# Integrated calorimetric microreactor in low-temperature cofired ceramic (LTCC) technology

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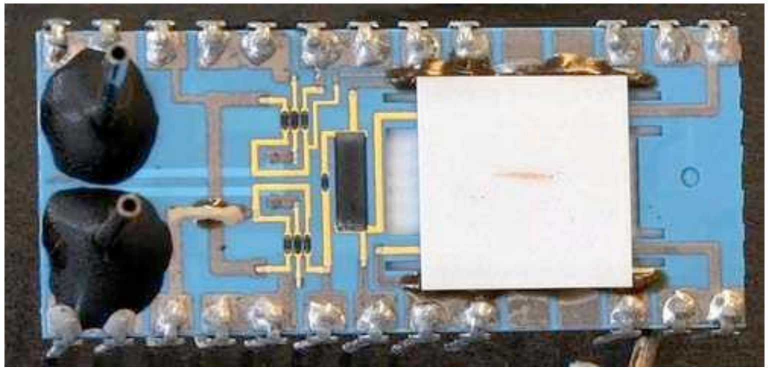

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# Object of this work

**Explore the feasibility of an LTCC microreactor**

- Chemical stability: compatible with HCl, NaOH, …
- Thermal stability to >100°C

**Achieve a high degree of integration**

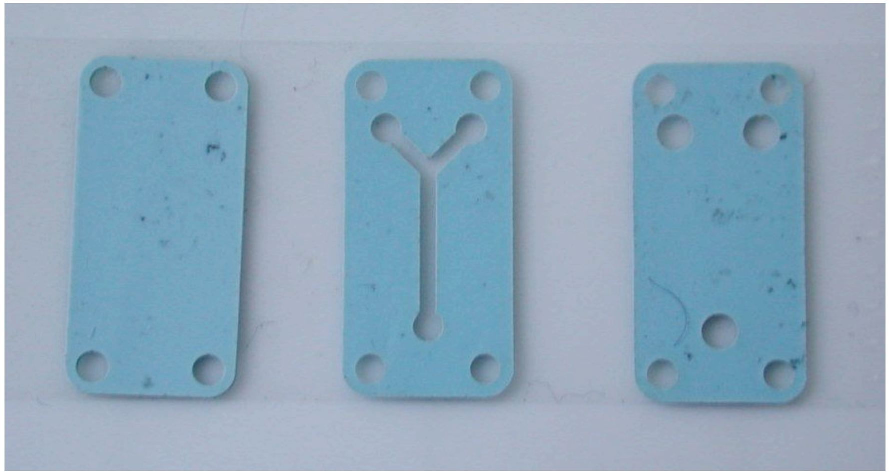
- Temperature measurement
- Reactant flow measurement
- Temperature control
- Calorimetric chamber

# Outline

- **Introduction**
- **Flow meter**
- **Microreactor**
- **Preliminary characterisation**

# Features of microreactors

- Very strong thermal coupling
- Safe study of very exothermic reactions
- Efficient mixing by diffusion (small channels)
- Control of residence time
- Equivalent to plug flow (usually)



# LTCC technology

- **L**ow-**T**emperature **C**ofired **C**eramic
- Originally for electronics
  - Radio frequency (RF): Bluetooth modules
  - Car electronics: engine control, ABS, etc.
- High reliability
- Hermeticity
- Thermal (>600°C) & chemical stability

