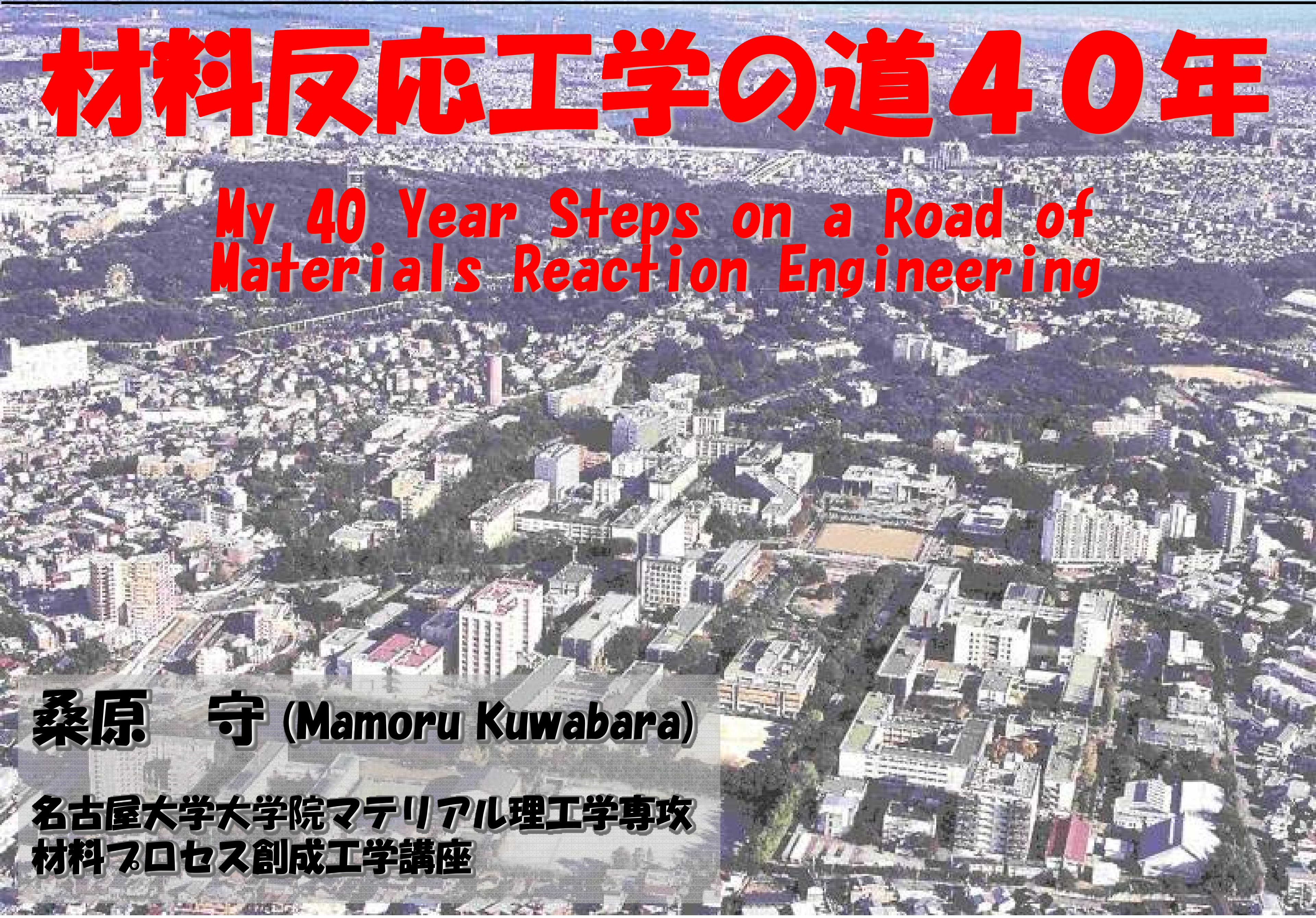
桑原最終講義, Feb. 29, 2008

材料反応工学の道４０年

My 40 Year Steps on a Road of Materials Reaction Engineering

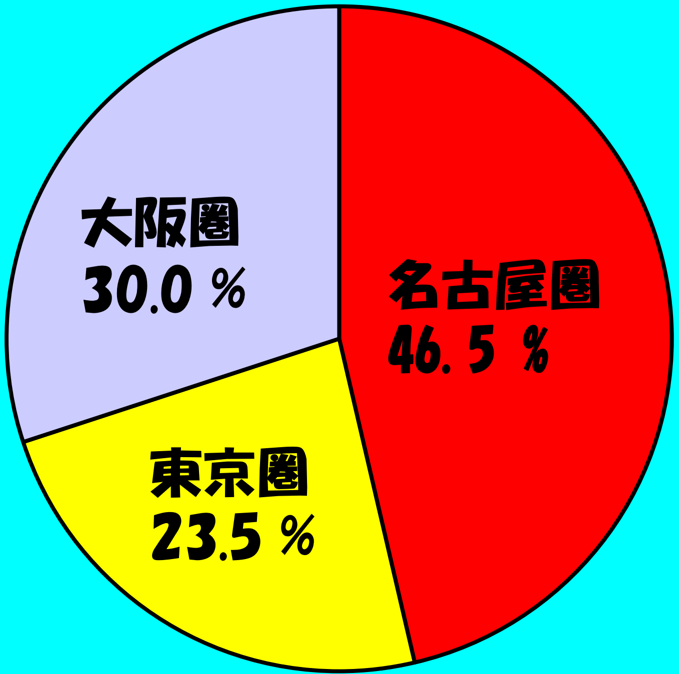


桑原　守 (Mamoru Kuwabara)

名古屋大学大学院マテリアル理工学専攻
材料プロセス創成工学講座

名古屋大学工学部鉄鋼工学科とその役割

昭和33年9月	東海製鉄㈱設立（出資率：富士製鉄51.7%、地元48.3%）
昭和37年4月	鉄鋼工学科第1期生入学（浅井、野村、松井名誉教授ら）
昭和38年4月	同上　　第2期生入学（桑原、藤井前JFE研究所長ら)
昭和42年8月	富士製鉄と合併、名古屋製鉄所として発足
昭和45年3月	富士･八幡製鉄合併、新日本製鉄名古屋製鉄所として発足



3大都市圏の製造業比率（平成15年）

名古屋は鉄鋼、車、セラミックス等、世界有数のものづくりの地

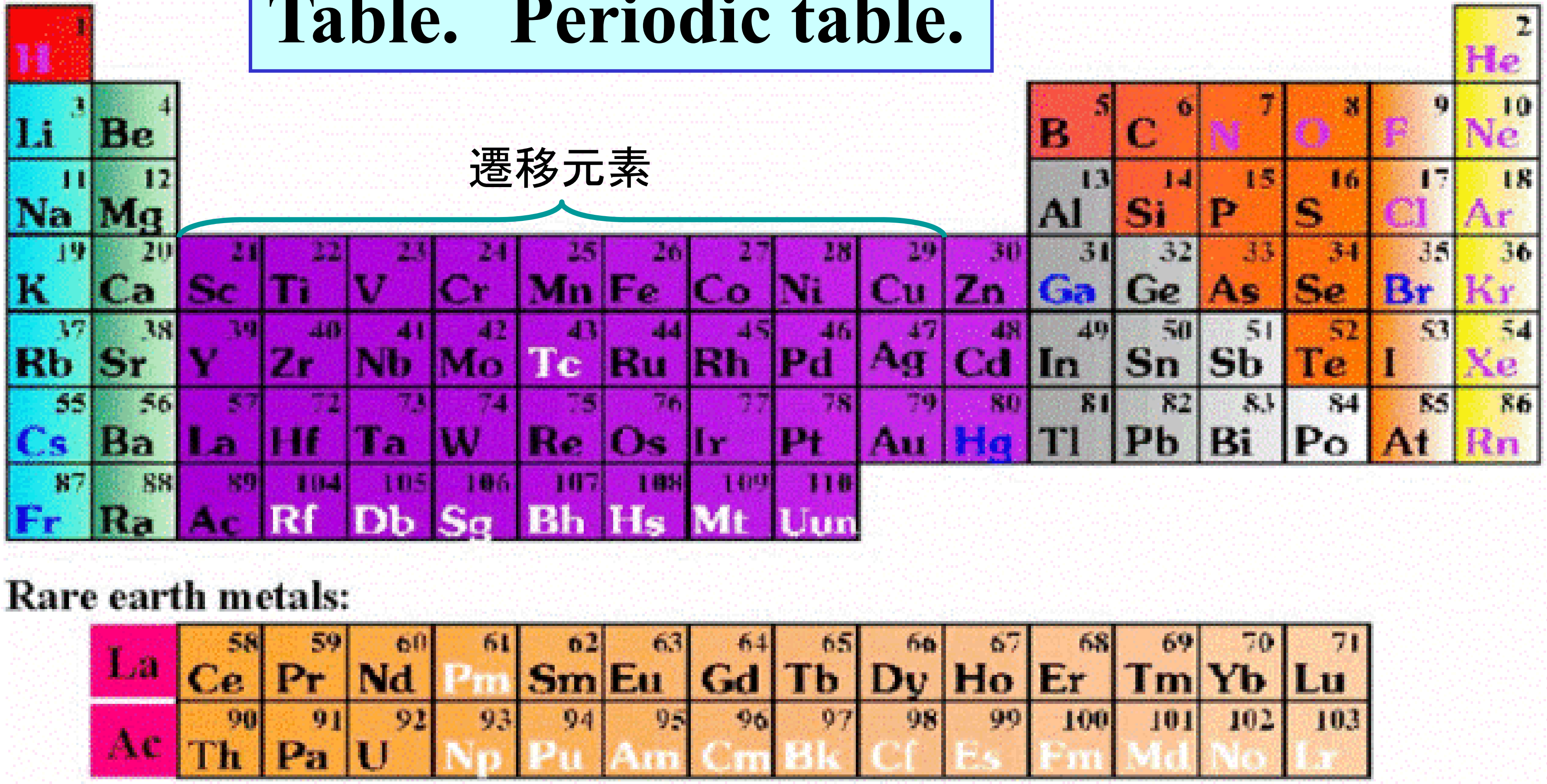
↓

ものづくりの技術、学理の構築

数学が専門科目と大学院入試に（全国材料系初）

資源と素材製造　：　物理的、化学的原理による分離と精製

Table.　Periodic table.



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun								

Rare earth metals:

La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

元素の殆んどが金属，数少ない非金属元素は気体が多く，両者の境目には両性の半金属、半導体がある。自然界に存在するのは90種類だけで，そのうち，金属元素は3/4を占め，残りが非金属元素。逆に，地殻中元素の質量分率では，種類の少い非金属元素が3/4を占め，多種類の金属元素と化合して多彩な物質世界を形成。

クラーク数1)（地殻表層部中元素の質量存在率%）

非金属元素　　（計 76.17 %）	金属元素　　（計 23.07 %）
1位　酸素　49.50 %	
2位　ケイ素　25.80 %	
	3位　アルミニウム　7.56 %
	4位　鉄　4.70 %
	5位　カルシウム　3.39 %
	6位　ナトリウム　2.63 %
	7位　カリウム　2.40 %
	8位　マグネシウム　1.93 %
9位　水素　0.87 %	
	10位　チタン　0.46 %
11位　塩素　0.19 %	
	12位　マンガン　0.09 %

（13位 P = 0.08, 14位 C = 0.08, 15位 S = 0.06, 16位 N = 0.03, 17位 F = 0.03・・・）

10位までで約 99.24 % となる。

地殻内部まで含めれば鉄が一番多い！

反応工学的研究の研究手法

- 熱力学
- 反応速度論
- 移動現象論
- 数学
- 反応器解析
- 数値解析法
- 確認実験

経歴の変遷

４年（鞭研：反応器解析）

修士（坂尾研：熱力学）

助手（鞭研）

その後

助教授（佐野研：反応速度）

教授（反応工学全般）

Ellingham Diagram[2)]

:酸化/還元の熱力学的原理

$$a\mathrm{Me}+\mathrm{O}_2=b\mathrm{Me}_{(a/b)}\mathrm{O}_{(2/b)}$$

$$\Delta G=\Delta G^\circ+RT\ln K_d$$

$$\Delta G^\circ=RT\ln P_{\mathrm{O}_2}$$

$$=\Delta H^\circ-T\Delta S^\circ$$

直線が下位の元素 Me_1は上位の元素Me_2 の酸化物を還元し、単体のMe_2 とMe_1の酸化物を生成する。また、そのときの反応熱は $(\Delta H_2{}^\circ-\Delta H_1{}^\circ)>0$.

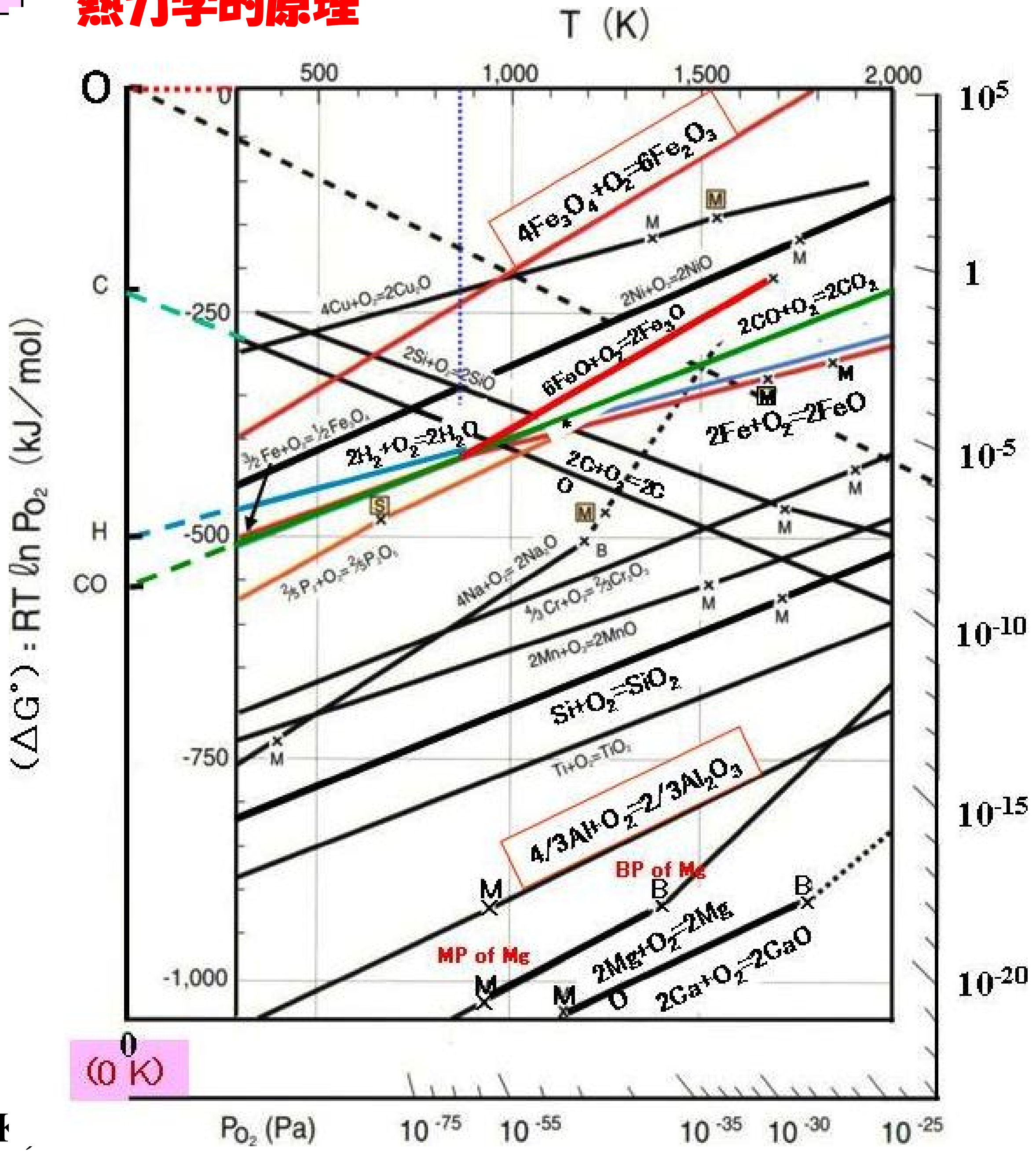
→

CやCOは酸化鉄$\mathrm{Fe}_x\mathrm{O}_y$の安価な還元剤, Alも良好な還元剤として利用できる

（例）テルミット反応:

$$2\mathrm{Al}+\mathrm{Fe}_2\mathrm{O}_3\rightarrow 2\mathrm{Fe}+\mathrm{Al}_2\mathrm{O}_3$$

+ 856 kJ/mol (273



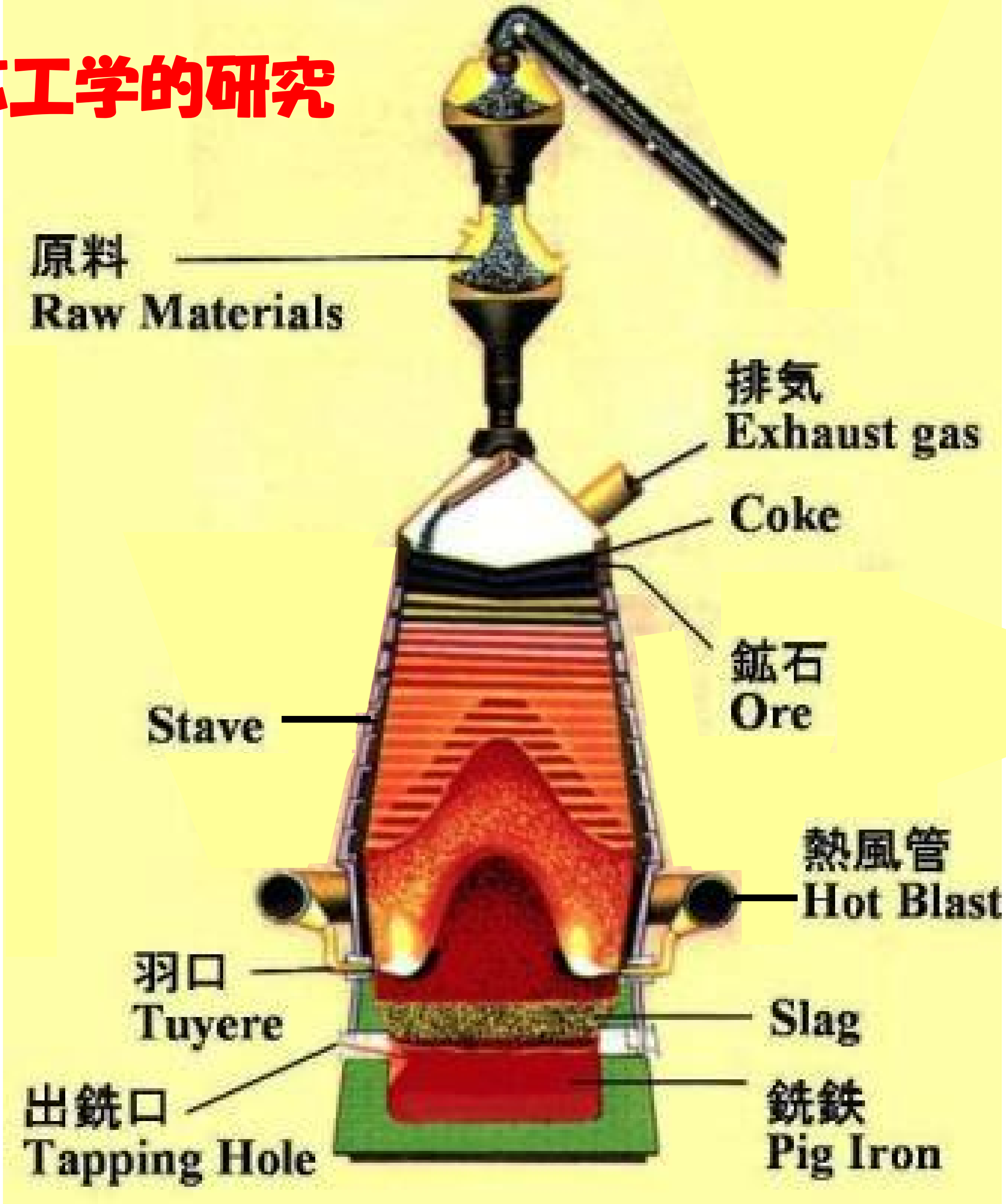
製鉄プロセスの反応工学的研究

- 多くの充填層型反応器が関与：

反応器の様式:

固定層 (Fixed bed)
移動層 (Moving bed)
流動層 (Fluidized bed)
回転炉（Rotary kiln）

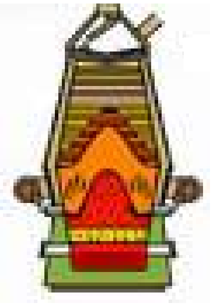
- 熱, 物質, 運動量の移動現象が深く関与



鉄－炭素系状態図上での高炉-転炉法と反応工学

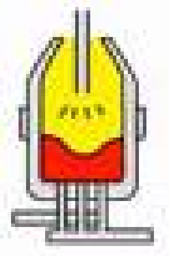
In BF

- Iron ore reduction with minimum consumptions of natural resources and energy
- Slag formation
- Carburization



In LD

- Refining
- Heating of melt
- 2nd refining
- Solidification



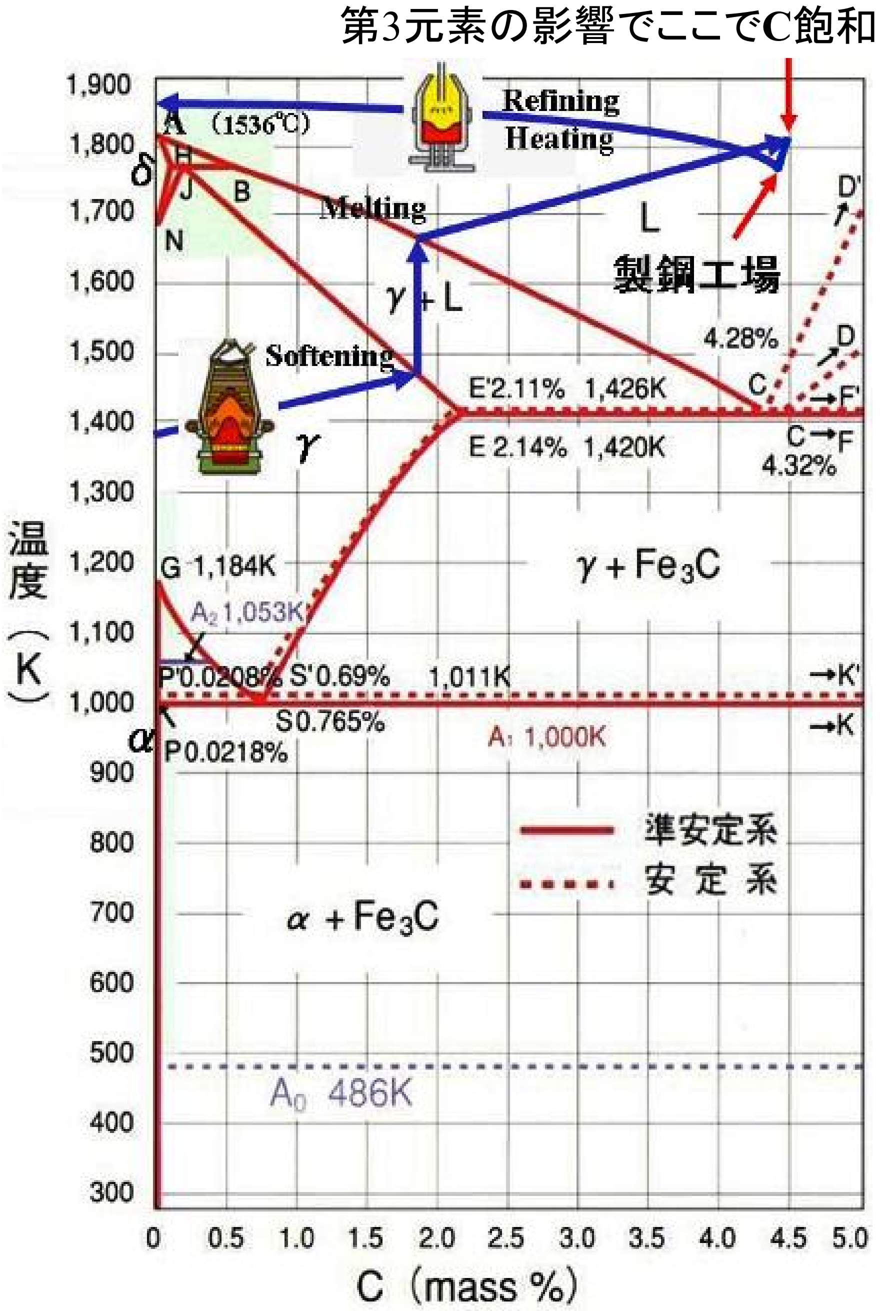


Fig. Phase diagram in Fe-C system.

高炉モデル（Blast furnace modeling）

過去40年に亘り、名古屋大学で開発してきた高炉モデルの歴史とコンセプト

1. **One-dimensional steady-state model called Muchi's model (1966-1970)**

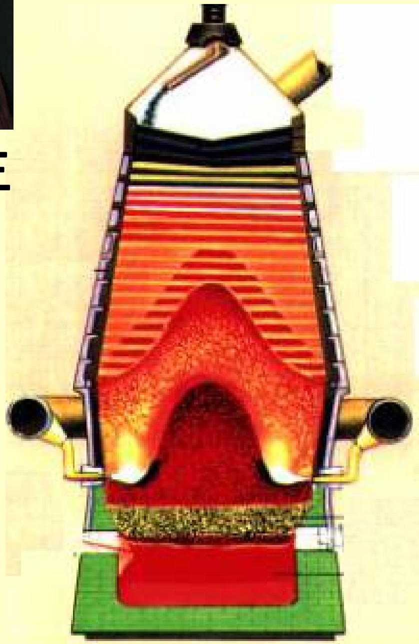
2. **Layered structure model (1975)**

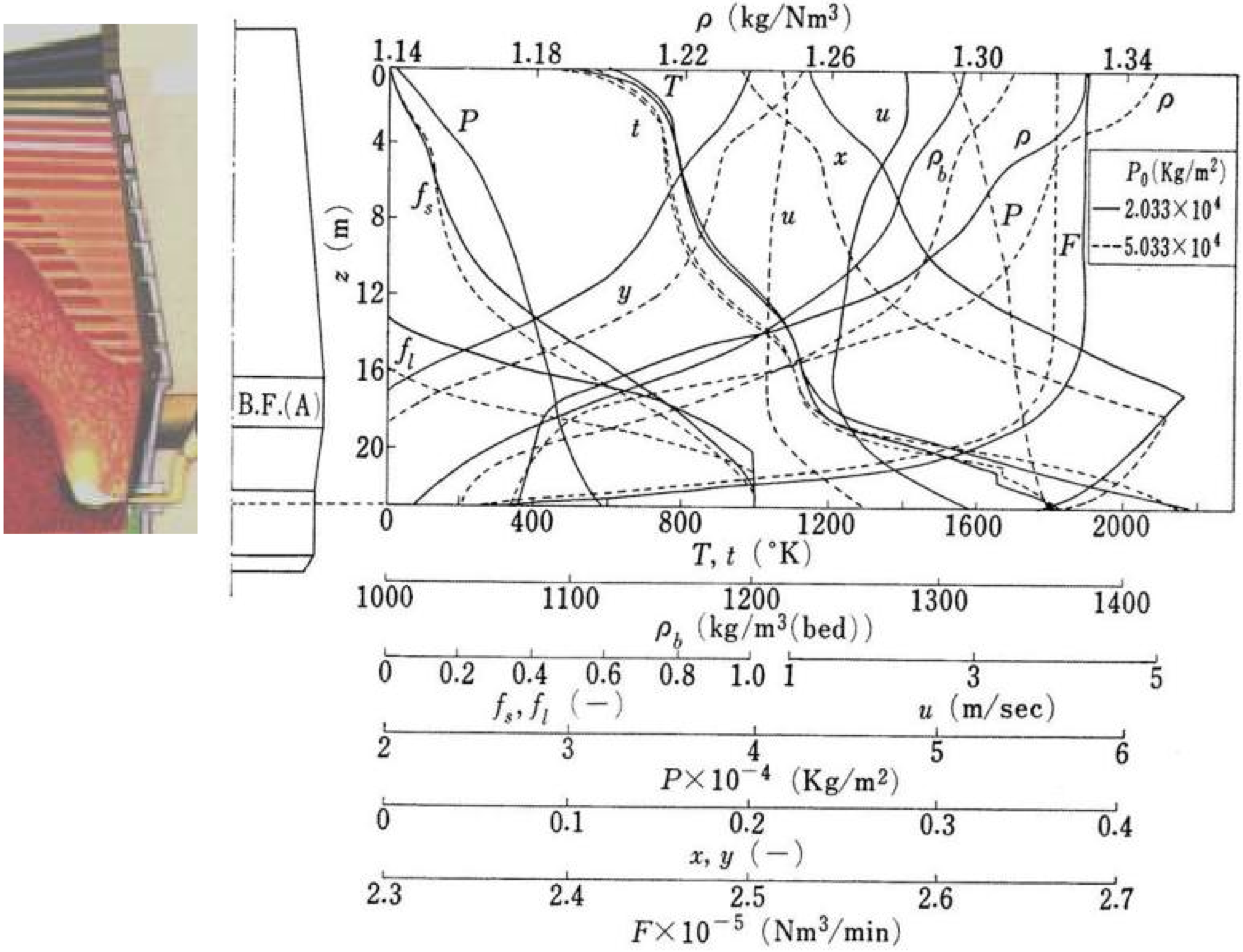
3. **Detailed formulation of transport and rate processes (1975-1988)**

4. **Two-dimensional model (1980-1991)**

5. **Divided region model for the lower part of blast furnace (2000)**

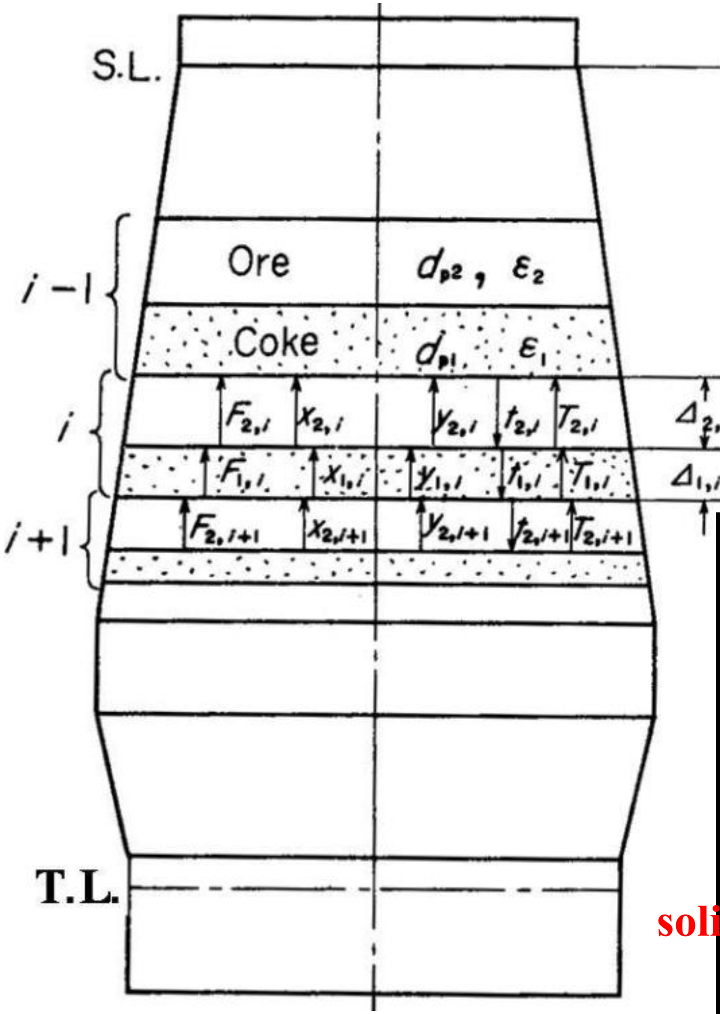
鞭巌先生





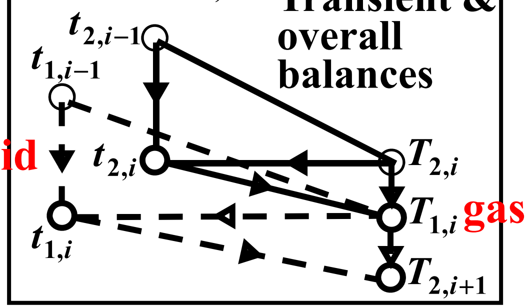
鉱石とコークスの混合装入を仮定した１次元モデル

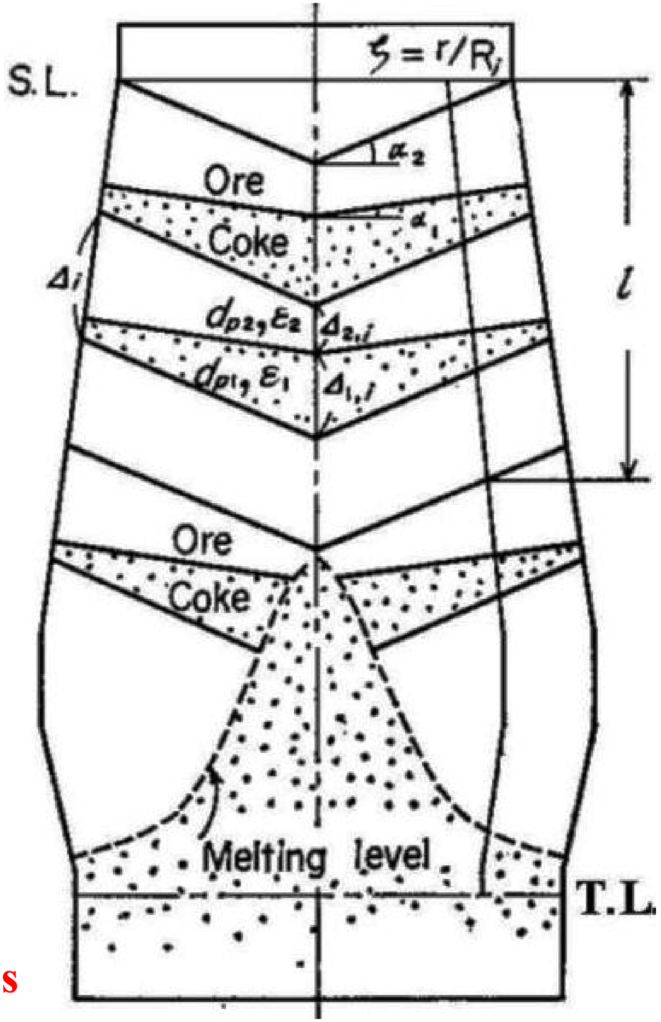
Fig. One-dimensional steady-state mathematical model of blast furnace (田村, 八木、鞭 (1966)) 3,4).



