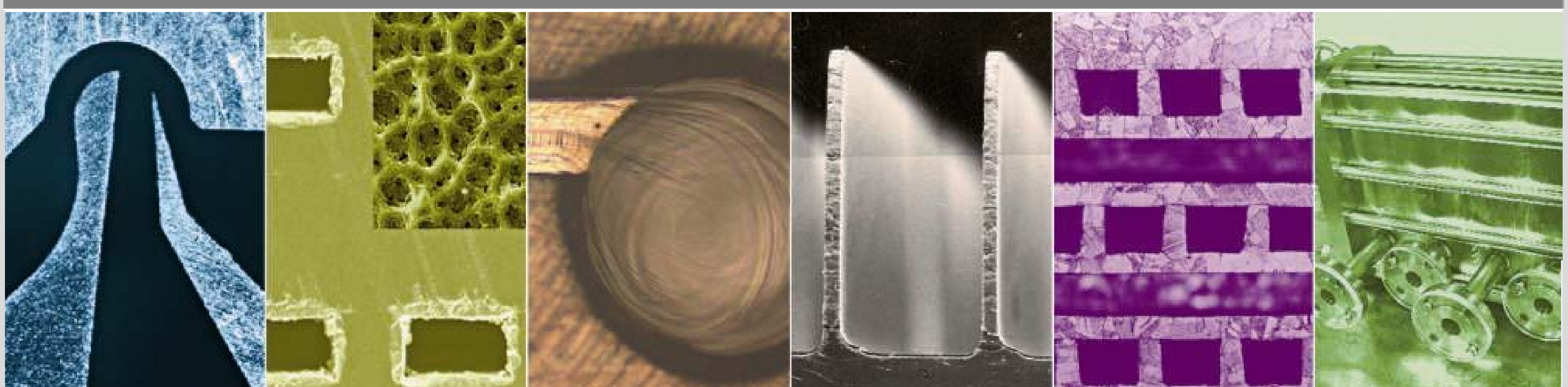
Opportunities and Challenges of Membrane Integration into Compact Microstructured Reactors

R. Dittmeyer, J. Thormann, O. Görke, P. Pfeifer, N. Schüler, M. Kraut

Chinese-German Workshop on Inorganic Membranes, Guangzhou, March 21-25, 2010

Institute for Micro Process Engineering (IMVT)



What is KIT?

Start: National Excellence Initiative 2006 - Success in all three funding lines

- **Graduate Schools:** Karlsruhe School of Optics and Photonics
- **Excellence Clusters:** DFG Center for Functional Nanostructures
- **Concept for the Future:** Merger of University and Research Center to form the Karlsruhe Institute of Technology (October 1, 2009)

KIT

North Campus

10	Programs
31	Institutes
3690	Employees
408 Mio €	Budget

+

South Campus

11	Faculties
118	Institutes
4269	Employees
299 Mio €	Budget
18353	Students

Natural and Engineering Sciences

KIT - Centers and Focuses

Institute for Micro Process Engineering (IMVT) North Campus

KIT Centers:

- Energy
- Nano & Micro Science and Technology
- Elementary Particle and Astroparticle Physics
- Climate and Environment

KIT Focuses:

- COMMputation
- Mobility Systems
- Optics and Photonics
- Humans and Technology
- Applied and New Materials

IMVT - Mission Statement

R&D for the manufacture of highly efficient microstructure devices for process engineering tasks in chemical, pharmaceutical and related industries

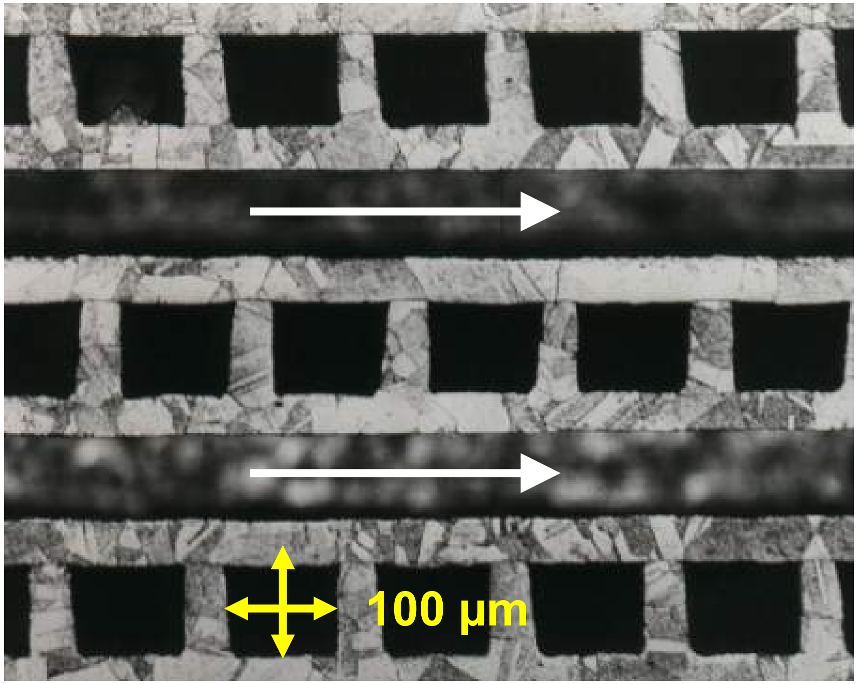
Renewing process engineering through “Process Intensification”

- **Safe:** Reduced reactive inventory, Quenching of reactions, Local production avoids transport
- **Efficient:** Energy and raw materials, Reduced heat and mass transport resistances and improved control on the process conditions
- **Compact:** Higher space-time-yield, Integration of additional functions, Compartmentalization
- **Cheap:** Looking at investment plus operating costs
- **Fast:** Standardized, well characterized equipment

Principles: *Microstructuring of the reactor volume (thin fluid layers)*

Supply or removal of material and energy on the spot (hierarchical structures)

Key Features of Microstructure Devices



Cross flow metallic heat exchanger

Advantages:

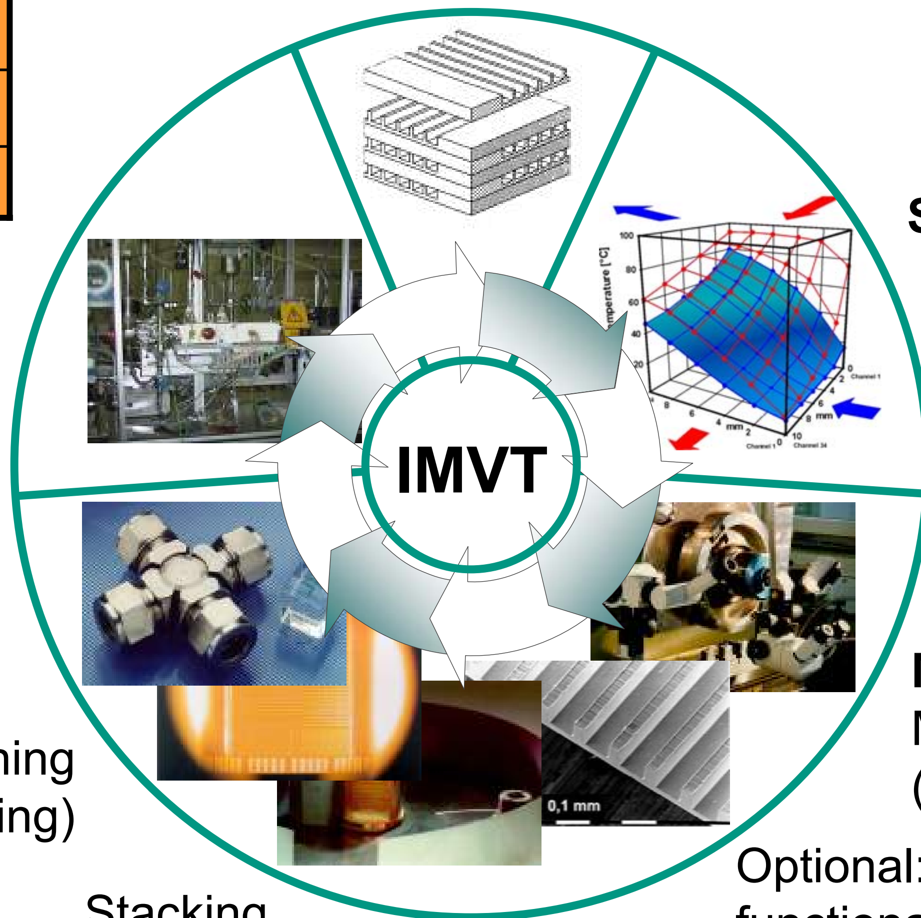
- Excellent heat transfer (up to 20 kW pro cm^3)
- Excellent mass transfer (channel to wall)
- High pressure resistance
- Inhibition or retardation of flames and explosions (depends)

Challenges:

- Prone to plugging
- Prone to corrosion
- High pressure drop (depends)

IMVT - Competences

Personnel	62 (5)
Manufacturing	15
Fundamentals	16
Applications	26 (4)
Administration	5 (1)



Why Membranes in Microstructure Devices ?

Two systems:

- Membrane reactor for hydrogen production: (1) reforming of natural gas / biogas, (2) dehydrogenation of methylcyclohexane
- Gravity-insensitive gas/liquid separation or contacting

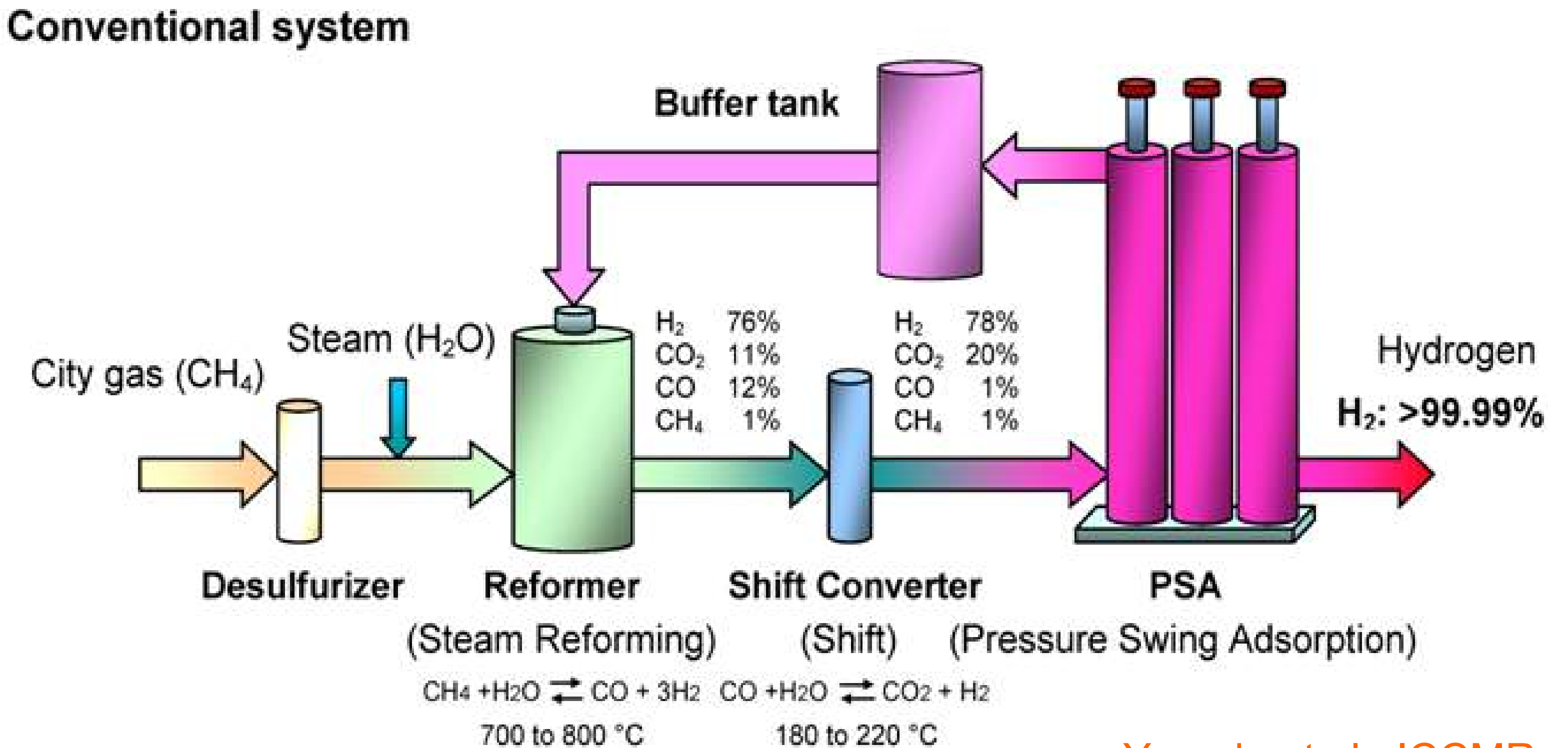
Microstructure devices do

- offer a large surface to volume ratio and can serve as hierarchical supports for very thin membranes,
- provide excellent indirect heat transfer,
- allow to supply reactants or withdraw products along the flow path through the channel walls,
- enable an influence on multiphase flow through the wetting properties of the channel walls.

