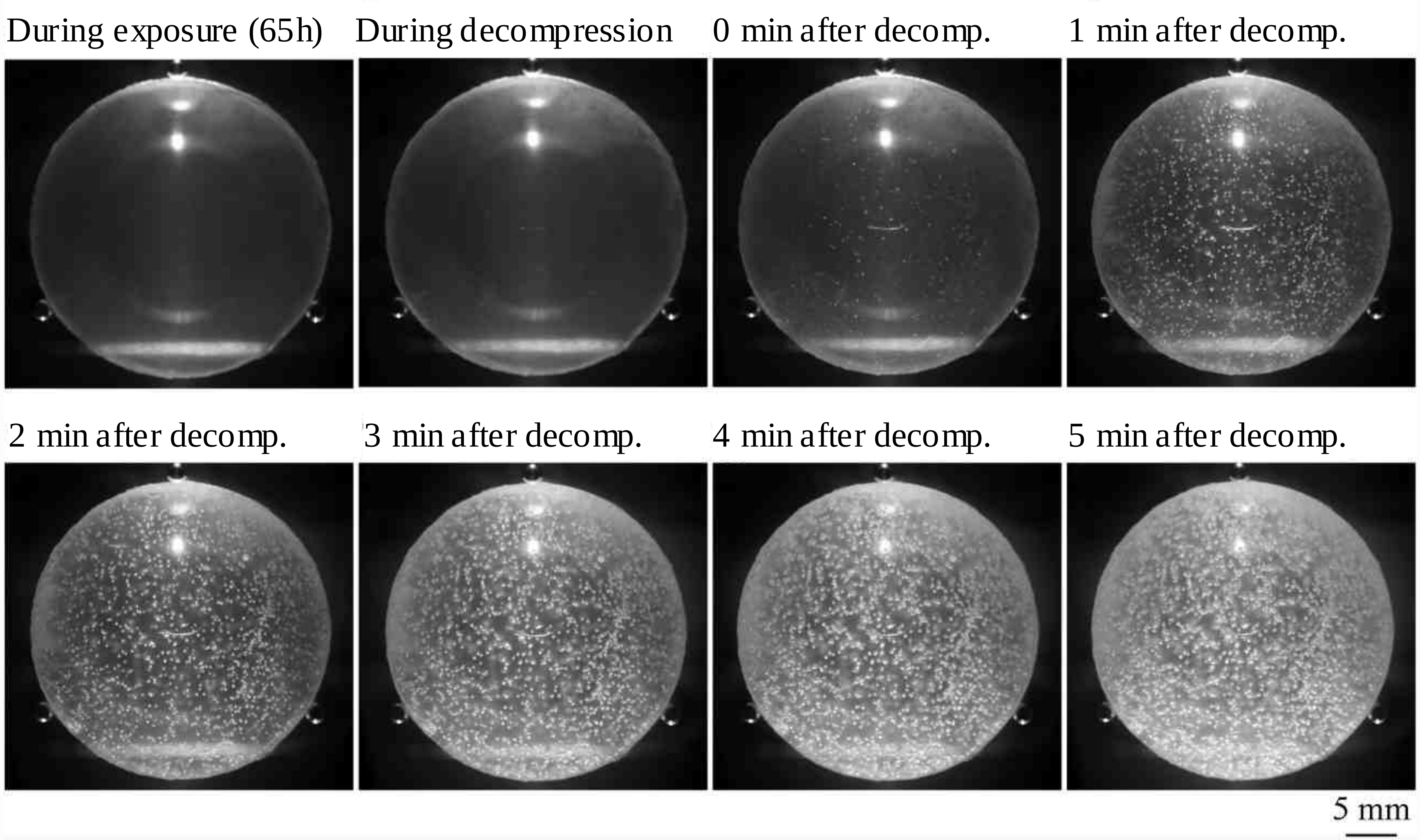
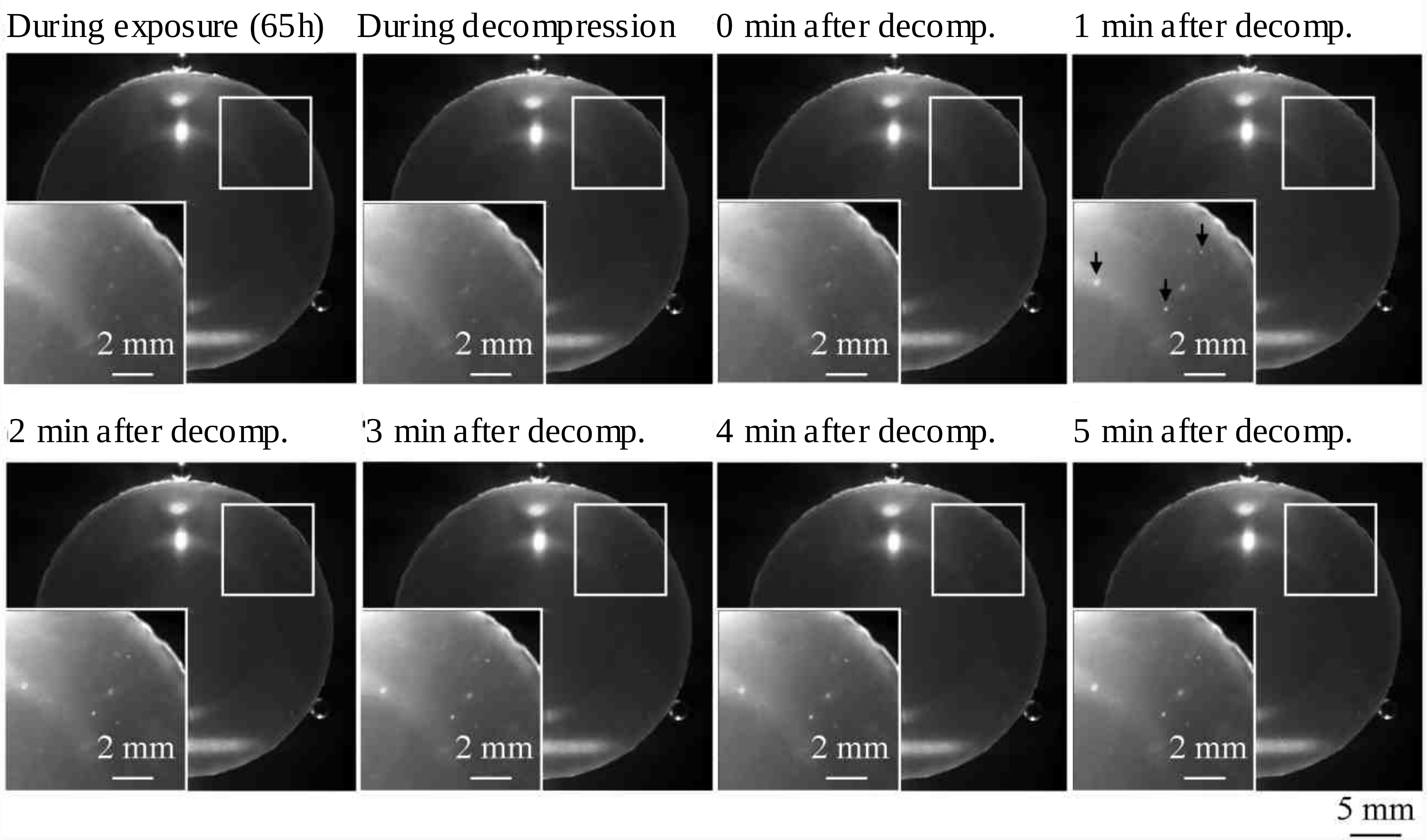
Results and discussion-10 MPa hydrogen exposure-

- The specimen was exposed to hydrogen gas at 10 MPa and 25 ^{o}C for 65 h.
- No cracks were observed during hydrogen exposure and during decompression.
- Many cracks were observed after decompression, and grew with the elapsed time after decompression.



Results and discussion-2 MPa hydrogen exposure-

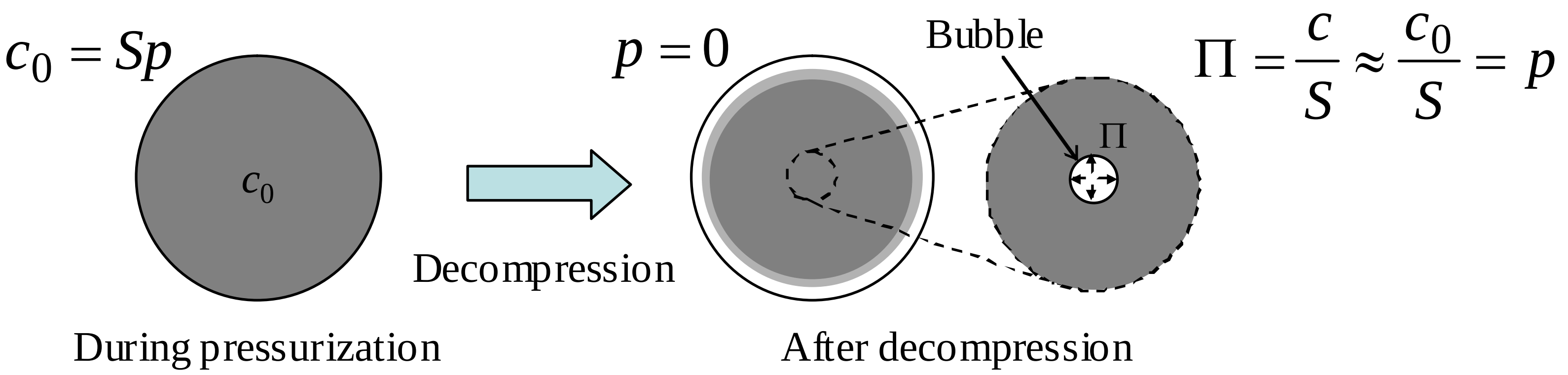
- The specimen was exposed to hydrogen gas at 2 MPa and 25 °C for 65 h.
- Cracks initiated after decompression as well as 10 MPa.
- The crack damage at 2 MPa was slighter that that at 10 MPa



Results and discussion-Relationship between hydrogen pressure and internal pressure-