Cyclic steady state for heat transfer in *i*-th cell during residence time :

$\Theta = \Delta_i / u_{s,i}$

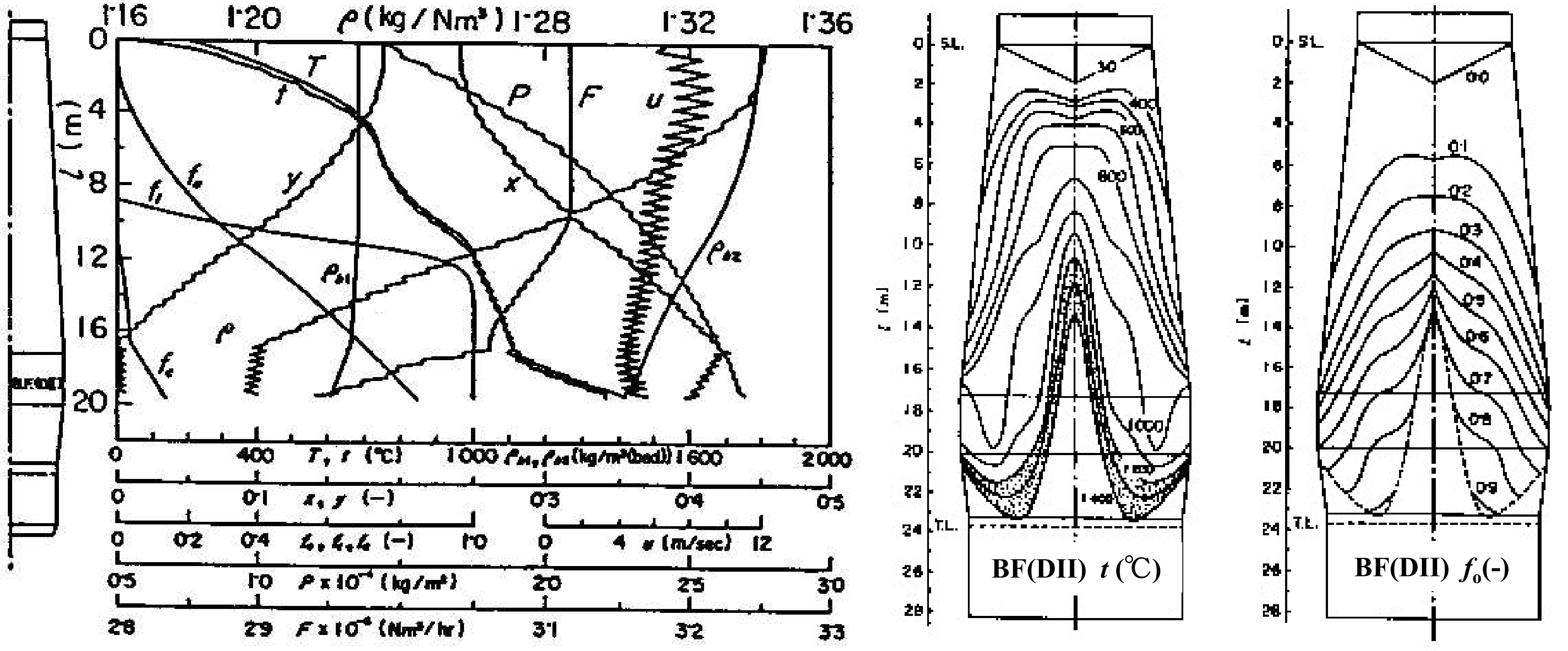




Cylic steady-state due to descent of layered burdens 5)

Radially distributed burdens and gas flow 6)

Fig. 層状装入の高炉操業の数学的モデル (桑原、鞭, 1975) 5,6) .



(a) longitudinal distribution of process variables 5)

(b) isotherms 6)

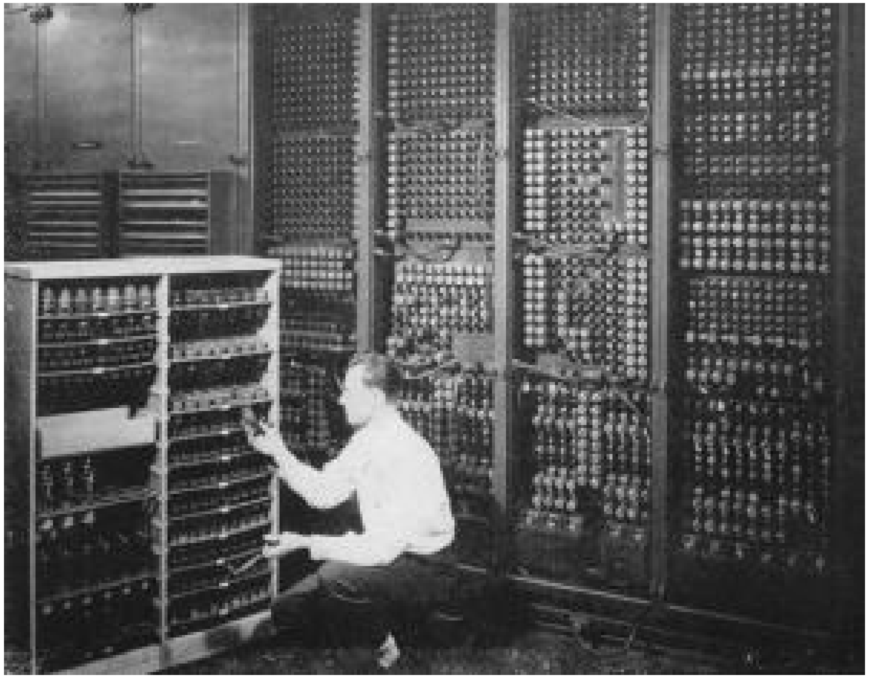
(c) equi-fractional reduction 6)

Theoretical bases to understand mixed burden model and non-uniform inner features of blast furnaces dissected in 1970s

Fig. Typical computed results by the layered structure model of blast furnace (Kuwabara and Muchi, 1975) 5,6).

日本鉄鋼協会俵論文賞：理論だけで受賞した最初の研究

1970年代
当時はまだ
電算機の
（数値解析
モデルの）
黎明期！



第2次大戦中、
大砲の弾道
計算用に開発

18800 本の
真空管を利用:

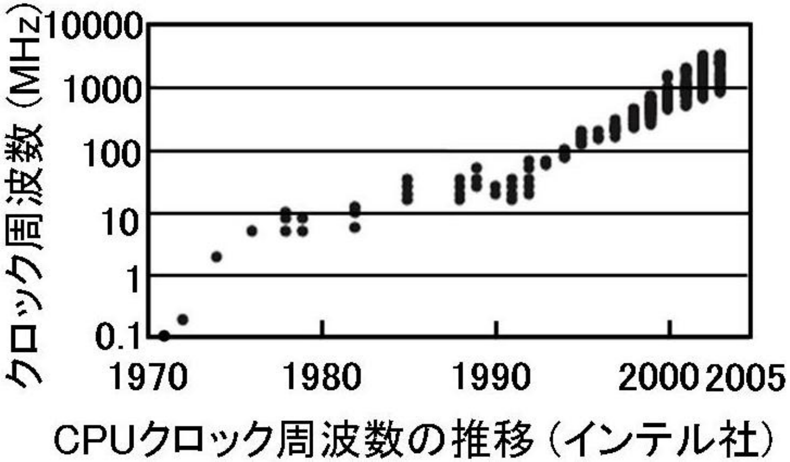
6分に1本を
故障で交換

世界初の真空管式電子計算機 ENIAC(1946) 7)

ENIAC (Electronic Numerical Integrator and Computer)

1946 ENIMAC
1952 世界最初のプログラム内蔵式実用計算機 EDVAC
1958 集積回路の発明
1964 集積回路を搭載した計算機 IBM 360
1971 最初の4ビットマイクロプロセッサ Intel4004
1972 8ビットマイクロプロセッサ
1979 16ビットマイクロプロセッサ

1971 名大大型計算機センター設置
（センターニュース第1号の巻頭言は鞭教授）



CPUクロック周波数の推移（インテル社）

充填層内ガス流れ（Fluid Flow through Packed Bed）
－偏微分方程式の数値解析に着手－

連続の式（質量保存式）

$$\nabla \bullet \vec{G}_g = \frac{1}{r}\left\{ \frac{\partial (rG_{gr})}{\partial r} + \frac{\partial (rG_{gz})}{\partial z} \right\} = 0$$ （非反応系）

運動方程式（運動量保存式）

$$\nabla P = -\left(f_1 + f_2 \left| \vec{G}_g \right|\right) \vec{G}_g$$: Ergun equation

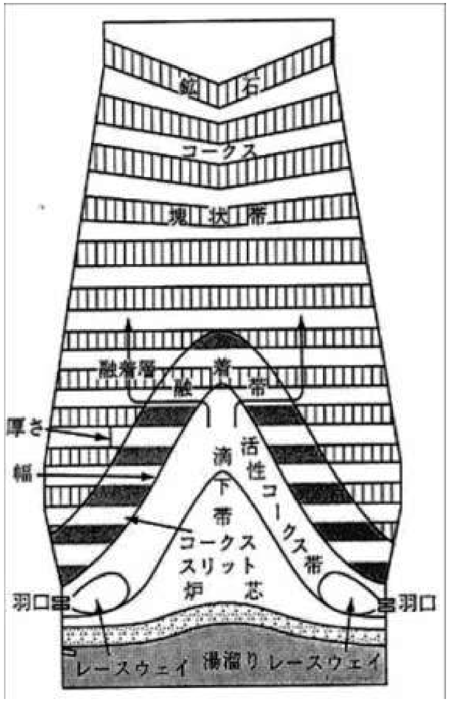
$$\vec{G}_g = \rho_g \vec{u}_g$$: 質量速度（**mass velocity**）**[kg/m²s]**

$$f_1 = 150(1-\varepsilon)^2 \mu_g / \rho_g (\phi d_p)^2 \varepsilon^3,$$

$$f_2 = 1.75(1-\varepsilon) / \rho_g (\phi d_p) \varepsilon^3$$

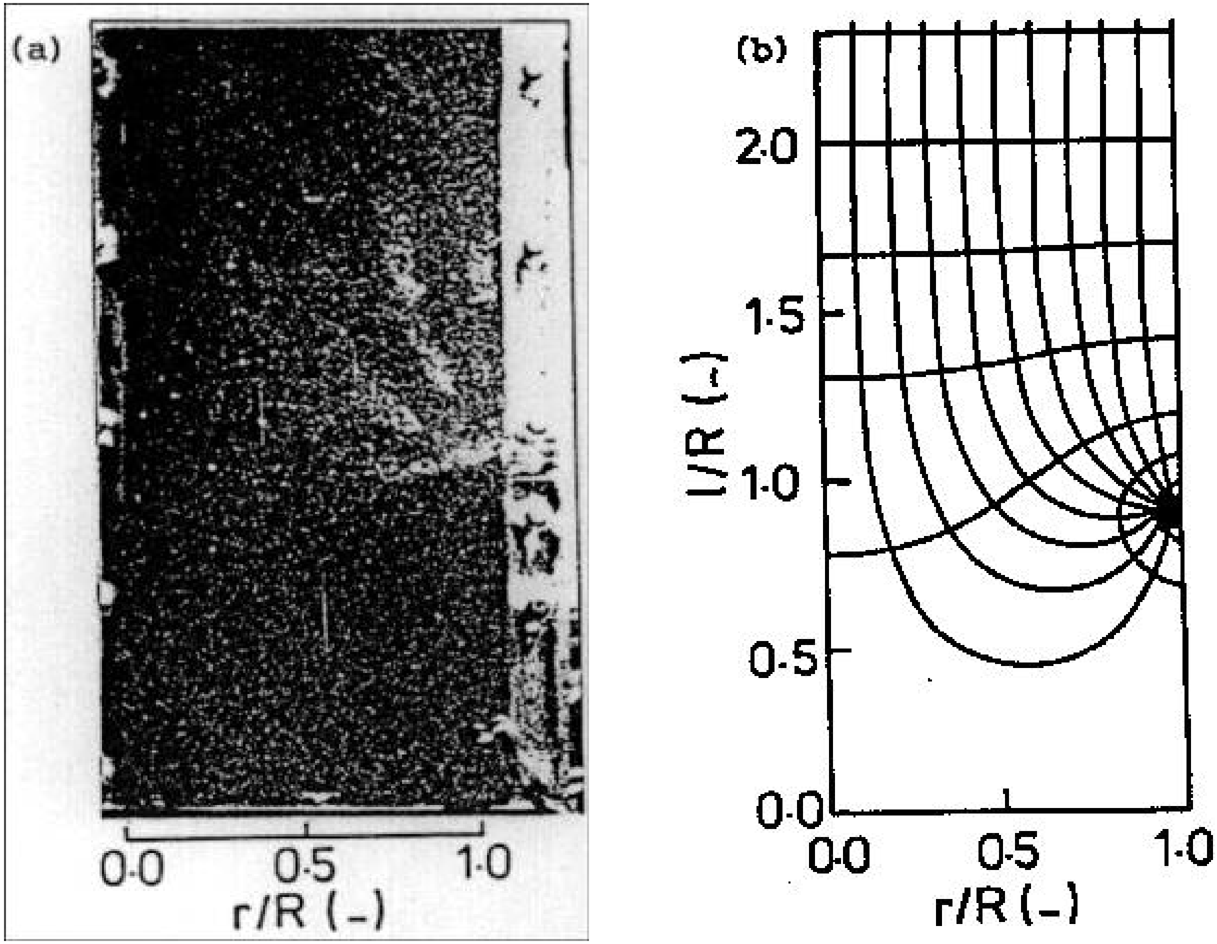
d_p:粒子径, ε:空間率, μ_g粘性係数

ρ_g :密度, ϕ :形状係数



Ore :$d_{po} \approx 2\,\mathrm{cm}, \varepsilon_o \approx 0.45$, **Coke**:$d_{pc} \approx 5\,\mathrm{cm}, \varepsilon_c \approx 0.45$ $\quad \frac{f_{1o}}{f_{1c}} \approx \left(\frac{d_{pc}}{d_{po}}\right)^2 \approx 6.25, \ \frac{f_{2o}}{f_{2c}} \approx \frac{d_{pc}}{d_{po}} \approx 2.5$

炉下部羽口先ガス流れ



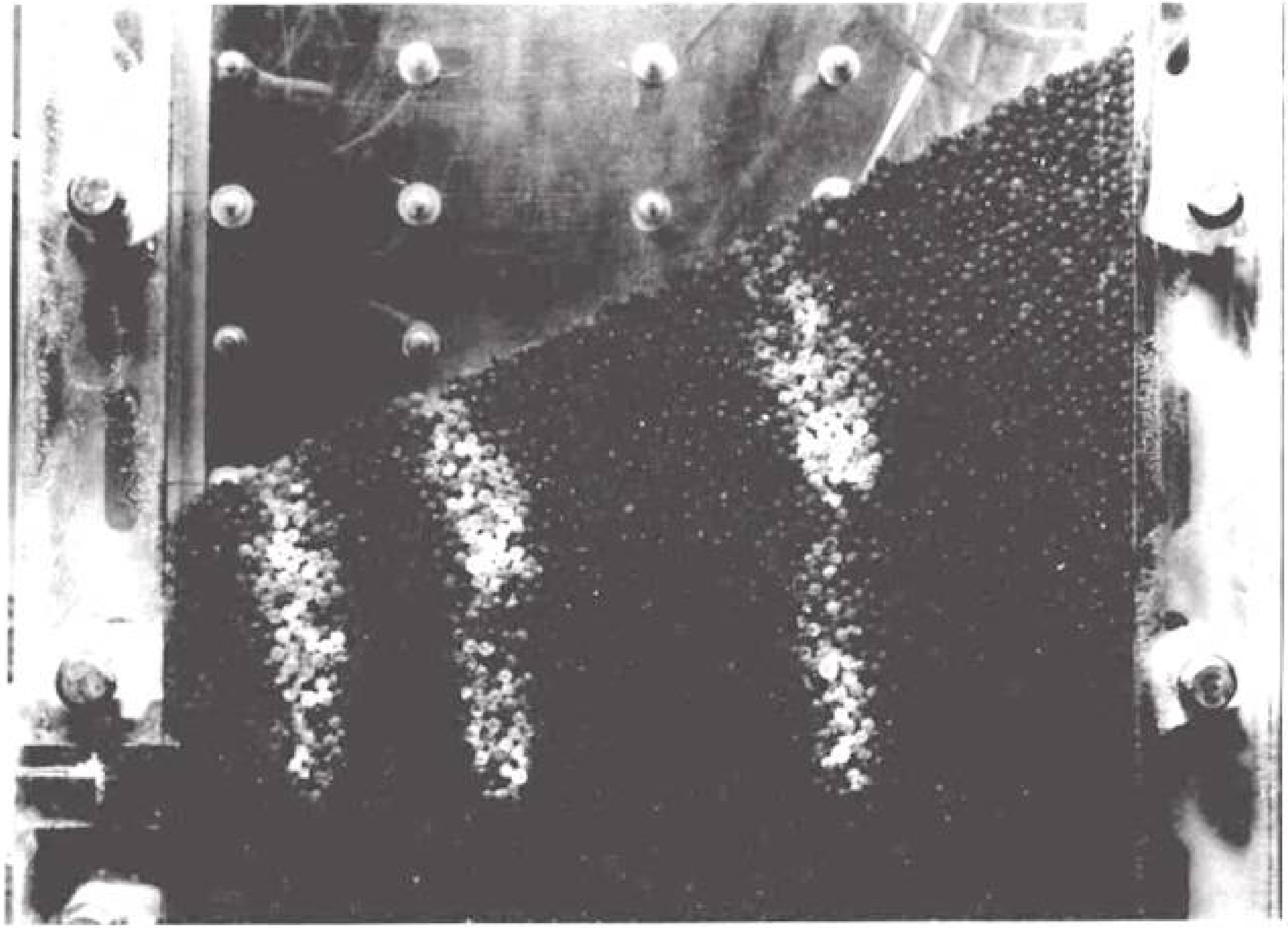
(a) Visualized streamlines

(b) Predicted streamlines and isobars

吹き込みの位置、方向によってガスは偏流する。

Fig. Comparison of gas-streamline around the raceway visualized in a two-dimensional bed packed with silica-gel particles with that numerically predicted (Kuwabara et al., 1976, 1981) 8) .

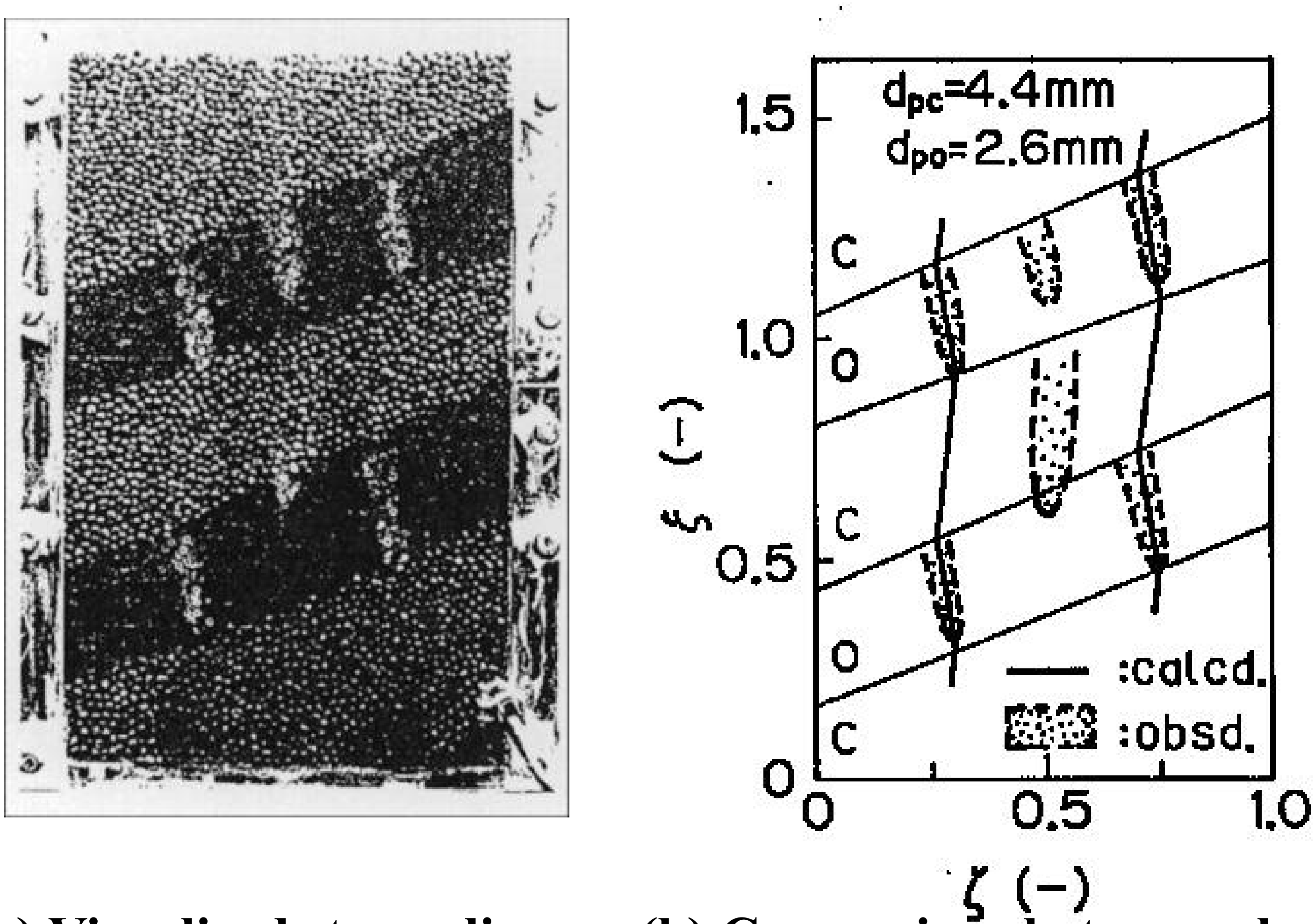
層頂部ガス流れ



層頂での堆積形状によっても偏流

Fig.　Gas-streamlines in a two-dimensional bed having the inclined top structure of silica-gel particles (Kuwabara et al., 1988)[9)].

層状装入物層内ガス流れ



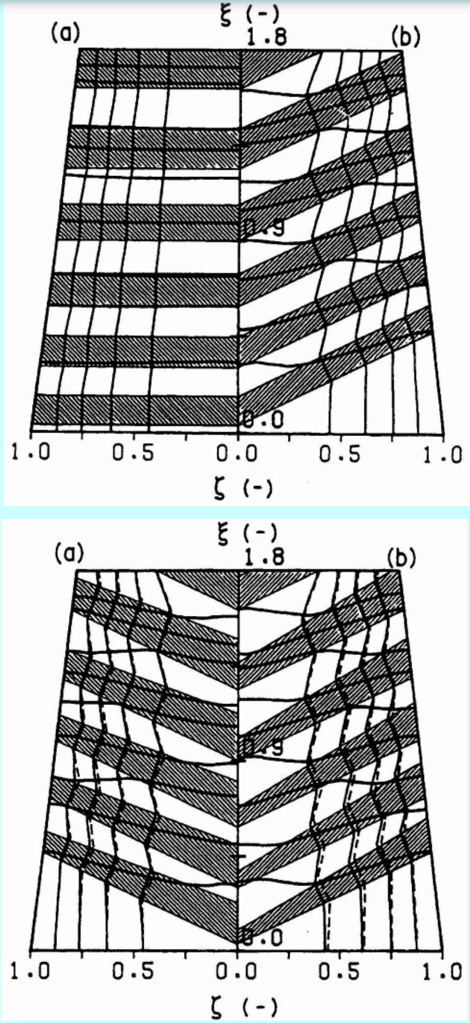
(a) Visualized streamlines

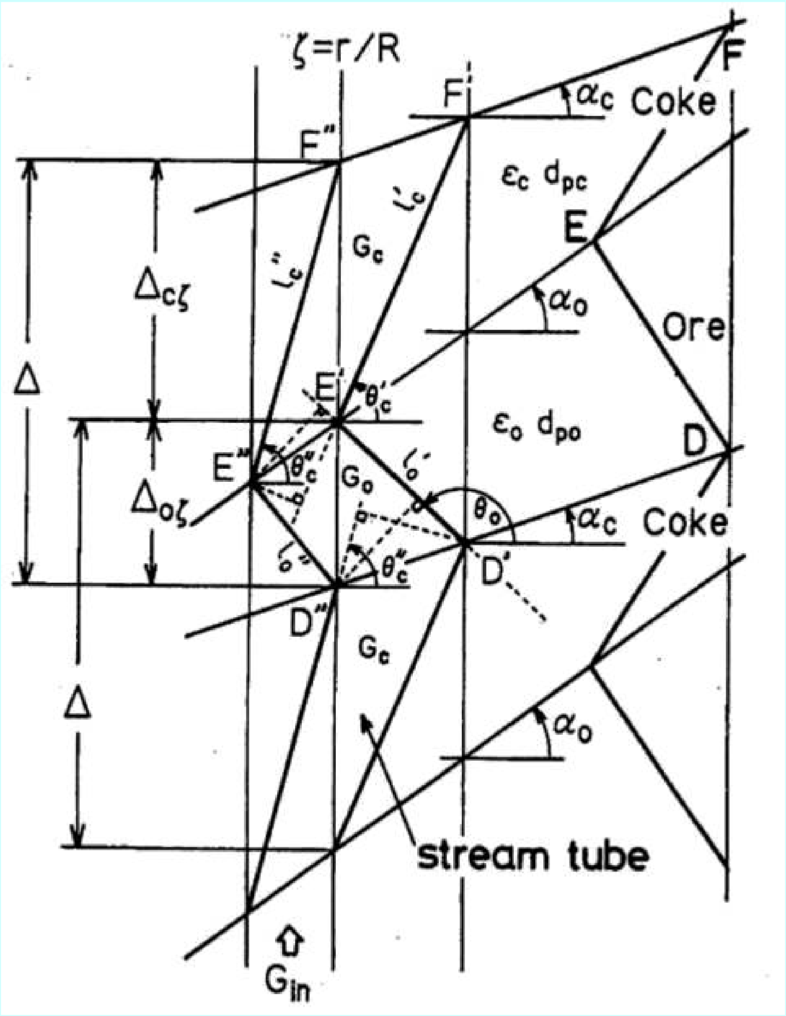
(b) Comparison between observed and predicted streamlines

鉱石、コークス層の粒径、空間率、堆積角、層厚比によっても偏流

Fig. Gas-streamlines in a two-dimensional bed having layered structure of silica-gel particles (Kuwabara et al., 1988) 10) .

層状装入物相内不均一ガス流れの近似解析
(Approximate Analysis of Non-uniform Gas Flow)



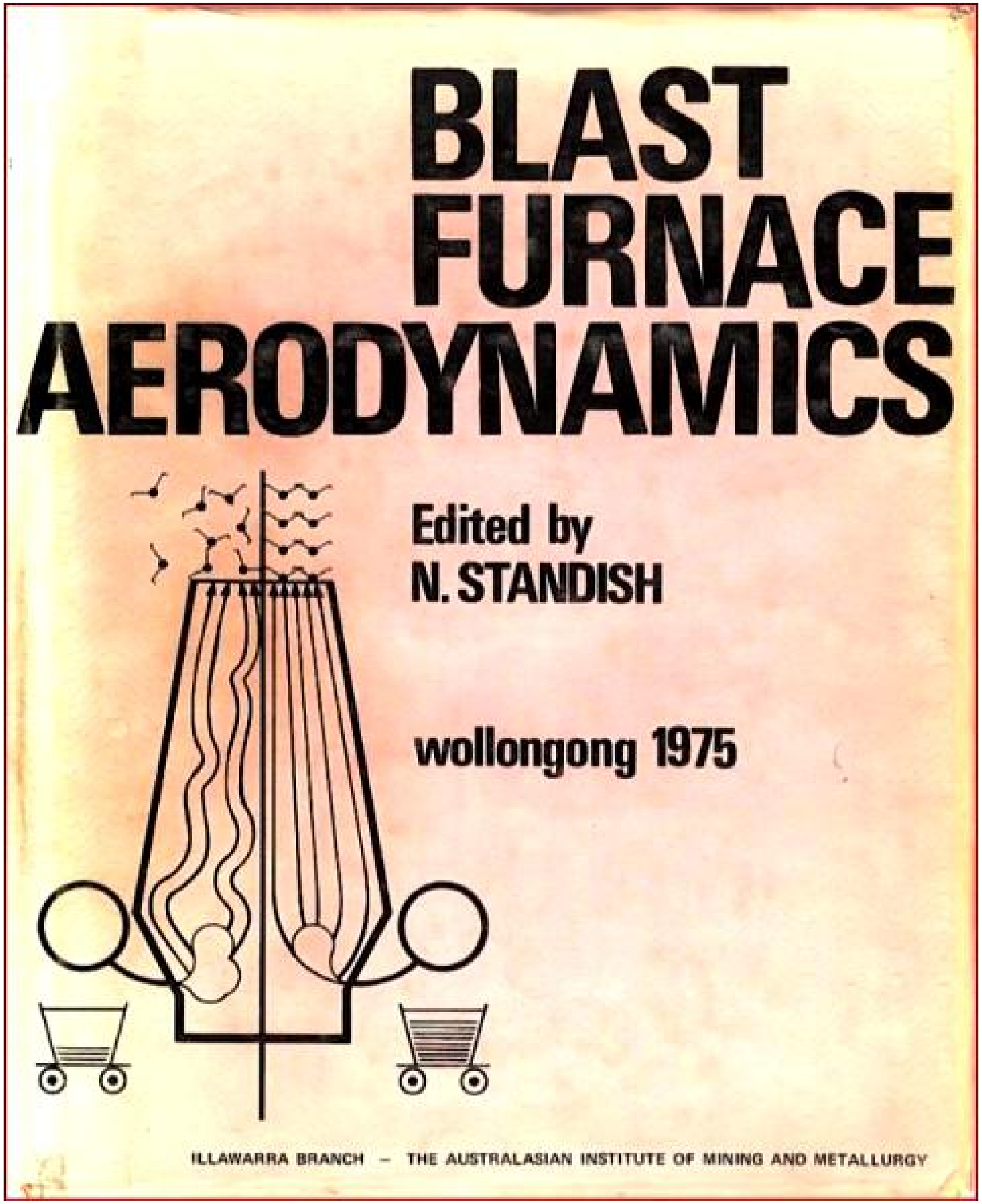


A streamline along a contour of stream - function φ which satisfies the continuity eqation may correspond to a wall of streamtube

Non-uniform flow stems from the principle that gas flows so as to minimize its pressure loss through a tube.