Membrane Reactor for Hydrogen Production

1) Membrane Steam Reformer for Natural Gas

- Idea dates back more than 20 years (Oertel et al., 1987, TH Aachen)
- >> 100 research papers; many patents; several industry-led consortia (Japan, US/Canada, Europe)



Yasuda et al., ICCMR-7, 2005

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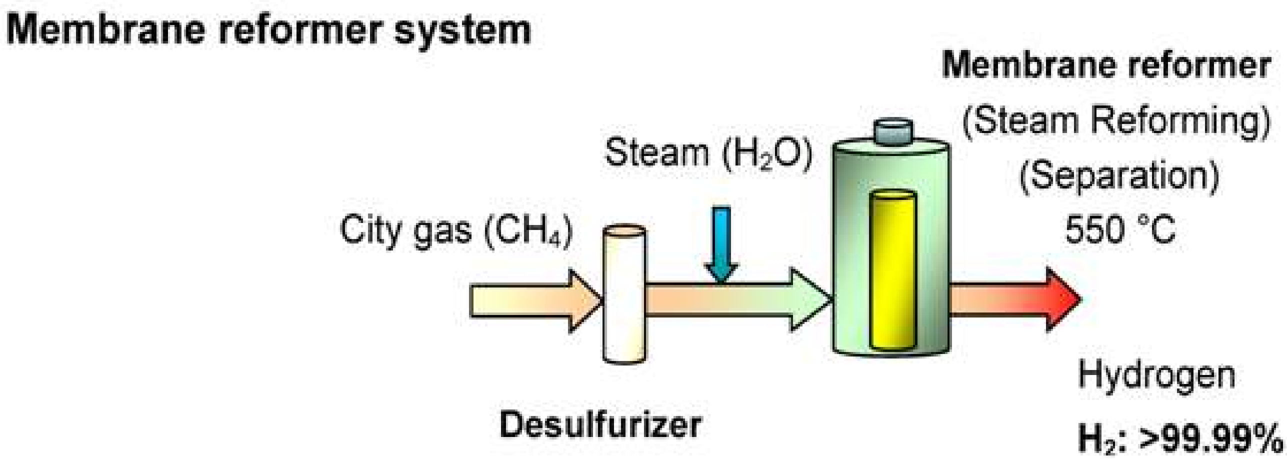
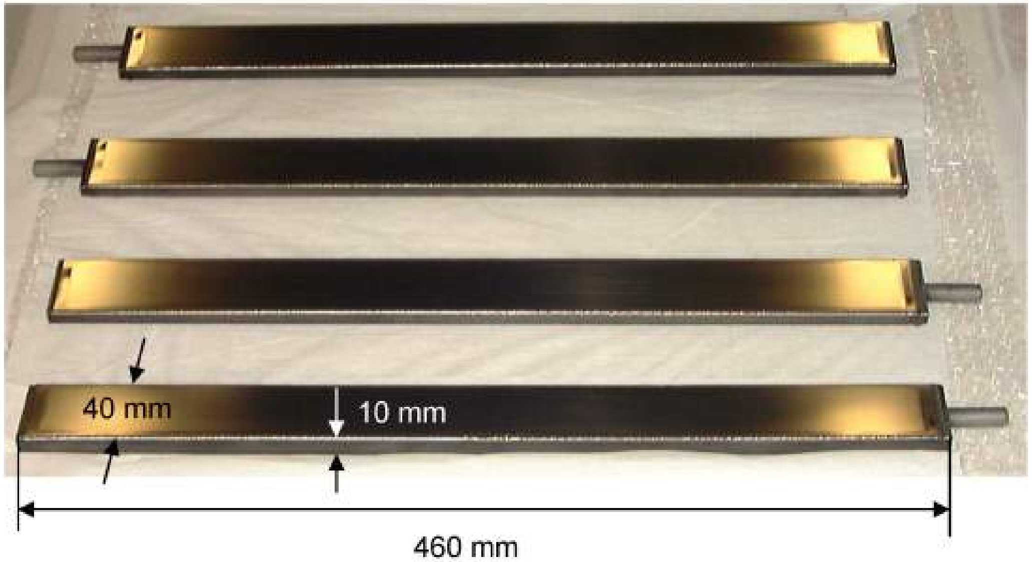


- Fewer steps / more compact unit
- Lower temperature due to synergy between reaction and separation
- Higher efficiency / lower cost

Yasuda et al., ICCMR-7, 2005

Tokyo Gas System – Membranes

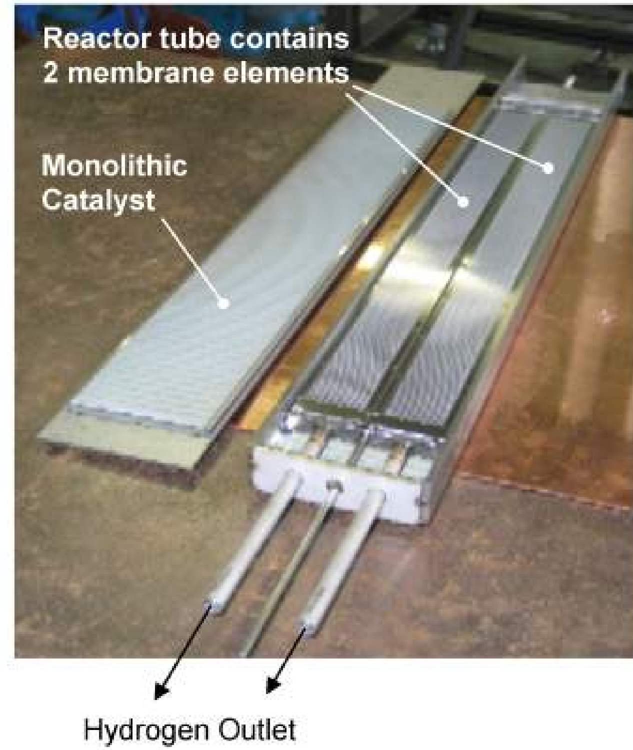


Membrane:

Cold-rolled Pd alloy foil with <20 µm thickness hot-pressed on a porous stainless-steel structural support using a porous blanket for protection against intermetallic diffusion.

Single tube hydrogen flux:

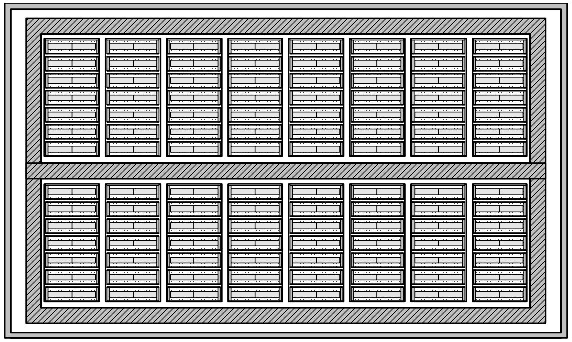
4.2 $m_N^3 \cdot m^2 \cdot h^{-1}$ at 550°C, Feed: Syngas with S/C = 3 at 9 bar, Permeate: Steam as sweep gas at 0.4 bar



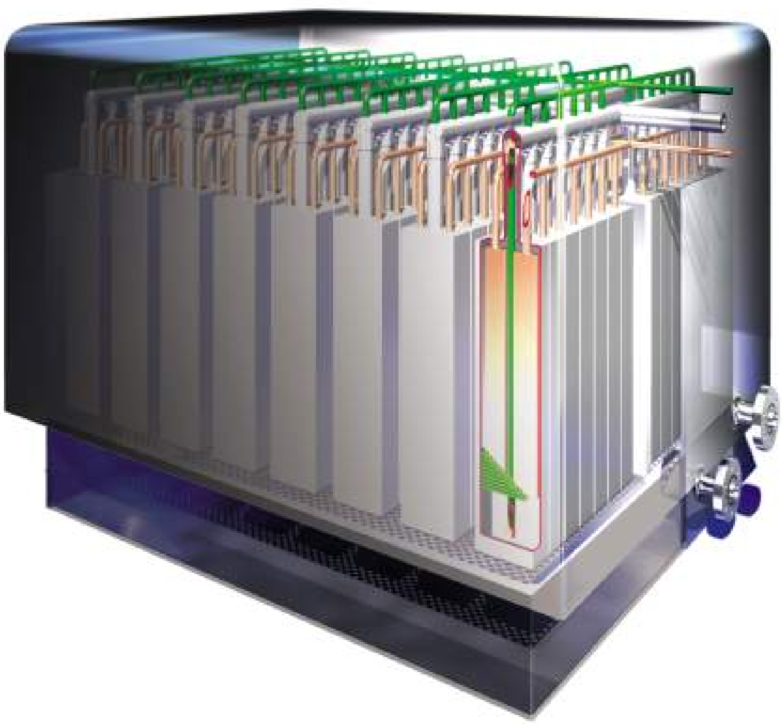
R. Dittmeyer, J. Caro, in: G. Ertl et al. (Eds.), Handbook of Heterogeneous Catalysis, 2nd Ed., Wiley-VCH, Weinheim, 2008, Ch. 10.7

Yasuda et al., ICCMR-7, 2005

Tokyo Gas System – Reactor Design



2 (Elements/Tube) × 7 (Tubes/Module) × 16 (Modules) = 224 Elements (membrane area: 10.3 m^2)



Reactor Size:

1.2 m × 0.75 m × 1.35 m
(with thermal insulation)

Yasuda et al., ICCMR-7, 2005

Technical Challenges

- Membrane and catalyst performance → thin membrane; active catalyst
- Integration of catalyst and membrane
- Minimization of the mass transfer resistances for hydrogen in the whole system
- Supply of the heat for the endothermic reaction on the spot

(Integration, minimization of mass transfer resistances, heat supply) → Reactor design

Heat demand (550°C):

$$CH_4 + 2H_2O \Leftrightarrow 4H_2 + CO_2 \qquad \Delta H_R^{823} = 186.1 \frac{kJ}{mol}$$

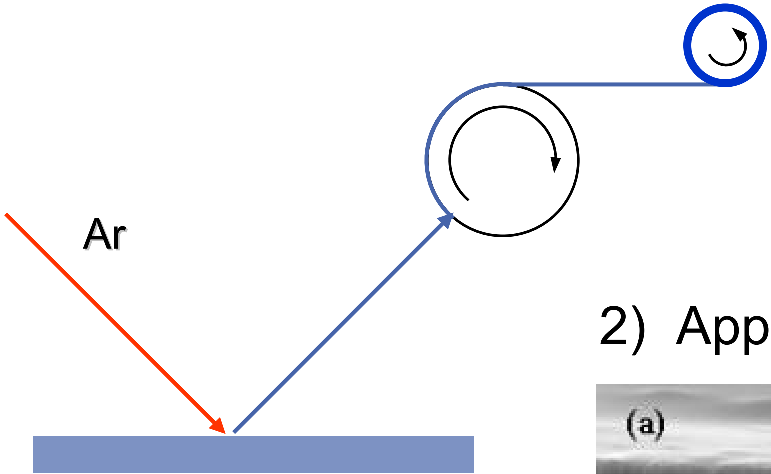
Heat release by burning of H_2:

$$H_2 + 0.5O_2 \Leftrightarrow H_2O \qquad \Delta H_R^{823} = -246.6 \frac{kJ}{mol}$$

→ 18.9% of the H_2 had to be burnt to provide the reaction heat

Thin Membranes

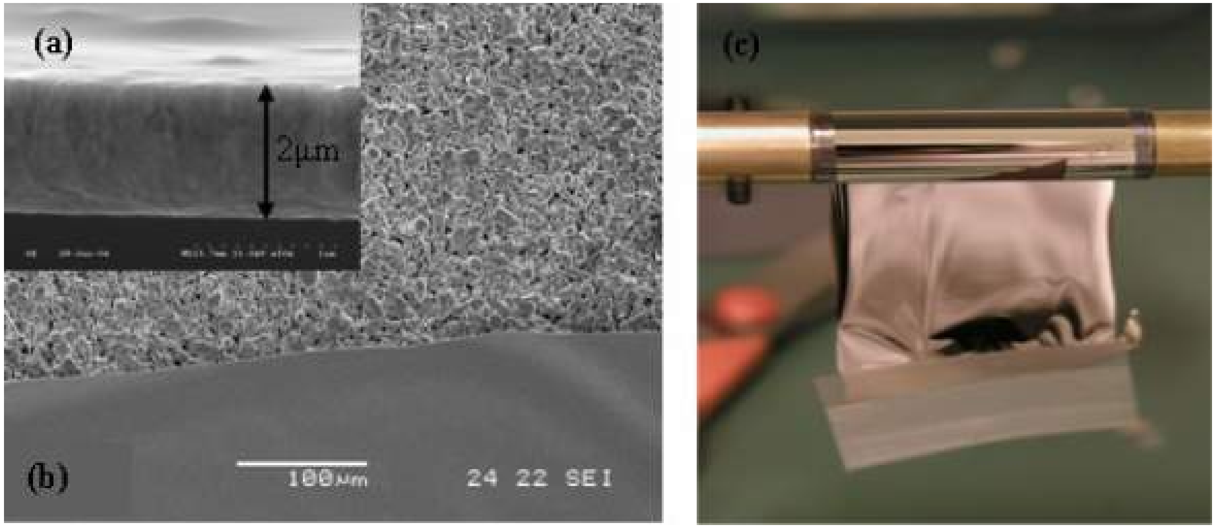
1) Magnetron sputtering of a thin film on a perfect surface (e.g. Si wafer)



- Perfect surface allows growth of a perfect film
- Good control of the composition
- Multiple layers and continuous manufacture possible

R. Bredesen, ForuM Workshop, SINTEF, Oslo, Nov. 2002

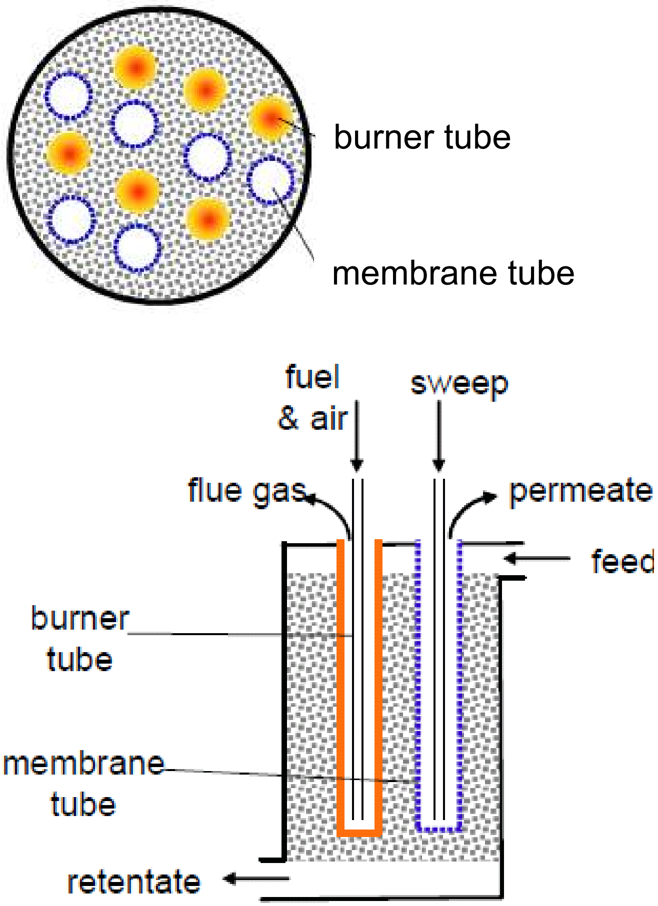
2) Application of the film on a supporting structure