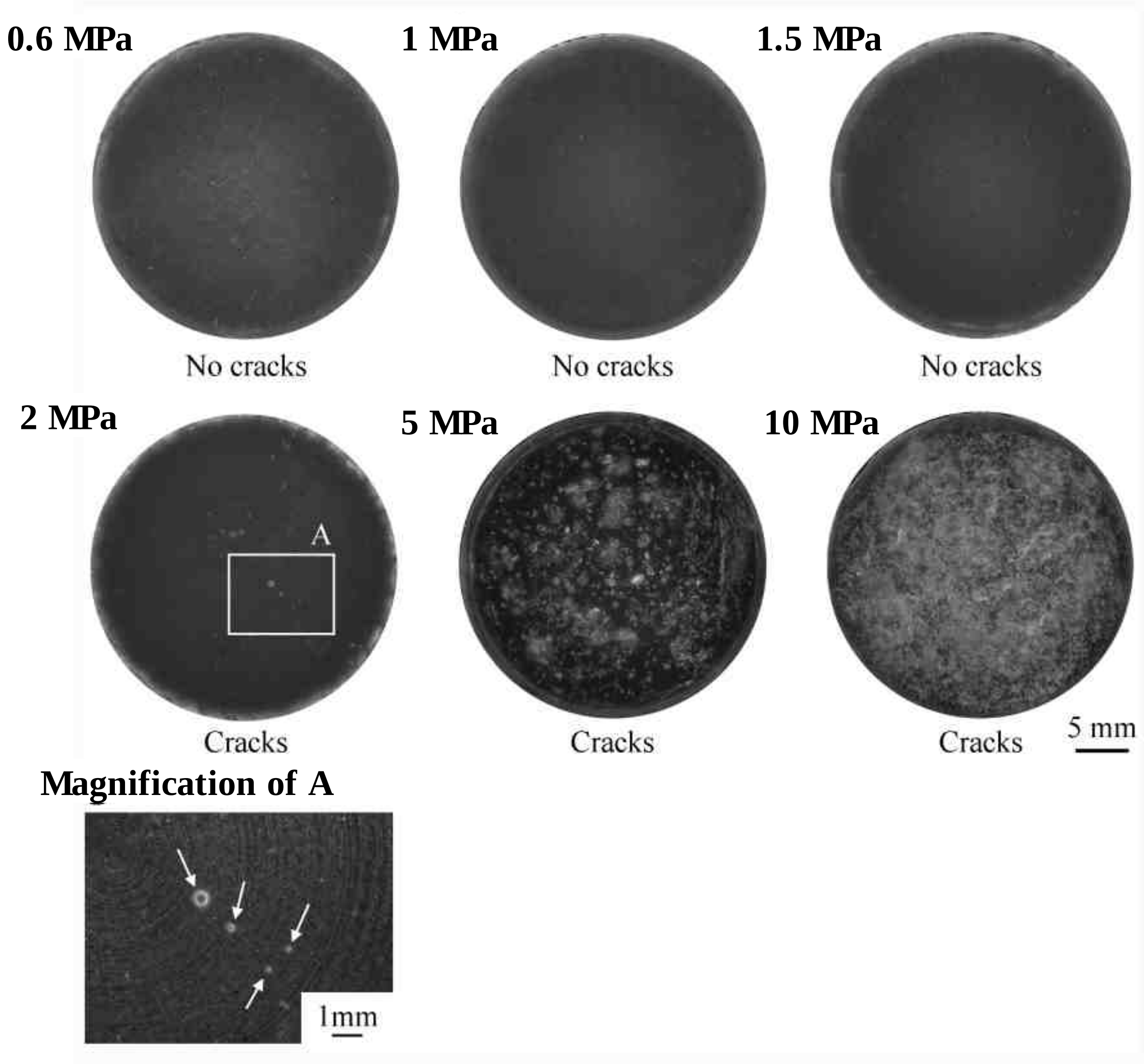
- The internal pressure (Π) of a bubble is nearly equal to hydrogen pressure (p).

⇒When a hydrogen pressure becomes higher, the internal pressure of the bubble also becomes higher.



Results and discussion-Influence of hydrogen pressure on crack damage-

- The crack damage was more serious with an increase in hydrogen pressure.
- The hydrogen pressure at crack initiation ranged from 1.5 MPa to 2.0 MPa.



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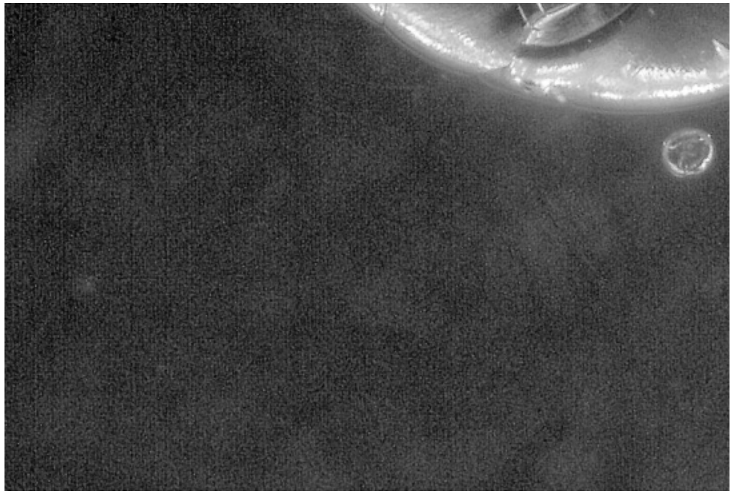
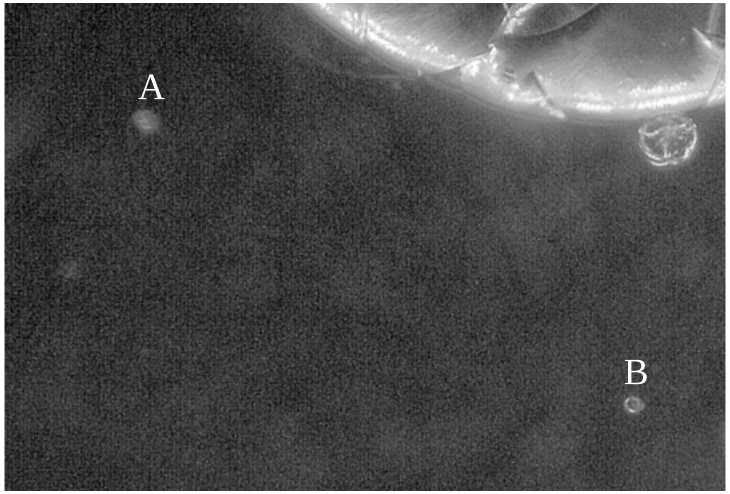
Results and discussion-3 MPa hydrogen exposure-

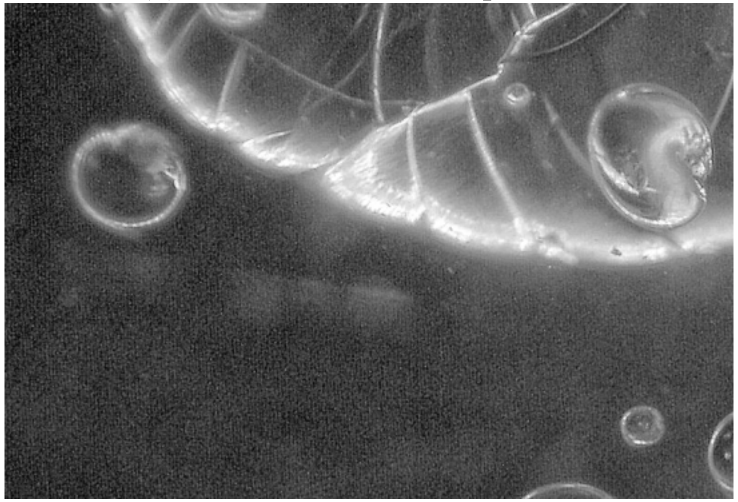
- Micrometer-size cracks initiated from the interior of rubber material.