(a) Numerical analyses (b) Schematic concept of approximate analysis

Fig. Numerical and analytical investigation of gas flow through layered burdens (M. Kuwabara et al., 1976, 1988) $^{10)}$.



BLAST
FURNACE
AERODYNAMICS

Edited by
N. STANDISH

wollongong 1975

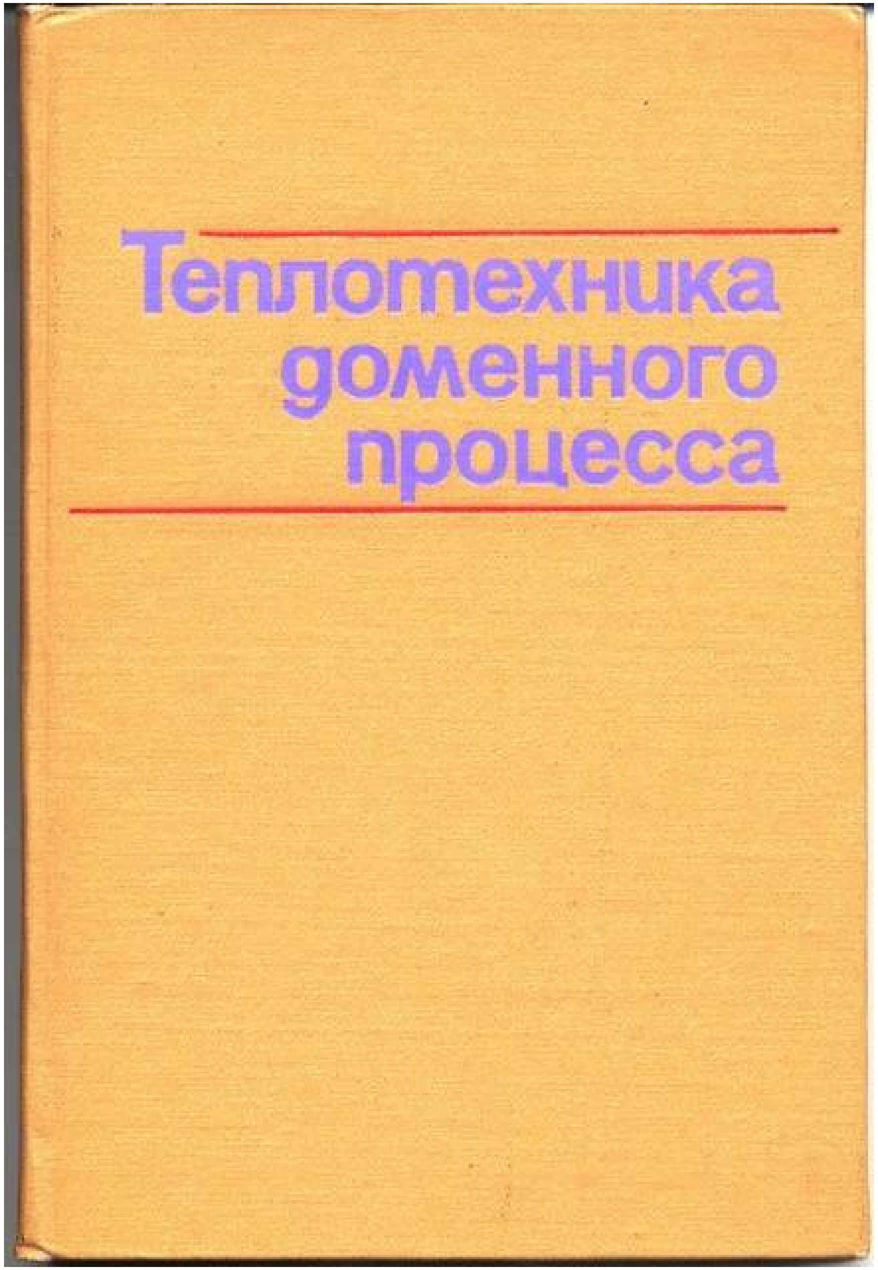
ILLAWARRA BRANCH – THE AUSTRALASIAN INSTITUTE OF MINING AND METALLURGY

世界最初の高炉の流体力学シンポジウム(1975) 11)

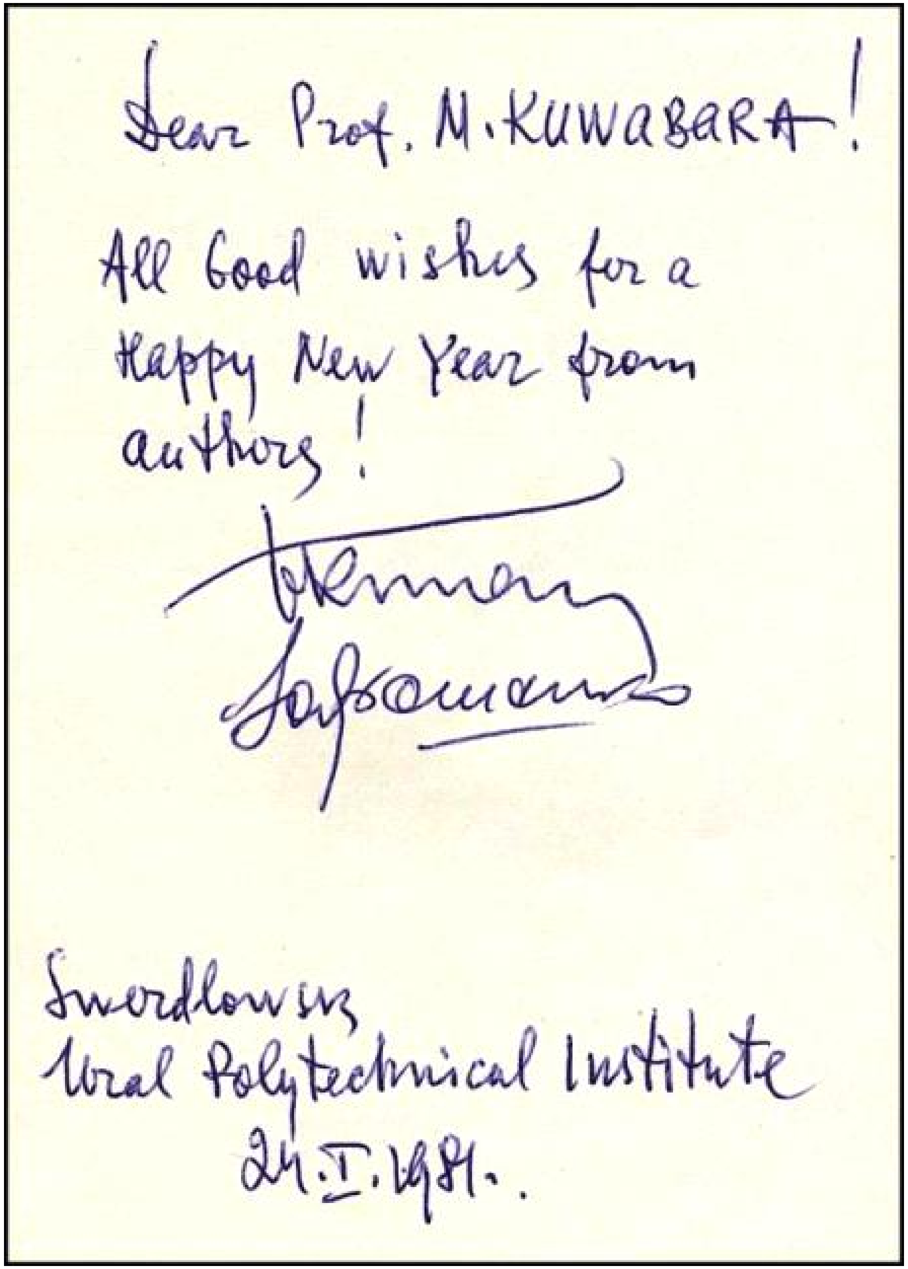
↓

自身初の国際学会出席（30才）

- 世界的な研究の潮流の先端をきることができた。
- 著名な研究者との交流機会を得た。



Теплотехника
доменного
процесса



Dear Prof. M. KUWABARA!

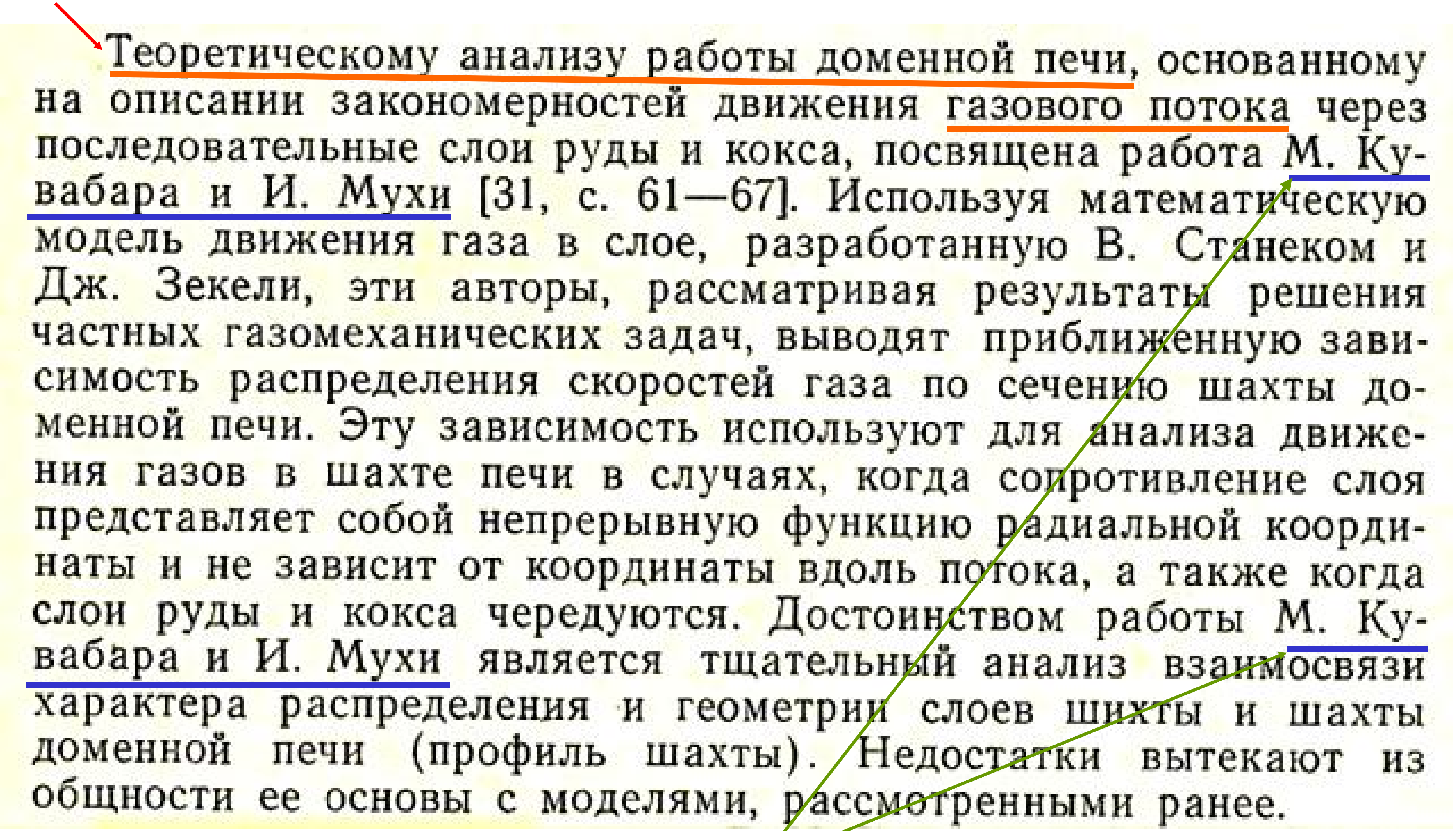
All Good wishes for a
Happy New Year from
authors!

Swerdlowsk
Ural Polytechnical Institute
24.I.1981.

当時世界的に著名であったロシアの **Prof. Kitaev** からの献本12) （1981）

Prof. Kitaev の著書に紹介された当方らの研究12)

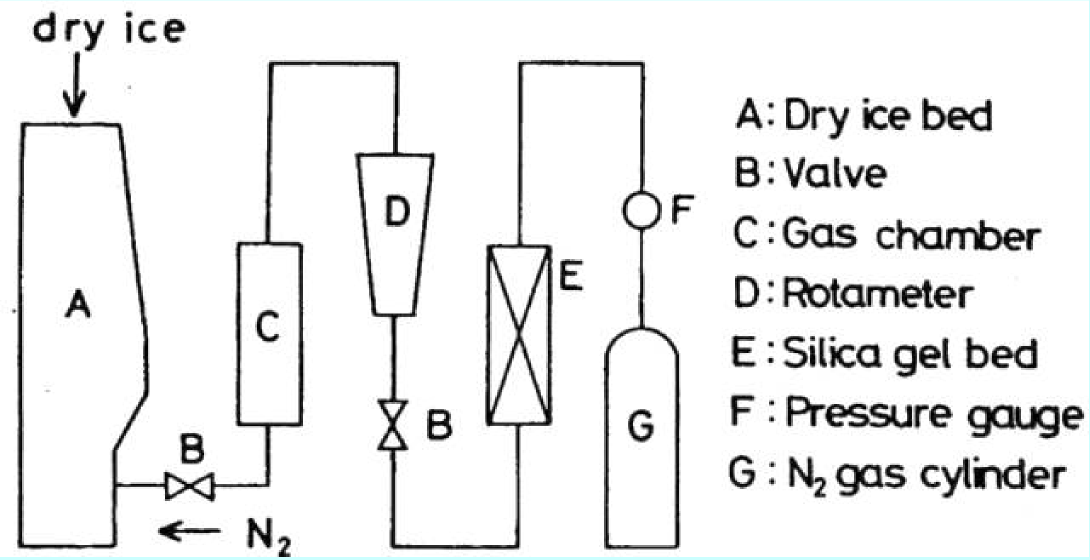
鉱石とコークスの層状装入物内ガス流れを考慮した高炉の理論解析



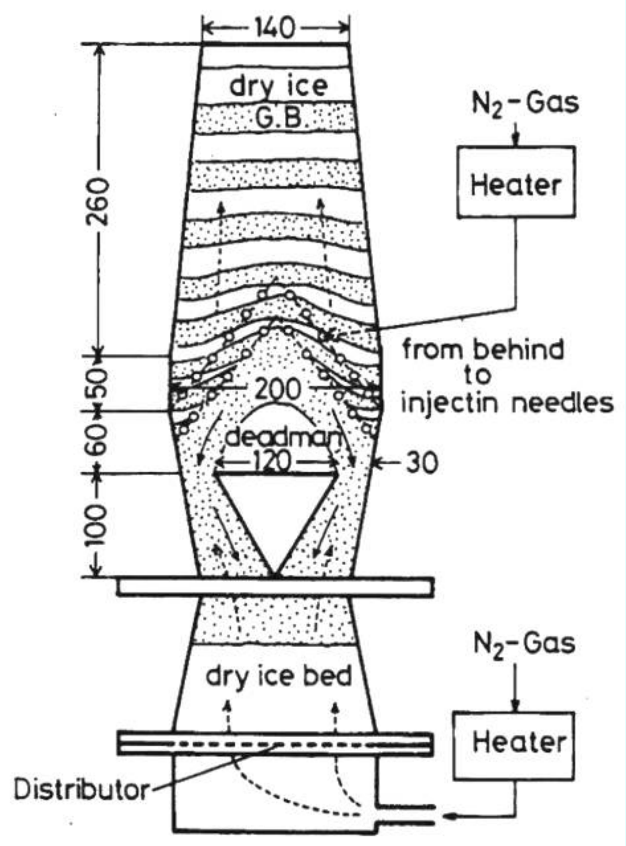
Теоретическому анализу работы доменной печи, основанному на описании закономерностей движения газового потока через последовательные слои руды и кокса, посвящена работа М. Кувабара и И. Мухи [31, с. 61—67]. Используя математическую модель движения газа в слое, разработанную В. Станеком и Дж. Зекели, эти авторы, рассматривая результаты решения частных газомеханических задач, выводят приближенную зависимость распределения скоростей газа по сечению шахты доменной печи. Эту зависимость используют для анализа движения газов в шахте печи в случаях, когда сопротивление слоя представляет собой непрерывную функцию радиальной координаты и не зависит от координаты вдоль потока, а также когда слои руды и кокса чередуются. Достоинством работы М. Кувабара и И. Мухи является тщательный анализ взаимосвязи характера распределения и геометрии слоев шихты и шахты доменной печи (профиль шахты). Недостатки вытекают из общности ее основы с моделями, рассмотренными ранее.

M. Kuwabara and I. Muchi

ドライアイスで模擬した高炉内装入物運動とその定式化



Experiment I
(羽口先コークス燃焼を駆動力とする運動)

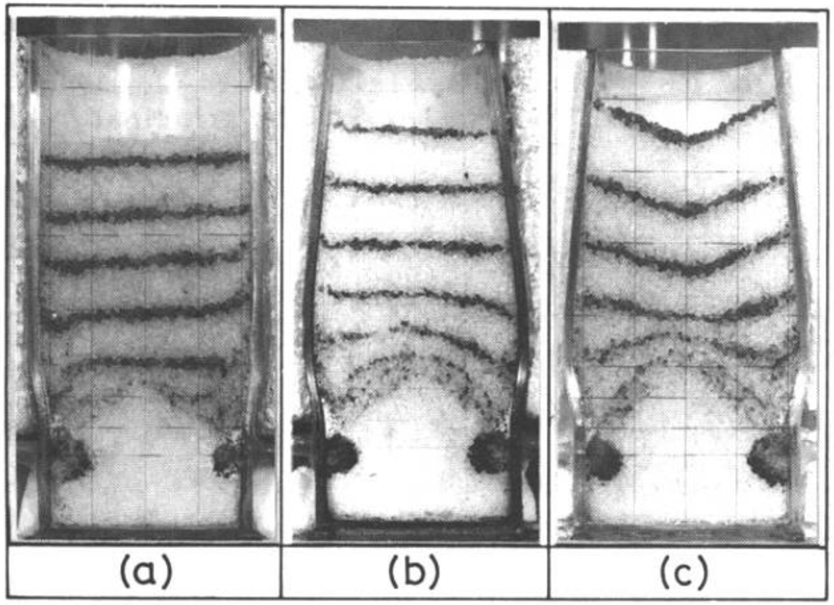


Experiment II
(鉱石溶融を駆動力とする運動)

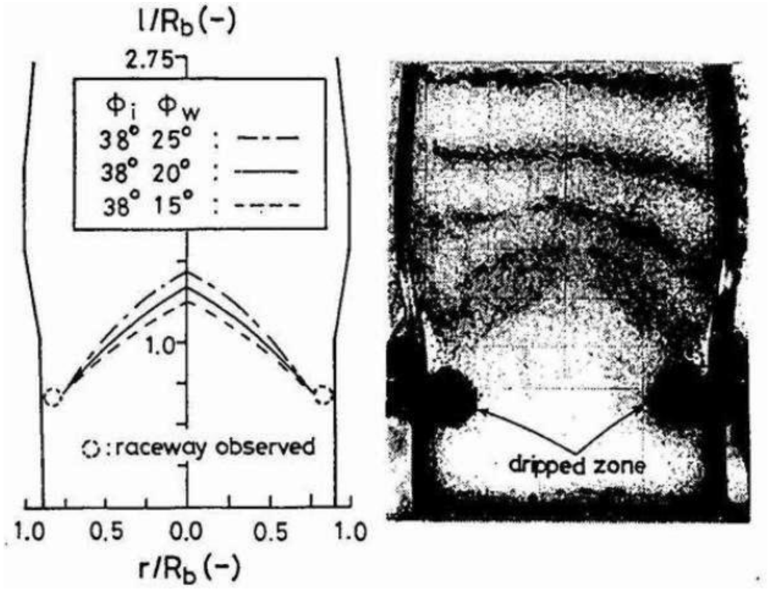
Newly revised experimental methods for simulating burden flows in BF without any mechanical discharging system

Fig. Solid flow experiments in cold models packed with Dry ice (Kuwabara et al., 1988) 13) .

Dry ice for coke (タイムラインは着色ドライアイス)



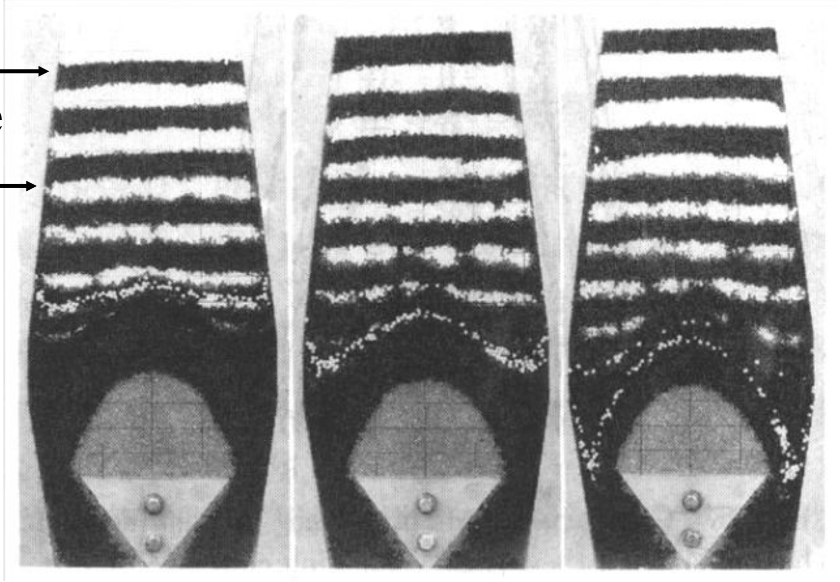
Burden flow in Experiment I.



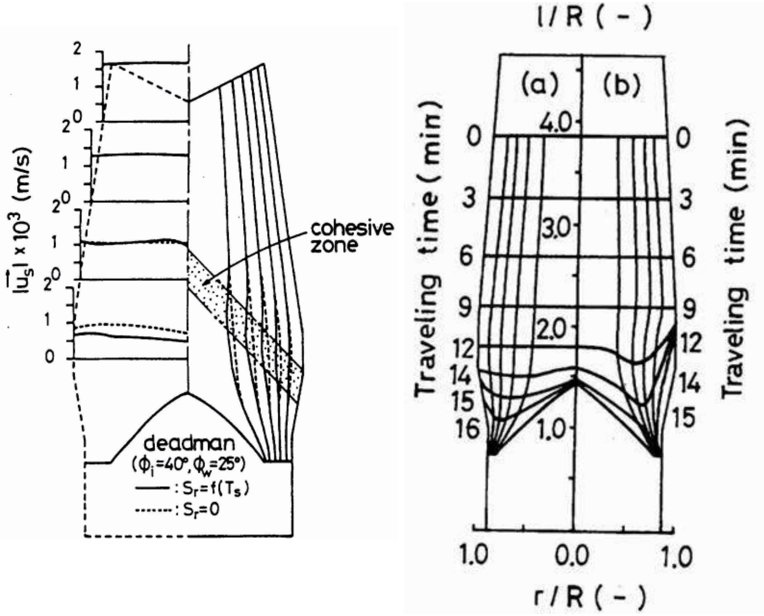
Formulation of deadman shape

G.B. for coke

Dry ice for ore



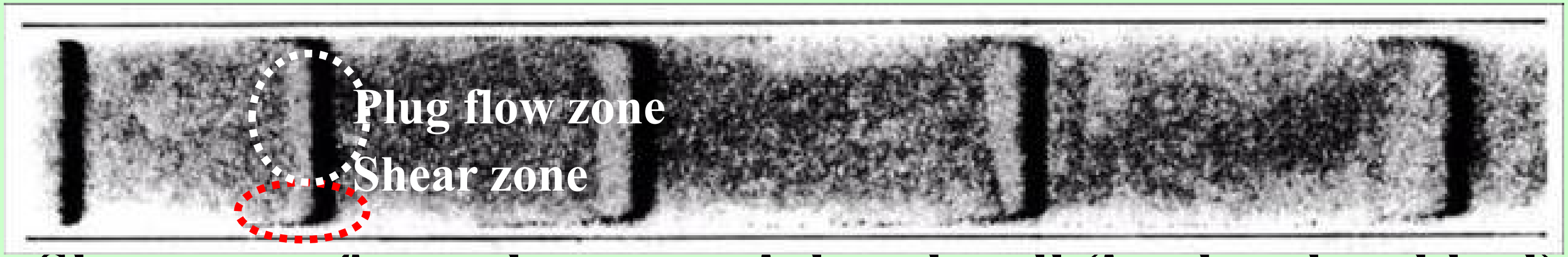
Burden flow in Experiment II.



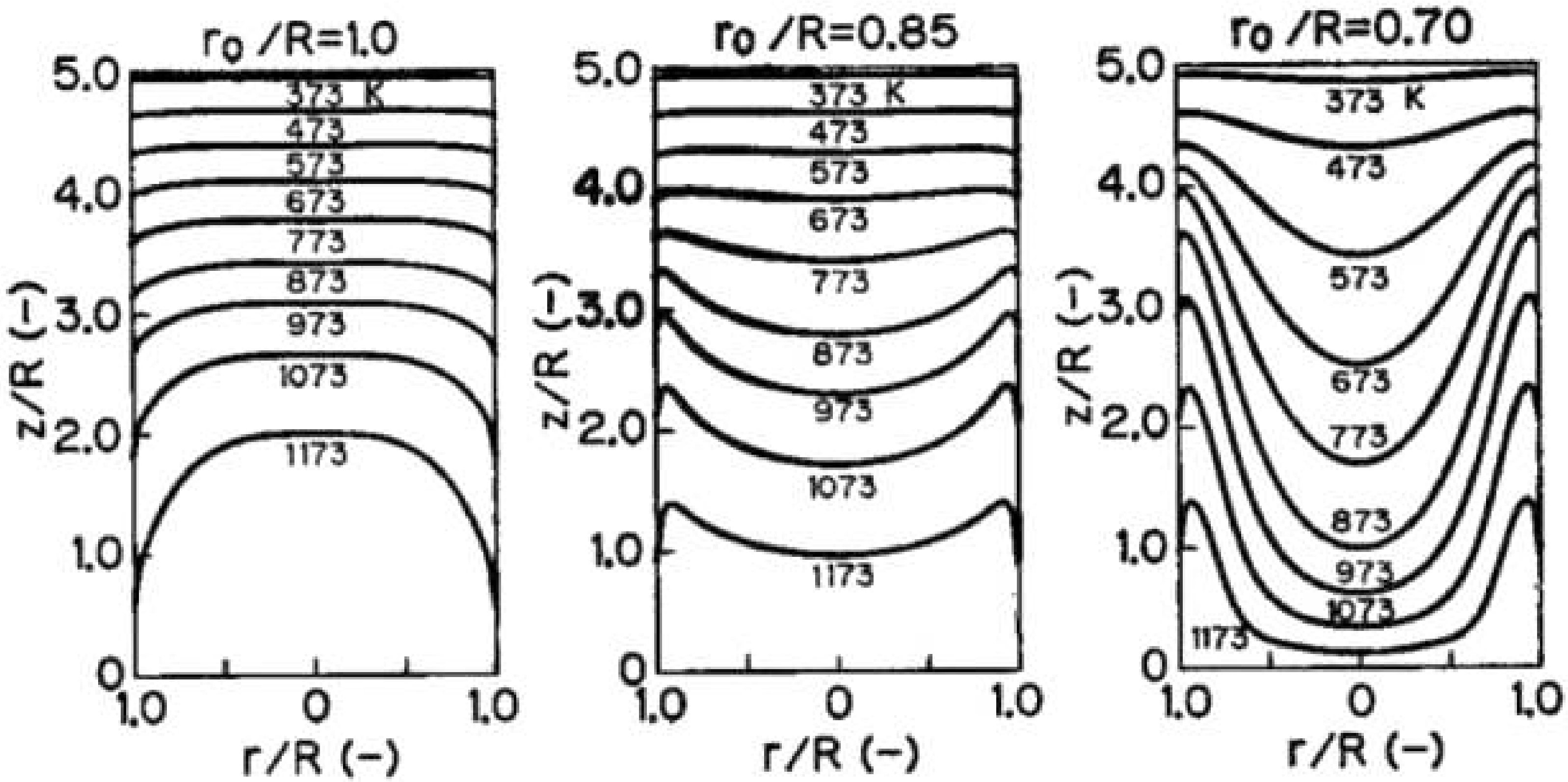
Formulation of flow pattern

Fig. Solid flow patterns and their mathematical formulations(1988)13)

固体流れが移動層内温度場に及ぼす影響



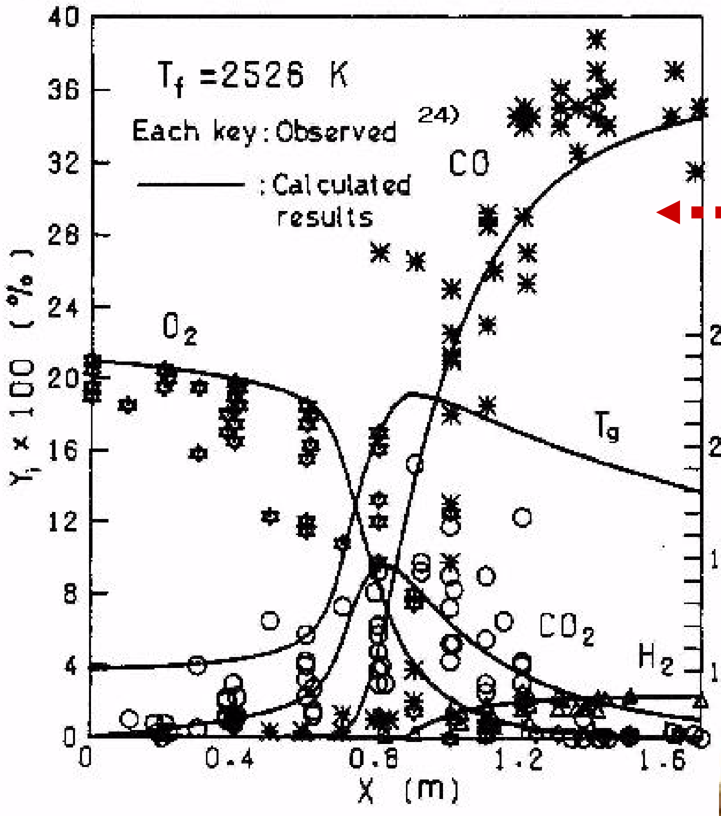
Shear zone formed near peripheral wall (in glass bead bed)

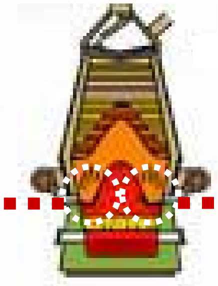


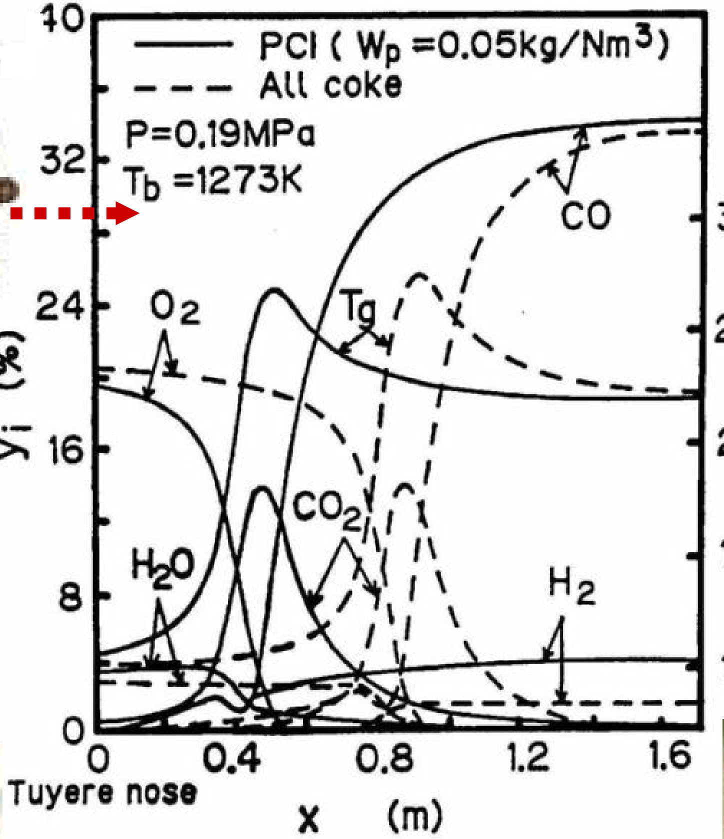
Prof. He

Fig. Effects of thickness of shear zone on gas isotherm in counter-current moving bed (Jicheng He, M.Kuwabara, I.Muchi, 1986)14) .