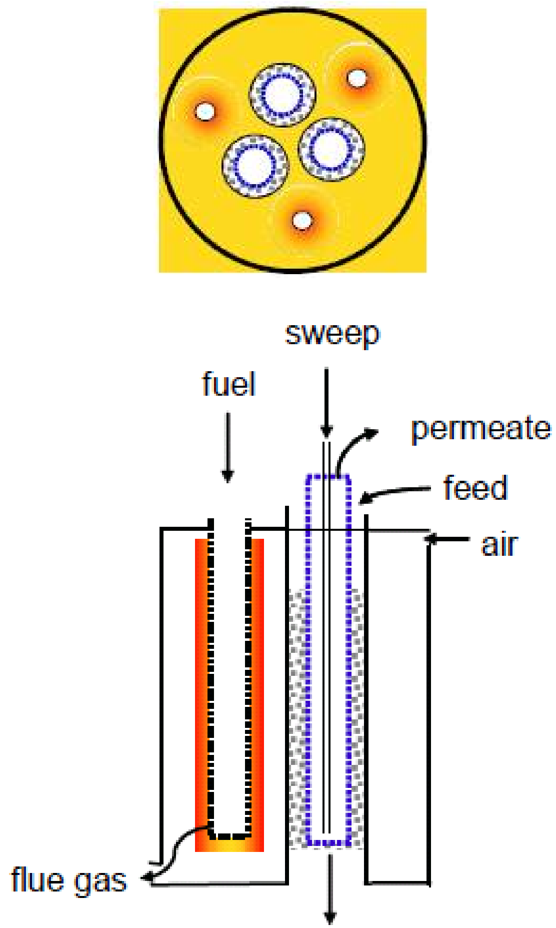
Jansen et al., Energy Procedia 1, 2009, 253

Tube-Based Reactor Design Options

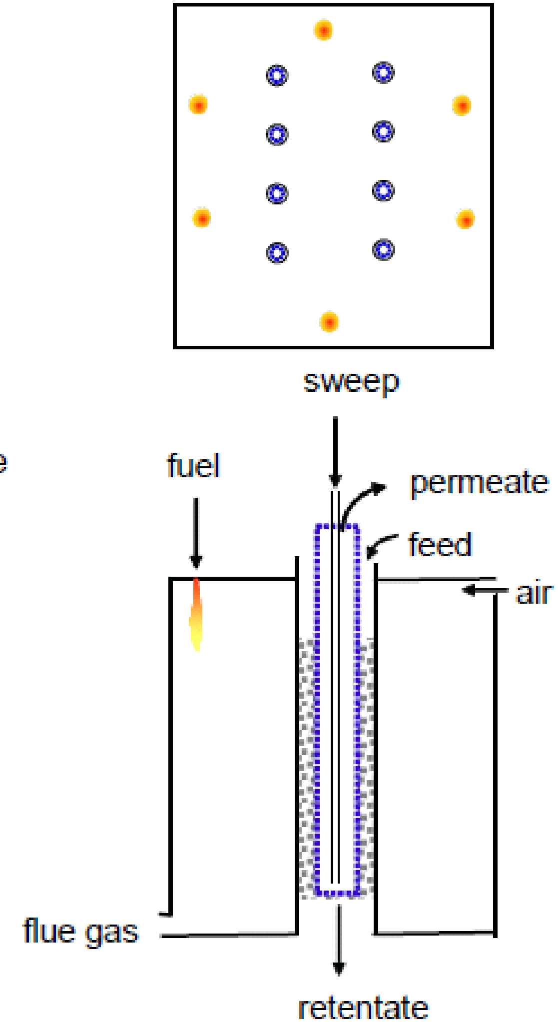
Catalyst in shell



Catalyst in annulus



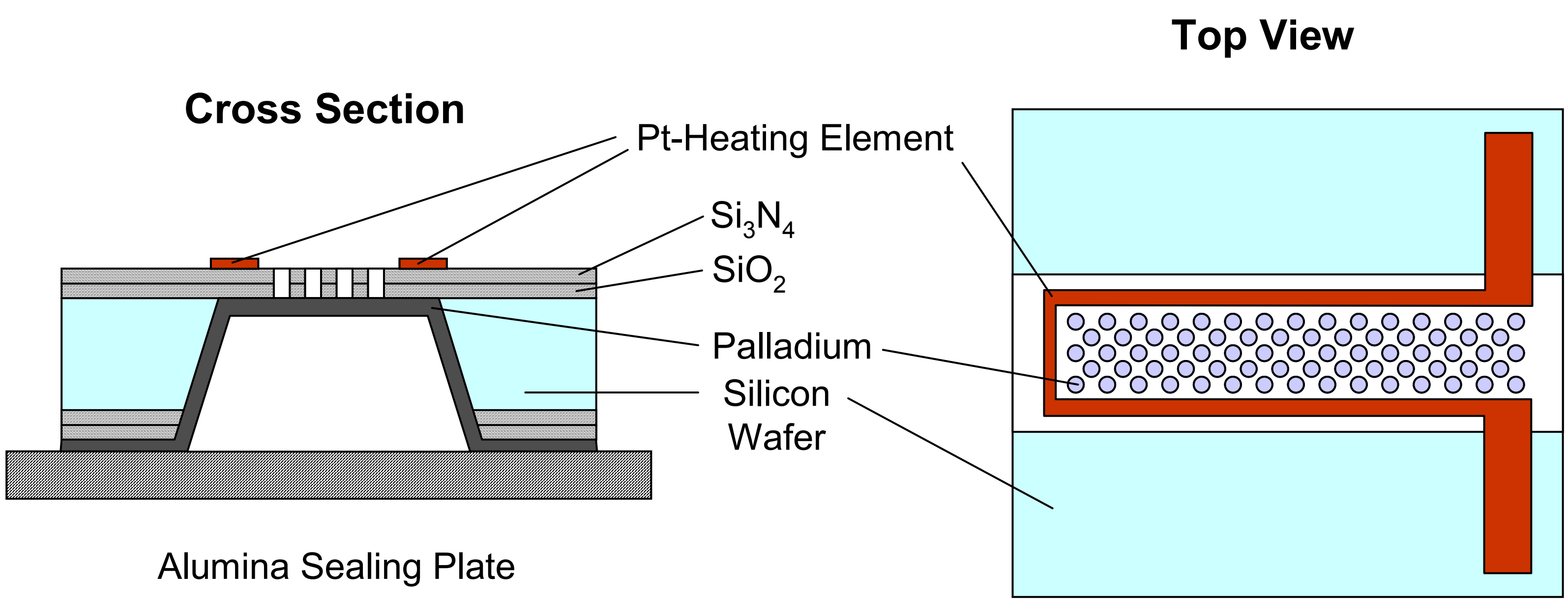
Box



Jansen et al., Energy Procedia 1, 2009, 253

The Microsystems Technology Approach

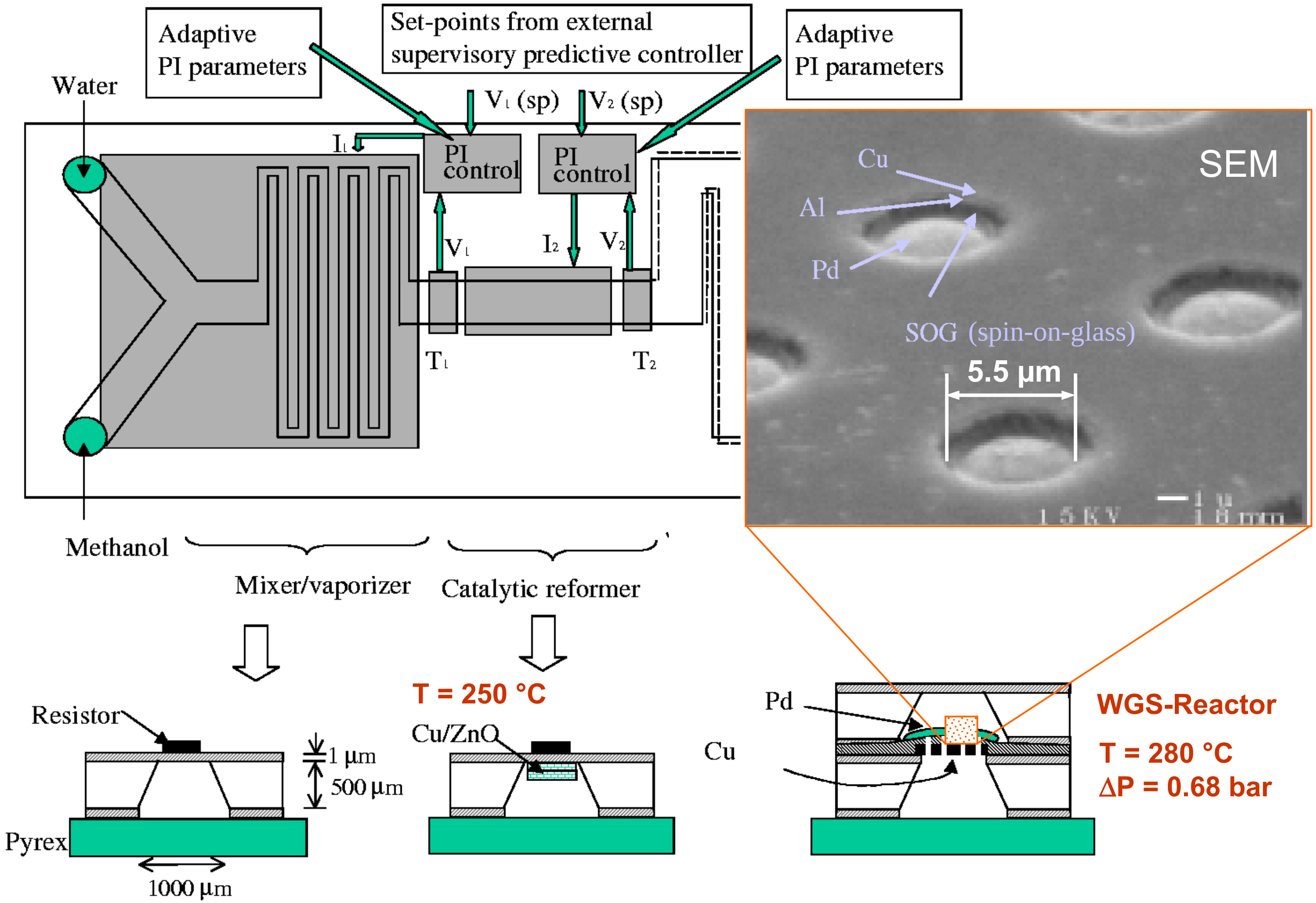
Palladium membrane microsystem for hydrogen separation



- Pd-Membrane
- H_2 Flux ~ 360 m^3/m^2h at 500°C and 0.1 bar
- $\alpha(H_2/N_2)$ ~ 1800

Franz et al., IEEE MEMS, 1999, 382

Microsystem for Methanol Reforming



Karnik et al., Proc. IMRET 5, Strasbourg, May 27-30, 2001

Palladium Membrane Microsystems – Status

- More recent work by several research groups
  - MESA+ Institute for Nanotechnology, Twente University, NL
  - MIT, Cambridge/MA, USA
  - AIST, Ibaraki and Sendai, JP
  - SINTEF, Oslo, NO
  - IMTEK, Freiburg/DE

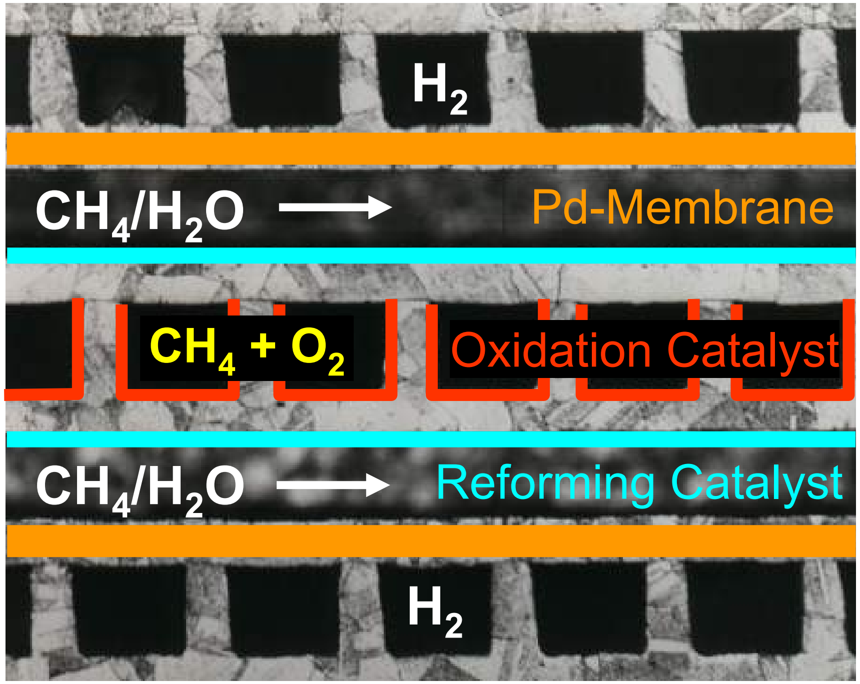
  …

- But reactor size and design options are very limited when relying on silicon-based microfabrication technologies

- Pd microsystems are focused on portable hydrogen generation (Holladay et al., Chem. Rev. 104, 2004, 4767-4790)