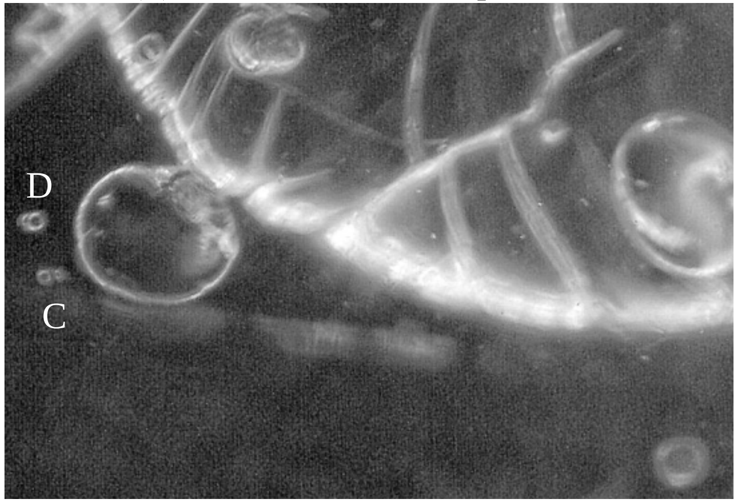
(a) 20 min after decompression



(b) 21 min after decompression



(c) 26 min after decompression

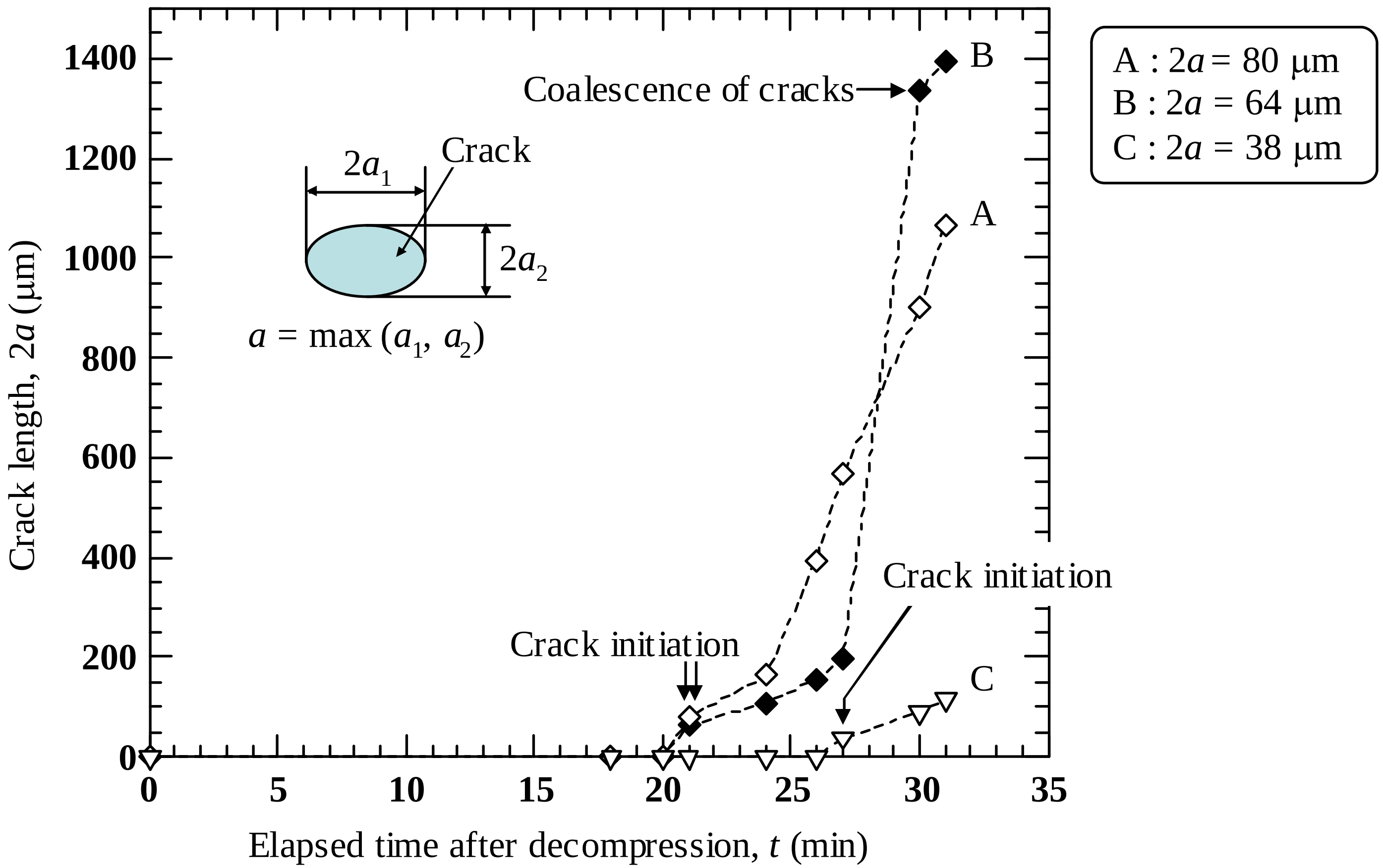


(d) 27 min after decompression

500 μm

Results and discussion-Relationship between crack length and time-

• The cracks grow with the elapsed time after decompression.
⇒This behavior is related to crack growth under constant loading.
This type of crack growth is generally referred to as static crack growth.



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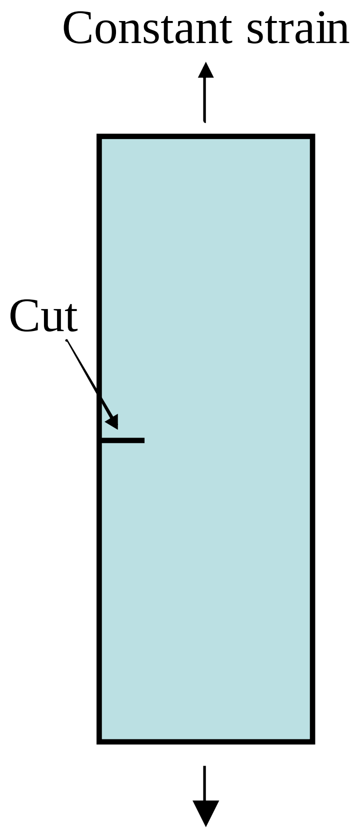
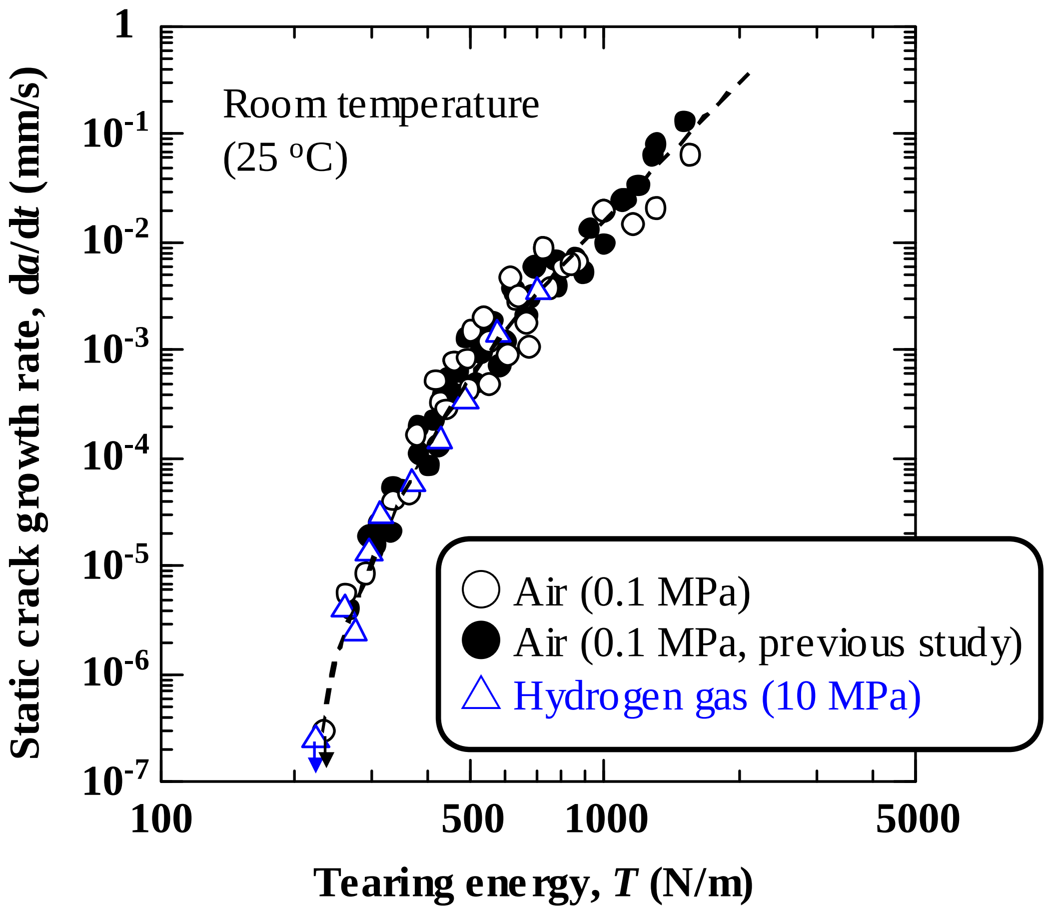
Results and discussion-Static crack growth behavior-

- Constant strain was applied to cut specimen.
- Relationship between static crack growth rate and tearing energy is obtained.





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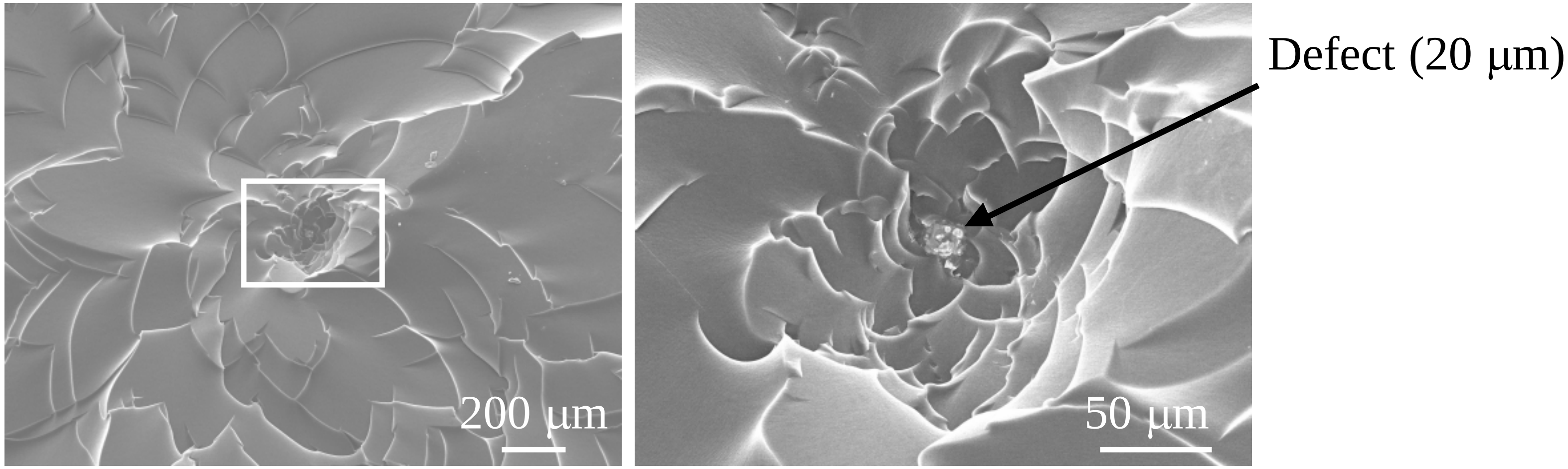
Results and discussion-SEM images of fracture surfaces-

Fracture origins can be divided into two types.

Case I : Fracture from the site with micrometer-size defect.