羽口先でのコークスおよび微粉炭燃焼







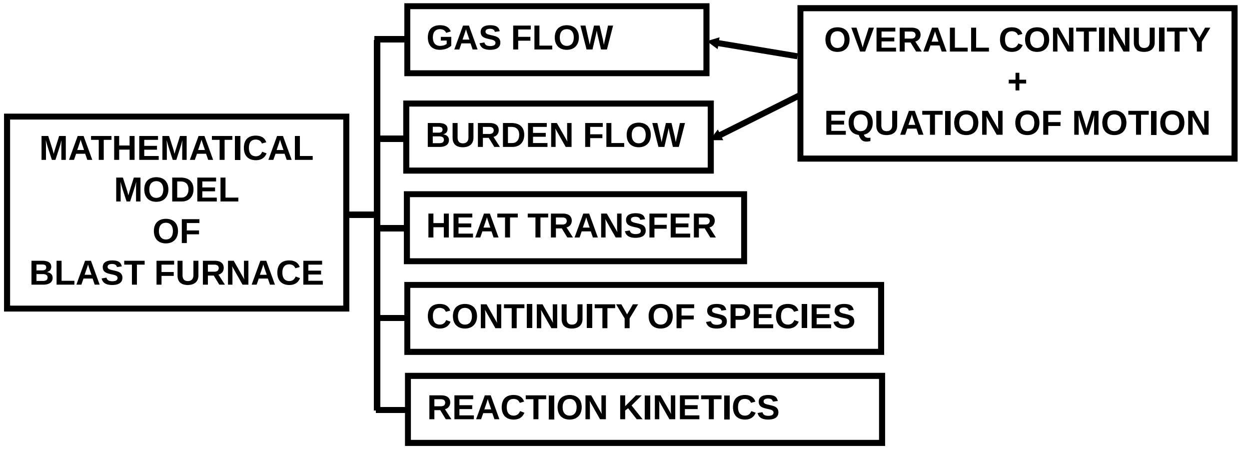
(a) coke combustion (1980)
(with Prof. Y. Xie) 15) →

(b) PC combustion (1986)
(with Prof. J. He) 16) →

⇨ **Theoretical basis of PCI operation initiated in 1983 in Japan**

Fig. Predicted axial-distributions of process variables in raceway by a kinetic model(Kuwabara et al., 198015) **, 1986** 16) **).**

高炉の二次元トータルモデルの開発



MATHEMATICAL MODEL OF BLAST FURNACE

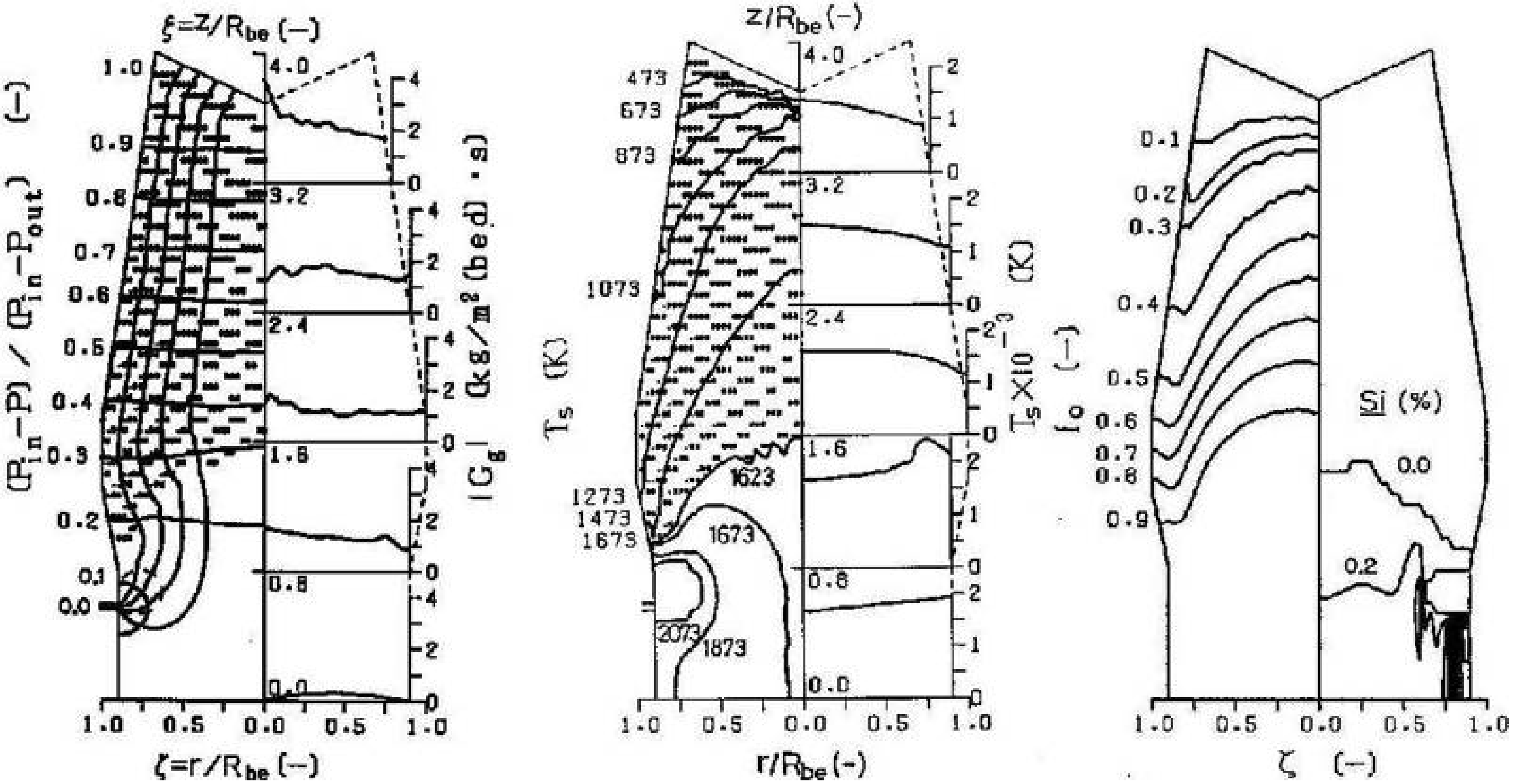
- **GAS FLOW**
- **BURDEN FLOW**
- **HEAT TRANSFER**
- **CONTINUITY OF SPECIES**
- **REACTION KINETICS**

OVERALL CONTINUITY + EQUATION OF MOTION

Table. Chemical rate processes considered.

$(1/3)\mathrm{Fe_2O_3} + \mathrm{CO} \rightarrow (2/3)\mathrm{Fe} + \mathrm{CO_2}$		$, R_1^*$
$(1/3)\mathrm{Fe_2O_3} + \mathrm{H_2} \rightarrow (2/3)\mathrm{Fe} + \mathrm{H_2O}$		$, R_2^*$
$\mathrm{CO_2} + \mathrm{C} \rightarrow 2\mathrm{CO}$		$, R_3^*$
$\mathrm{H_2O} + \mathrm{C} \rightarrow \mathrm{H_2} + \mathrm{CO}$		$, R_4^*$
$\mathrm{H_2O} + \mathrm{CO} \rightarrow \mathrm{H_2} + \mathrm{CO_2}$		$, R_5^*$
$\mathrm{FeO(l)} + \mathrm{C(s)} \rightarrow \mathrm{Fe(l)} + \mathrm{CO}$		$, R_6^*$
$\mathrm{C(s)} = \underline{\mathrm{C}}$		$, \mathit{Equilibrium}$
$\mathrm{SiO_2} + 3\mathrm{C} = \mathrm{SiC} + 2\mathrm{CO}$	$(T = T_{cr})$	$, \mathit{Equilibrium}$
$\mathrm{SiO_2} + \mathrm{C} = \mathrm{SiO(g)} + \mathrm{CO}$	$(T < T_{cr})$	$, \mathit{Equilibrium}$
$\mathrm{SiC} + \mathrm{CO} = \mathrm{SiO(g)} + 2\mathrm{C}$	$(T > T_{cr})$	$, \mathit{Equilibrium}$
$\mathrm{SiO(g)} + \underline{\mathrm{C}} \rightarrow \underline{\mathrm{Si}} + \mathrm{CO}$		$, R_7^*$

Fig. Two-dimensional model of blast furnace (Kuwabara et al., 1983 [17] , 1991 [18]).



(a) gas flow

(b) temperature

(c) fractional reduction and Si

The first comprehensive two-dimensional model possible to predict Si content and temperature of hot metal

Fig. Typical computed results from mathematical two-dimensional model (Kuwabara et al., 1983 17) , 1991 18)).

人生、良いことばかりは続きません！
必ず大きな試練があります。

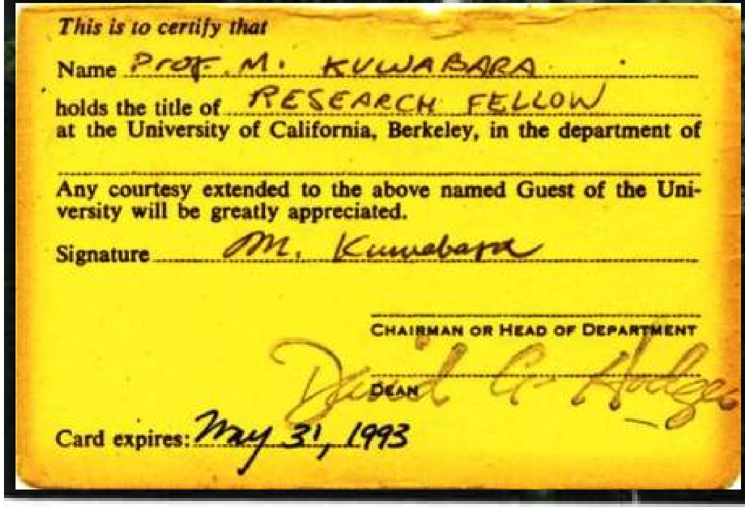
33-43才（さらに・・）
奇病(RLH)の克服（?）

禁煙、禁酒(?)、ソフトボールで気分転換：
1988: 公式審判員3種（日本ソフトボール協会）
1989: 公式審判員2種（ 同上 ）
名大スポーツ大会ソフトボールの部でも何度か優勝、準優勝。栄光の工学部Bチーム！


千種区ソフト
敢闘賞メダル

そして海外体験

かって声をかけていただいていた Prof. James W. Evans のもとへ



This is to certify that

Name PROF. M. KUWABARA

holds the title of RESEARCH FELLOW

at the University of California, Berkeley, in the department of

Any courtesy extended to the above named Guest of the University will be greatly appreciated.

Signature M. Kuwabara

CHAIRMAN OR HEAD OF DEPARTMENT

David A. Hodges

DEAN

Card expires: May 31, 1993

小さな種から大きな成果
を得る研究思想を学ぶ

1992 - 1993：　University of California at Berkeley

新しい発想での研究とプロセス開発

例：

1. 熱力学原理と反応工学によるプロセス開発

2. 現象、プロセスのアナロジー的発想

3. 既存プロセスの技術の限界打破

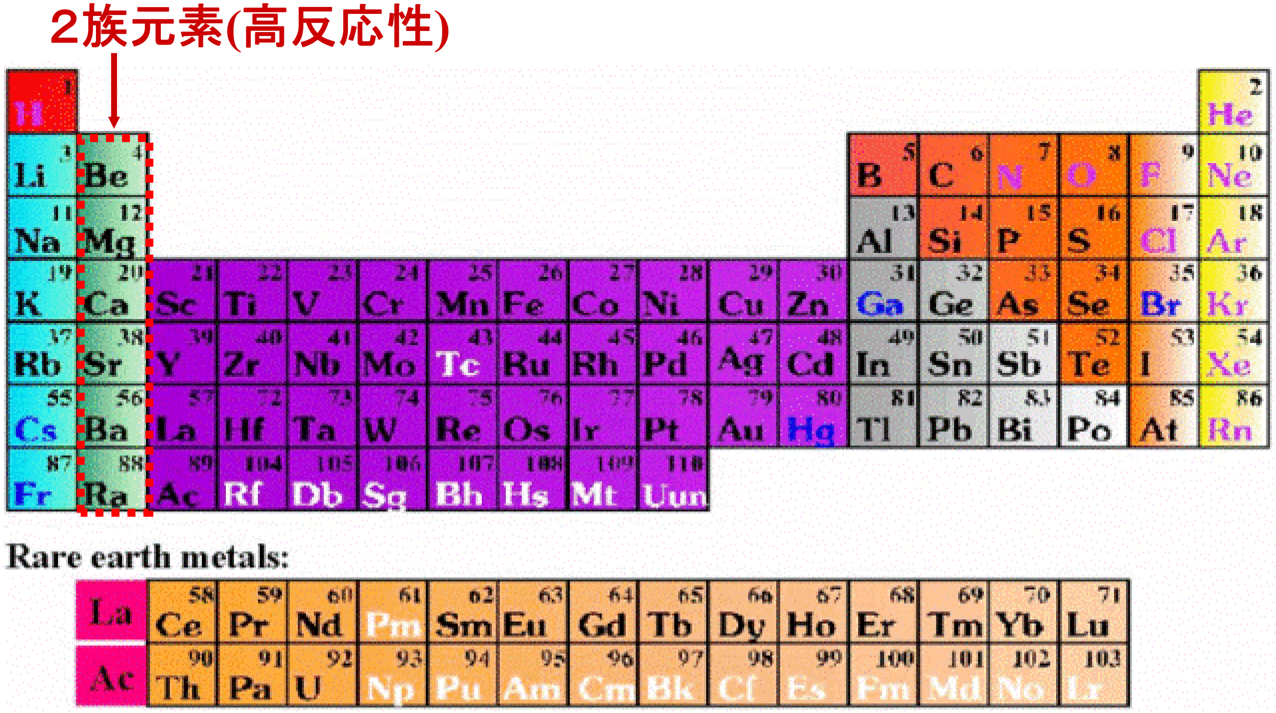
1. 熱力学原理と反応工学によるプロセス開発

Mg蒸気利用−溶銑脱硫、溶鋼脱酸

Desulfurization and Deoxidation of Iron Melt by Injecting Mg-gas In-situ Produced

$\mathrm{Mg(g)} + \underline{\mathrm{S}} = \mathrm{MgS(s)}$, $\mathrm{Mg(g)} + \underline{\mathrm{O}} = \mathrm{MgO(s)}$: 安全性、操作性、効率的Mg供給

Table. Periodic table of elements.

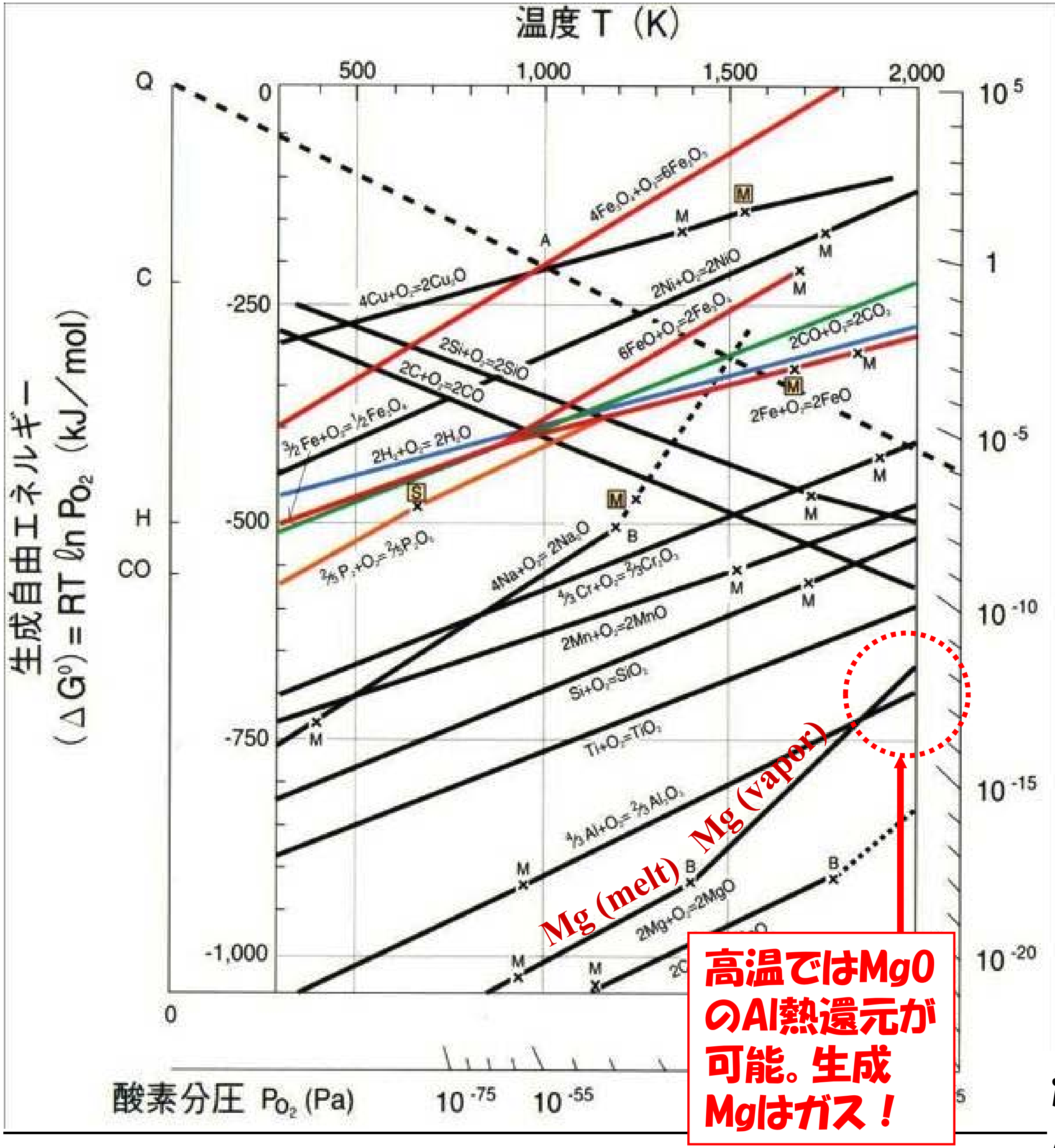


２族元素(高反応性)

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun								

Rare earth metals:

La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr



高温ではMgOのAl熱還元が可能。生成Mgはガス！

Mg(g)生成反応(吸熱):

$4MgO(s) + 2Al(l) =$

$3Mg(g) + MgO\cdot Al_2O_3(s)$ (1)

$3(MgO\cdot Al_2O_3)(s) + 2Al(l) =$

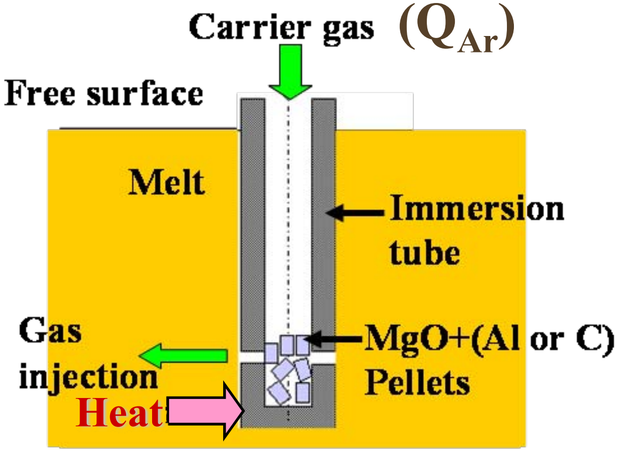
$3Mg(g) + 4Al_2O_3(s)$ (2)

脱硫、脱酸反応：

$Mg(g) + \underline{S} = MgS(s)$ (3)

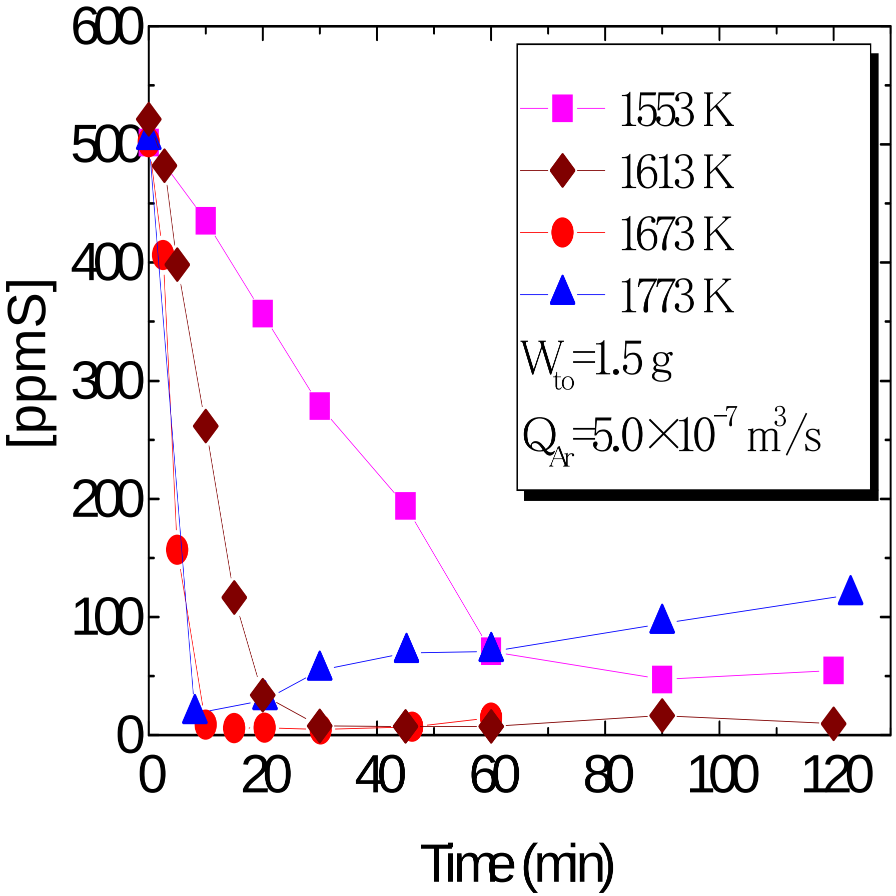
$Mg(g) + \underline{O} = MgO(s)$ (4)

プロセス化



浸漬ノズル中の熱還元Mgを、Arガスで溶鋼中に吹込む。

Mgガスによる溶銑脱硫の検討項目



硫黄濃度の経時変化20)

温度は還元反応では高く、
脱硫反応では低い方が有利
→　温度制御が肝要。

脱硫の目標に対し、最適な
ペレット使用量(W_{to})がある。

ガス流量(Q_{Ar})や気泡径調節で
脱硫効率の最適化が可能。

特徴と効率向上化要因

楊ら19,20)：　日本鉄鋼協会澤村論文賞受賞（2002）

化学反応速度と反応開始温度21)

Ignition Temperature for SHS Reaction

1. $2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$

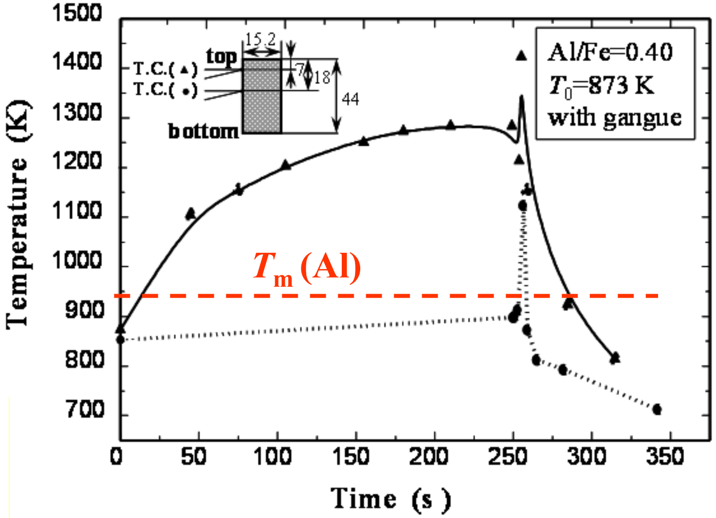


Fig. Variation of temperature of specimen during self-propagating thermit reaction.

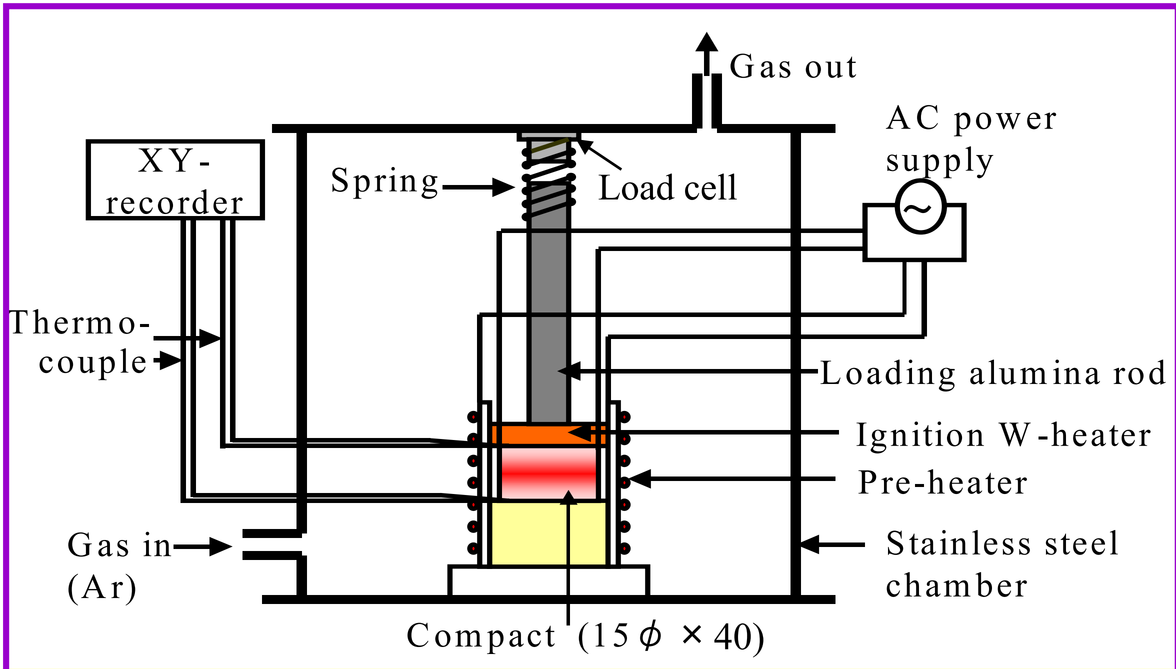


Fig. Experimental apparatus for SHS reaction.

2. $Mo + 2\,Si = MoSi_2$

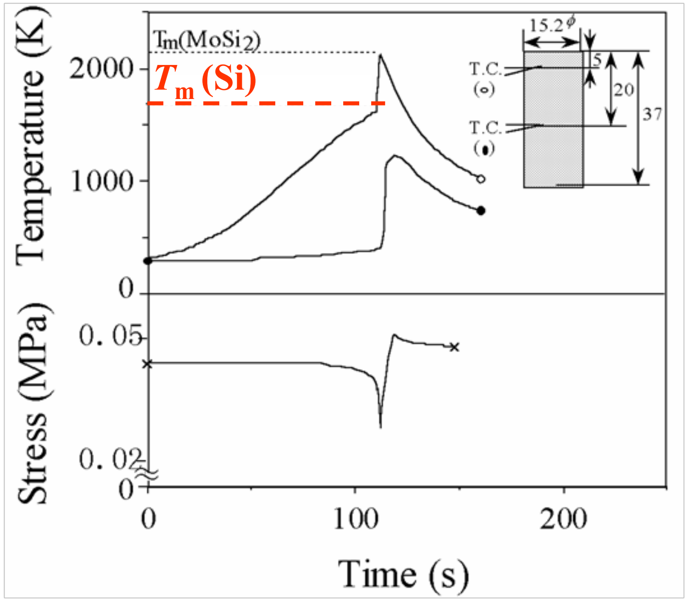
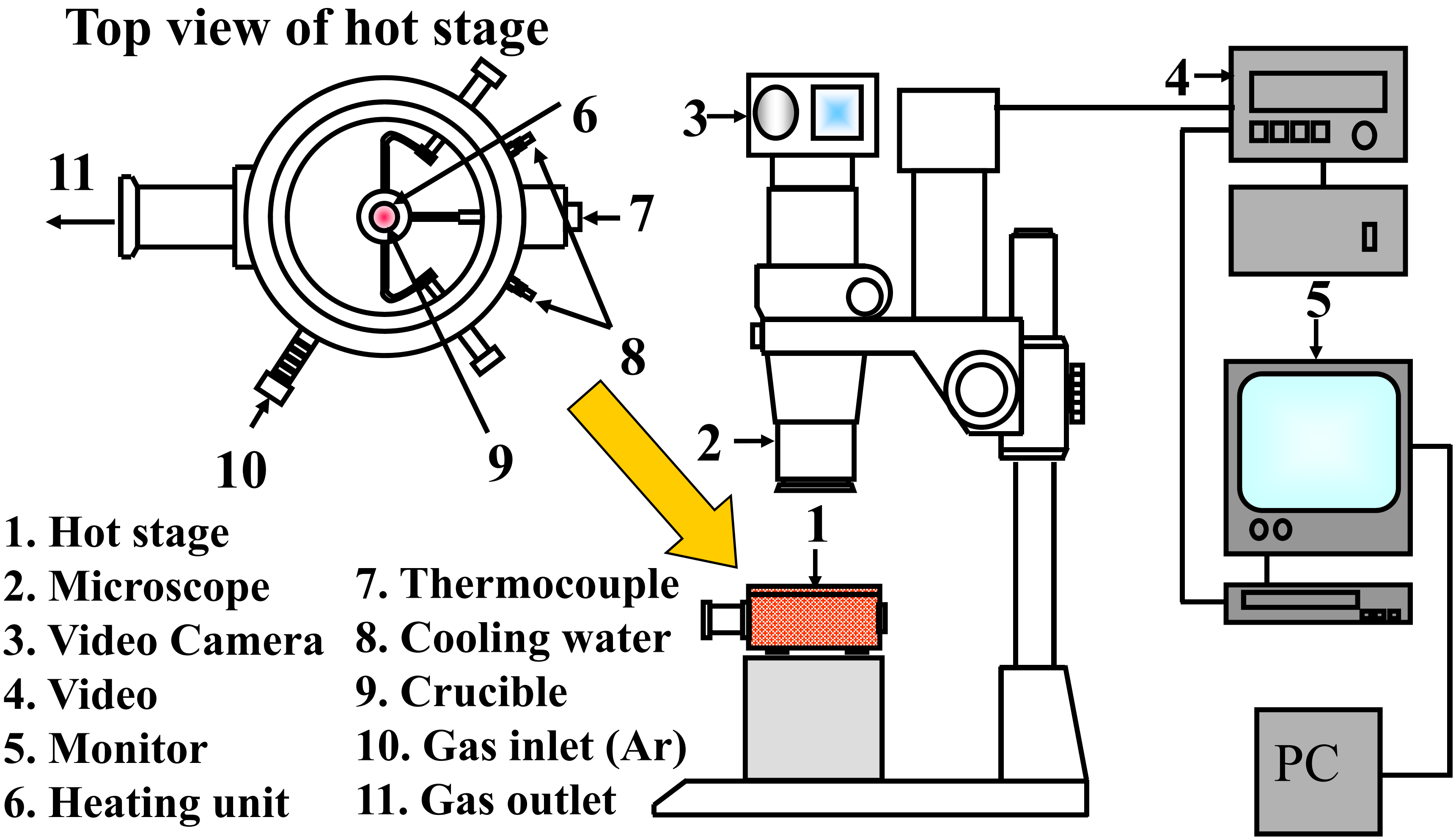


Fig. Variation of temperature during SHS of molybdenum disilicide ($MoSi_2$).