Systems Based on Micromachining of Metals

Stacked design using diffusion bonding of thin Pd foils and micro-structured metal sheets



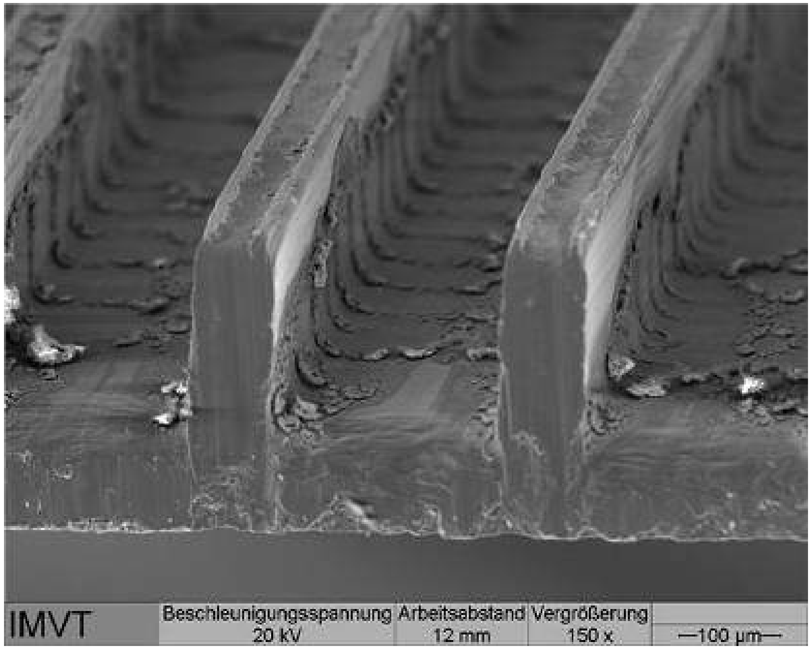
- Operating temperature is limited (interdiffusion of metals)
- Coating of sheets and foils with lower melting metals possible (soldering)
- Options for heating

  Alternating layers for H_2 removal and oxidation

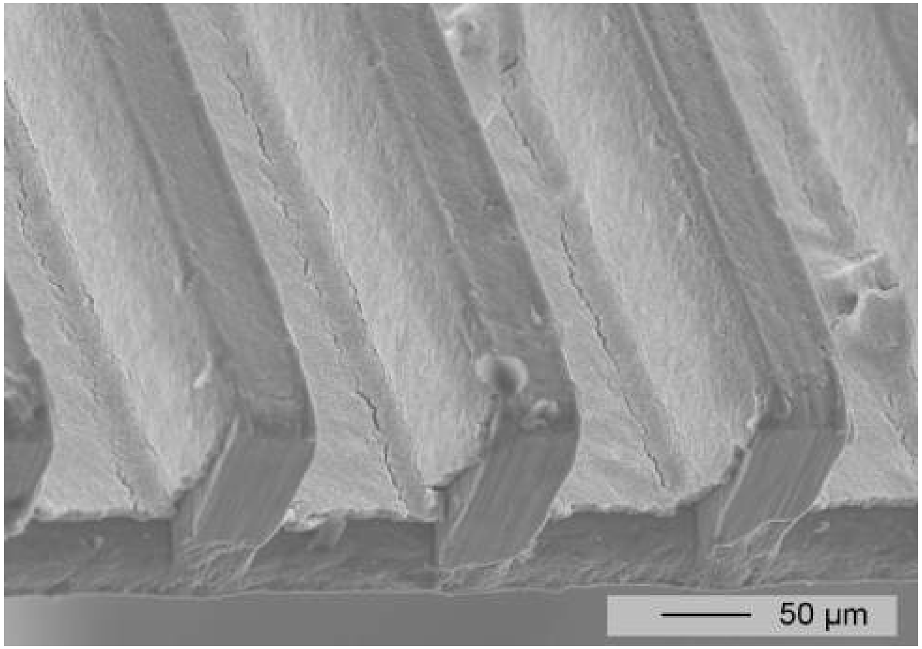
  Alternating channels (in each layer) for H_2 removal and oxidation

Catalyst Coating of Microstructured Metal Sheets

Sol-Gel



Washcoat

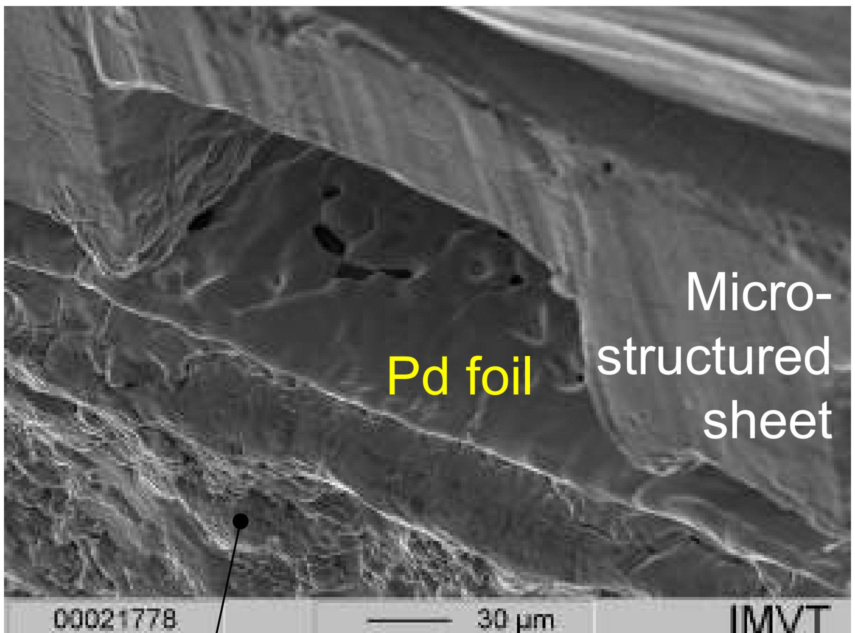


Catalyst coating can be applied before or after stacking/joining of the sheets depending on the joining method

Diffusion Bonding of Pd foils to Stainless Steel

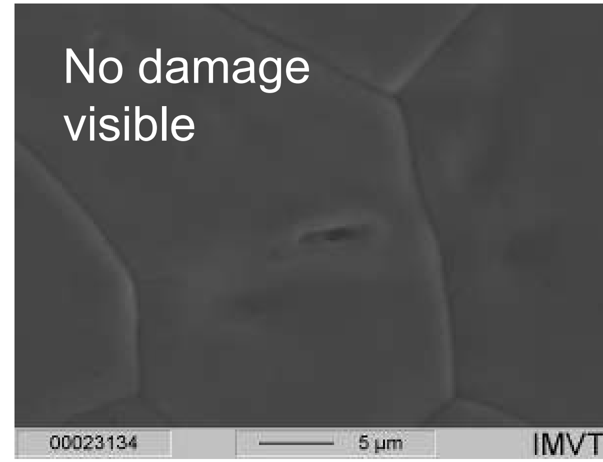
First attempts at IMVT for bonding of 5 µm thick Pd foils (CETH, Marcoussis/FR) to micro-structured stainless steel sheets (1.4404)

Bonding with IMVT standard conditions for stainless steel:



Support (solid frame, porous interior)

T ↓



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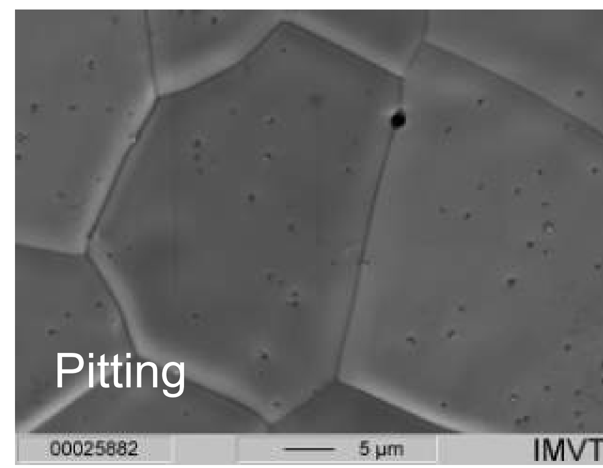
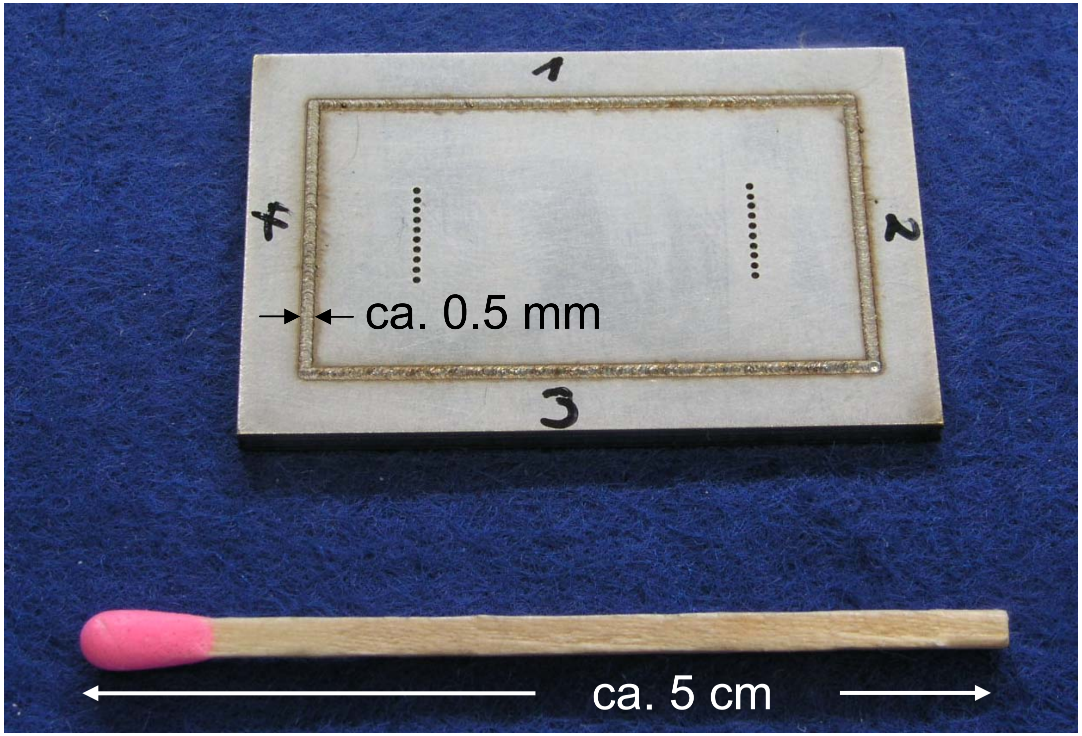


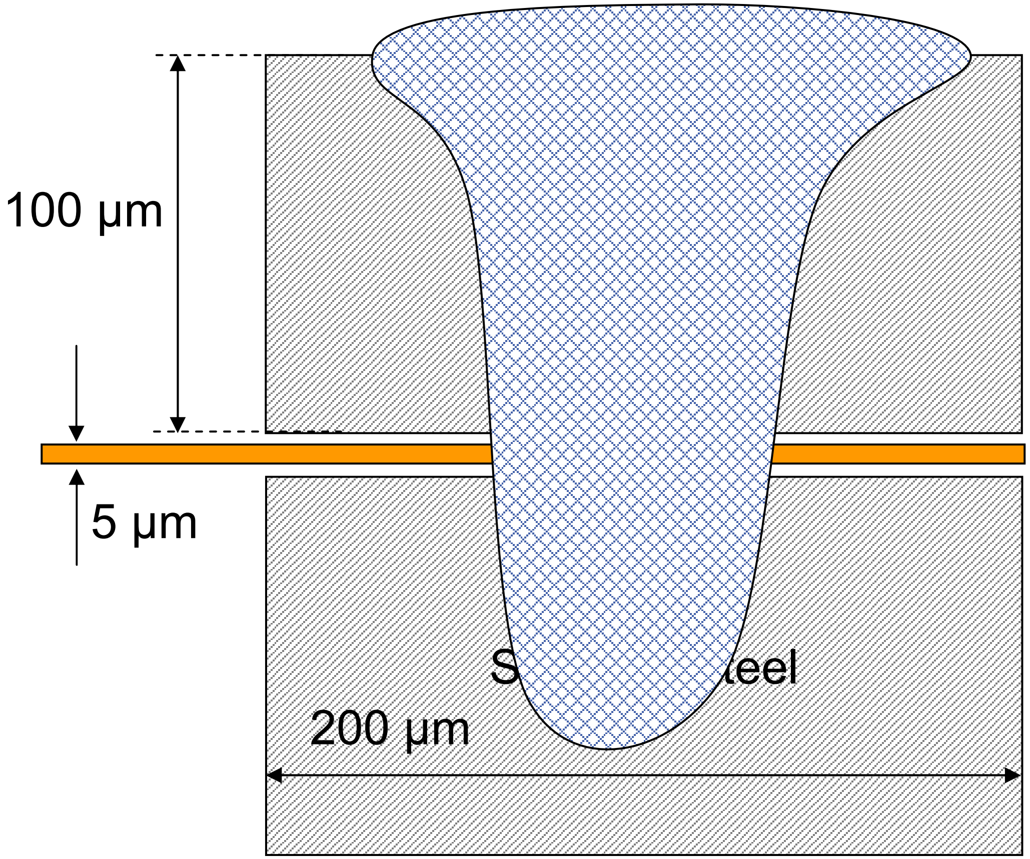
Laser Welding of Pd foils to Stainless Steel

First attempt at IMVT with laser welding of thin Pd foils to microstructured stainless steel sheets



- 5 µm thick Pd foil between two micro-structured stainless steel sheets
- Coplanar sheets with burr-free microstructure
- Performed with a multi-purpose pulsed laser
- Leak-free integration achieved