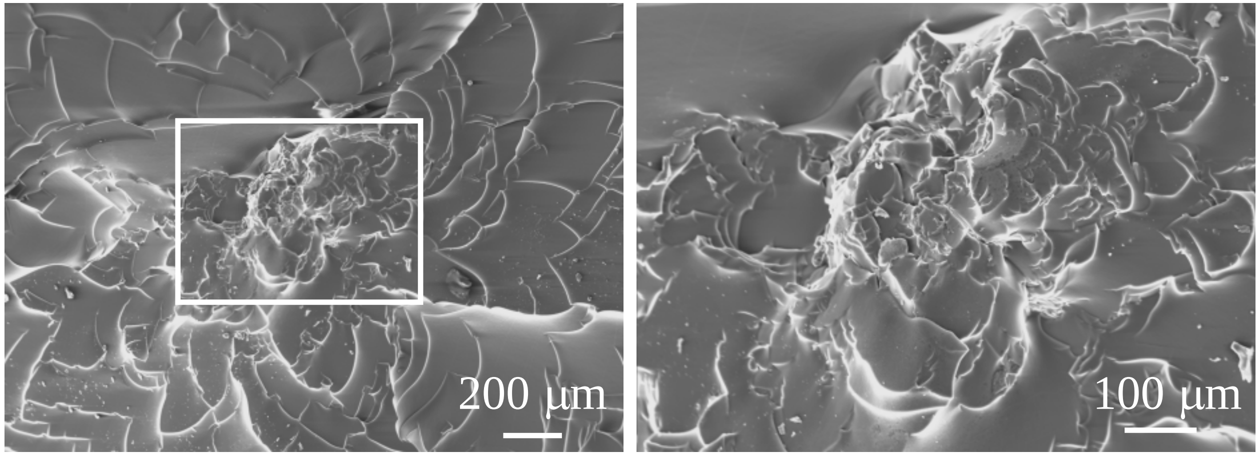
Case II : Fracture from the site without anything.

Case I



Low magnification High magnification

Case II



Low magnification High magnification

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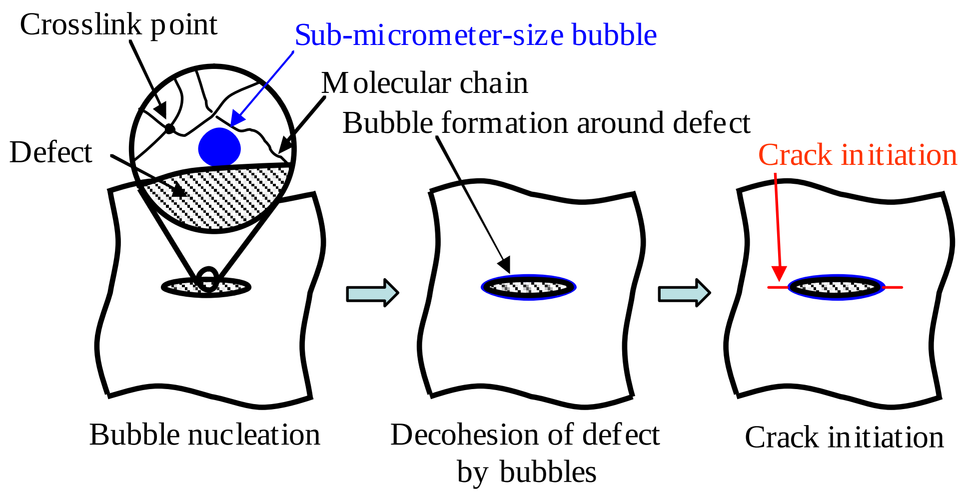
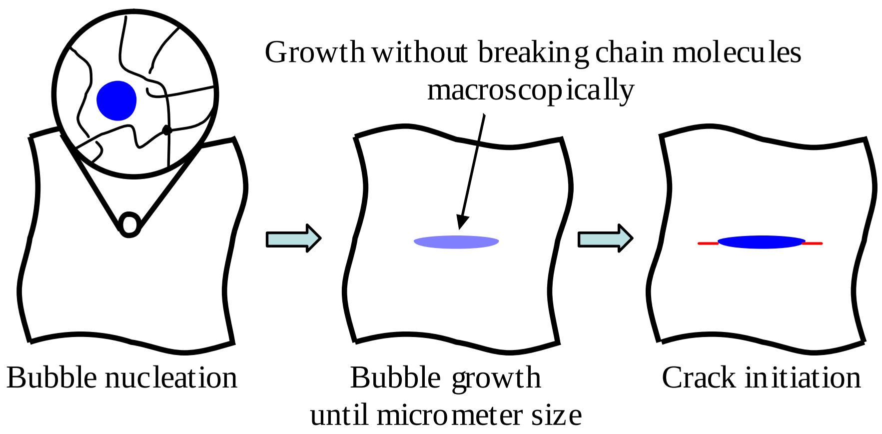
Results and discussion-Suggested fracture processes of internal fracture-

Case I
Fracture from micrometer-size defect



Case II
Fracture from site without anything



This process is not clear, since we can not see nanoscale fracture process by optical microscopy.

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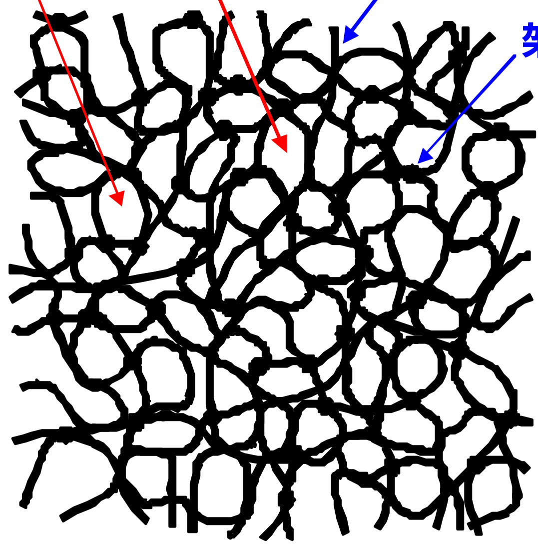
Bubble formation by change in free energy

J.

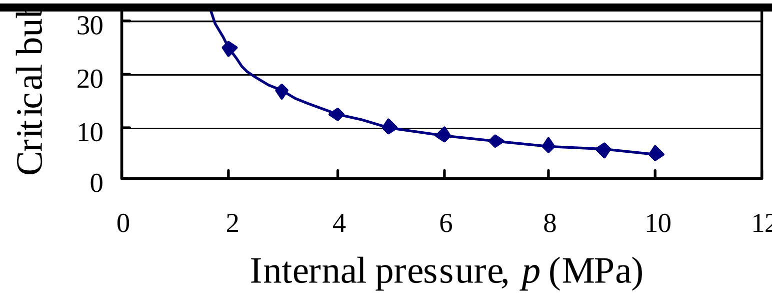
均一な構造では，圧力0.6MPaの
気泡形成を説明できない！
⇒不均一構造の存在が示唆される.

均一な網目構造のイメージ



$$a_{\mathrm{cr}} = \frac{\quad}{p}$$

$$\gamma = 25\times10^{-3}\ \mathrm{N/m}$$



* J. C. Fisher, *Journal of Applied Physics*, **19**, 1062 (1948).