真の反応速度推算のために微視的反応機構を観察



1. Hot stage
2. Microscope
3. Video Camera
4. Video
5. Monitor
6. Heating unit
7. Thermocouple
8. Cooling water
9. Crucible
10. Gas inlet (Ar)
11. Gas outlet

Fig. Experimental unit of high temperature microscope (HOMS) for observing morphology change.

アルミ熱還元反応（Alによる酸化物還元）の反応機構

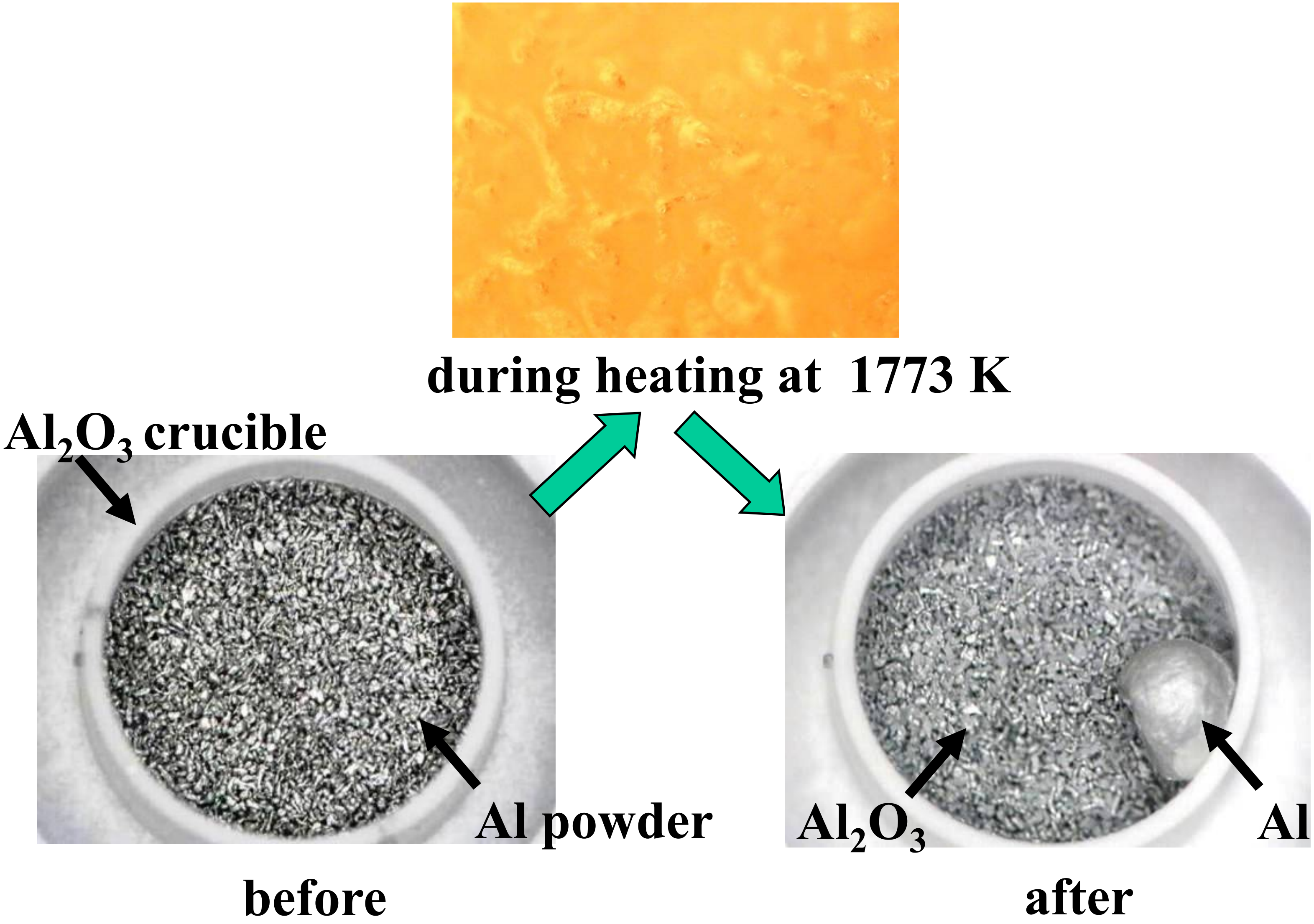
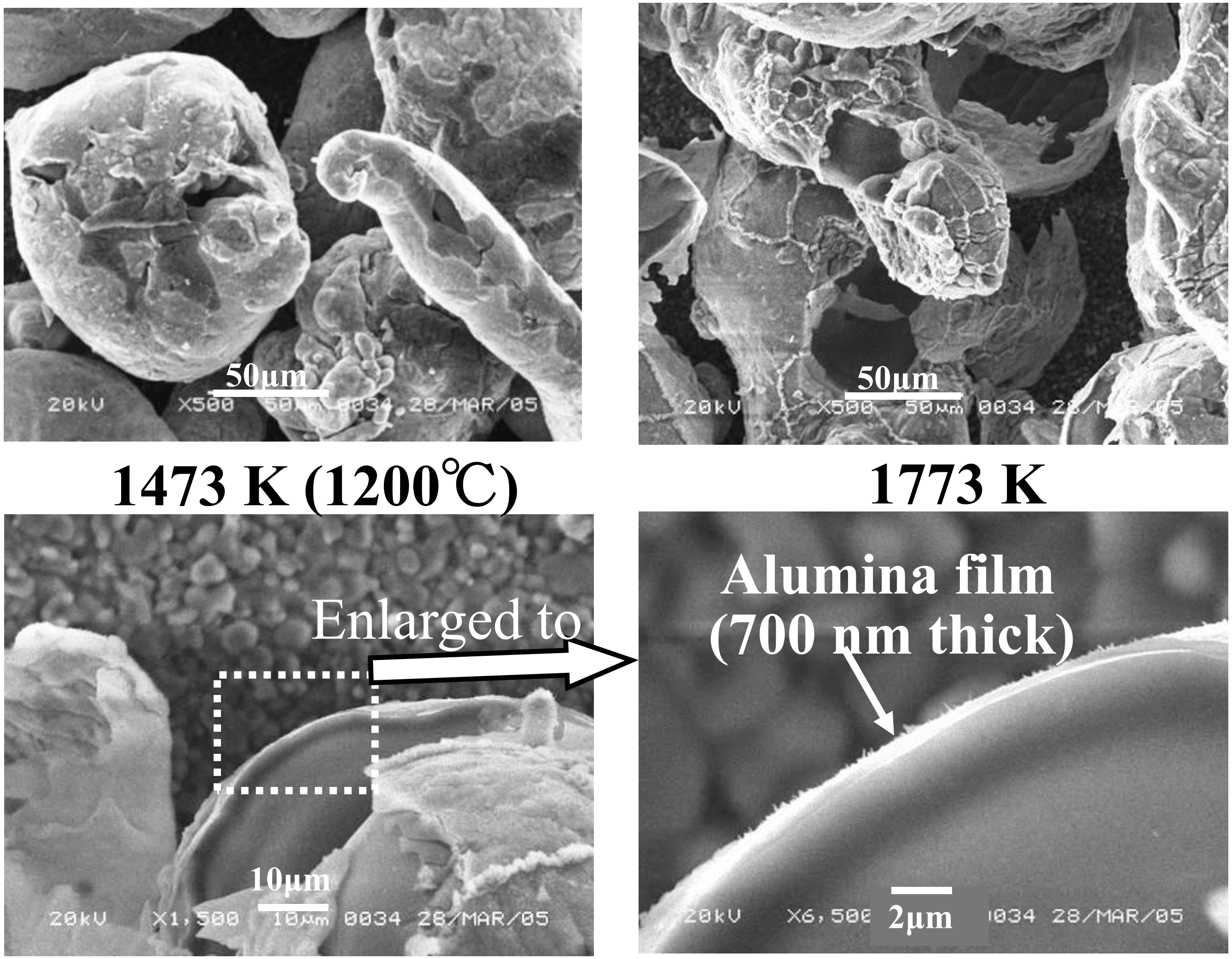


Fig. Morphology change in aluminum powders before and after heating up to 1773 K in Ar gas[22].



1473 K (1200℃)

1773 K

1773 K

1773 K

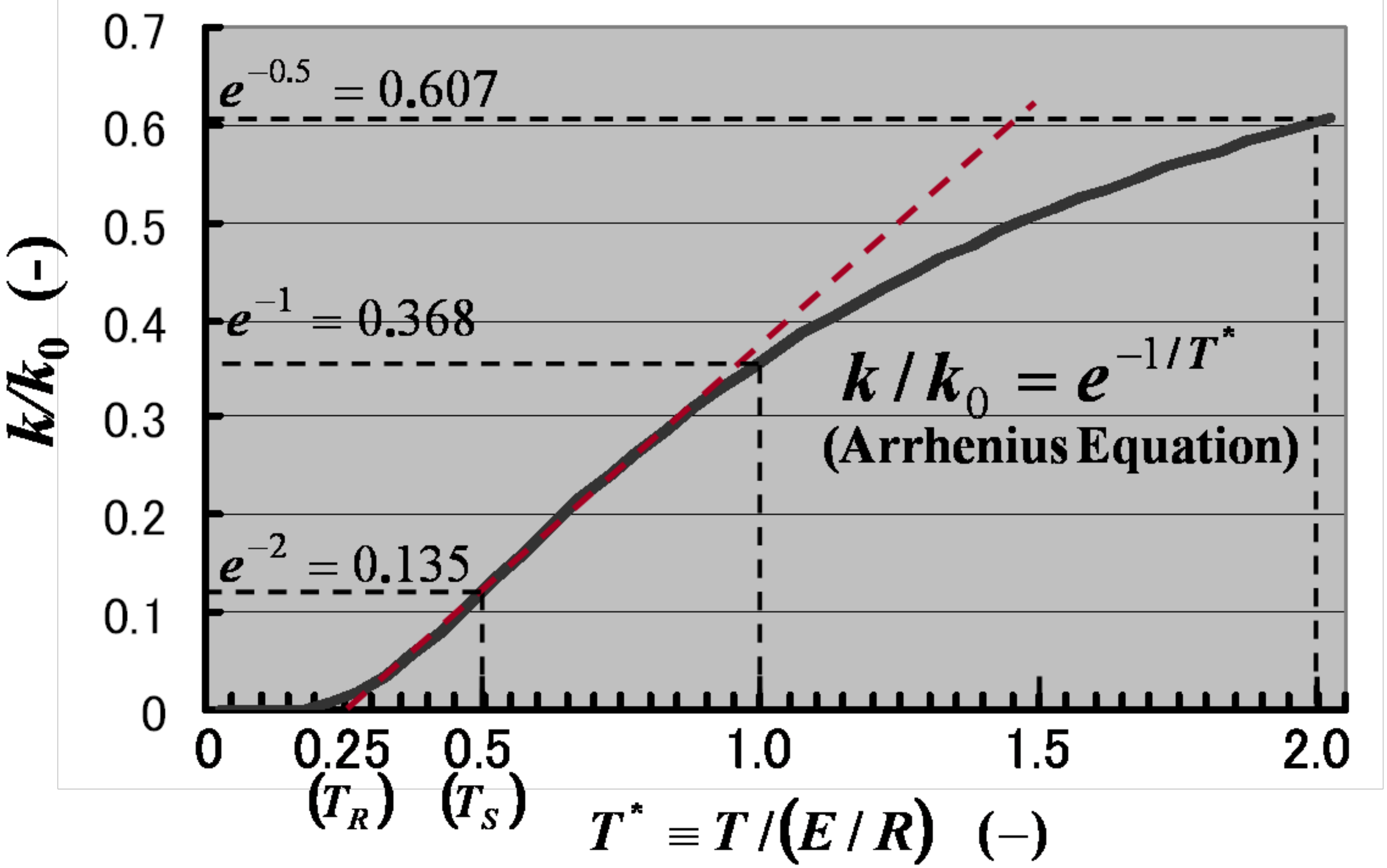
金属Alの
表面はア
ルミナ薄
膜で覆わ
れていた。

Fig. SEM image of morphology change in aluminum powders during heating up to 1773 K and after cooling down in Ar [22].

Al熱還元反応の速度は、アルミナ皮膜の破壊と周りの多孔質粉体層へのその後の溶融アルミの浸透の速度に律速されている。

Arrheniusの式 $k = k_0 e^{-E/RT}$ は信頼できるか？

$$k/k_0 = e^{-(E/R)/T} = e^{-1/[T/(E/R)]} = e^{-1/T^*}$$

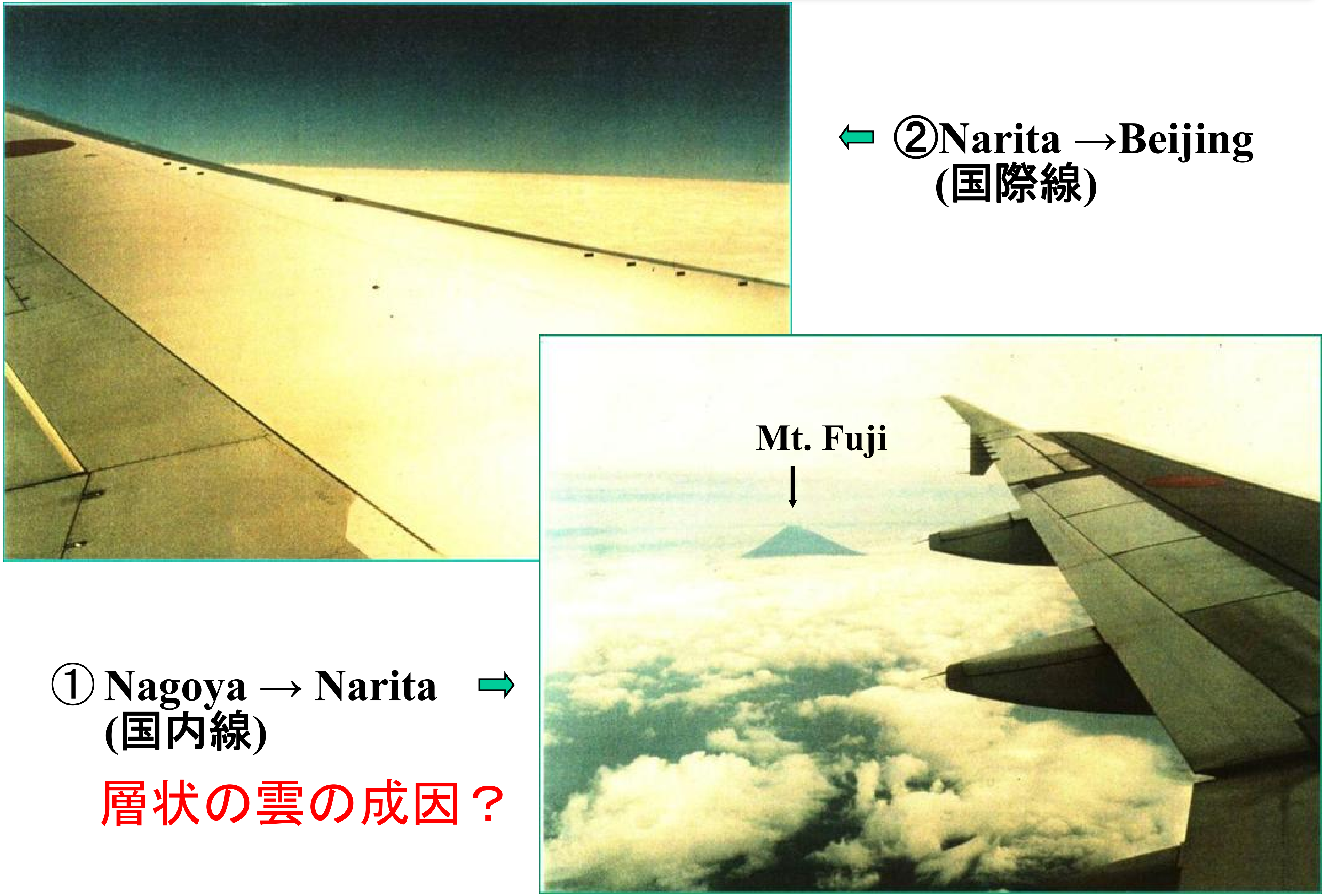


T_R (≒12500 K での $k/k_0 = e^{-4} \approx 0.018$ であるから，

反応速度が頻度因子の1%に達することさえ至難の業23)

2. 現象、プロセスのアナロジー的理解と研究の発想

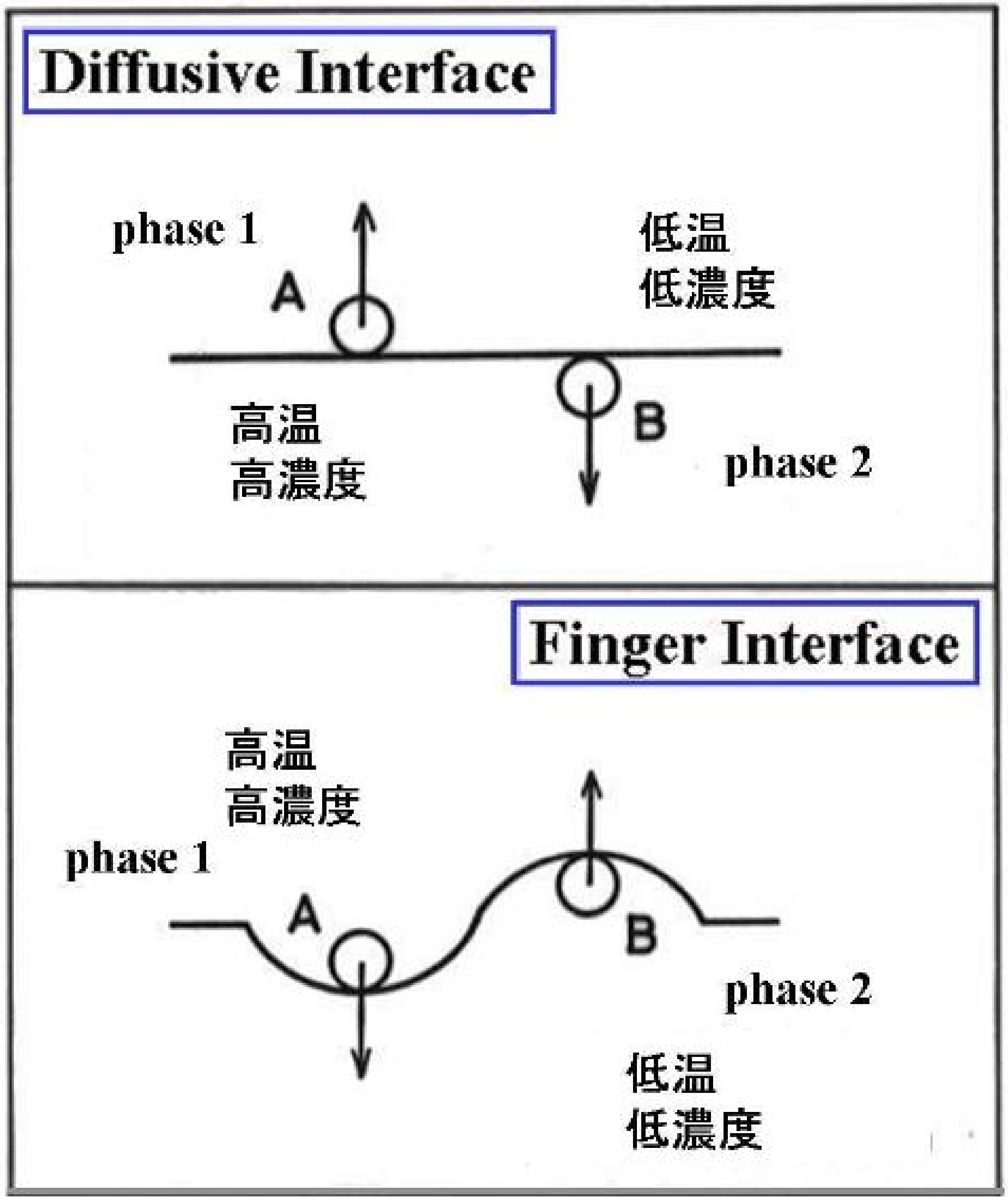
雲と凝固 - 二重拡散の話23)

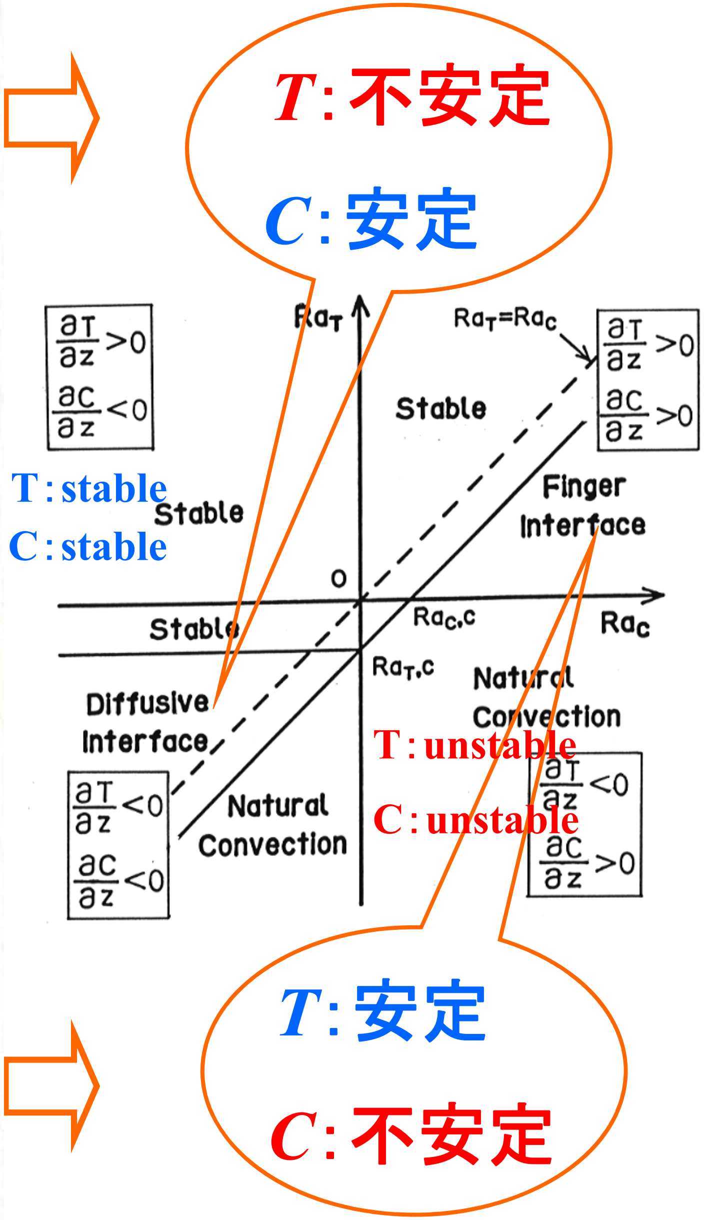


⇦ ②Narita →Beijing
(国際線)

① Nagoya → Narita ⇨
(国内線)

層状の雲の成因？



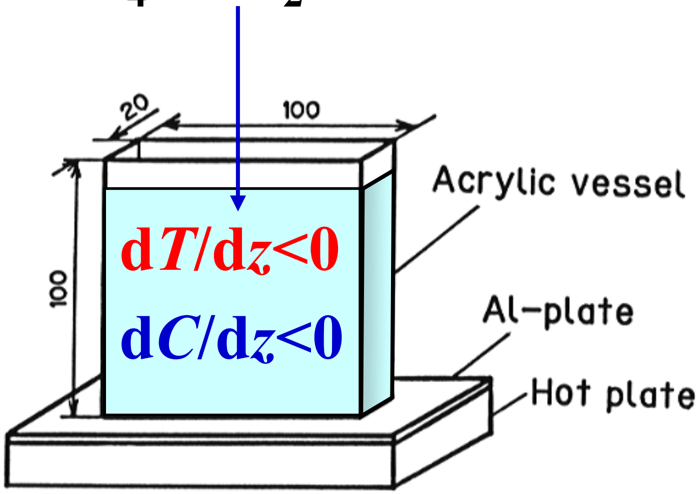


図．温度‐濃度レイリー数線図上での対流様式24)

Diffusive 型と Finger 型二重拡散の可視化実験

1. Diffusive interface

NH$_4$Cl-H$_2$O solution



T: 不安定
C: 安定

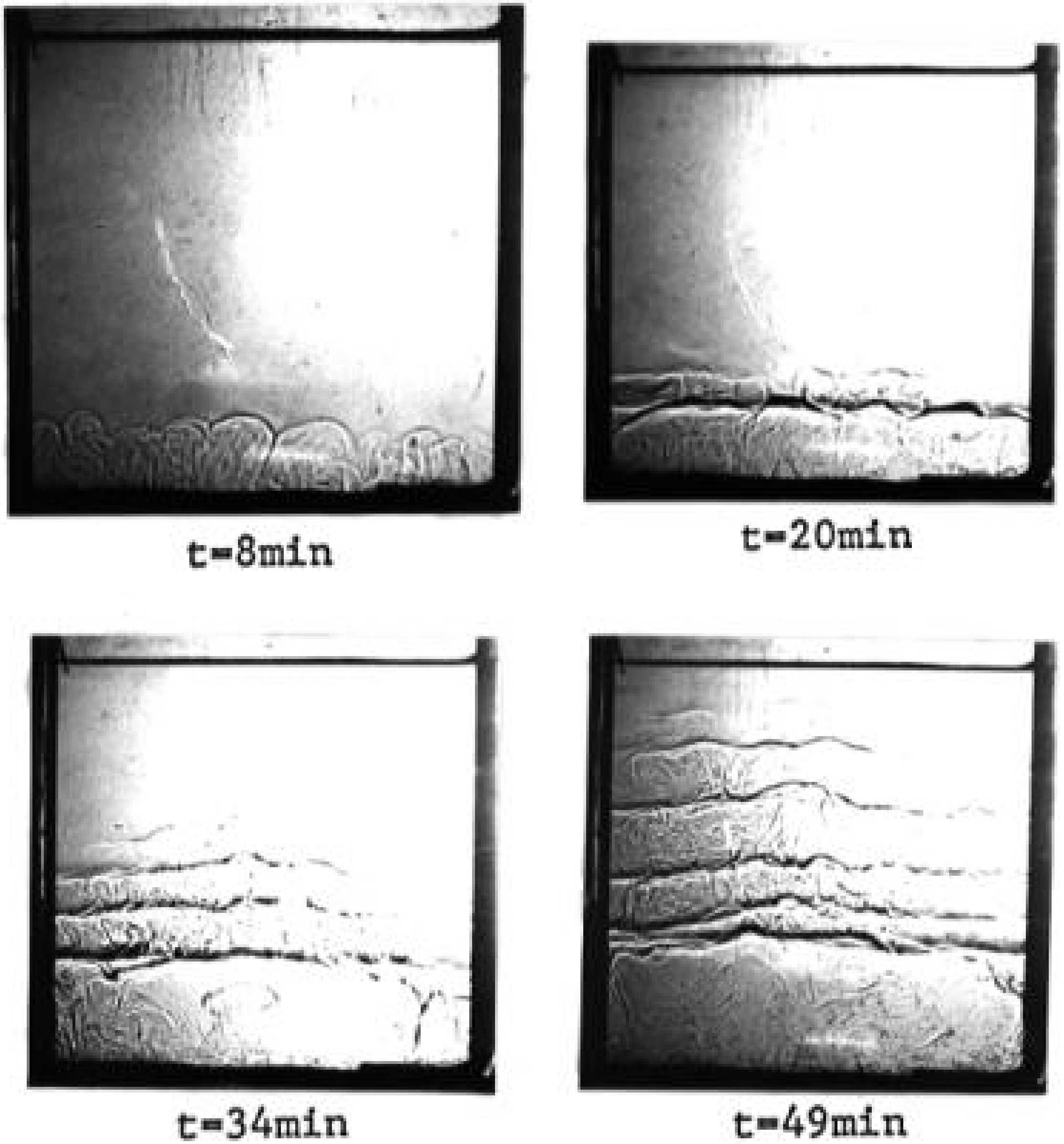
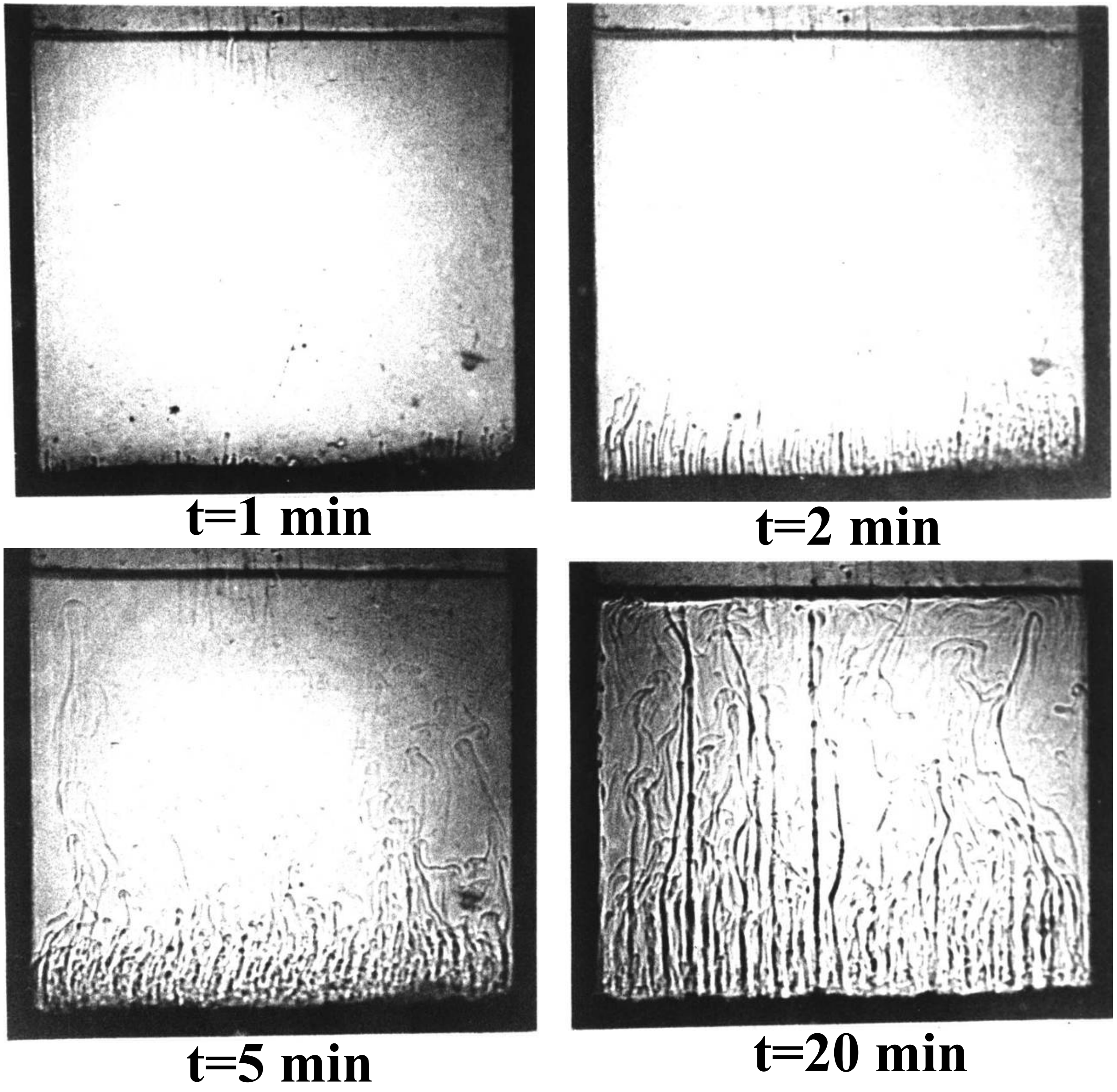

t=8min
t=20min
t=34min
t=49min

Fig. Transitional change in the diffusive interfaces visualized by the shadowgraph method [24].