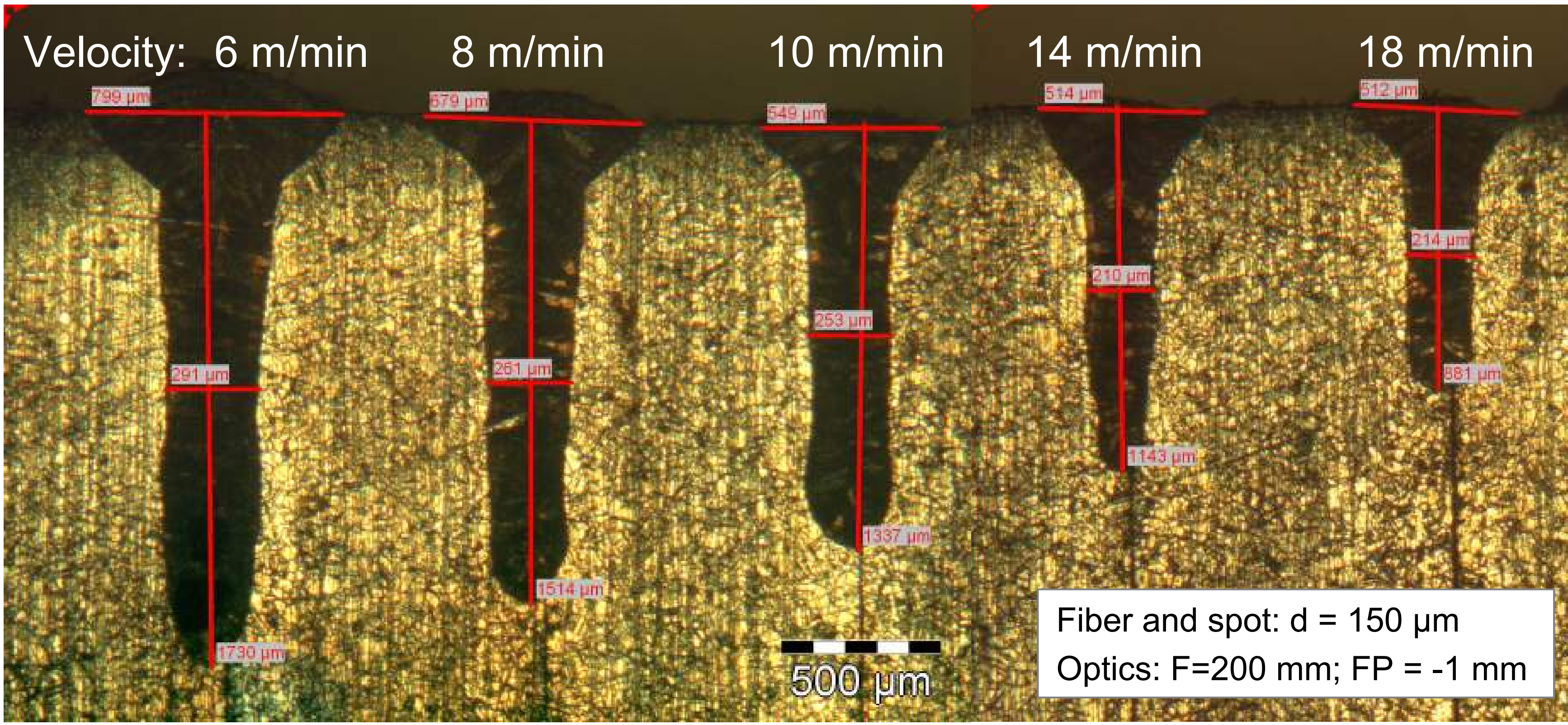
Technical Challenges



- High geometrical precision and subtle control of the energy input per unit length required
- High aspect ratio of the weld seam needed for joining of multiple layers / stacks from the top
- High power, high speed continuous wave laser system with precise control (positioning, laser power, linear velocity, dynamic control)

Weld Seam Geometry for Different Energy Input

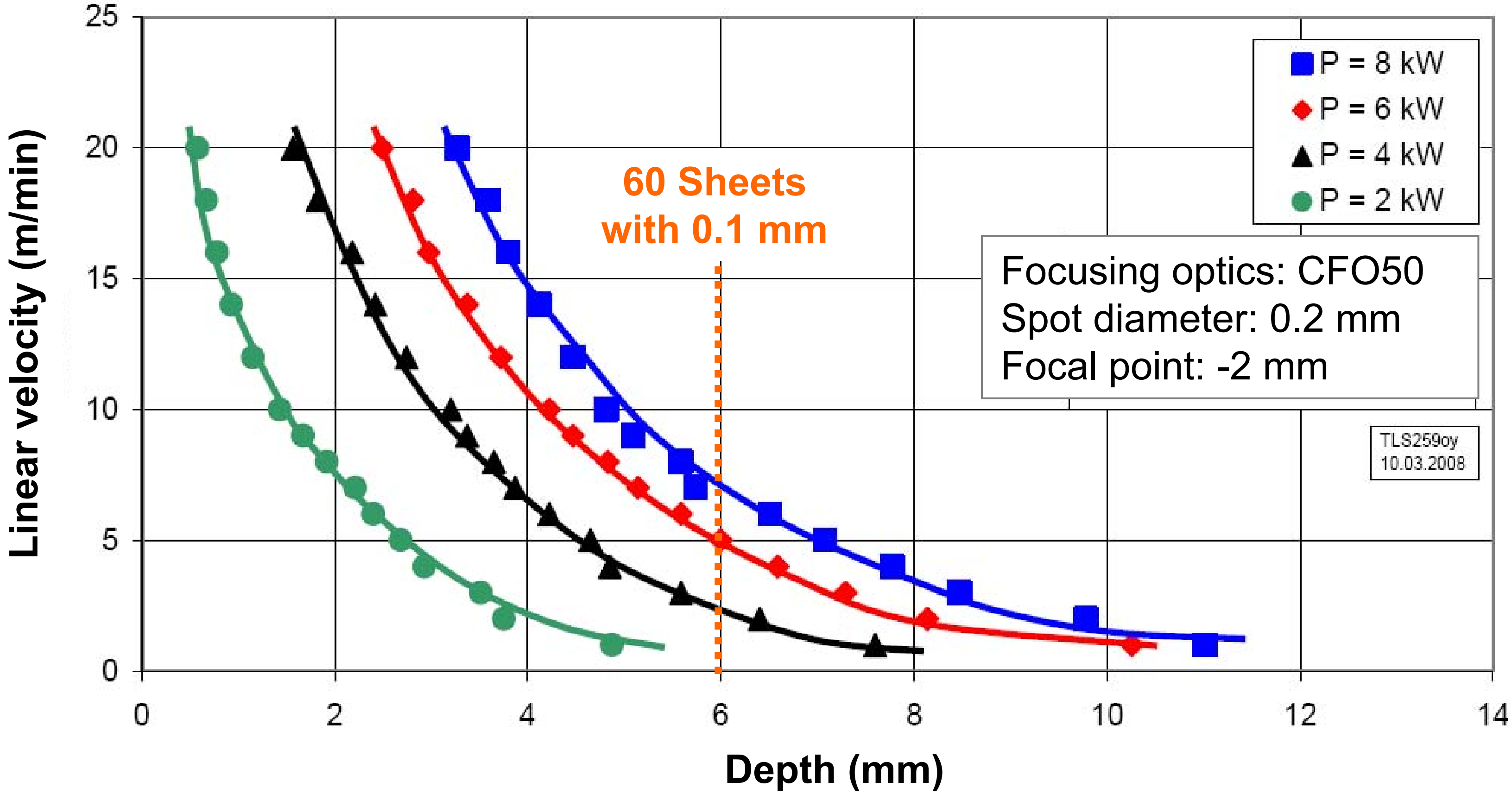
- Linear velocity determines energy input per unit length
- Material: Hastelloy C-22



1 kW continuous wave CO_2 fiber laser (Rofin-Sinar Laser GmbH, Hamburg/Germany)

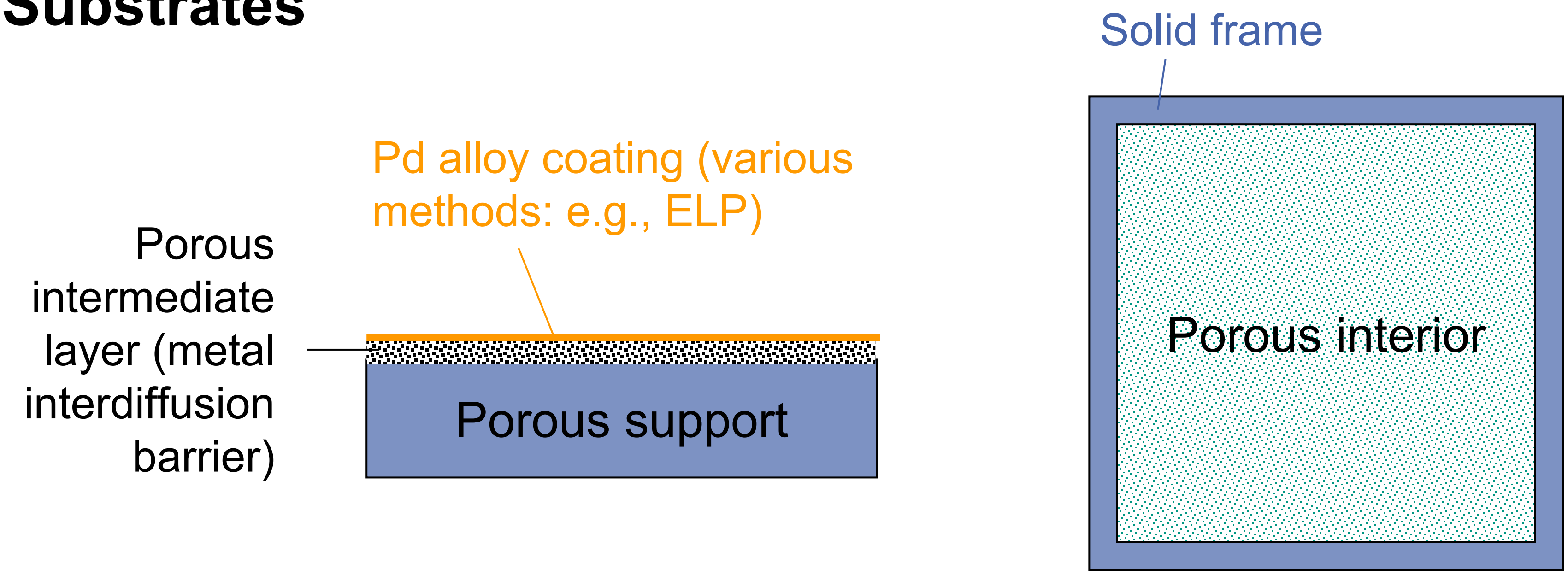
Velocity versus Depth for Different Laser Power

- Material: Standard construction steel



Continuous wave YAG disk laser (Trumpf Laser Technology, Schramberg/Germany)

Alternative to Pd Foils – Coating of Porous Substrates



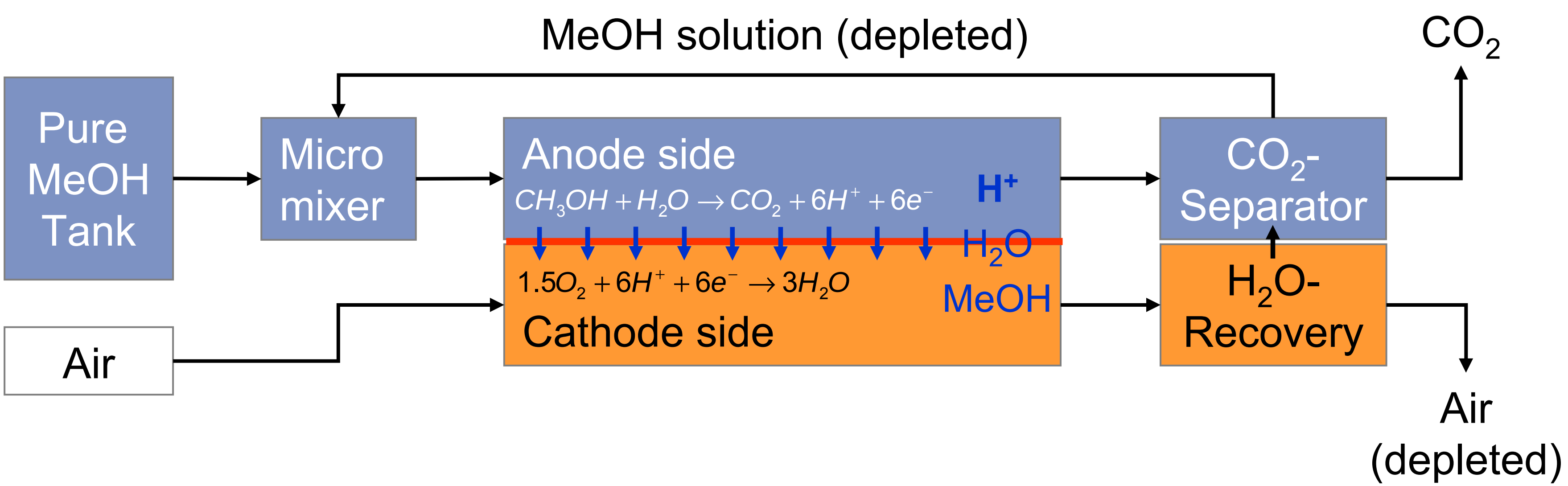
- Not compatible with diffusion bonding due to ceramic interdiffusion barrier
- Ceramic membrane coatings applicable (comparable to metal supported SOFCs)