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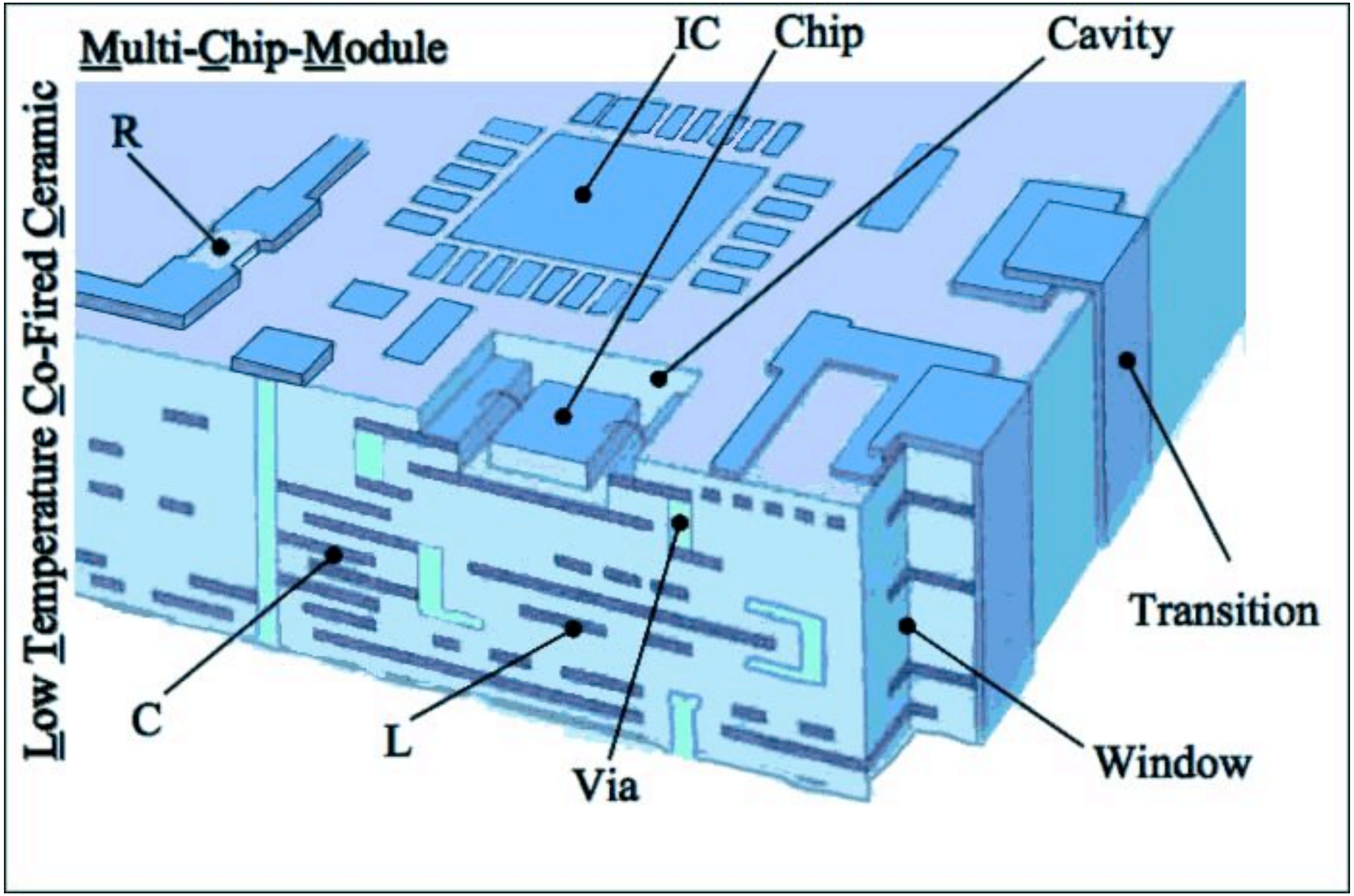
# LTCC electronics modules



# What is LTCC?

- Calcium aluminosilicate + Mg, Na, …
- Obtained by firing tapes of glass + filler
- Cofired with itself & thick-film materials

| | **COMPONENTS** | | |
|---|---|---|---|
| | **SUBSTRATE** | **PASSIVES** | |
| **Components** | **Tape** | **Conductor** | **Resistor** |
| ***Function*** | Dielectric layer | Thick-film paste | Thick-film paste |
| ***Functional group*** | Dielectric powder | Precious metal, fine size powder | Conductive oxide, fine size powder |
| ***Glass*** | ✍Lowers $T_{firing}$,<br>✍increases dielectric strength and density | ✍Lowers $T_{firing}$,<br>✍increases adhesion to substrate and density | ✍Lowers $T_{firing}$,<br>✍increases density<br>✍surrounds conductive powder |
| ***Organics*** | Binder, solvent, dispersant for appropriate rheology | | |