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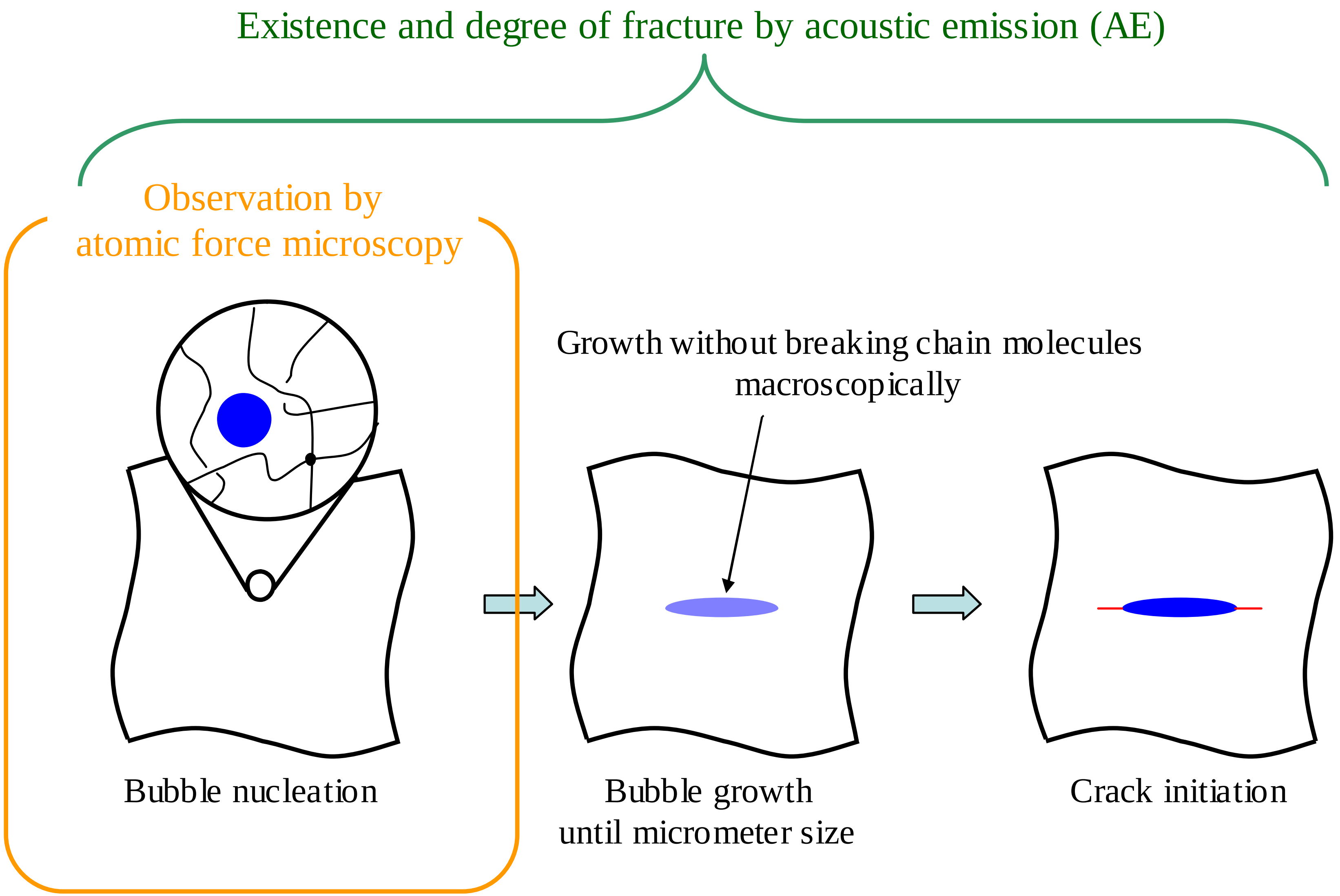
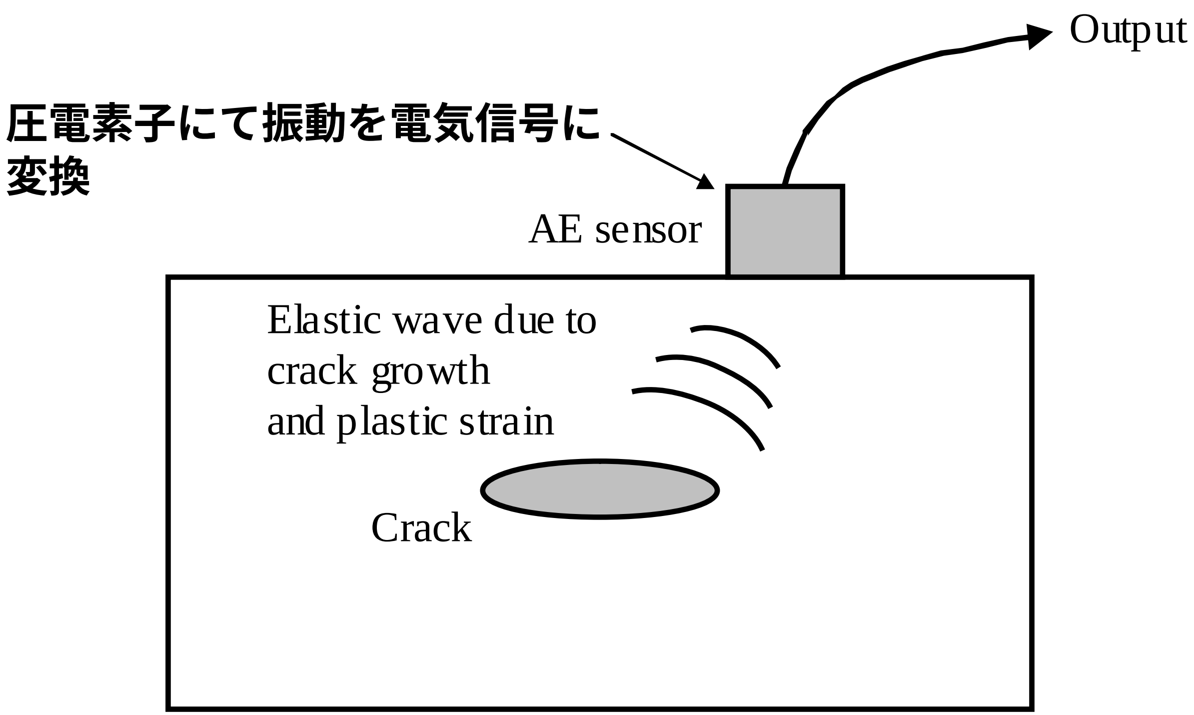
Results and discussion-Detection of Nanoscale fracture by AE and AFM-



Introduction-Acoustic emission (AE)-

・アコースティックエミッション（AE）とは
⇒き裂進展や塑性変形によって材料内部で発生する弾性波現象
　（主として20kHz以上の弾性波を対象）
・AE法
⇒AEを検出して，内部き裂を非破壊で検知する方法であり，金属材料，コンクリートおよびCFRPのき裂検知に使用されている．

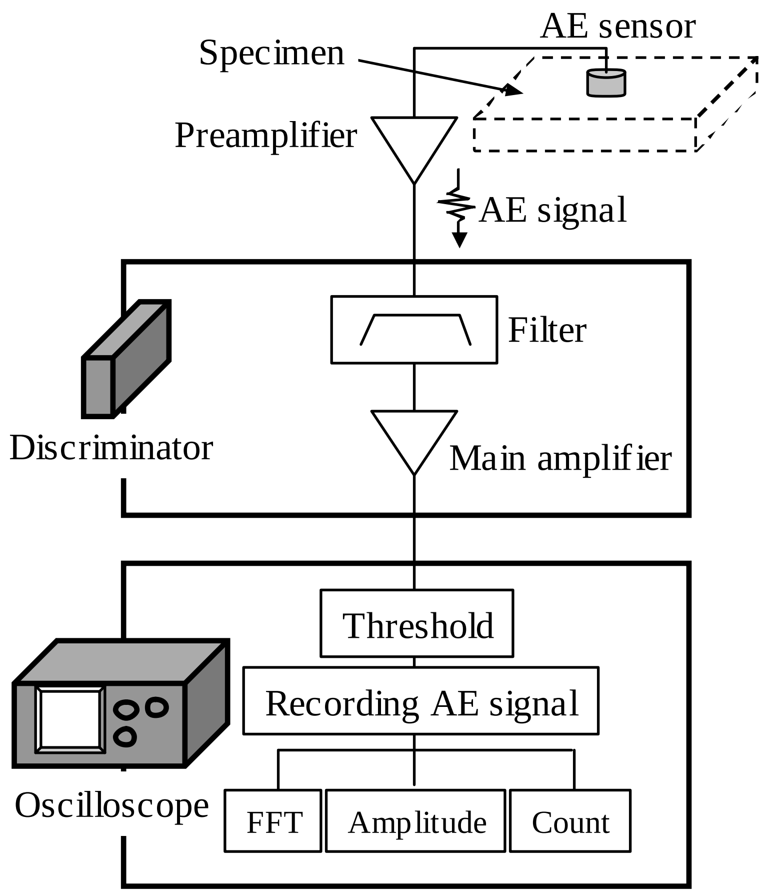


Experimental-AE measurement in air-

- 室温（20〜25 ºC）・大気中において，引張試験および静き裂進展試験を実施し，発生するAEを計測．
- 水素曝露した試験片では，減圧後5〜10分から室温・大気中においてAE計測を開始．

Room temperature in air

・AE sensor (FUJI CERAMICS M204A)
  Resonance type AE・・・200kHz
・Preamplifier (FUJI CERAMICS A1002)
  Gain・・・55dB
・Discriminator
  Frequency property・・・1kHz〜2MHz (-3dB)
  Filter
    H.P.F ・・・100kHz
    L.P.F ・・・THRU
    GAIN ・・・30dB
・Oscilloscope
  Threshold・・・400mV
  Dead time・・・1 sec



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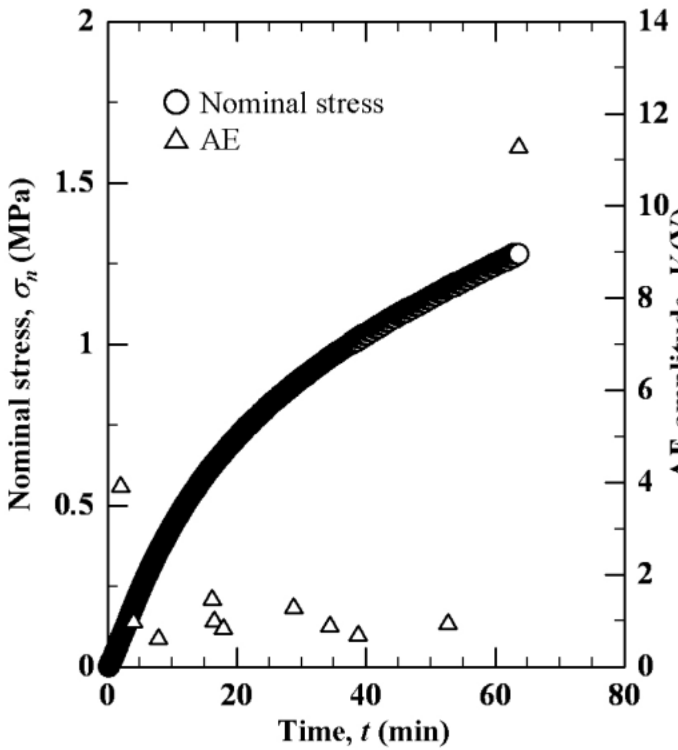
Results and discussion-Preliminary tests by AE-

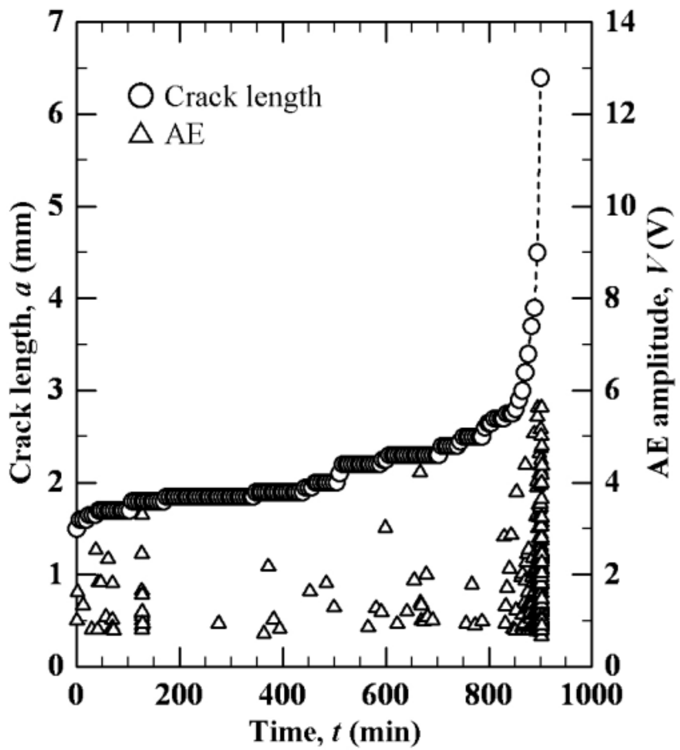
- As preliminary tests, tensile test and static crack growth test were conducted.
- AE signals were detected at crack growth test, whereas these were hardly detected at tensile test.