→ **High precision laser welding for joining of stacks**

Gravity-insensitive Gas/Liquid Systems

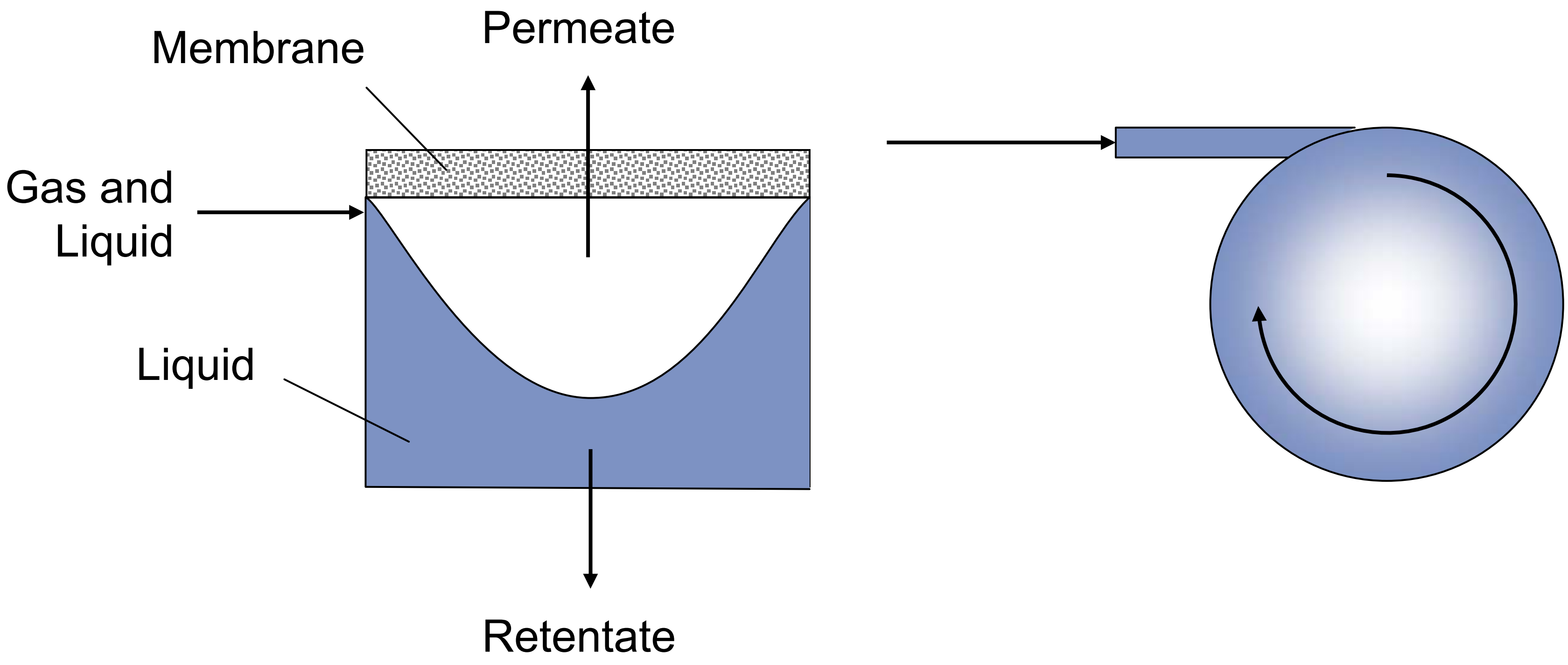
Why Gas/Liquid-Separation in Microstructures ?

- For processes fully based on compact „intensified“ microstructure equipment often phase separation is a bottleneck
- Gas-Liquid separation is important in many multiphase reactions (e.g., liquid-phase hydrogenation or oxidation)
- Application: Development of a „Micro“-DMFC supported universal battery charging system

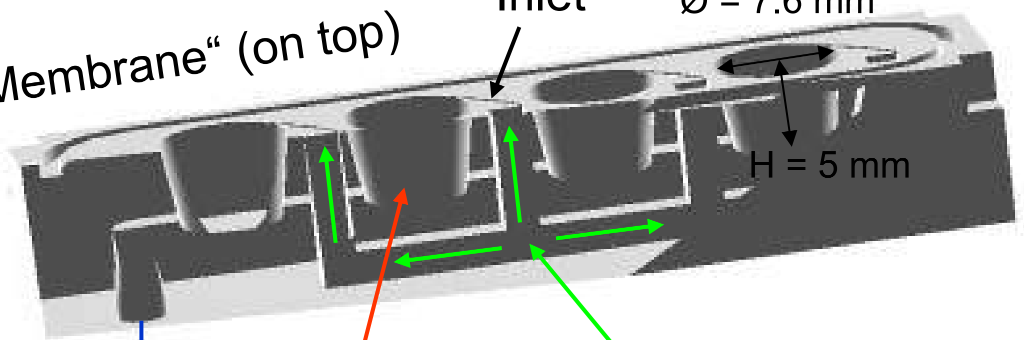


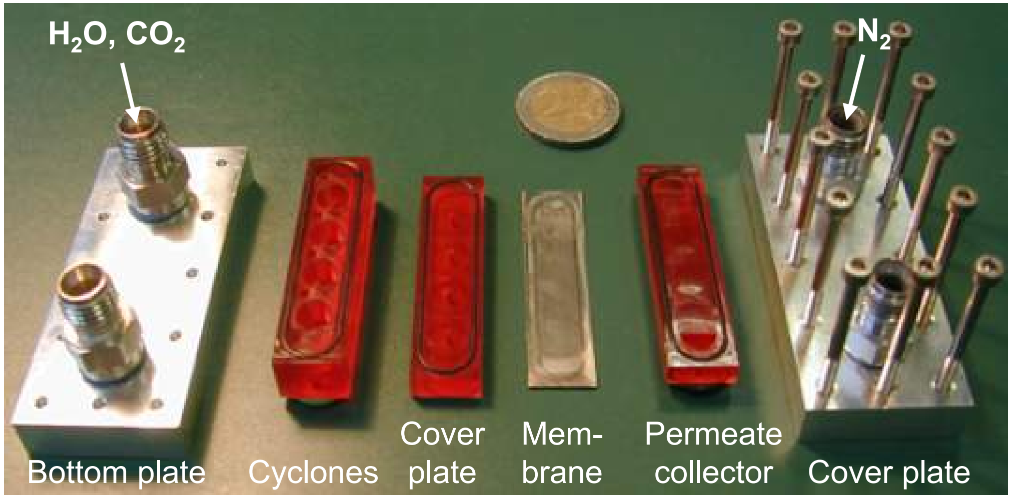
Preliminary Work on G/L-Separation at IMVT

- Cyclone separator combined with a fine-porous metallic membrane
- Targets: high recovery of the gas; low pressure drop
- Tested with CO_2 in water

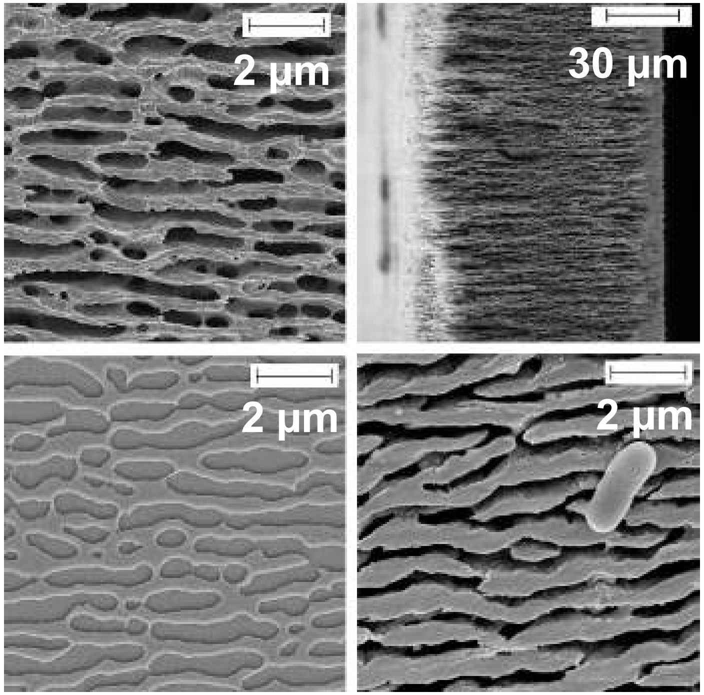


Cyclone/Membrane Separator – Design



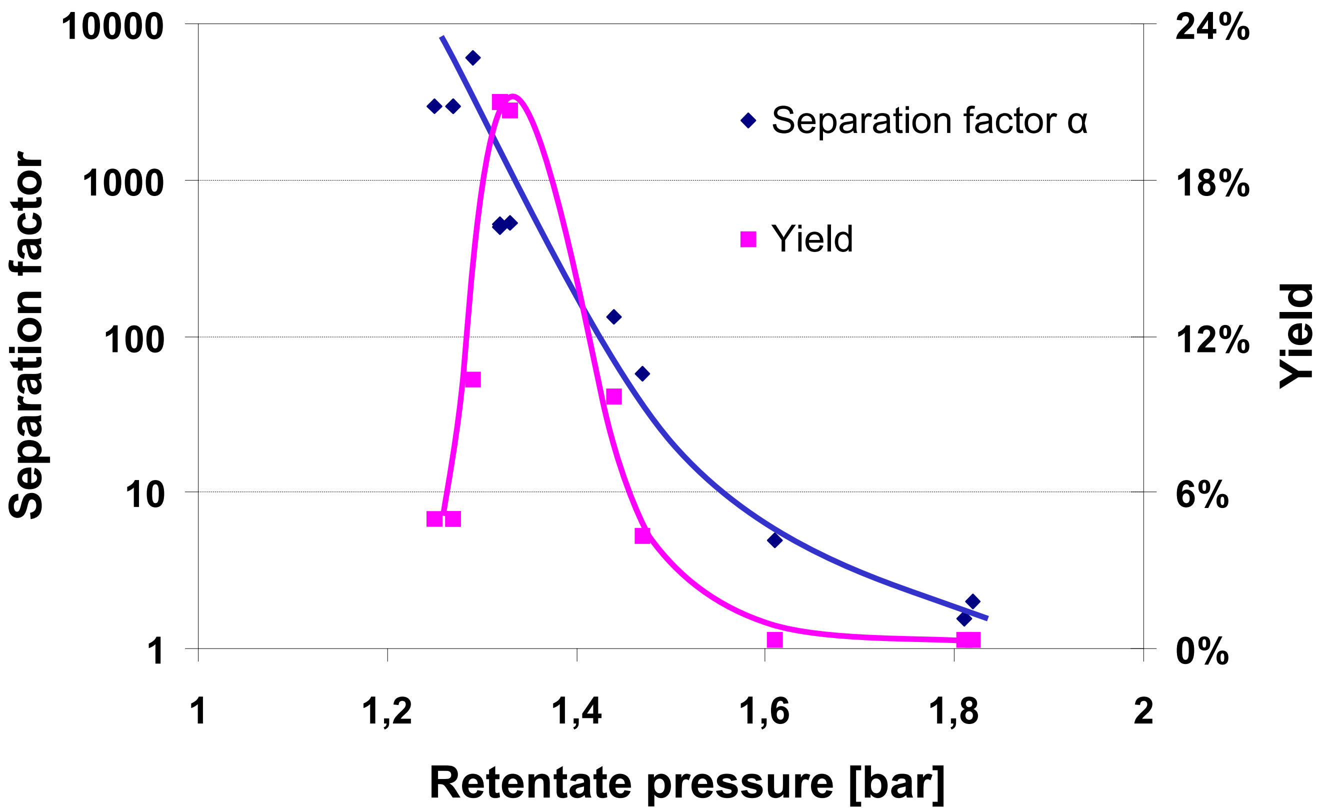


Metallic superalloy membranes prepared be electrochemical etching at TU Braunschweig



J. Rösler, D. Mukherji, Adv. Eng. Mat. 5, 2003, 916-918

Cyclone/Membrane Separator – Results



<u>Conditions:</u>

T = 26 +/-2 °C

3 ml/min H_2O

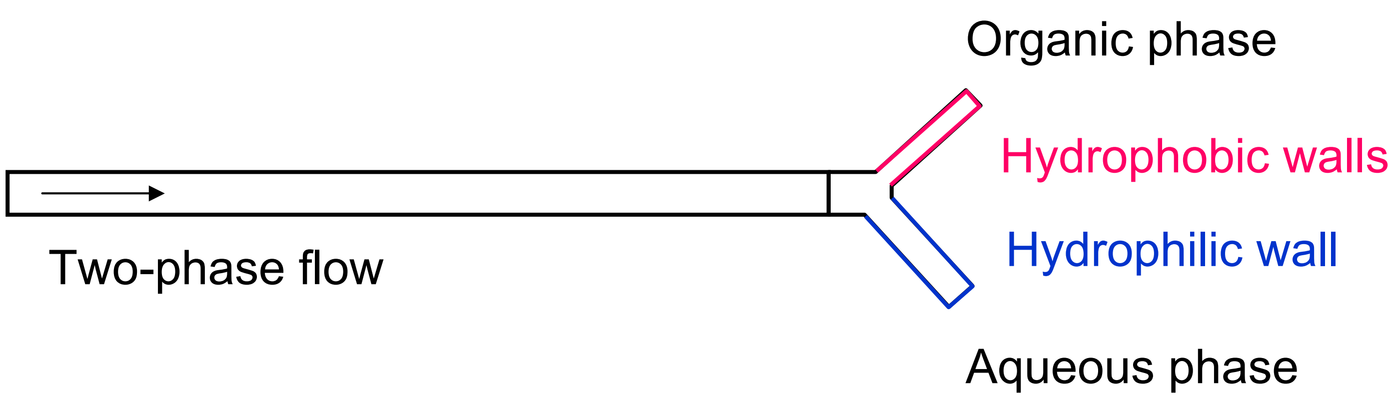
6 ml/min CO_2

Separation factor: $\alpha = \left(\frac{w_{CO_2}}{w_{H_2O}}\right)_P / \left(\frac{w_{CO_2}}{w_{H_2O}}\right)_F$