# LTCC physical properties

- Relatively low thermal conductivity
- Can be enhanced by using Ag thick films

| | LTCC* (DP951) | $Al_2O_3$ 96% | $Al_2O_3^+$ pure | BeO 99.5% | AlN 98% | $ZrO_2$ |
|---|---|---|---|---|---|---|
| **MECHANICAL CHARACTERISTICS** | | | | | | |
| **Flexural Strength (MPa)** | 320 | 274 | 300-400 | 241 | 340 | 980 |
| **Young's Modulus (GPa)** | 120 | 314 | 400 | 343 | 340 | 206 |
| **Density** | 3.1 | 3.8 | - | 2.8 | 3.3 | 6 |
| **THERMAL CHARACTERISTICS** | | | | | | |
| **Thermal expansioncoefficient ($10^{-6}$ /°C)** | 5.8 | 7.1 | 8.1 | 7.5 | 4.6 | 10.5 |
| **Thermal Conductivity (W/mK) and (25-300)°C** | 3 | 20.9 | - | 251 | 180 | 3.8 |
| **ELECTRICAL CHARACTERISTICS** | | | | | | |
| **Rel. dielectric constant (@1MHz)** | 7.8 @10MHz | 9.6 | - | 6.5 | 8.6 | 8.5 |
| **Dissipation factor ($x10^{-4}$)** | 0.15% @10MHz | 3 | - | 2 | 5 | - |

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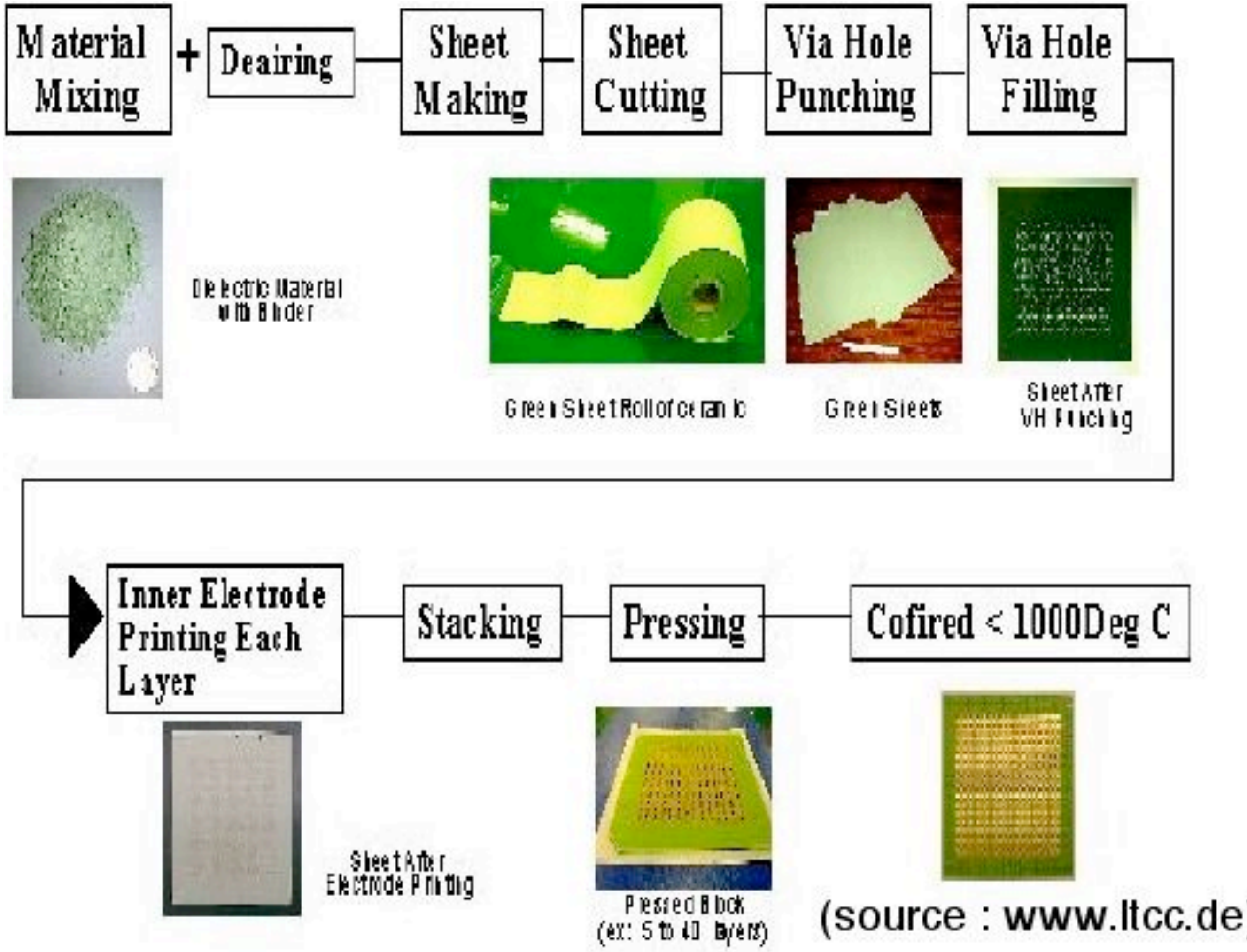
# LTCC process flow