2. Finger interface

$\mathrm{d}C/\mathrm{d}z>0$ C: 不安定

$\mathrm{d}T/\mathrm{d}z>0$ T: 安定


t=1 min

t=2 min

t=5 min

t=20 min

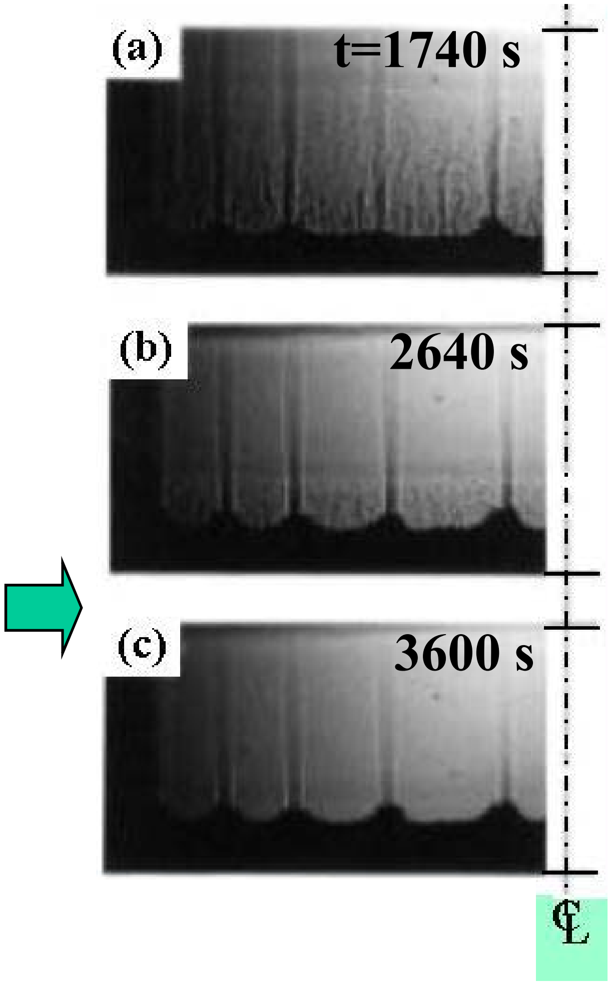
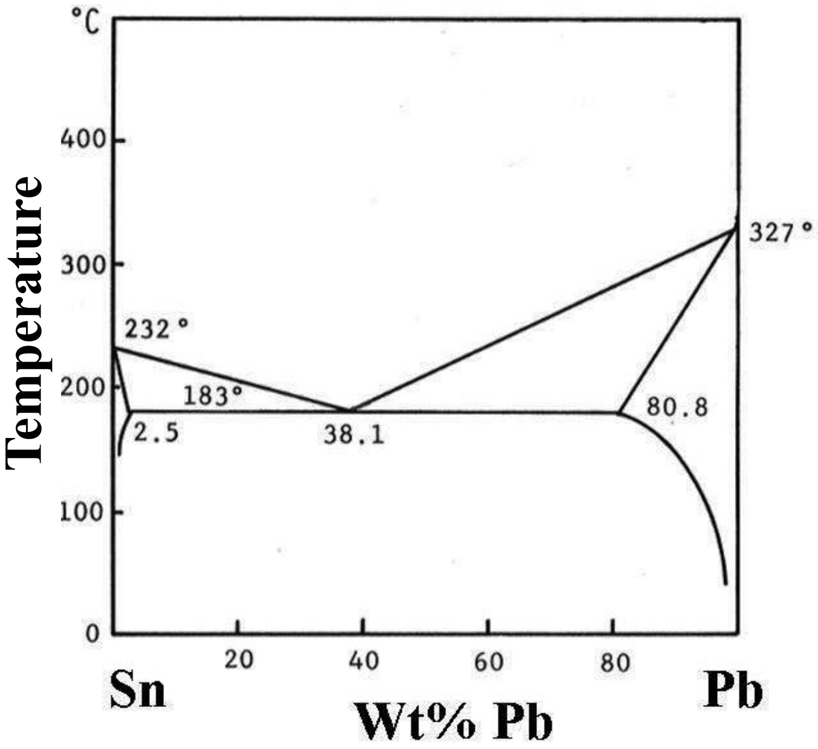


Fig. Transitional change in the finger interfaces visualized by the shadowgraph method [24).

2元合金系でも Finger 型2重拡散に基づく線状欠陥の形成を確認



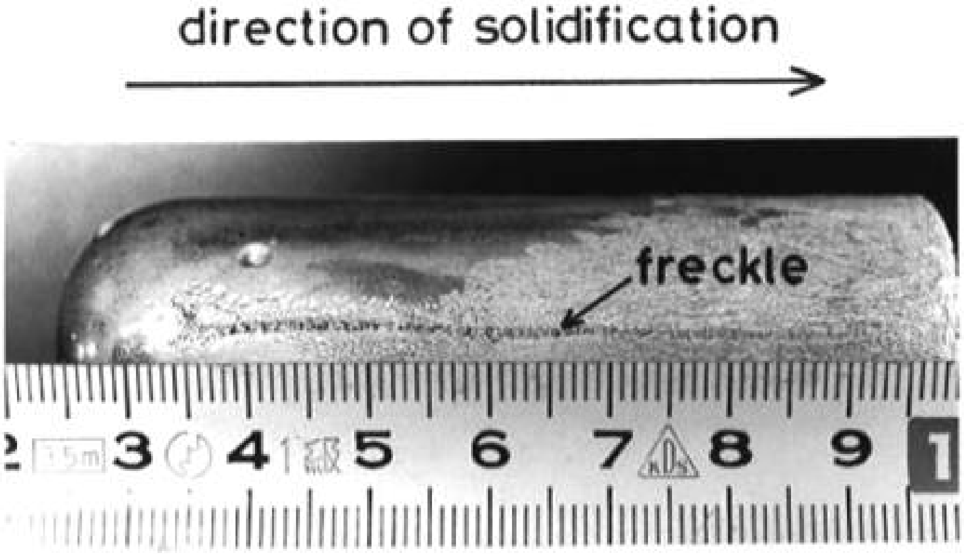


Photo. Overview of the surface of Solidified Sn-Pb ingot.

Fig. Freckle formation in uni-directionally solidified Sn-Pb binary alloy [24].

2元共晶合金系エンジンの一方向凝固時に発生するフレックル欠陥の原因と防止策を示唆

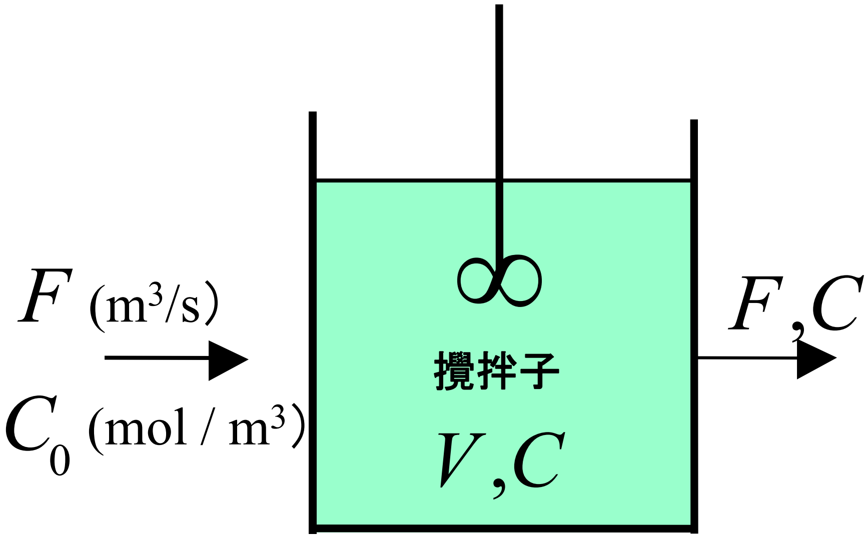
多くの現象とプロセスは完全混合槽的？

$$V\frac{dC}{d\theta}=FC_0-FC\ ,\quad \mathrm{I.C.}:\ \theta=0:C=C_i$$

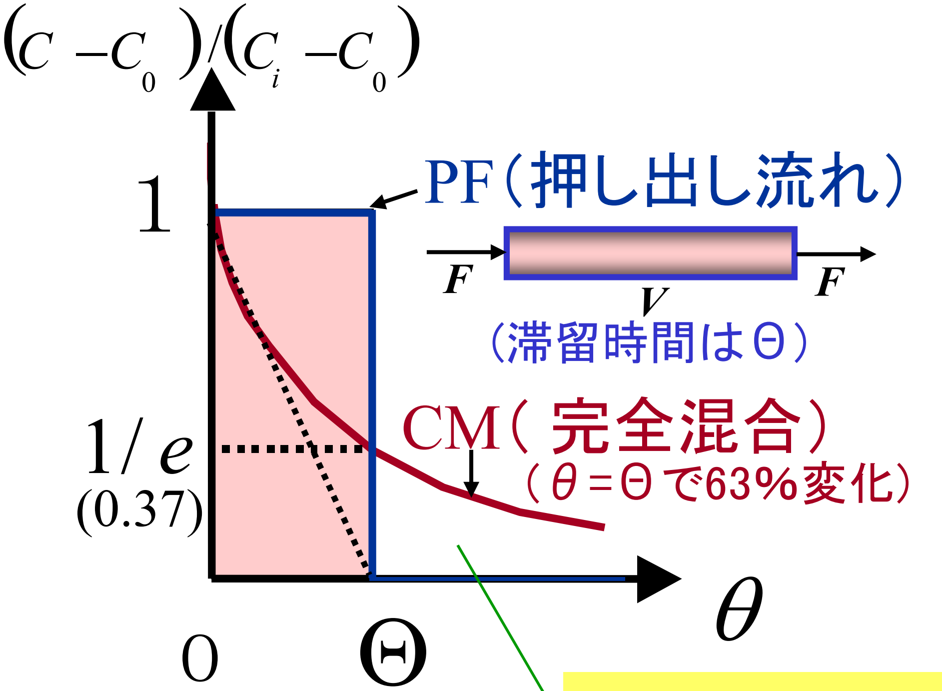
$$C=C_0+\left(C_i-C_0\right)e^{-\theta/\Theta}\quad ,\ \Theta=V/F$$

:時定数 (Time constant)

（系の特性時間）



(a) 完全混合槽(CSTR)の操作（槽内は完全混合）



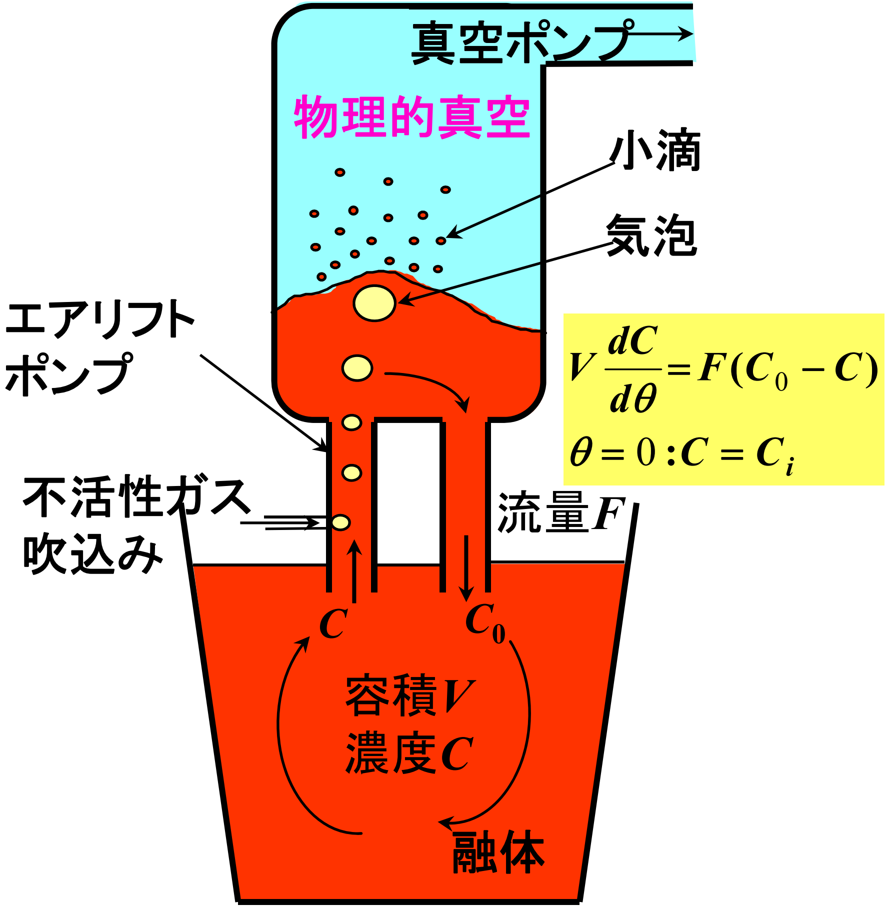
$$\int_0^\infty e^{-\theta/\Theta}\mathrm{d}\theta=\Theta$$

(b) 濃度変化

お風呂とRH脱ガス装置23)

RHでの脱ガス過程は，お風呂での湯沸し過程と等価であり，概略は完全混合槽モデルで表される．

RH脱ガス装置での濃度変化

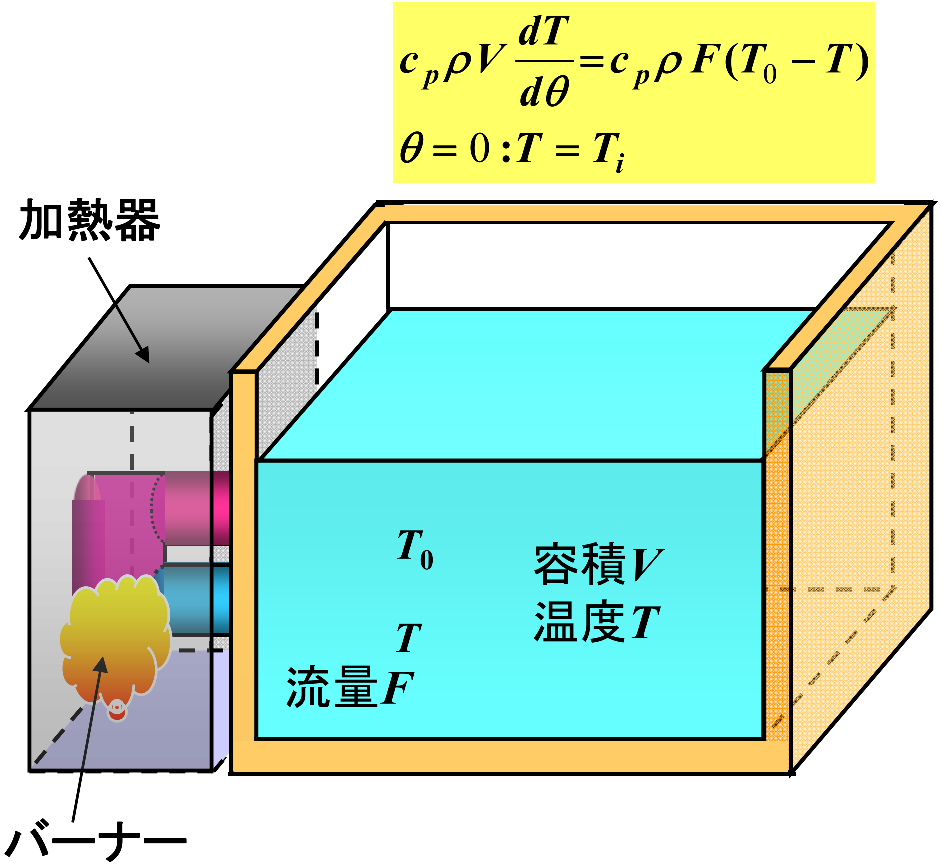


$$V\frac{dC}{d\theta}=F(C_0-C)$$

$$\theta=0:C=C_i$$

Fig. RH degassing unit.

循環加熱型浴槽での昇温速度



$$c_p\rho V\frac{dT}{d\theta}=c_p\rho F(T_0-T)$$

$$\theta=0:T=T_i$$

Fig. Bath with a recirculating heating unit.

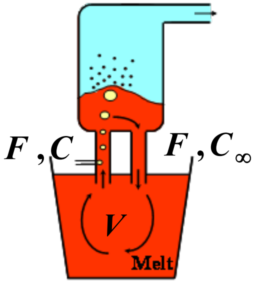
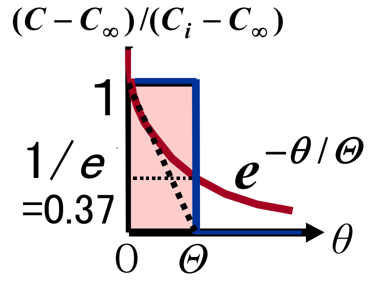
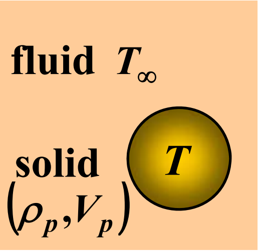
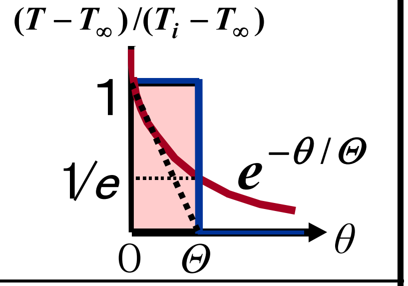
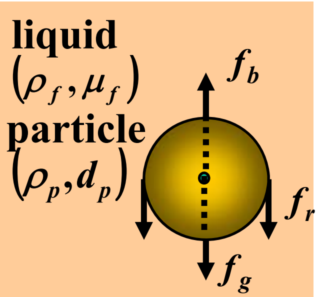
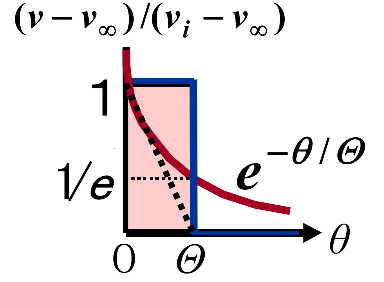
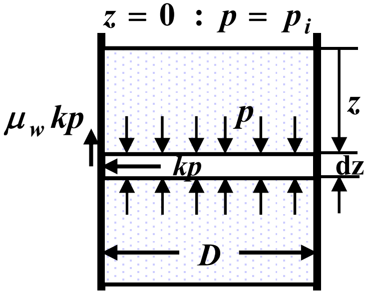
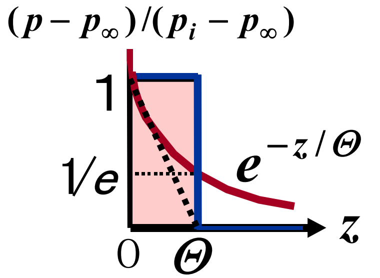
System of interest	Formulation	Process indices	Process variation
Transient purification of melt during RH degassing 	$\Theta \frac{dC}{d\theta} = C_\infty - C$ $\theta = 0 : C = C_i$	$\Theta = \frac{V}{F}$ $C_\infty = C_{equilibrium}$	
Convective step heating/ cooling of a particle in fluid 	$\Theta \frac{dT}{d\theta} = T_\infty - T$ $\theta = 0 : T = T_i$	$\Theta = \frac{c_p \rho_p V_p}{h_p A_p}$ $T_\infty = T_{ambient}$	
Gravitational acceleration of a particle to its terminal velocity (Stokes Eq.) 	$\Theta \frac{dv}{d\theta} = v_\infty - v$ $\theta = 0 : v = v_i$	$\Theta = \frac{d_p{}^2 \rho_p}{18\mu_f}$ $v_\infty = \frac{\rho_p d_p g(\rho_f - \rho_p)}{18\mu_f}$	
Increase in pressure of burden in a cylindrical packed bed (Janssen Eq.) 	$\Theta \frac{dP}{dz} = P_\infty - P$ $z = 0 : P = P_i$	$\Theta = \frac{D}{4\mu_w k} \approx 2D$ $p_\infty = \rho_b g \Theta$	

Fig. 完全混合槽（CSTR）と同様な挙動をするプロセスの例[23)]．

3．現存工業プロセス、技術の限界と新プロセスの開発

３．現存工業技術の限界と新プロセス

Solid Resource
as
a physical mixture of phases with impurities

Liquid Phase Processing
with mechano-chemical treatments

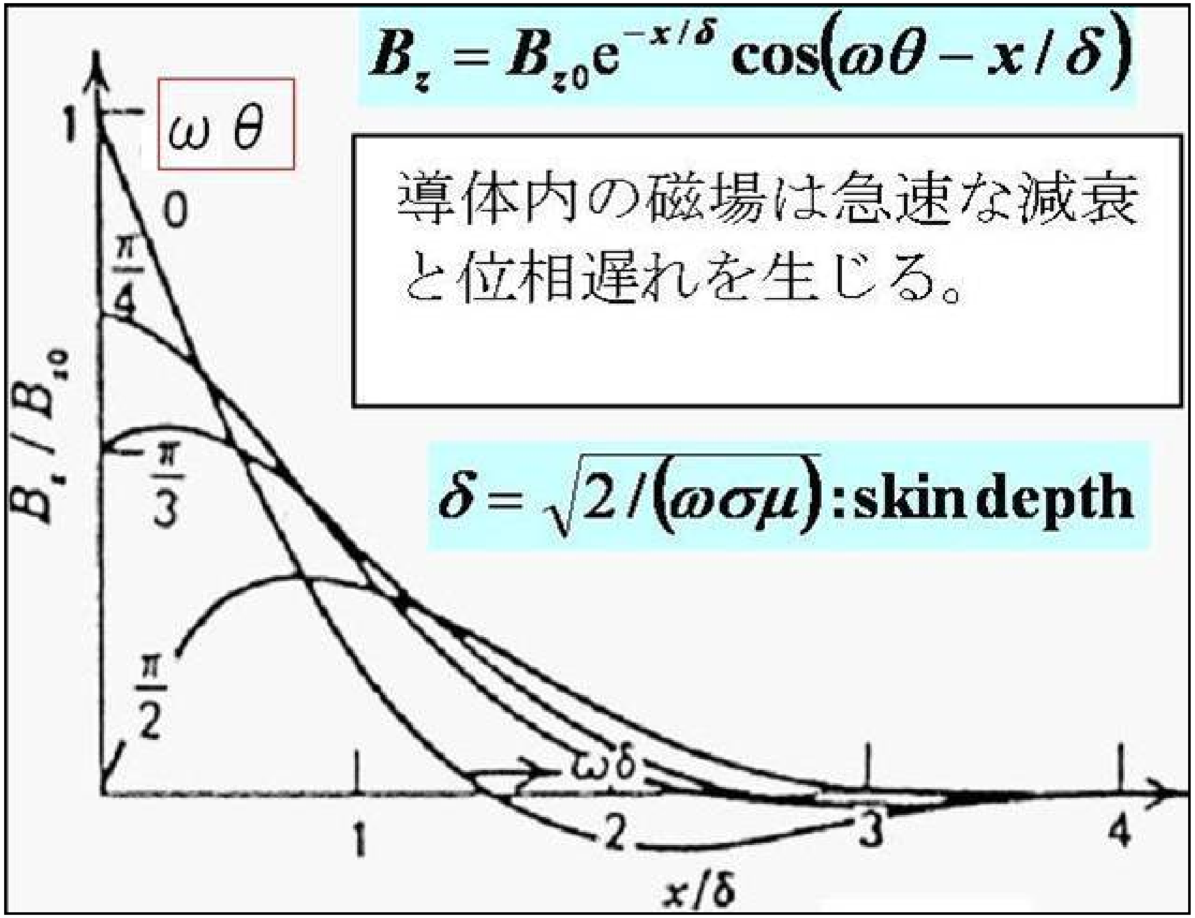
Solid Material
as
a homogeneous phase without impurities

Increasing issues arise to eliminate gravitational, atmospheric, thermal constraints

(Ex.) Time for 1m floatation of inclusions in molten iron:
d_p=100 µm: t =4.4 min ; d_p=10 µm : t =7.3 hr
(clean steel) **(ultra-clean steel)**

➡ このままでは不可能！

対策1： 電磁力の応用(材料への電磁場浸透)



$$B_z = B_{z0} e^{-x/\delta} \cos(\omega\theta - x/\delta)$$

導体内の磁場は急速な減衰と位相遅れを生じる。

$$\delta = \sqrt{2/(\omega\sigma\mu)} : \text{skin depth}$$

図　材料への磁場浸透に及ぼす無次元深さ x/δ と無時限時間 $\omega\theta = 2\pi(\theta/T)$ の影響

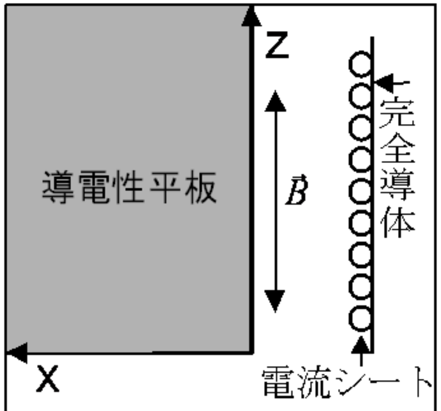
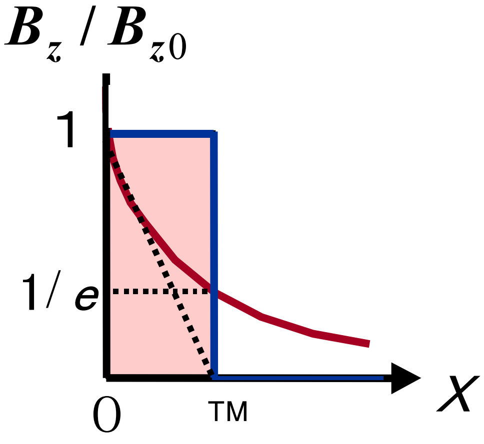
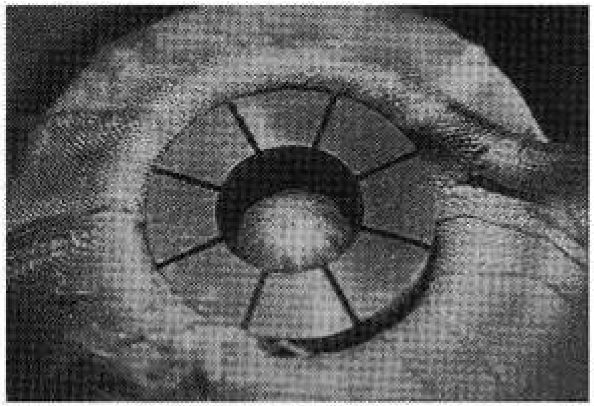


図７ :一次元電磁場



Electromagnetic Field around An Induction Cold Crucible 25)



Induction cold crucible is a segmented and internally water-cooled conductive mold in which materials can be electro-magnetically heated, melted and held without contacting with the mold. Important thing is to design the electromagnetic field for its practical use.

(コールドクルーシブルによる材料の非接触溶解・保持)

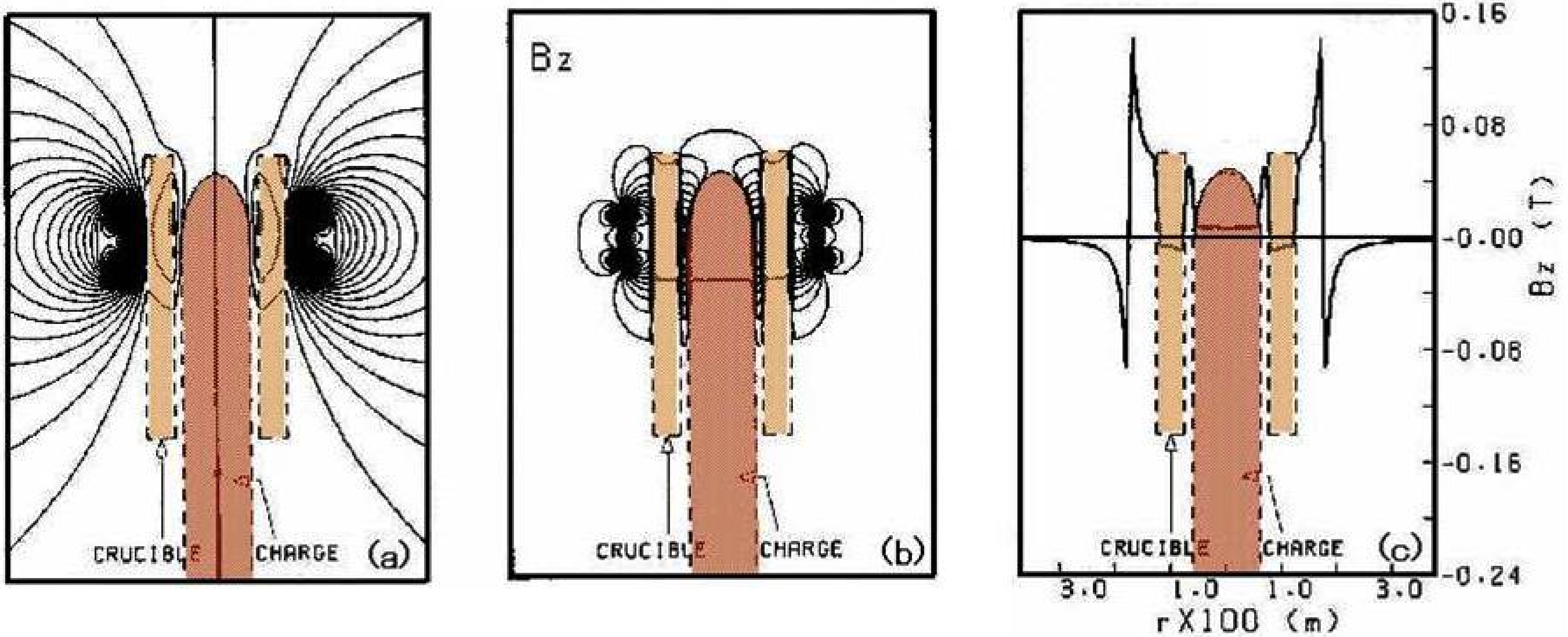
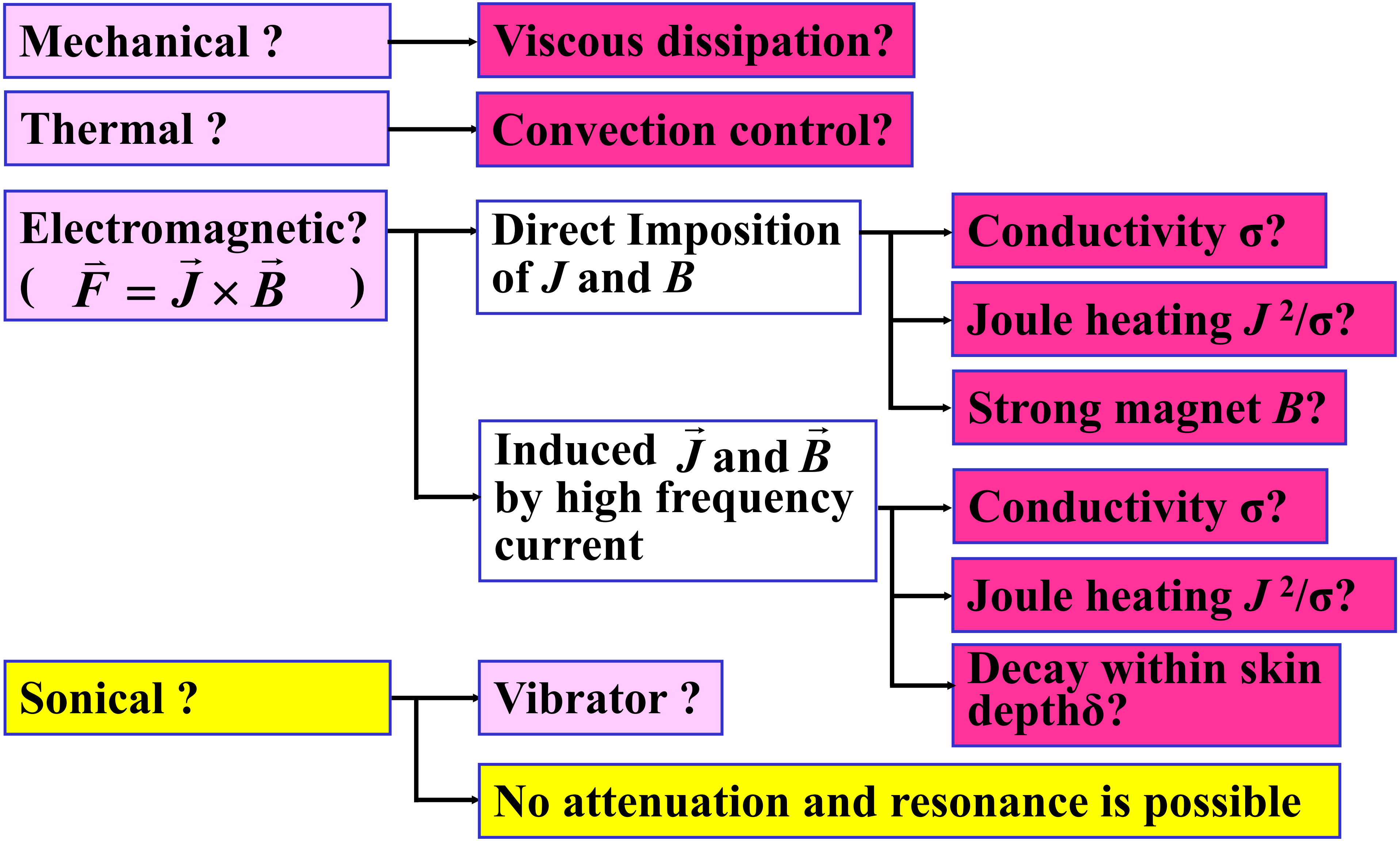


Fig. Computed results of (a) magnetic flux lines, (b)contour lines of B_z and (c) radial distribution of B_z around the cold crucible (Kuwabara et.al., 1990).