Permeate yield: $Y = \frac{\dot{V}_P}{\dot{V}_F}$

Separation Based on Wetting Properties of Wall

- Demonstrated for liquid-liquid systems in capillaries

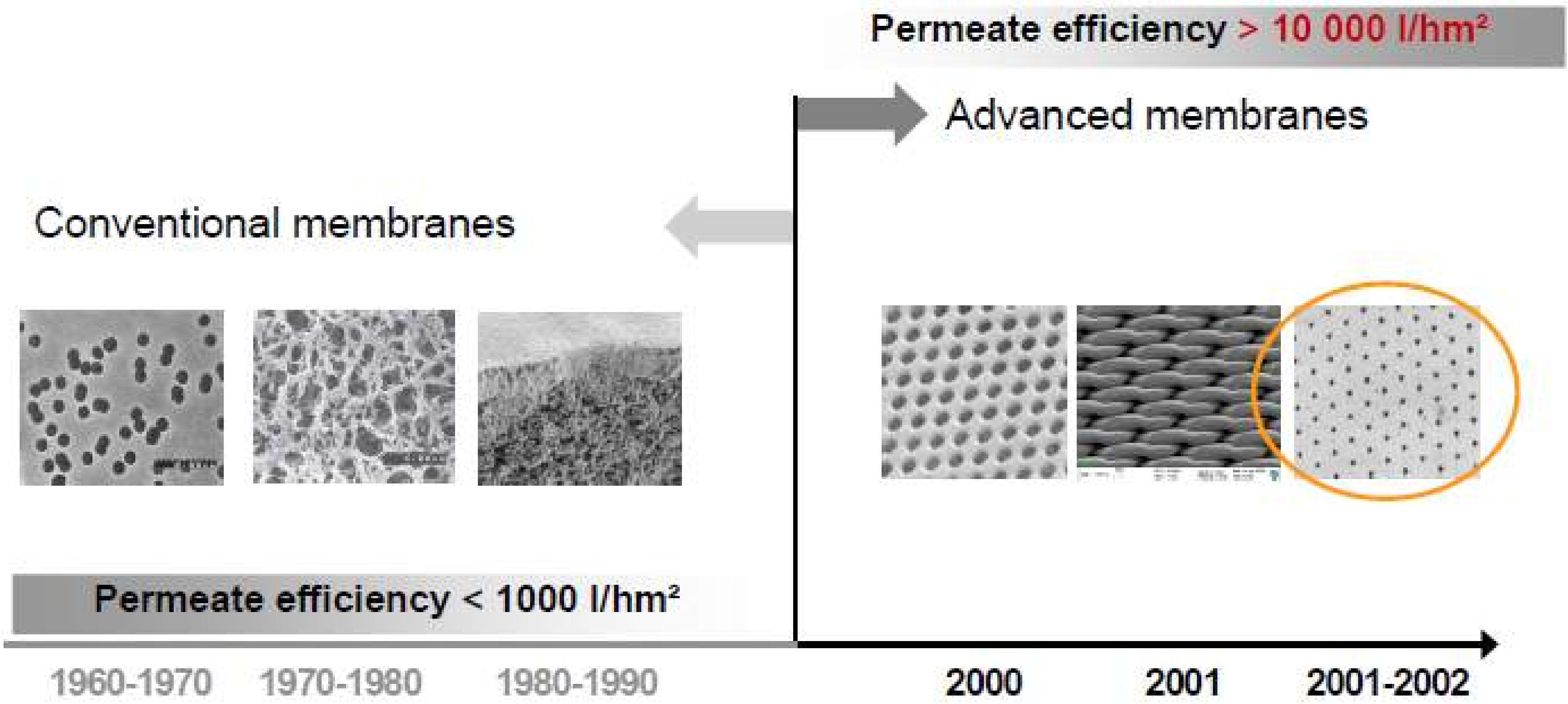


- Demonstrated also for liquid-liquid as well as gas-liquid systems in porous membrane contactors (pertraction, degassing)

Hydrophobic asymmetric porous membranes (hollow fibers or sheets)

Materials: Polymers (PTFE, PP, etc.)
Silica
Carbon

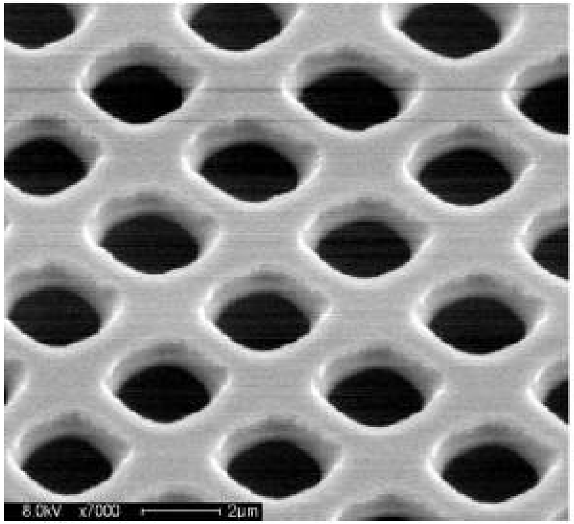
Basics of Microsieves

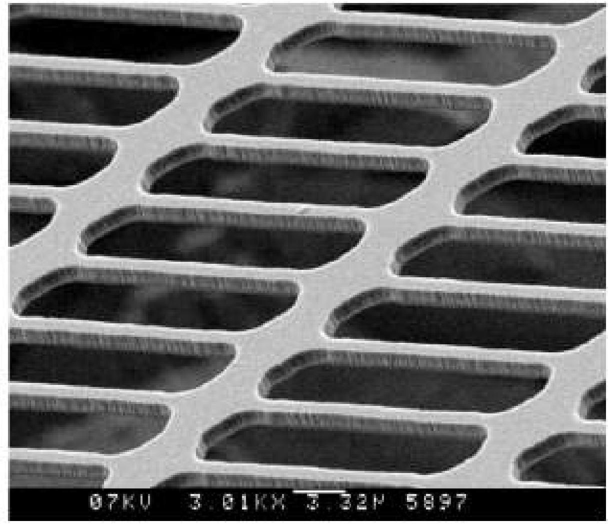


L. t. r.: Co. Oxyphen, GER; Co. Membrana, GER; Co. Aquamarijn, NL, Co. Haver & Boecker, GER; Fraunhofer UMSICHT

Gehrke and Keuter, EuroNanoForum, 02.-05.06.09, Prague

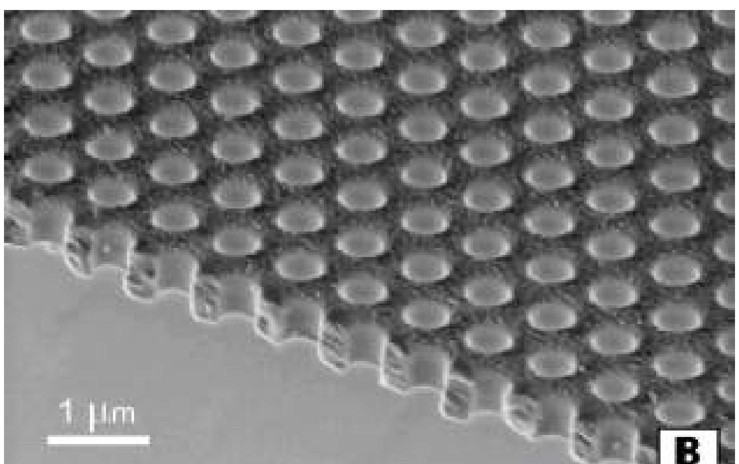
Silicon-based Microsieves





Pore size 1-2 μm

S. Kuiper, R. Brink, W. Nijdam, G.J.M. Krijnen, M.C. Elwenspoek, J. Membr. Sci. 196,2002, 149-157

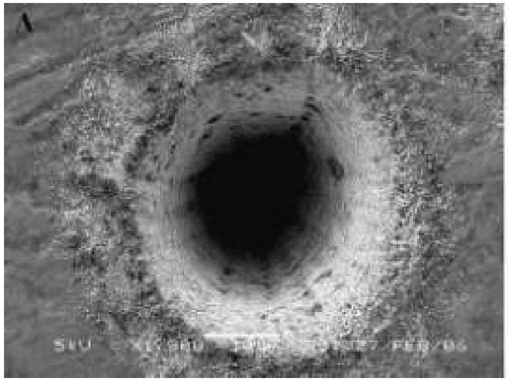


Pore size 500 nm

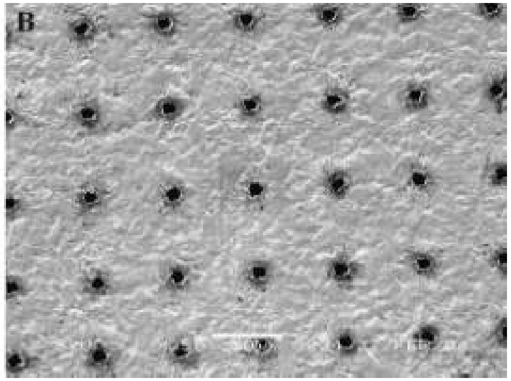
Juaz et al., J. Membr. Sci. 323, 2008, 347-351

Metal-based Microsieves

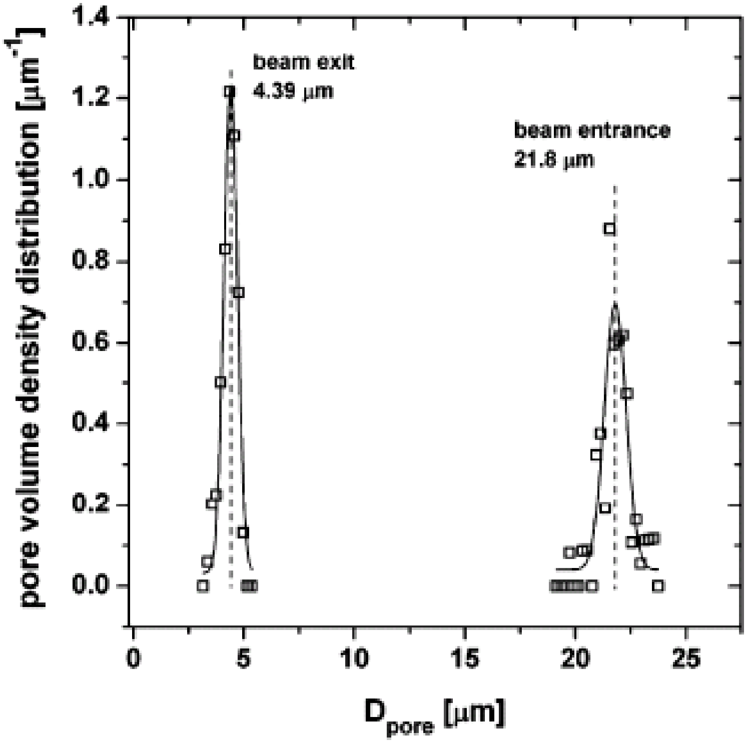
Laser ablation with a femtosecond laser



Inlet



Exit



50 µm thick stainless steel foil

M.J. Geerken, M.N.W. Groenendijk, R.G.H. Lammertink, M. Wessling, J. Membr. Sci. 310, 2008, 374-383

Metal-based Microsieves – Options

- Electron beam lithography followed by galvanic deposition of Ni or other metals (LIGA process) (KIT, Karlsruhe/Germany)
- Track etching of polymers followed by galvanic deposition of Ni or other metals (GSI, Darmstadt/Germany)
- Micro galvanics and laser ablation (Fraunhofer IUSE, Oberhausen/Germany)

Stable G/L-Interface: $$\Delta P \leq f \frac{\sigma \cos \alpha}{d}$$ f = 4 for circular pores

State of the art (IUSE): d = 0.5 - 1 µm

Summary/Outlook

Membrane integration in microstructures is on the agenda

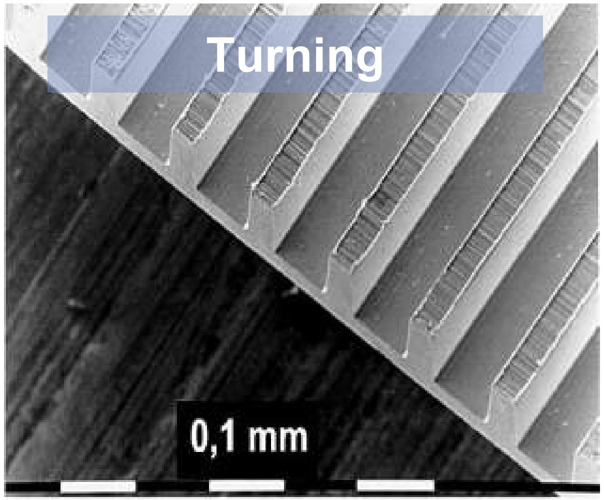
- Unit design and fabrication technology is (at least) equally important as membrane and catalyst development if working devices are targeted
- Microsystems are not in the focus at IMVT

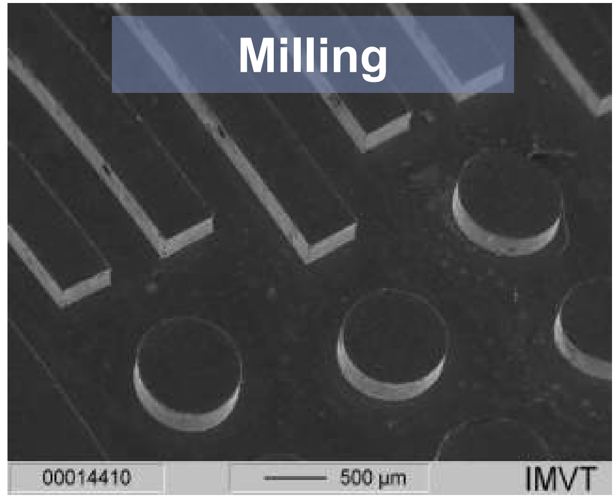
Current targets

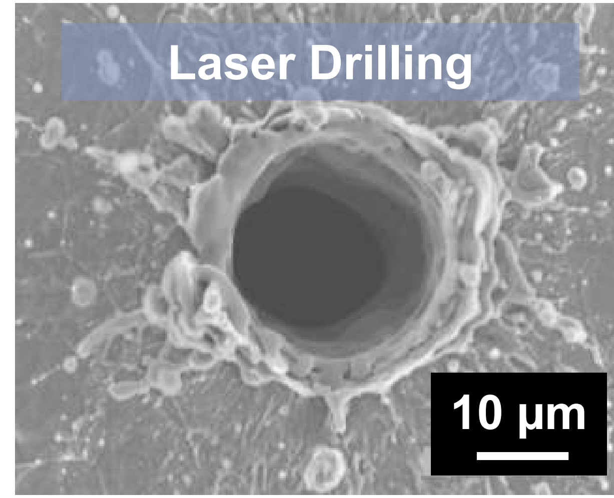
- Compact hydrogen production systems (Pd alloy membranes)
- Gas/liquid separation based on porous membranes (metal-based microsieves)
- Water removal from organic reaction mixtures via selective membranes
- Integrated oxygen-separation from air for high-temperature oxidation reaction with ceramic membranes on metallic substrates is being considered