(source : www.ltcc.de)

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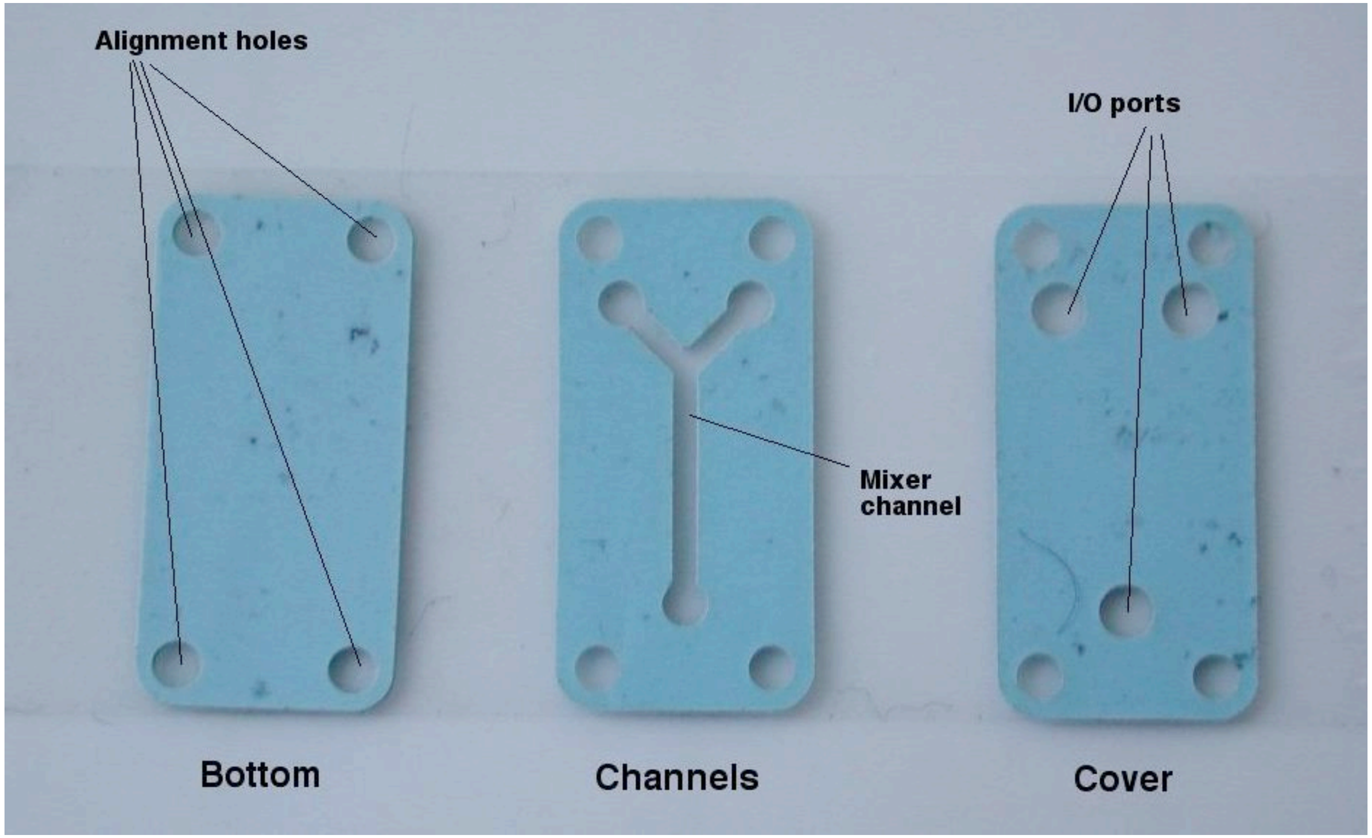
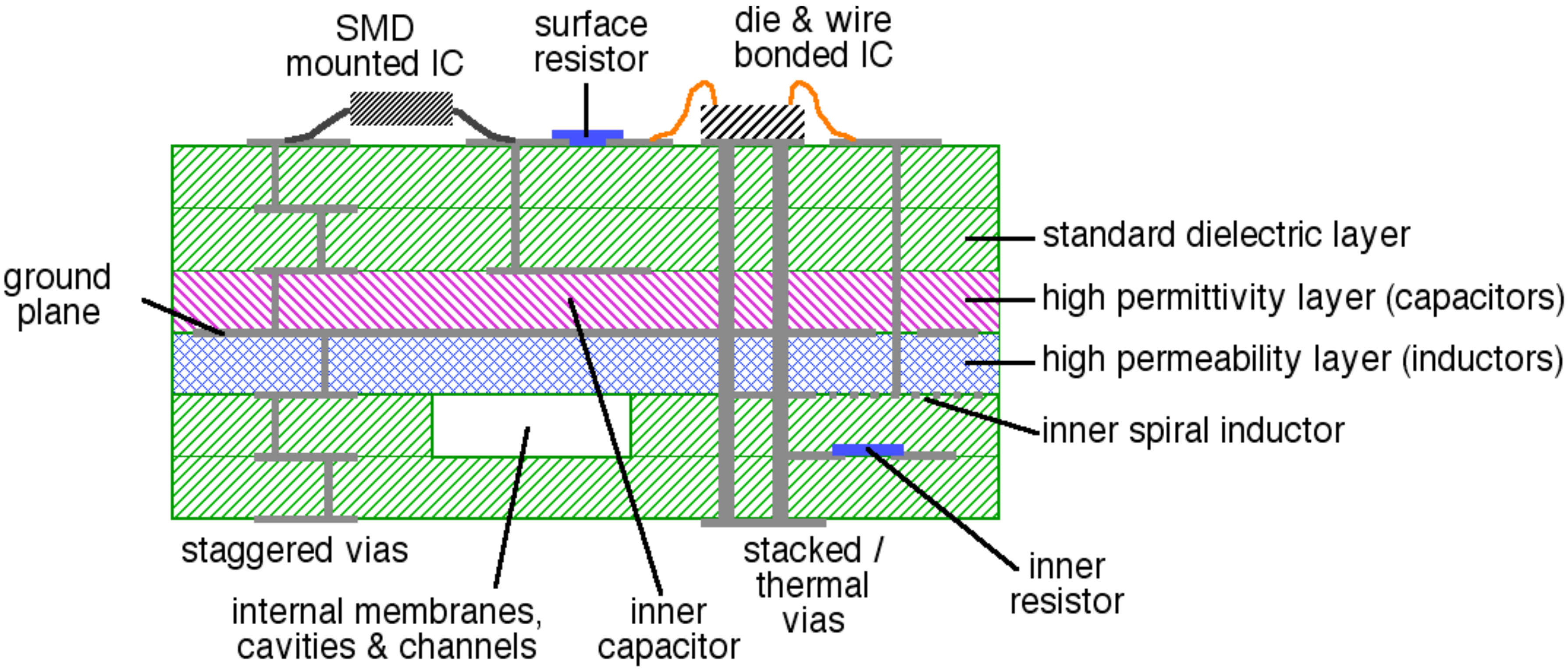
# Why LTCC (1) ?