⇒This result implies that the AE signals were mainly generated during fracture process of chain molecules, not deformation process.

Tensile test



Static crack growth test



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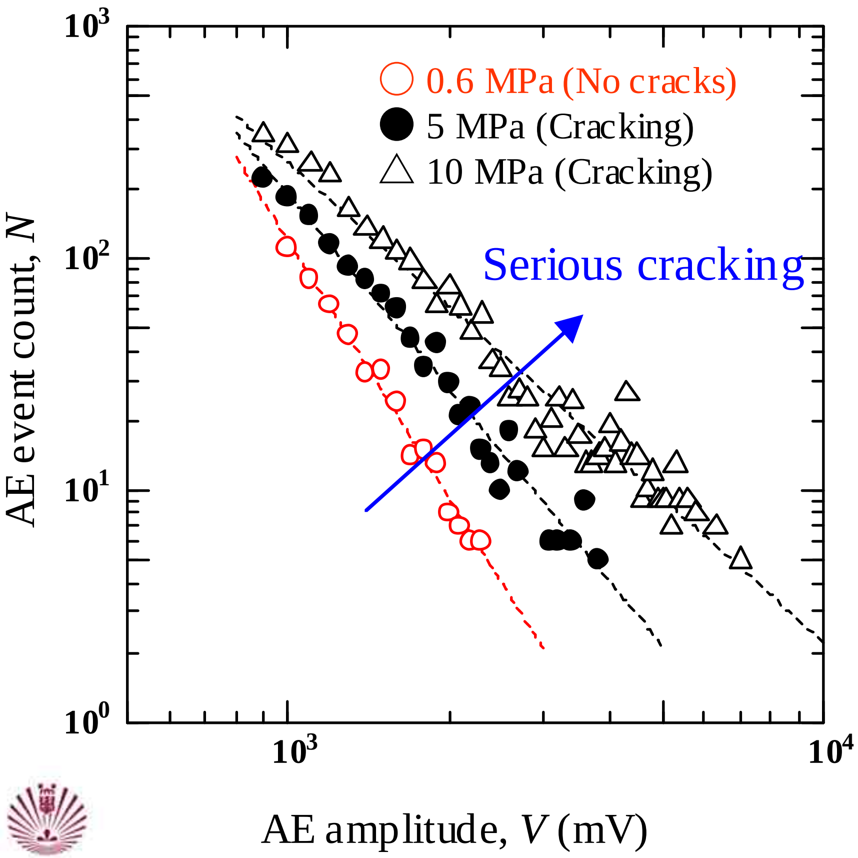
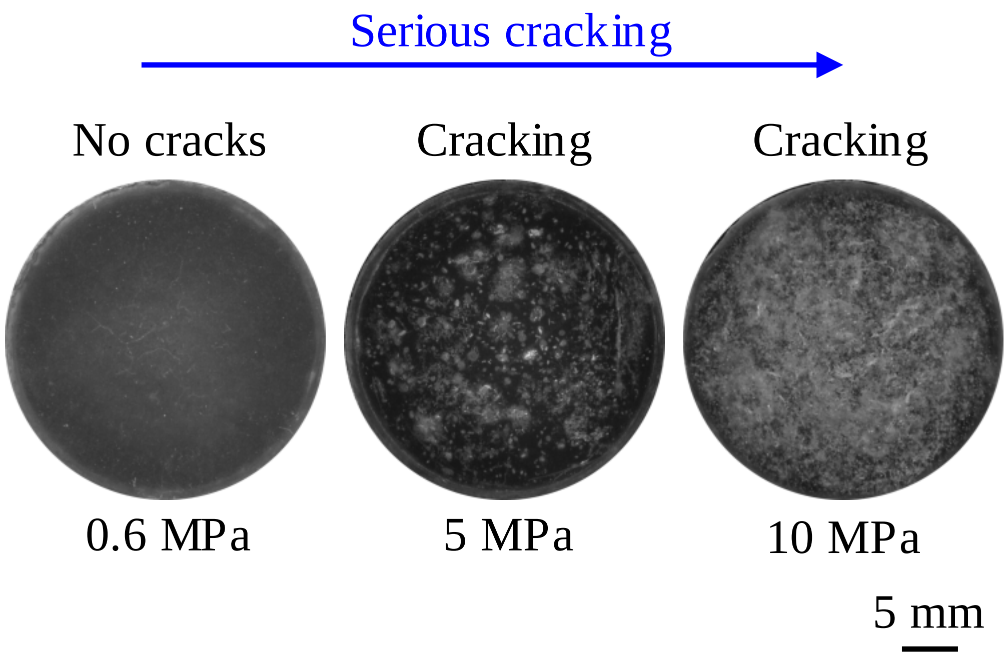
Results and discussion-Hydrogen exposure tests by AE-

- AE event counts and amplitude increased with an increase in hydrogen pressure.
- In spite of the specimen exposed to 0.6 MPa hydrogen gas where no cracks initiate, AE signals were detected.

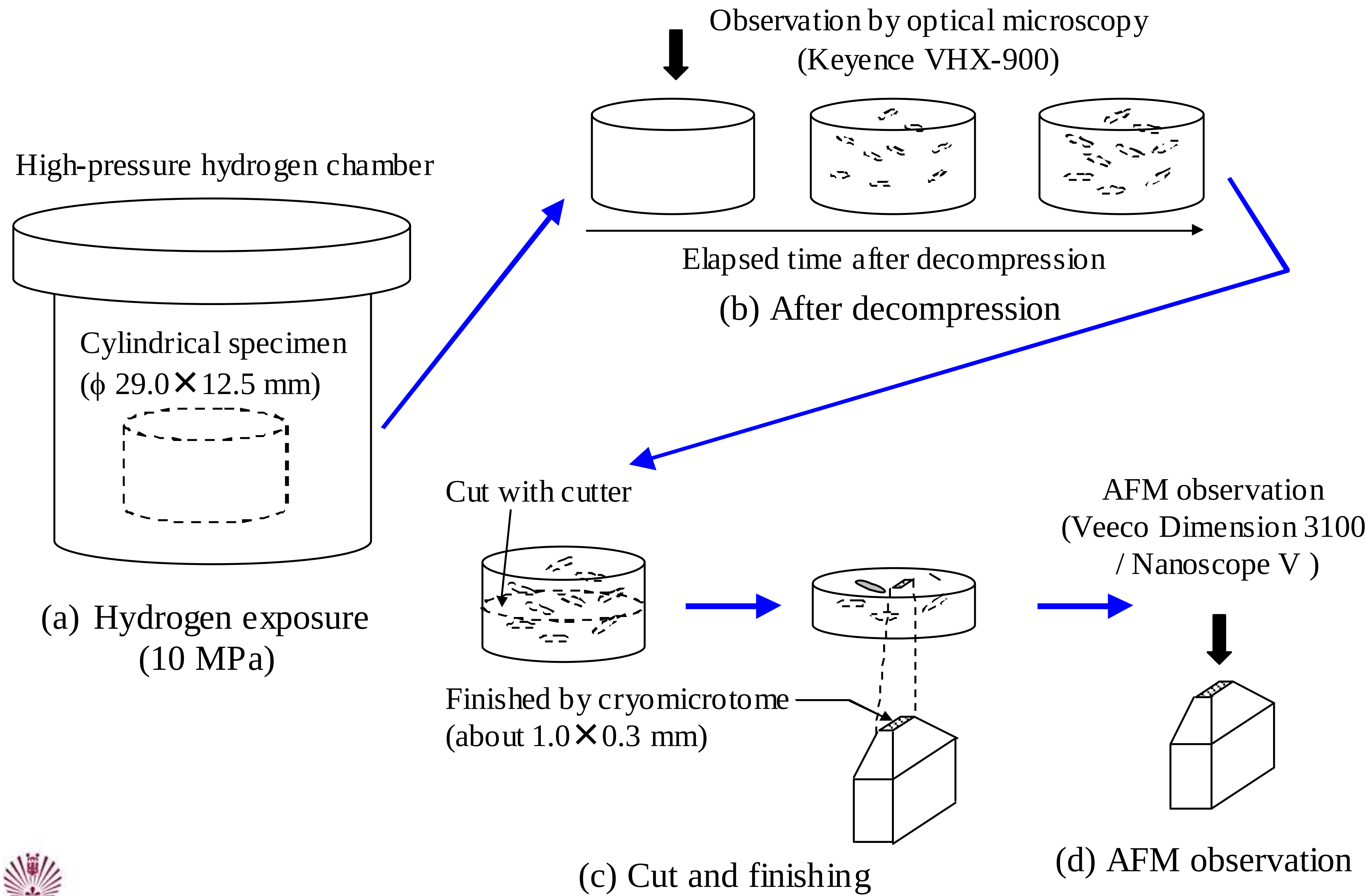
⇒Nanoscale fracture occurs although no cracks are observed by optical microscopy.

⇒This result implies sub-micromter-size bubbles initiate although no cracks initiate.