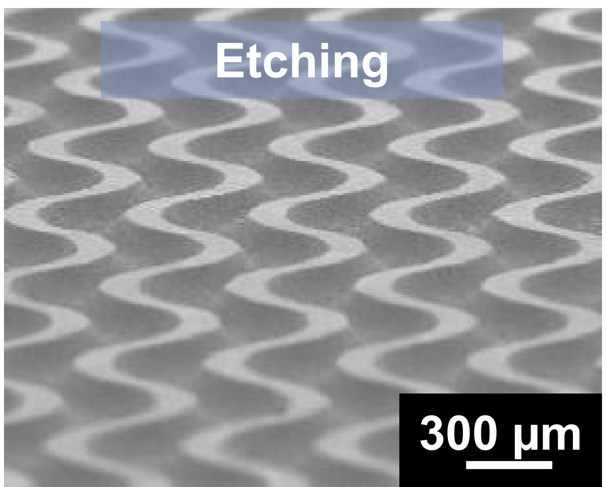
Backup – IMVT

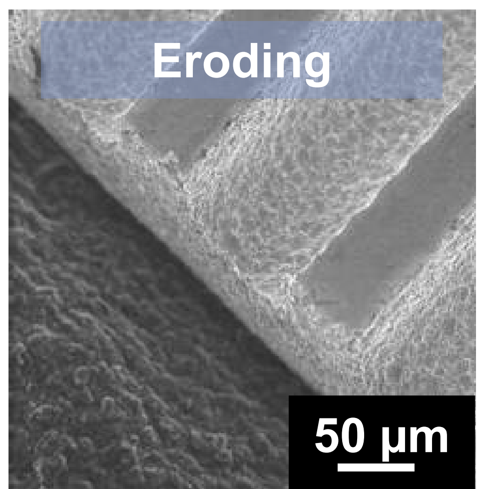
Microstructuring

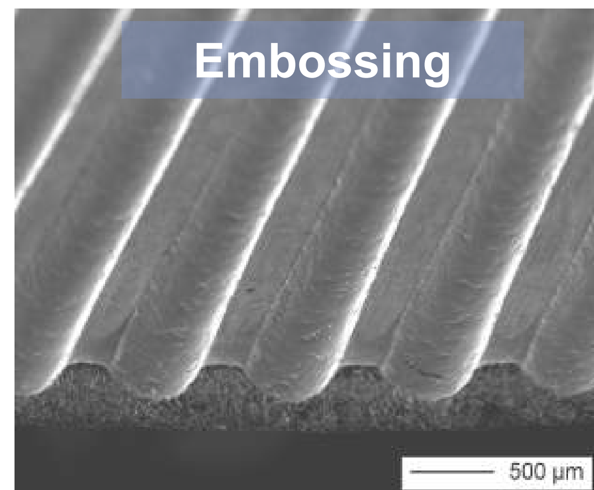




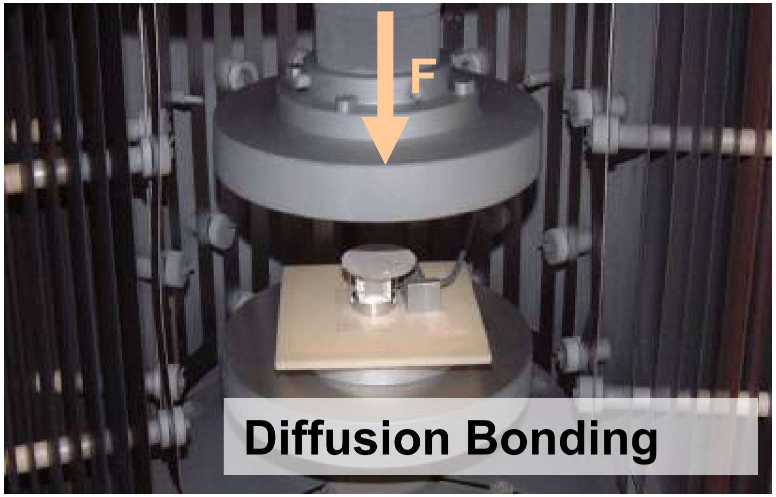




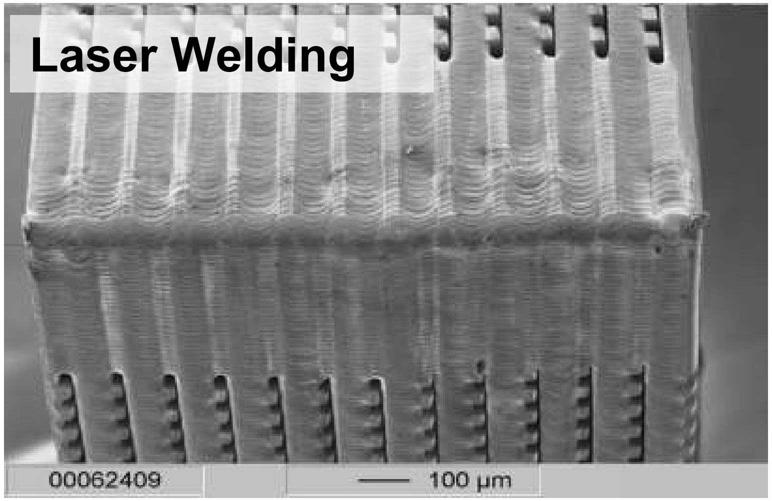


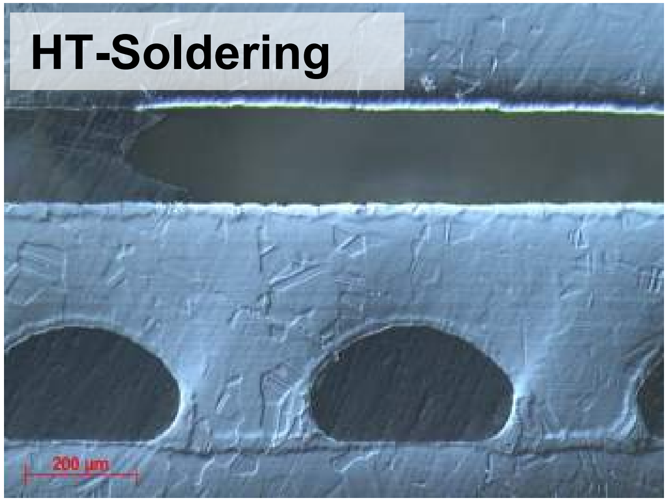


Joining

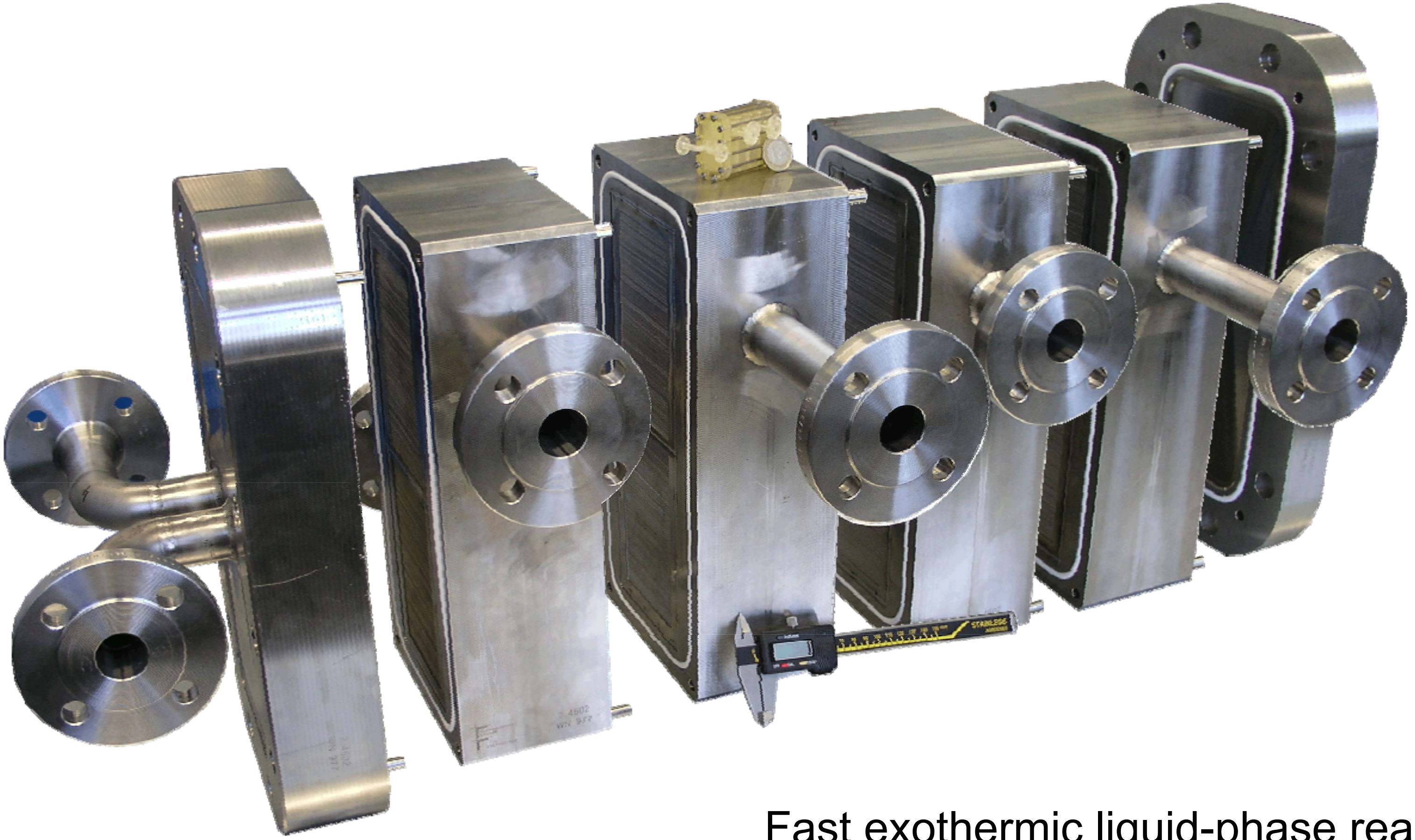

F
Diffusion Bonding


Electron Beam Welding


Laser Welding
00062409
100 µm


HT-Soldering
200 µm

Microstructured Reactor for 1500 kg/h



Fast exothermic liquid-phase reaction in hot concentrated sulfuric acid

Material: Hastelloy C-22

IMVT - Personnel

Karlsruhe Institute of Technology

Direction (2)
R. Dittmeyer, A. Karcher

Administration (4)
W. Ratajczak, M. Götz, A. Schäfer, W. Schneck

Thermal µ-PE (TMV) [12]
J. Brandner, E. Anurjew, *F. Brighenti*, J. Bucko, C. Grehl, E. Hansjosten, M. Jäger, N. Kamaruzaman, S. Maikowske, H. Maria Joseph, A. Vitoriosi, W. Wibel

Chemical µ-PE – Gas Phase / Multi Phase (CMV1) [12]
P. Pfeifer, O. Görke, K. Hecht, H. Kreuder, P. Piermartini, C. Spiegel, S. Tauro, J. Thormann, G. Straczewski, *N.N., N.N., N.N.*

Chemical µ-PE – Liquid Phase (CMV2) [6]
M. Kraut, K. Haas-Santo, A. Hensel, A. Kölbl, N. Schüler, *N.N.*

Materials for µ-PE (WMF) [6]
Th. Gietzelt, *A. Dubbe*, L. Eichhorn, U. Gerhards, F. Messerschmidt, M. Zürker

Modelling and Simulation (MSM) [5]
A. Wenka, W. Benzinger, C. Fräulin, F. Özkan, U. Schygulla

In situ Analytics and Sensors (ASM) [5]
G. Rinke, A. Ewinger, *S. Heidecker*, S. Kerschbaum, A. Urban

Mechanical µ-Structuring and Manufacturing Development (MF) [15]
L. Bohn, R. Dürrschnabel, M. Hofheinz, A. Hüll, H. Lambach, G. Rabsch, D. Scherhaufer, M. Schmidt, M. Schöffler, C. Schorle, J. Schwab, S. Schweikert-Joß, V. Toth, T. Wunsch, J. Dörflinger

Backup – Hydrogen Production

2) Methylcyclohexane Dehydrogenation

Heat demand (300°C):

$$C_7H_{14} \Leftrightarrow C_7H_8 + 3H_2 \qquad \Delta H_R^{573} = 215.3\ \frac{kJ}{mol}$$

Heat release by burning of H_2:

$$H_2 + 0.5O_2 \Leftrightarrow H_2O \qquad \Delta H_R^{573} = -244.5\ \frac{kJ}{mol}$$

} 29.4% of the H_2 had to be burnt to provide the reaction heat

- <u>Background:</u> storage of excess electricity or heat (nuclear, renewable)

  Chemical storage of hydrogen produced by electrolysis
  Capacity: 6.1 wt.-% or 43 kg H_2 / m^3

  Heat storage for solarthermal power plants
  Capacity: 215 kJ/mol or 2194 kJ/kg

  For comparison: heat capacity of molten $NaNO_3$: 1.83 kJ/kg·K

Pd Membrane Microsystems (not exhaustive)

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- F.C. Gielens, H.D. Tong, M.A.G. Vorstman, J.T.F. Keurentjes, Measurement and modeling of hydrogen transport through high-flux Pd membranes, J. Membr. Sci. 289, 2007, 15-25
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