- Ease of structuration

# Why LTCC (2) ?




- Integration of many functions

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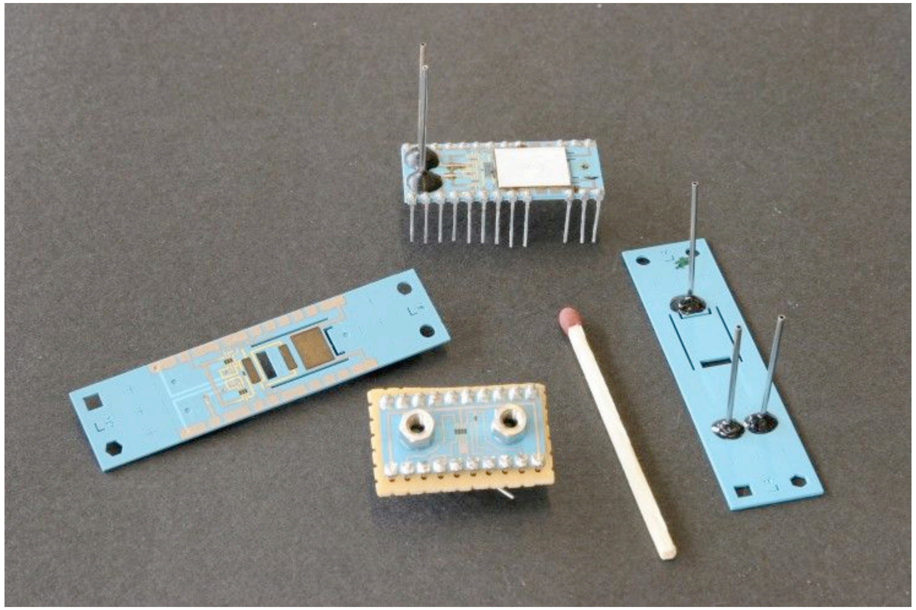
# Why LTCC (3) ?