Experimental-Preparation of specimen for AFM-



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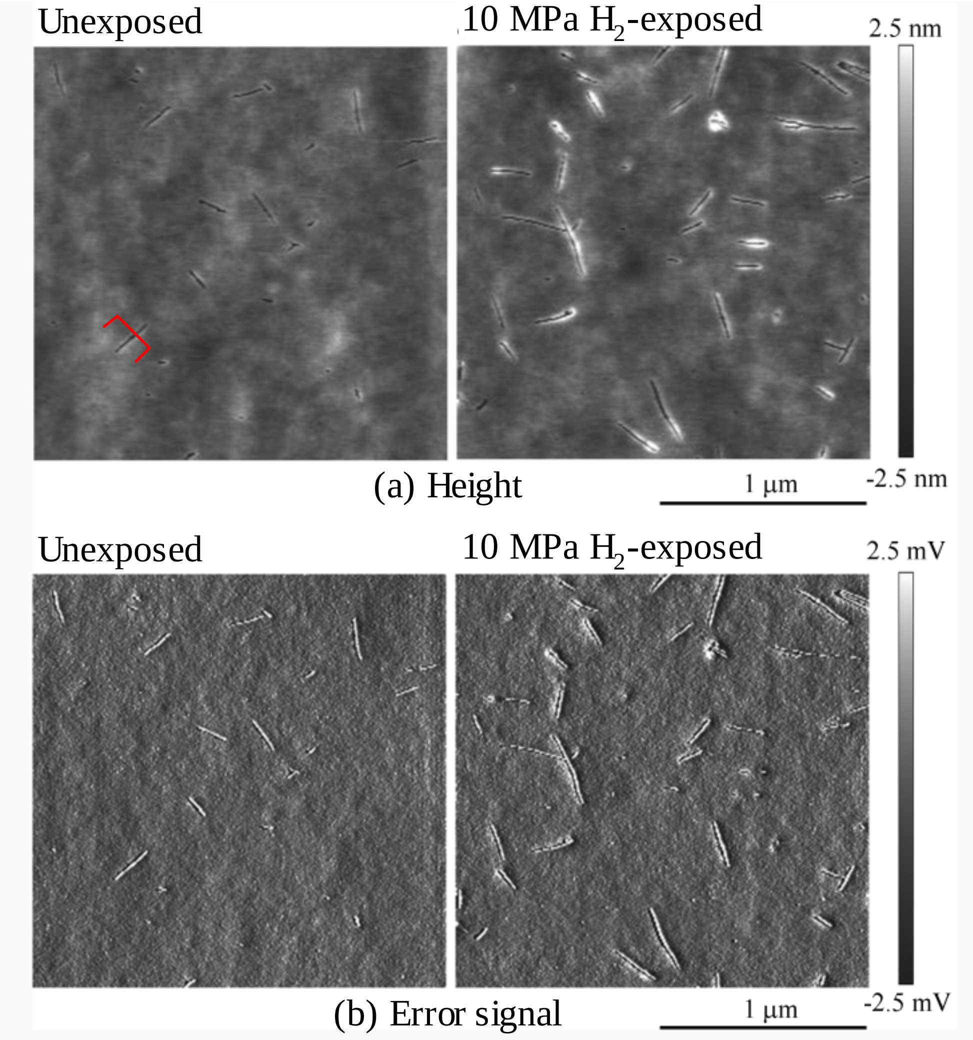
Results and discussion-AFM observation of rubber structure-

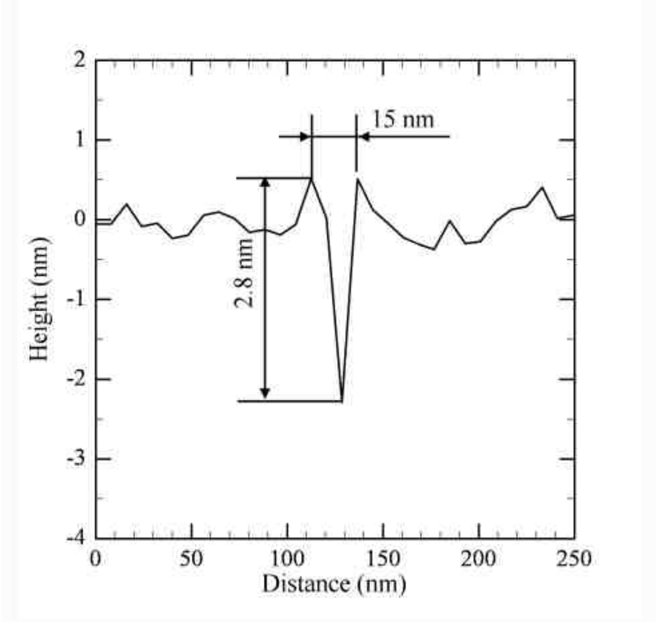
- In spite of unexposed specimen, nanoscale dents were observed.

⇒The rubber structure is not homogeneous at nanometer size.

- The length and number of the nanoscale dents increased by hydrogen exposure.

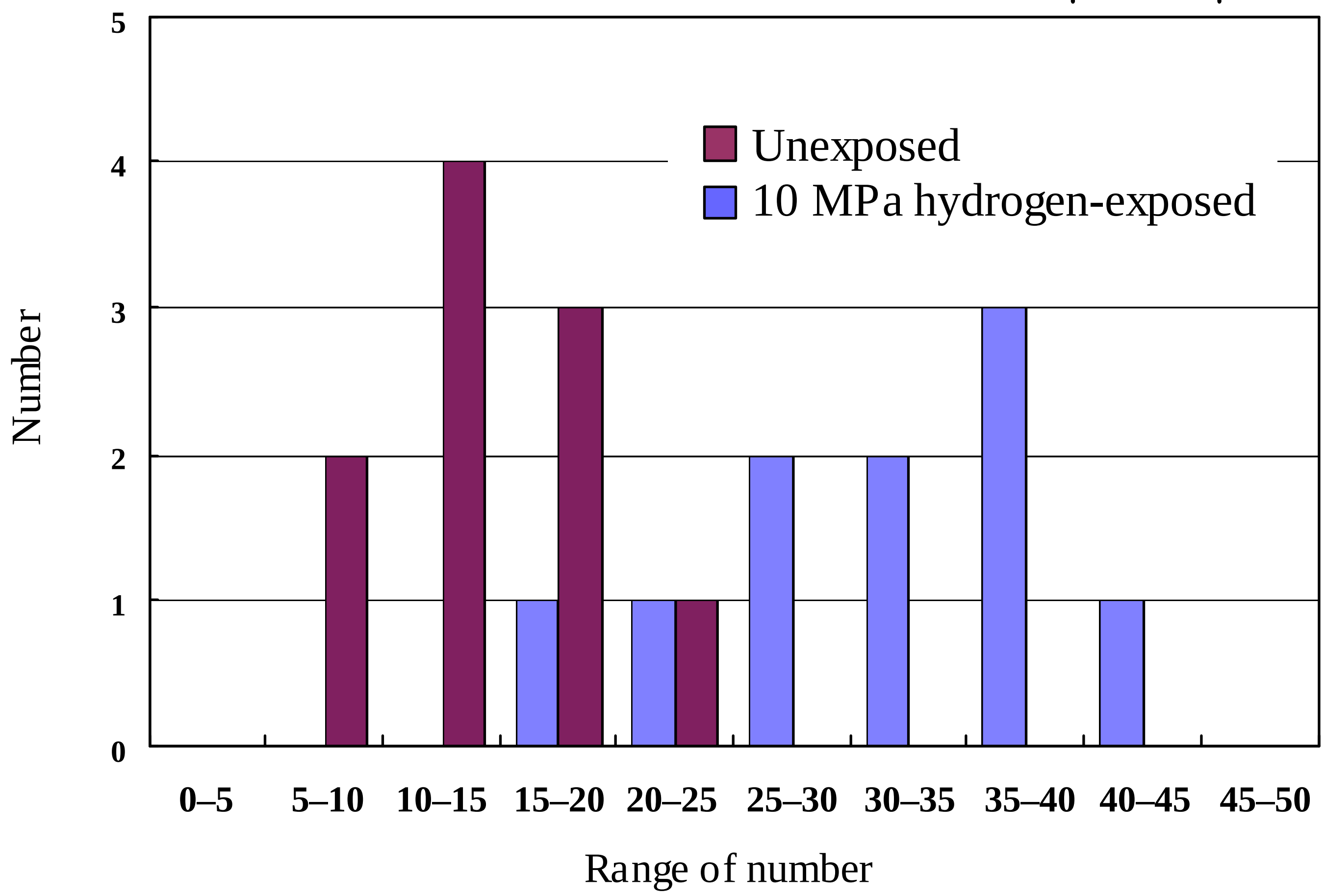
⇒Nanoscale fracture occurs by hydrogen exposure.





- When the scatter of data is considered, the number of nanoscale dents increased by hydrogen exposure.

Number of observation areas: 10
Observation area: 2 μm×2 μm



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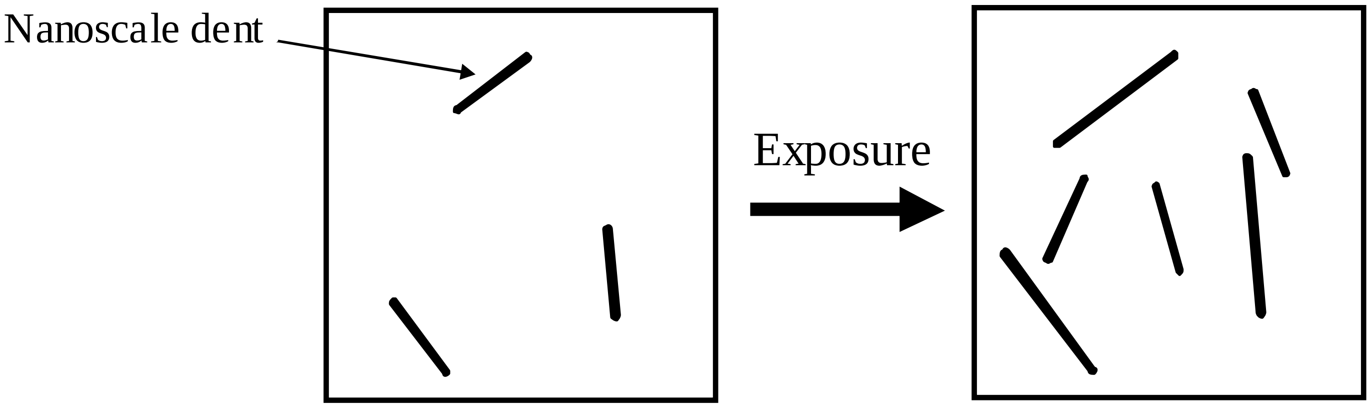
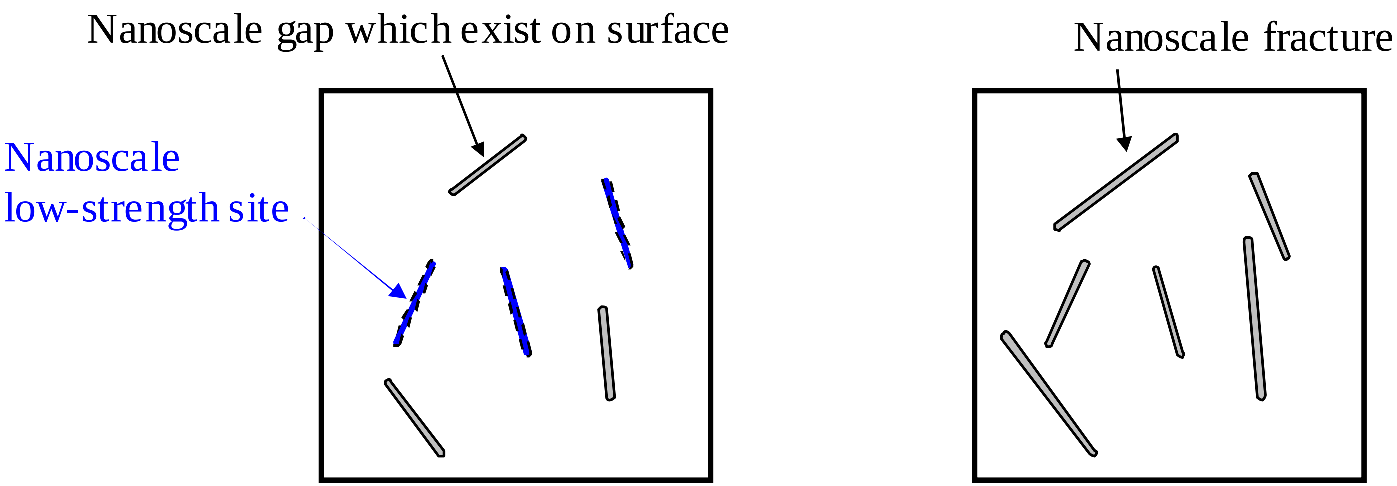
Results and discussion-Suggested nanoscale rubber structure and fracture-