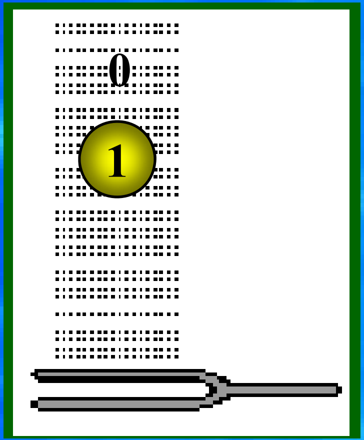
重力以外に液中に付加できる有効な外力は？



- Mechanical ?
  - Viscous dissipation?
- Thermal ?
  - Convection control?
- Electromagnetic? ($\vec{F} = \vec{J} \times \vec{B}$)
  - Direct Imposition of J and B
    - Conductivity σ?
    - Joule heating J^2/σ?
    - Strong magnet B?
  - Induced $\vec{J}$ and $\vec{B}$ by high frequency current
    - Conductivity σ?
    - Joule heating J^2/σ?
    - Decay within skin depthδ?
- Sonical ?
  - Vibrator ?
  - No attenuation and resonance is possible

対策2： 音響放射圧の利用

Radiation force in liquid(0) acting on a particle (1) [26)]



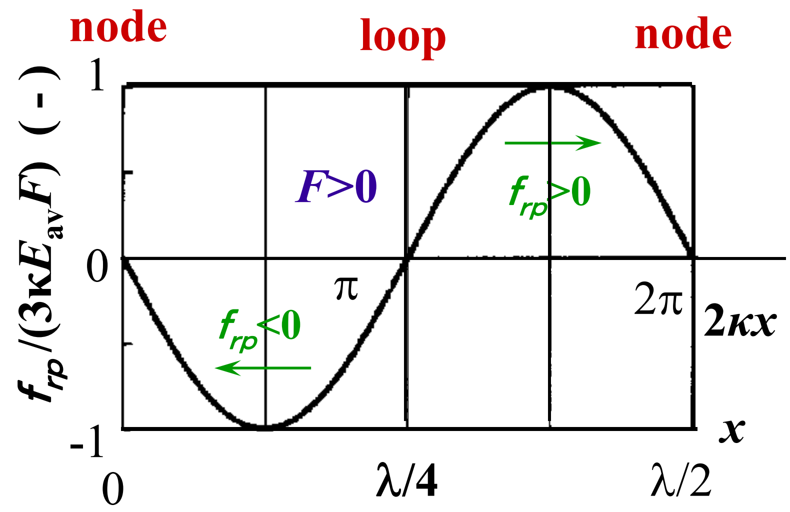
$$f_{rp} = -3V_p \kappa E_{av} \sin(2\kappa x) \cdot F(\Lambda, \sigma)$$

$$F(\Lambda,\sigma)=(\Lambda+2(\Lambda-1)/3)/(2\Lambda+1)-1/(3\Lambda\sigma^2)$$

where V_p: particle volume, E_{av}: energy density,

κ : wave number ($=2\pi f/c$), x : distance from a node,

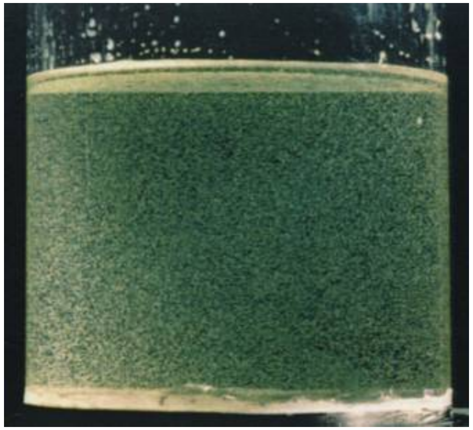
Λ: density ratio ($=\rho_1/\rho_0$), σ: sound velocity ratio ($=c_1/c_0$)



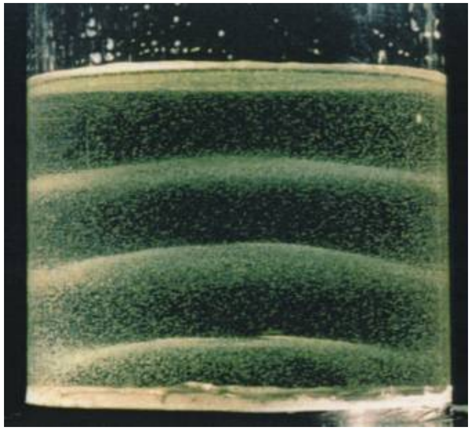
$F>0$: f_{rp} acts towards nodes.

Ultrasonic Separation of Suspended Inclusions

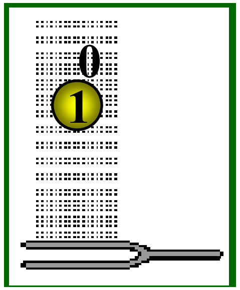
Vertical irradiation of ultrasound



(a) t = 0 s

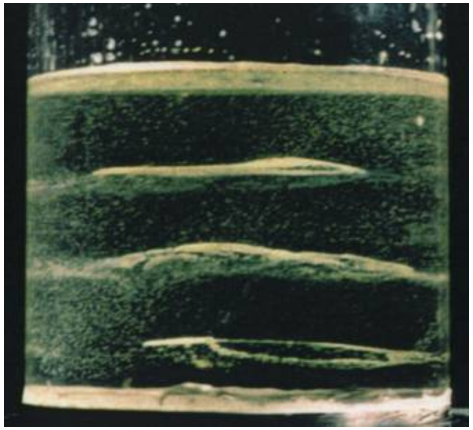


(b) t = 10 s

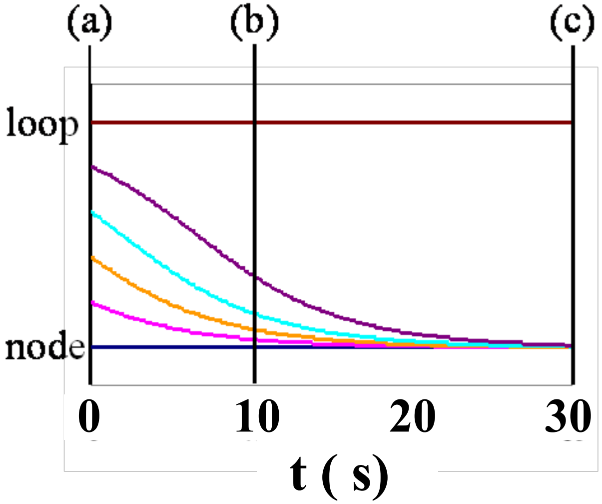


$$(\rho_p V_p + M)\frac{d^2x}{dt^2} = f_{rp} + f_b + f_d$$

f_{rp} : radiation force,
f_b : buoyancy force,
f_d : drag force



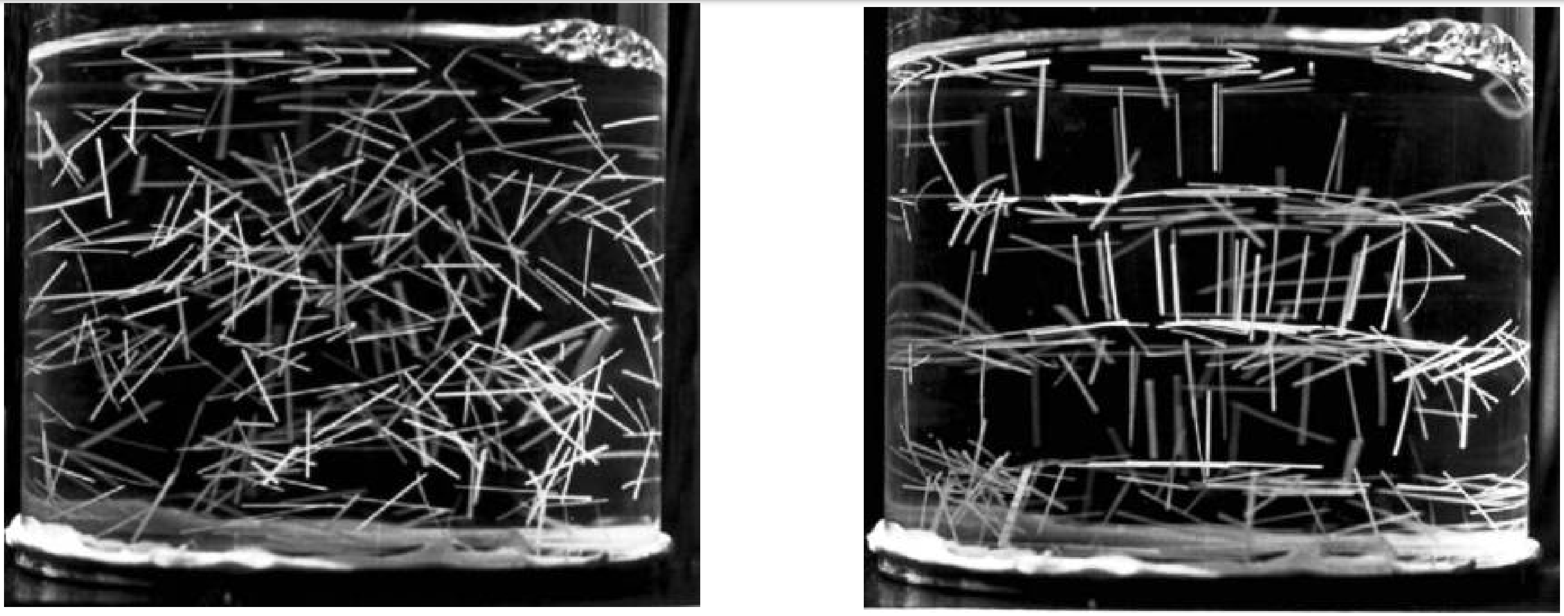
(c) t = 30 s



Arbitrarily specified five particles all gather around a nodal plane.

Fig. Transitional coagulation of suspended polystyrene particles in aqueous sugar solution through which an ultrasound of 48.5kHz is irradiated vertically$^{27)}$.

Orientation of Fibers in Composite Engineering



(a) without ultrasound (b) with ultrasound

Fig. Behavior of polystyrene fibers in aqueous sugar solution under the conditions with and without incidence of ultrasound 28). (l=10mm, f=49.0kHz, h_r=60mm)

The equation of motion for a fiber

translational : $$M\frac{d^2x}{dt^2} = f_{rp} + f_b + f_d$$

rotational : $$I\frac{d^2\theta}{dt^2} = T_{rp} + T_b + T_d$$

M : mass I : inertia moment

f : force T : torque

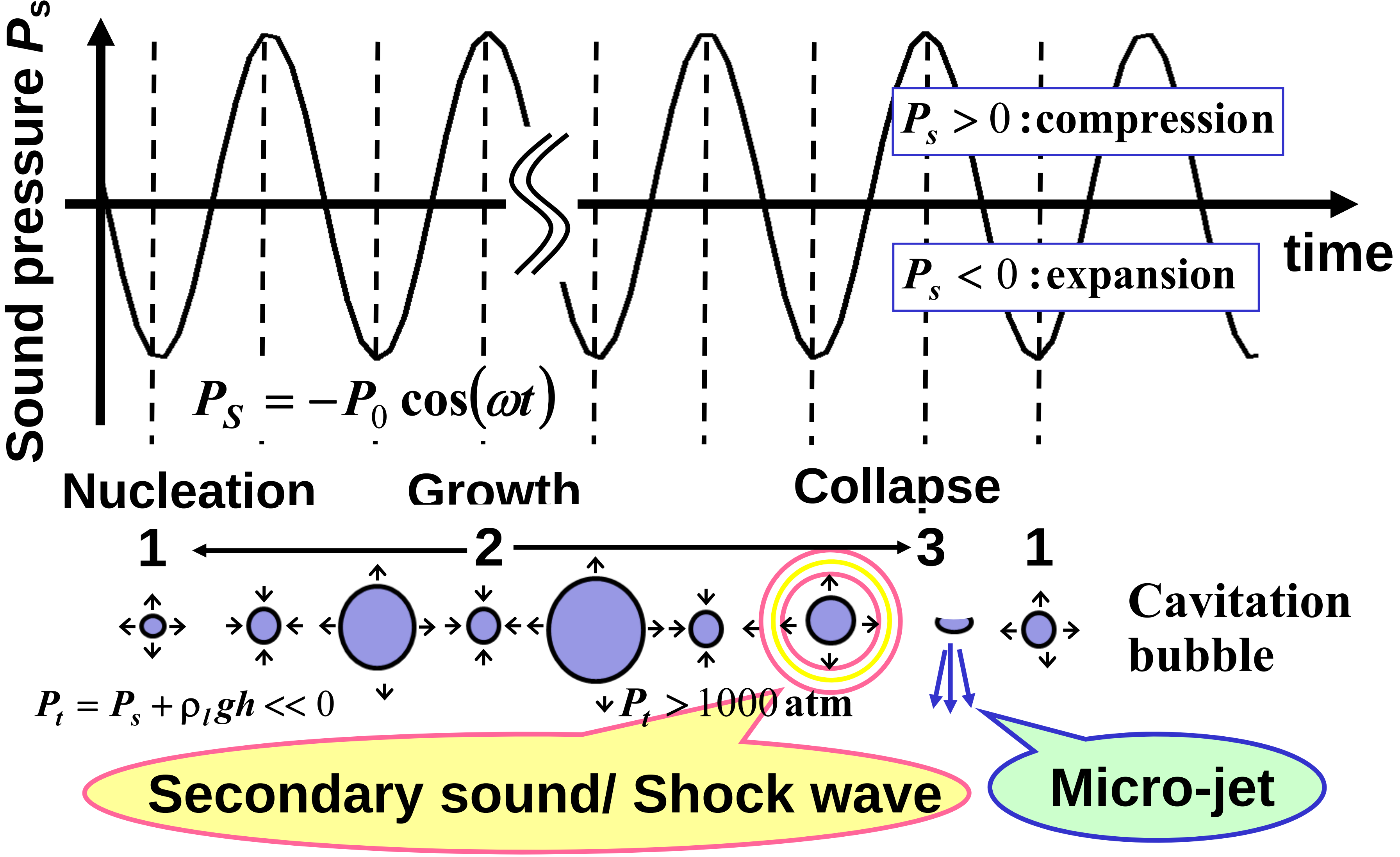
subscript

rp : radiation pressure

b : buoyancy force

d : drag force

対策3：音響キャビテーションとマイクロジェットの応用



$$P_S = -P_0 \cos(\omega t)$$

$P_s > 0$: compression

$P_s < 0$: expansion

$P_t = P_s + \rho_l g h << 0$

$P_t > 1000$ atm

Secondary sound/ Shock wave

Micro-jet

Fig. Schematic illustration of the generation of a cavitation bubble and micro-jet.

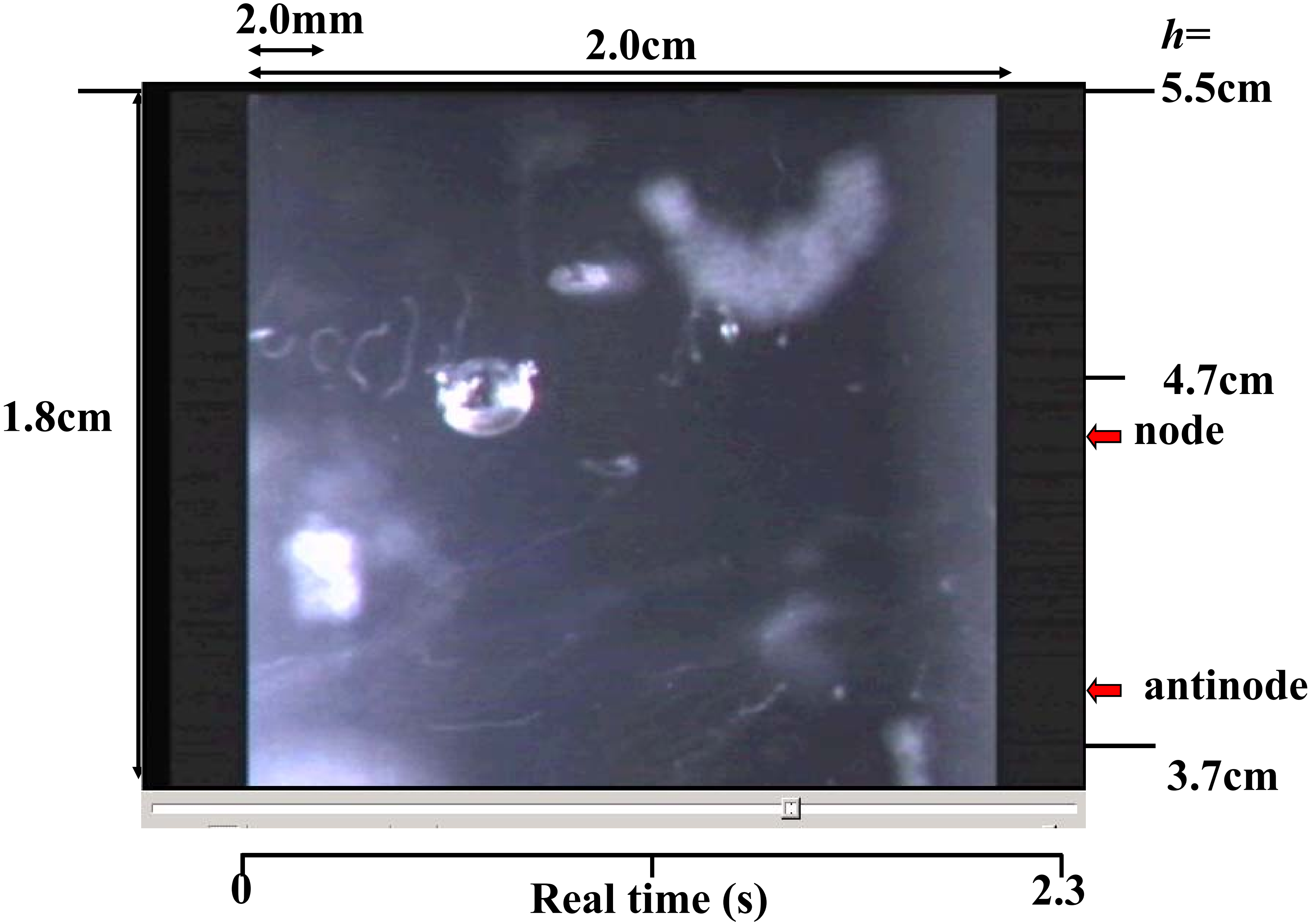
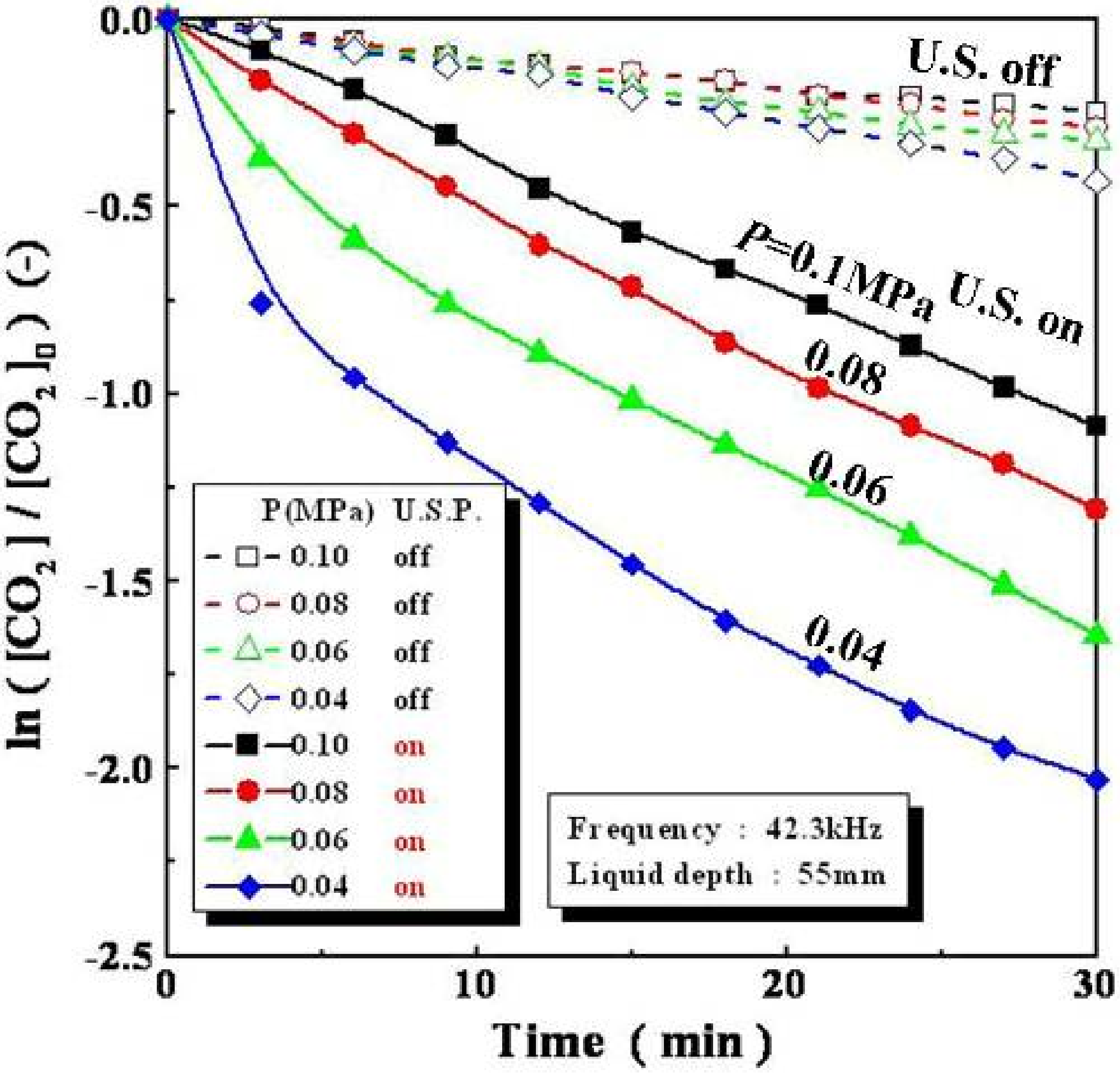
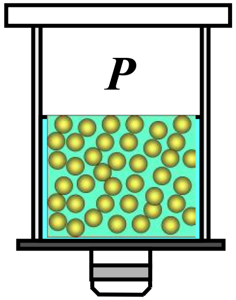


Fig. Stereo view of cavitation multibubble in water at 42.3 kHz [29].

キャビテーションの応用1：　超音波脱ガス

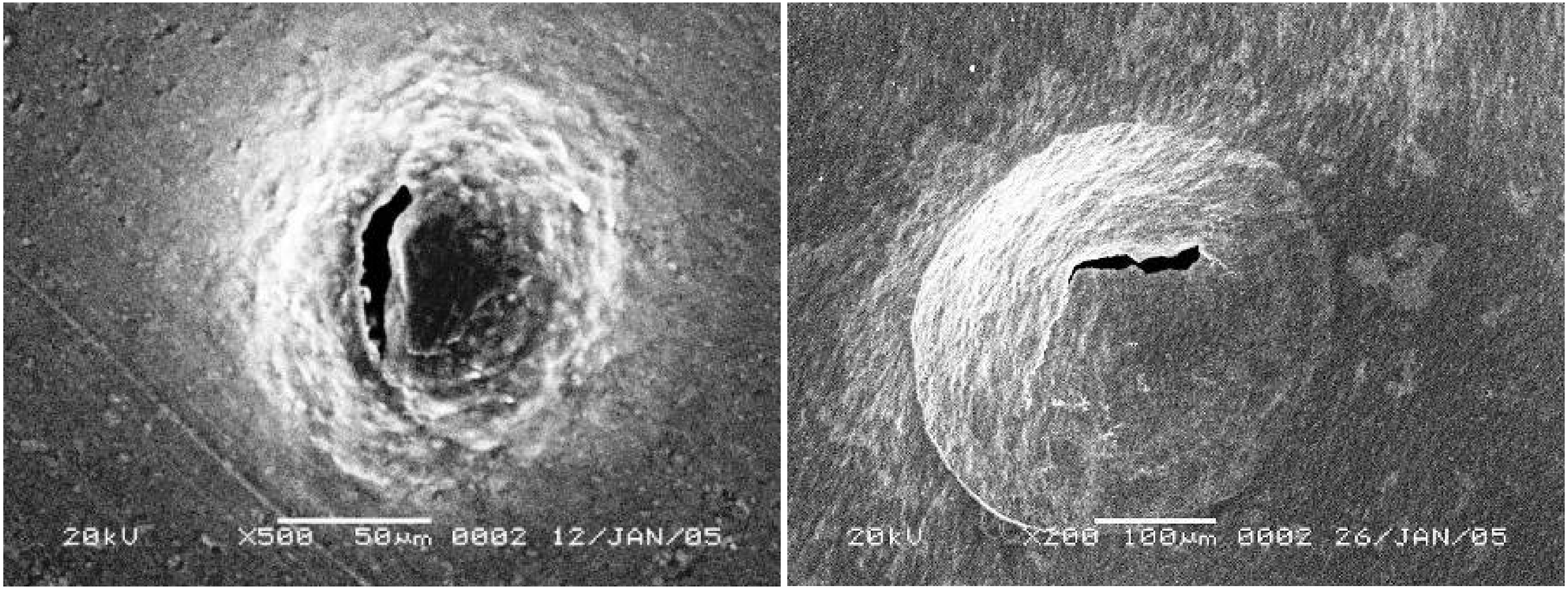




- **Irradiation of US** remarkably accelerates degassing rate due to increase in not only effective surface area but also mixing intensity in the liquid.
- **Decreased atmospheric pressure** is preferable.

Fig. Effect of atmospheric pressure on the rate of degassing with or without irradiation of ultrasound 30) .

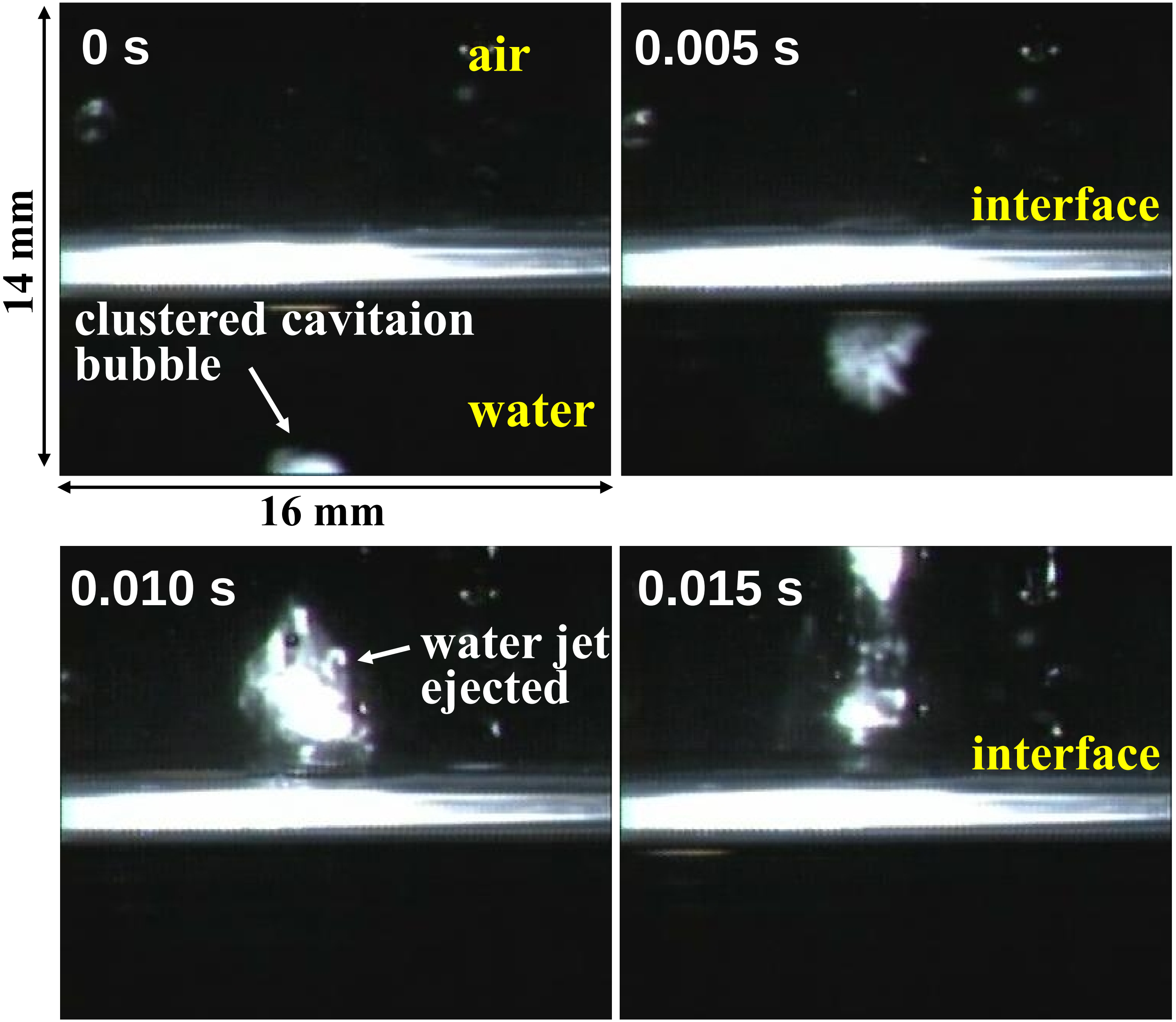
キャビテーションの応用２：Microjetによるエマルション



(41.88 kHz, 50W)

(20 kHz, 1.4 kW)

Fig. SEM image of one indentation on aluminum foil surface attacked by an acoustically induced cavitation bubble followed by a microjet [31) .