(a-1) Before exposure (a-2) After exposure

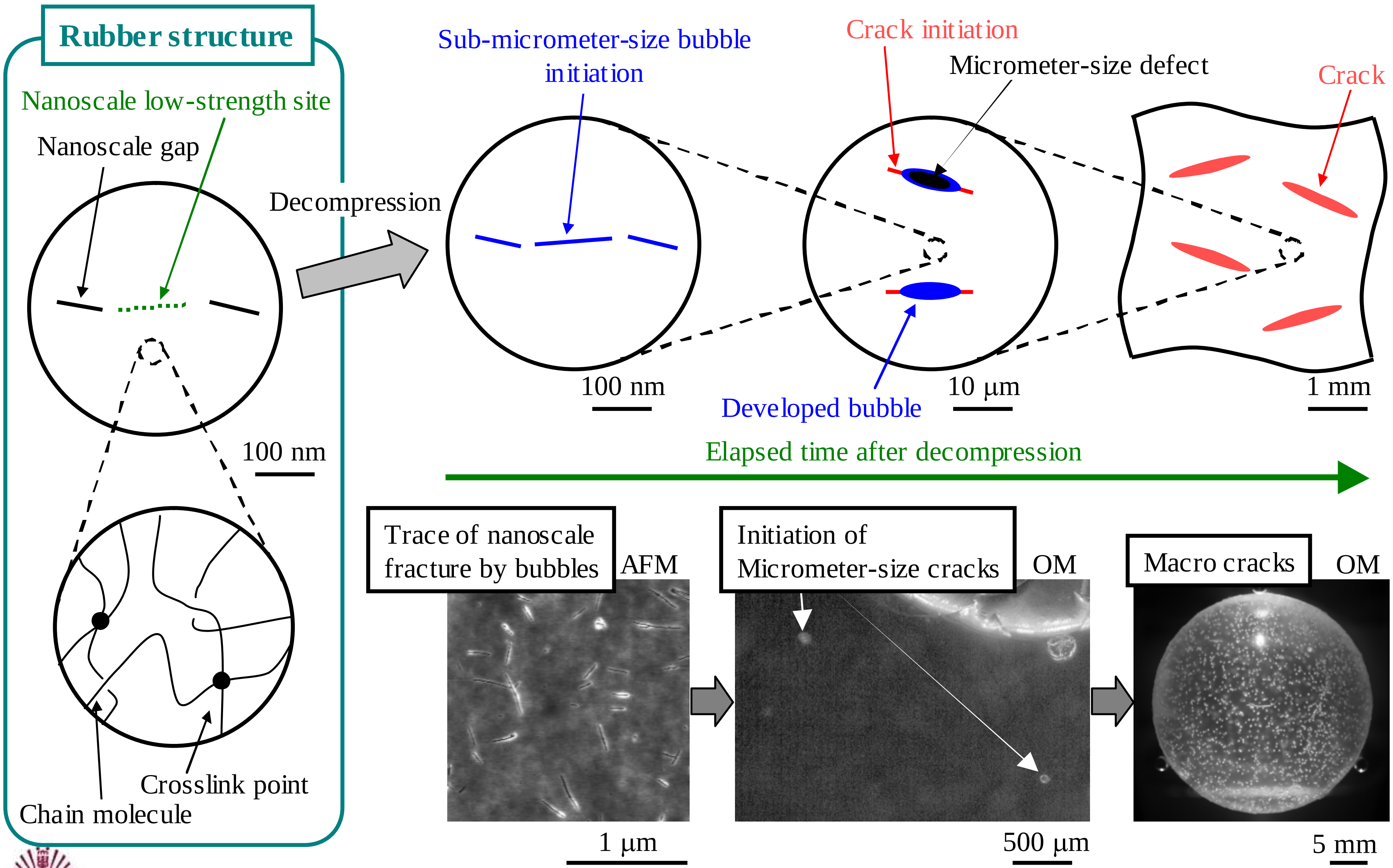
(a) AFM image



(b-1) Before exposure (b-2) After exposure

(b) Real structure

Results and discussion-Summary of multi-scale fracture processes-



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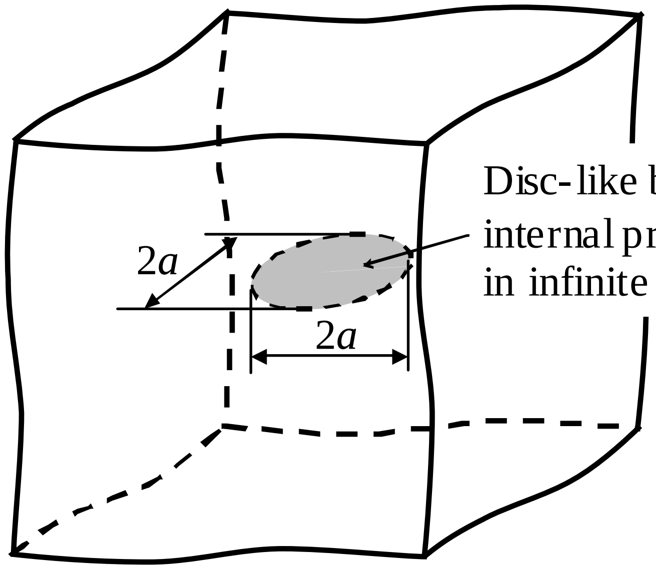
Results and discussion-Estimation of critical hydrogen pressure-

Criterion of crack initiation by fracture mechanics

$$T = f(p,a) \geq \Gamma_F$$

T : Tearing energy of bubble

Γ_F : Fracture energy



Calculation of tearing energy by FEM

Total energy method was employed.

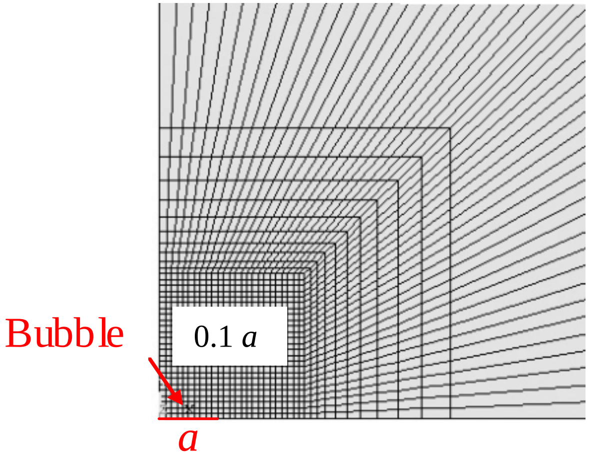
$$T \approx \frac{\Delta W}{\Delta A} = \frac{W(A+\Delta A) - W(A-\Delta A)}{2\Delta A}$$

T : Tearing energy (N/mm)

W : Strain energy (MPa)

A : Bubble area (mm^2)

Eight-node element (axisymmetric)



Meshing pattern near bubble tip

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Results and discussion-Estimation of critical hydrogen pressures-

- Bubble formation

  $T \geq \Gamma_{BF}$

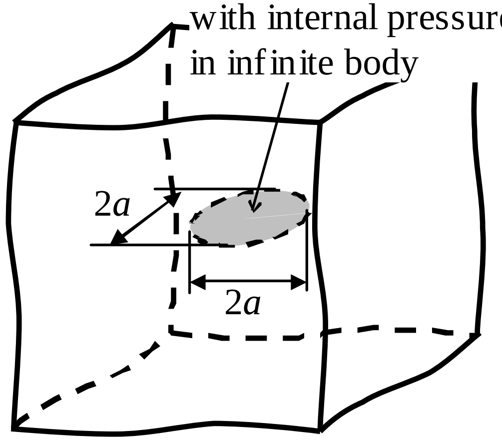
  It is considered that the values of Γ_{BF} are not constant.

  Therefore, the minimum value is assumed to be 50×10^{-3} N/m.

  (This value corresponds with the energy when bubbles grow in simple liquids.)

- Crack initiation

  $T \geq \Gamma_{CI} = T_{s,th} (= 55 \text{ N/m})$



Items	Experiment (MPa)*1	Method	Energy (N/m)	Size (μm)	Estimation (MPa)*1
Bubble formation (Nanoscale fracture)	0.5–0.6	Acoustic emission	50×10^{-3}	0.3	0.57
Crack initiation (Microscale fracture)	1.5–2.0	Optical microscope	55*2	14	1.53

*1) Gage pressure (=absolute pressure – 0.1 MPa)
*2) This value was obtained from static crack growth tests.

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謝　　　辞

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