Frequency：41.6 kHz
Water depth : 65 mm
U.S.P. : 50 W

A clustered bubble can eject a water jet against gravity.

The power is strong enough to induce micro and macro mixing of liquid as well as emulsification of two liquids.

Fig. Sequential motion of a clustered cavitation bubble near the free surface accompanied by an ejected liquid jet [32).

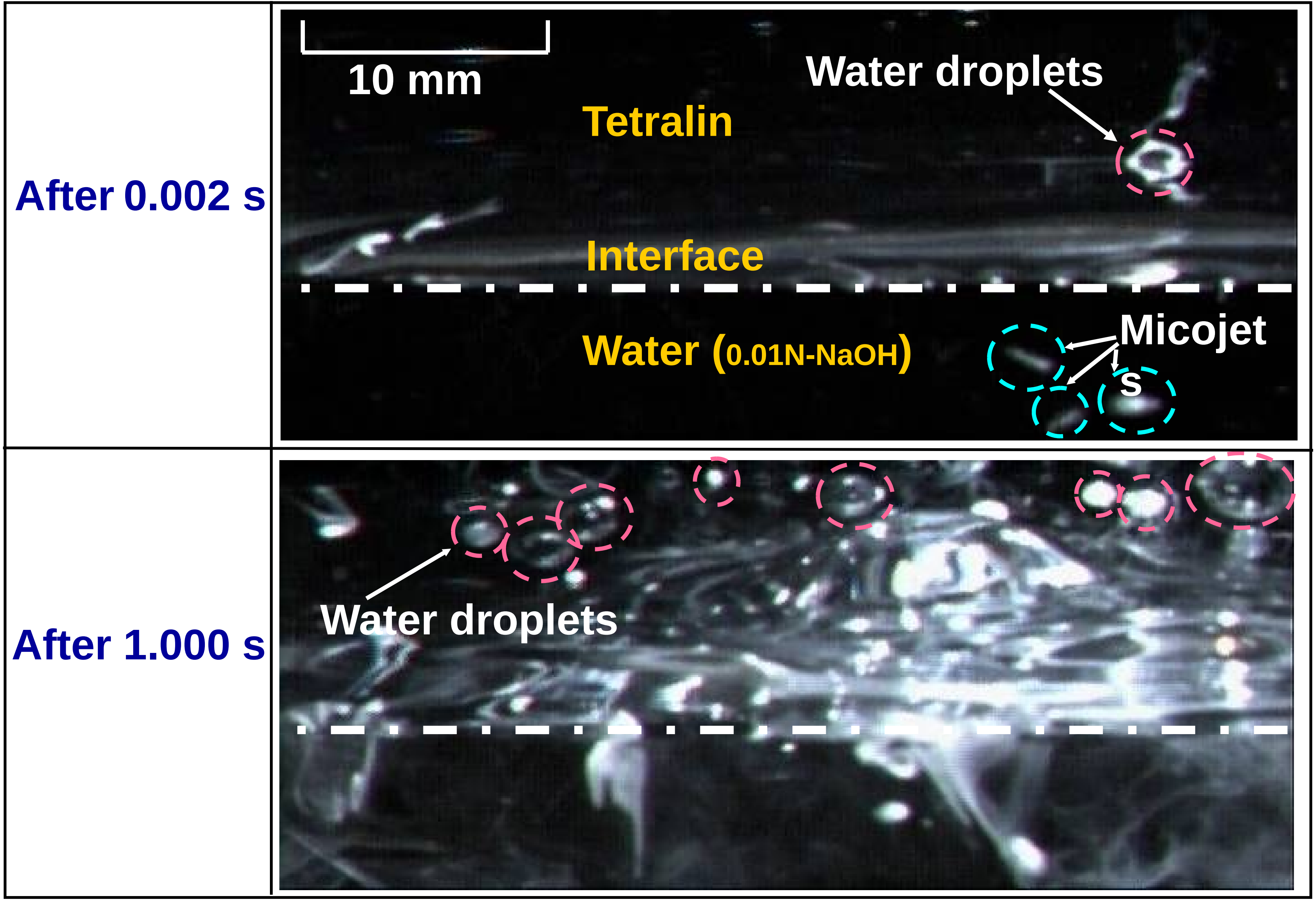
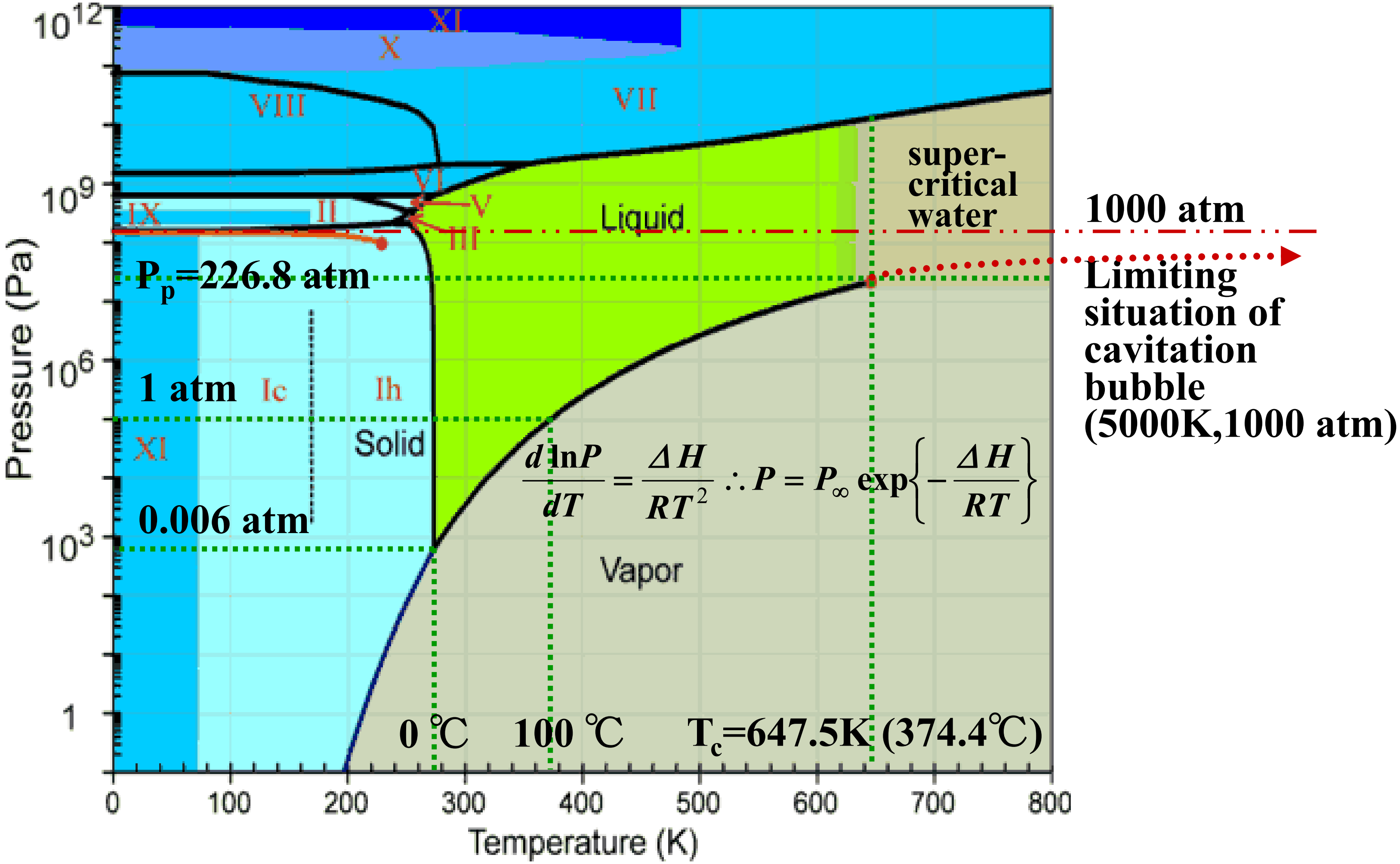


Fig. High-speed stereo view of emulsification of tetralin-water (0.01NNaOH) system 33) . (*f* = 41.3 kHz, U.S.P= 50 W, 500 frames/s)

キャビテーション気泡内では超臨界も可能！

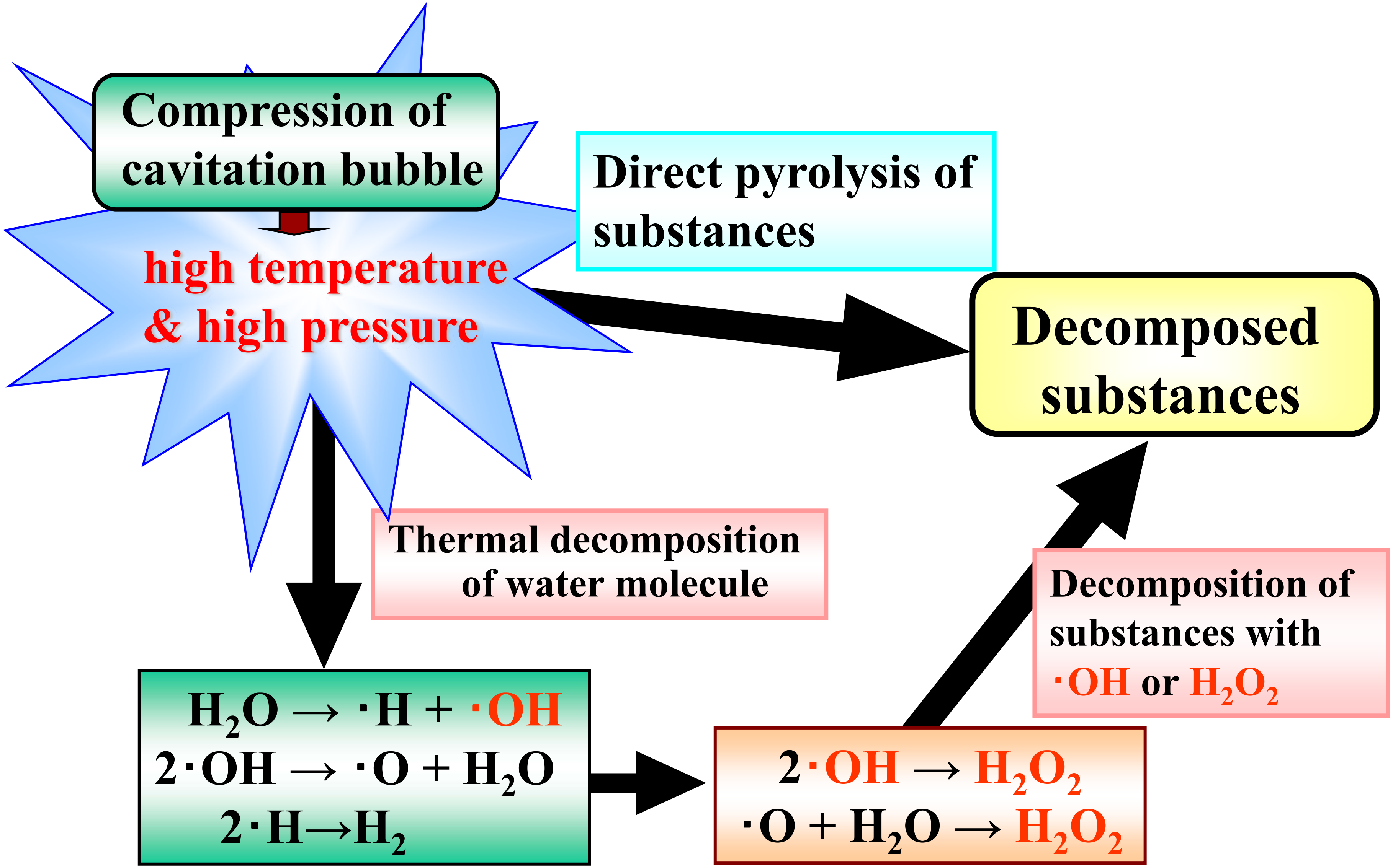


$$\frac{d\ln P}{dT}=\frac{\Delta H}{RT^2}\ \therefore P=P_\infty \exp\left\{-\frac{\Delta H}{RT}\right\}$$

Fig. The phase diagram of water 34) .

Limiting situation of the bubbles is considered at around 5000 K and 1000 atm. This state should be really the supercritical fluid one in which no surface tension exists and highly activated chemical sate would come across.

キャビテーションの応用３：　化学物質の分解



Compression of cavitation bubble

high temperature & high pressure

Direct pyrolysis of substances

Decomposed substances

Thermal decomposition of water molecule

$H_2O \rightarrow \cdot H + \cdot OH$

$2 \cdot OH \rightarrow \cdot O + H_2O$

$2 \cdot H \rightarrow H_2$

$2 \cdot OH \rightarrow H_2O_2$

$\cdot O + H_2O \rightarrow H_2O_2$

Decomposition of substances with $\cdot OH$ or H_2O_2

0 min

20 min

40 min

60 min

$C_i = 5.0 \times 10^{-4}$ mol/l

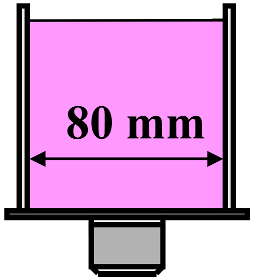
V=160 ml

U.S.P = 50 W

f = 42.0 kHz

T = 20 ℃

h_{water} = 125 mm



Possible reaction ?

$$2KMnO_4+2H_2O_2 \rightarrow 2MnO_2+2KOH+H_2O+5/2O_2$$

Fig. Transitional change in color of $KMnO_4$ solution after irradiation of ultrasound (Decomposition of an inorganic substance)35). ⇨ Action of H_2O_2

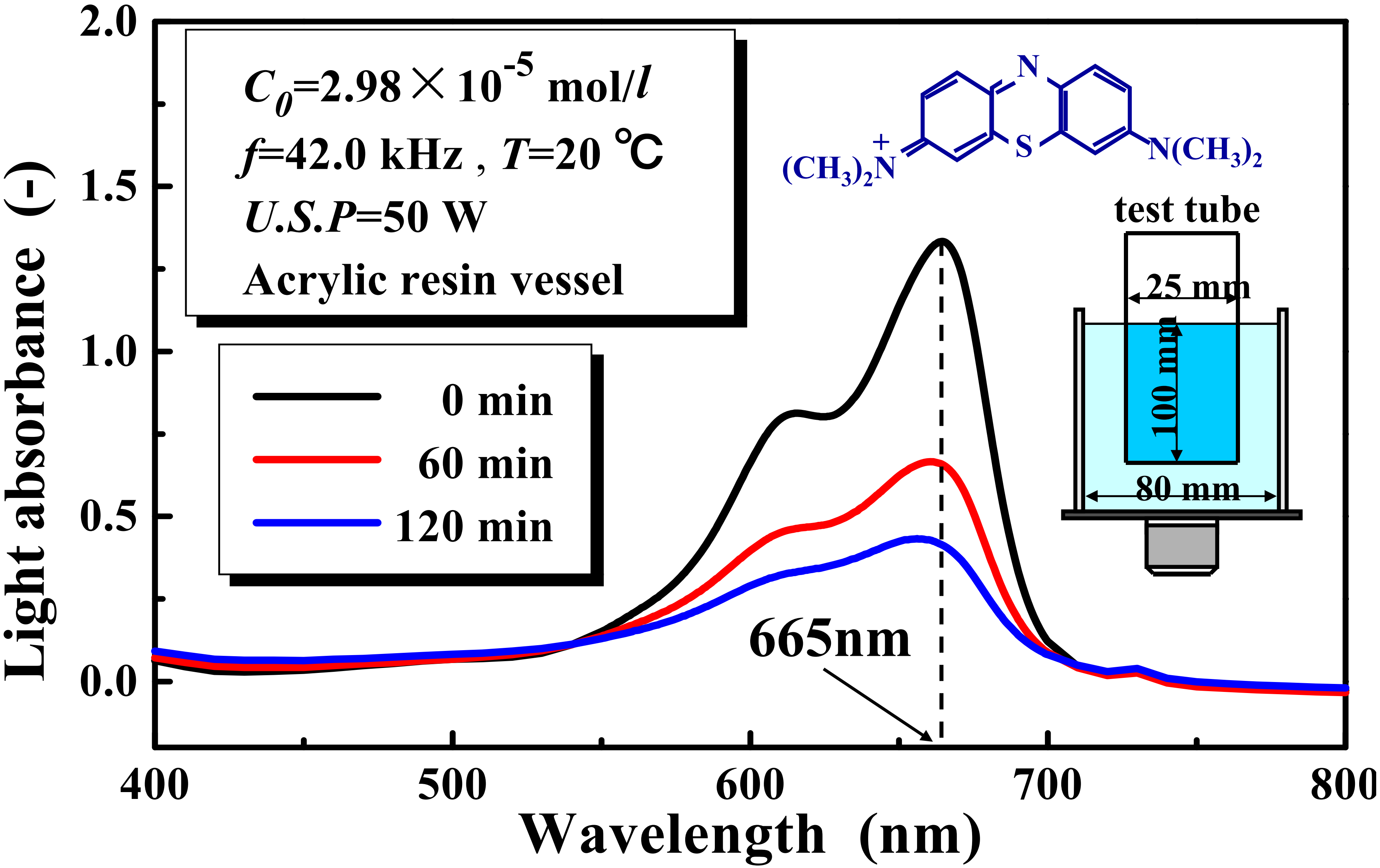
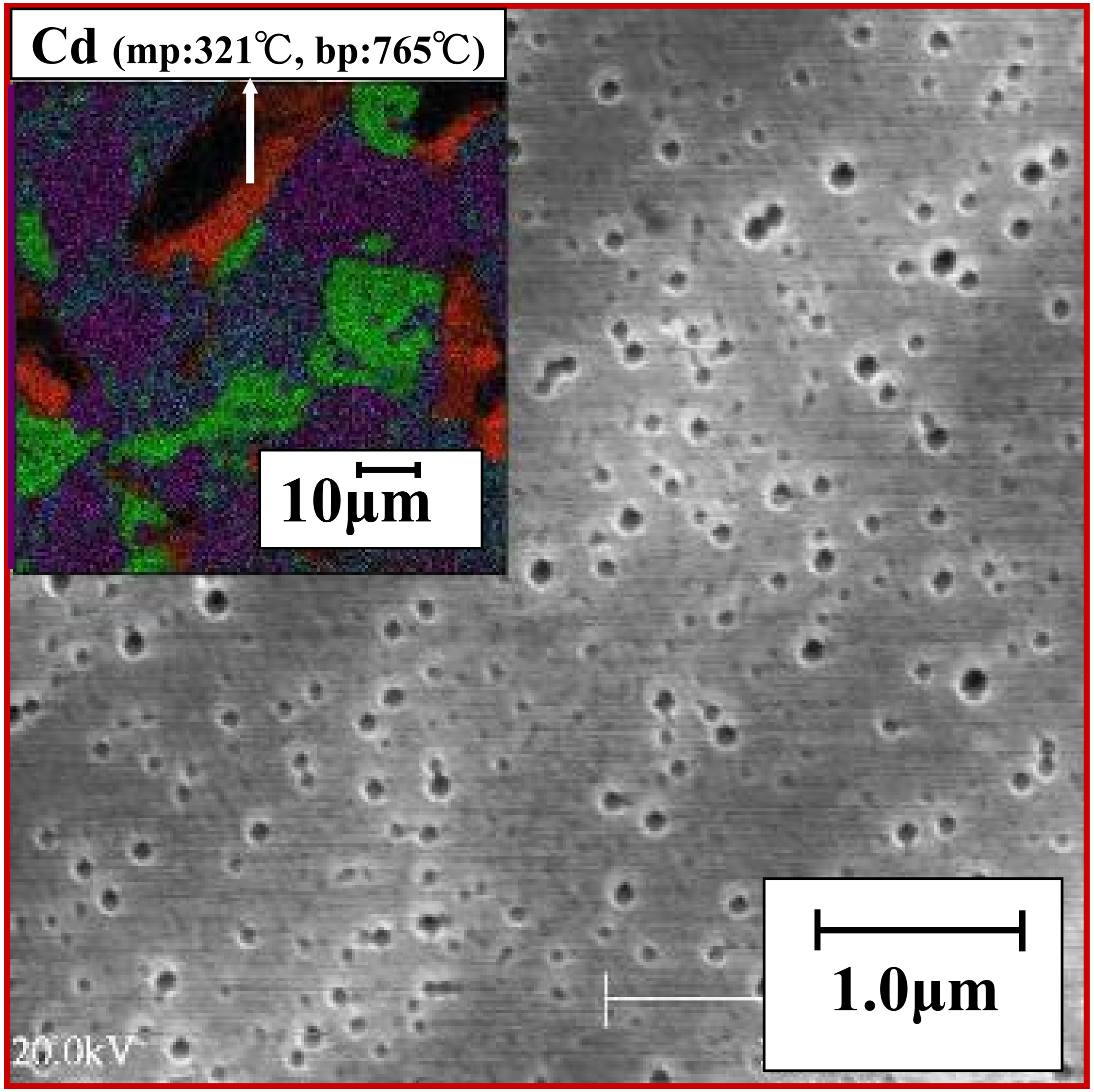
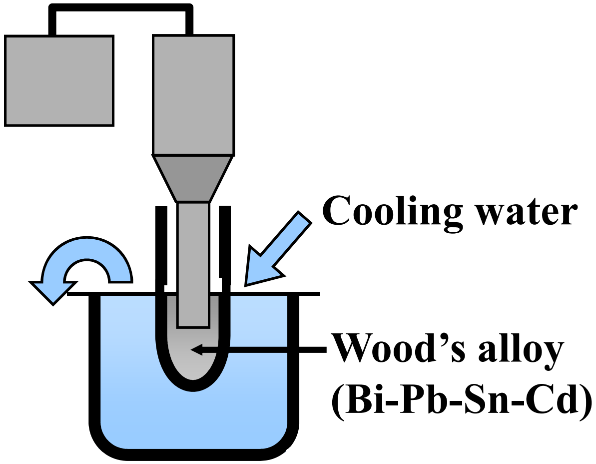


Fig. Relation between light absorbance and wavelength during irradiation of ultrasound on aqueous methylene blue solution 33). ⇨ Action of ·OH

キャビテーションの応用4：ナノ発泡材料の製造

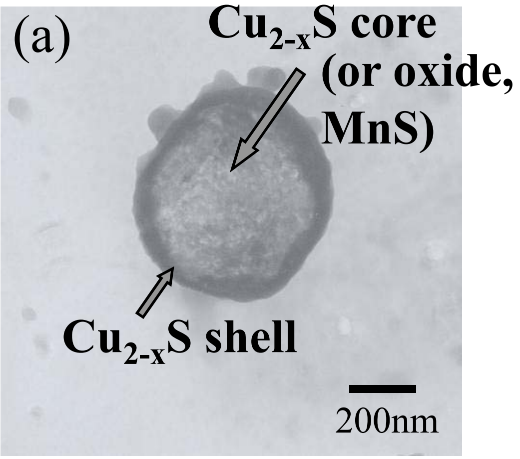




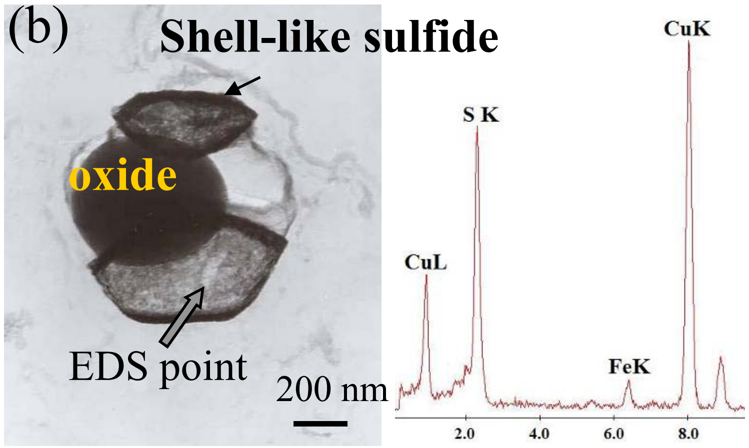
→ **Production of foamed material with small grain size**

Fig. SEM image of foamed structure of Wood’s alloy after irradiation of ultrasound (20kHz, 600 W 10 s) [36].

凝固過程での硫化銅の析出形態制御による鉄中銅の無害化



Shell-like copper sulfide



duplex oxide-sulfide

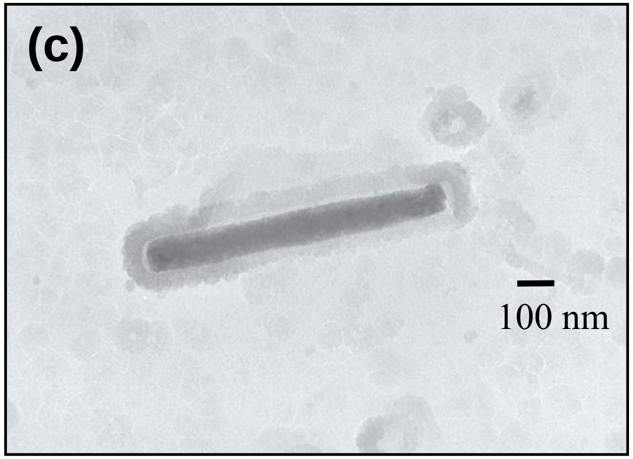
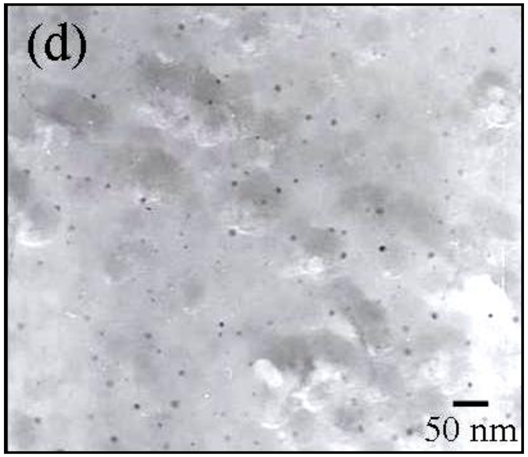


Plate-like copper sulfide
(low P steel)



Nano-scale copper sulfides
(high P steel)

車スクラップ鉄のリサイクルで濃化し、赤熱脆性の原因となる有害なCuを、やはり、有害なSとの間で微細な硫化銅として析出させて無害化。もう一つの有害元素Pは硫化銅を更に微細化するのに有効。

劉ら37)： 日本鉄鋼協会澤村論文賞受賞（2007）

正しい理解で現象はシンプルとなる！

プロセス、モデル、人生　・・・

混沌からシンプルへ！

Simple is the best!

教育・体制に関する思い出

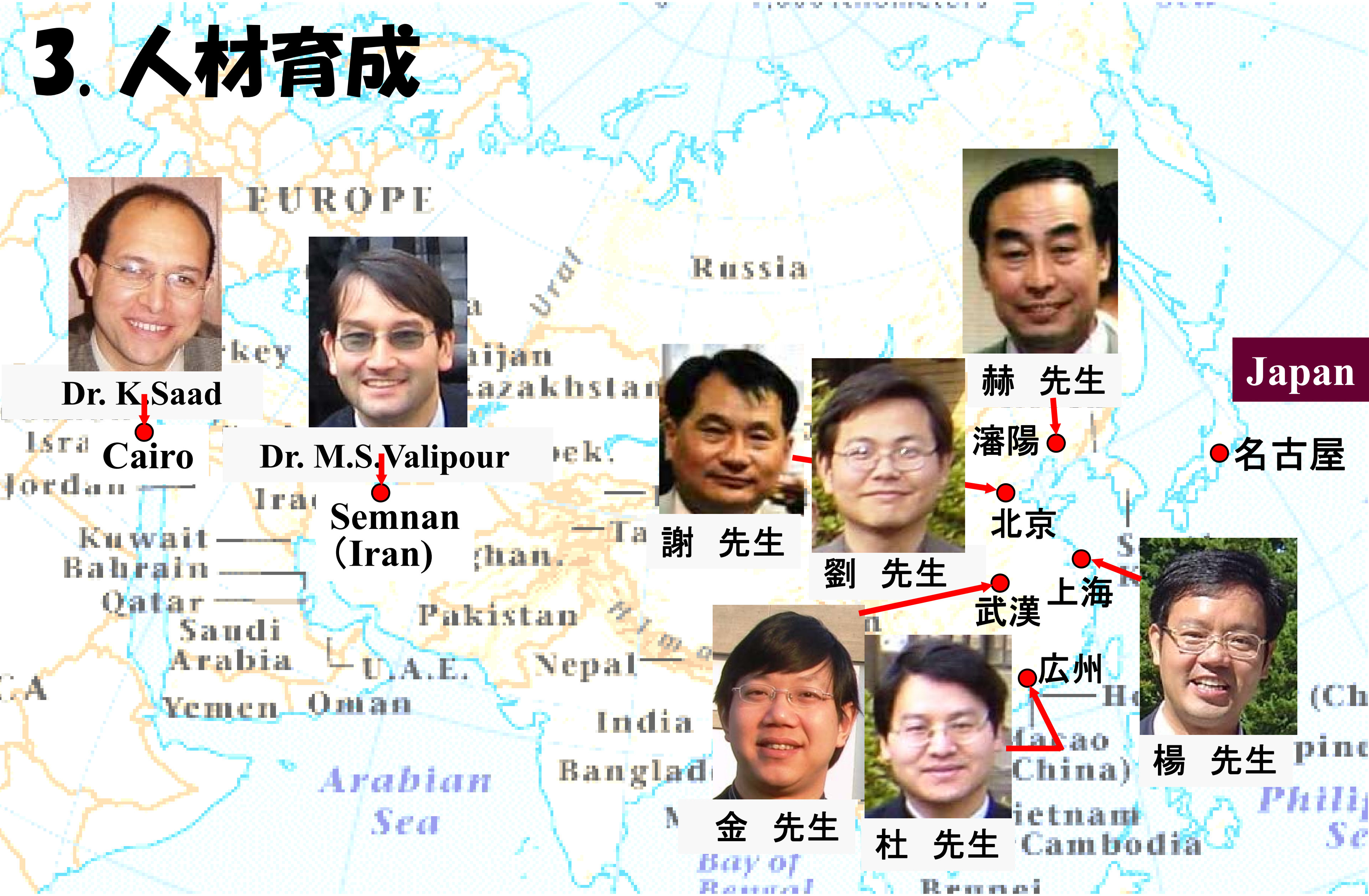
1. 法人化元年の主任
（マテリアル理工学専攻副専攻長）

2. 関連大講座の呼称と研究内容の決定

材料プロセス創成工学講座

高度の物理的および化学的原理に基づく制御手段を駆使し、先進材料創製のプロセス設計、およびナノからマクロのレベルに至るまでのプロセス設計に関する研究と教育を行う。

3. 人材育成



図．主な留学生、訪問研究者と帰国後の活躍地

謝　裕生　氏　(Prof. Y. Xie)　　　　赫　冀成　氏（Prof. J. He）
（前 北京化工冶金研究所所長）　　（瀋陽、東北大学校長）
（中国第１期研究生）　　　　　　（中国第１期大学院生）

(Materials Processing Symposium, June 6, 2001, 名古屋大学)

今後も国際交流・・

天安門前にて（北京, 2008, 1.25）

完成間近の首鋼技術研究院
（北京, 2008, 1.24）

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