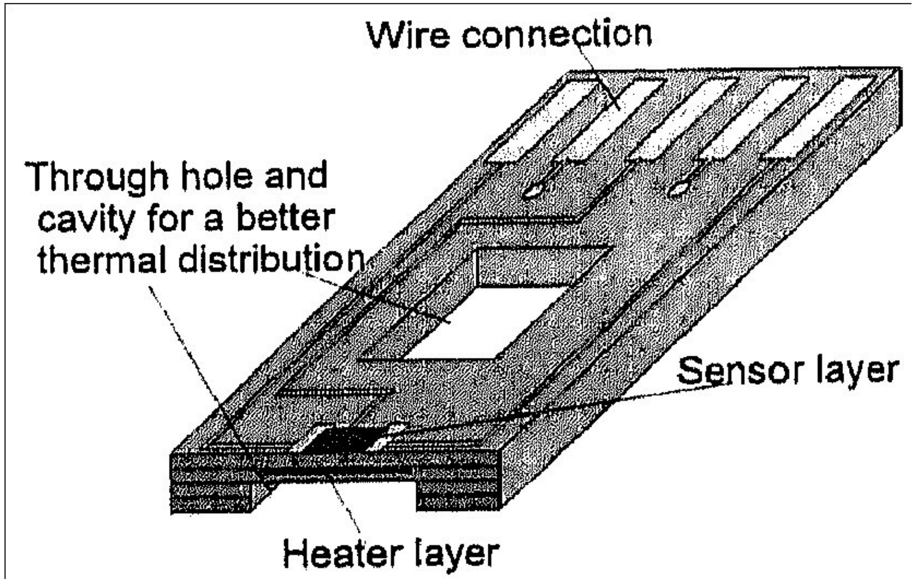


- Microreactor & flow sensor

# Why LTCC (3) ?

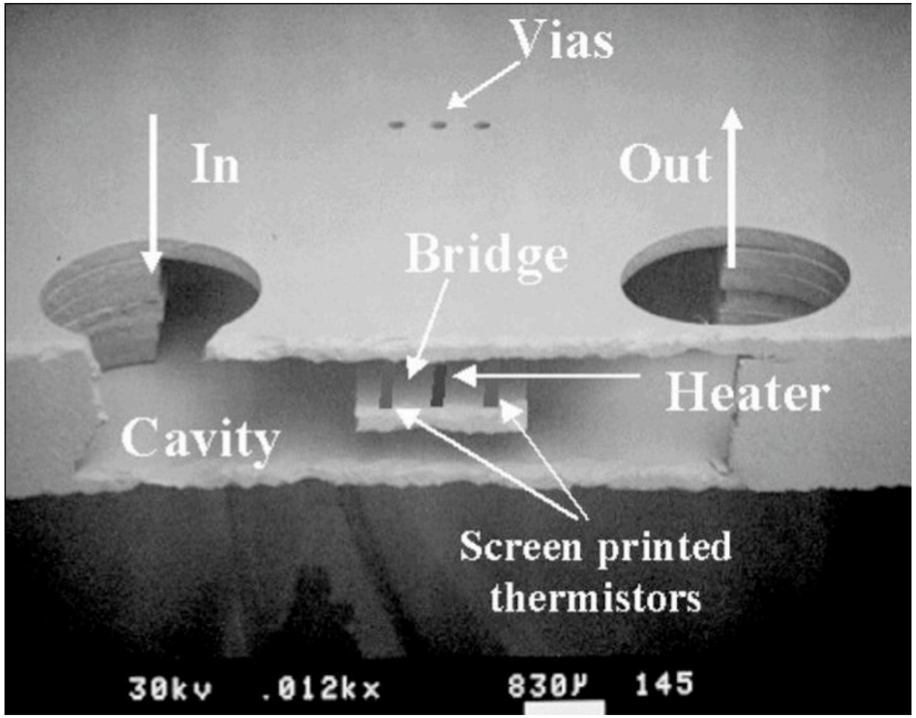
- Microreactor & flow sensor
- Inclination sensor

# Why LTCC (3) ?




- Microreactor & flow sensor
- Inclination sensor
- Gas sensor (Golonka et al., 1998)

# Why LTCC (3) ?

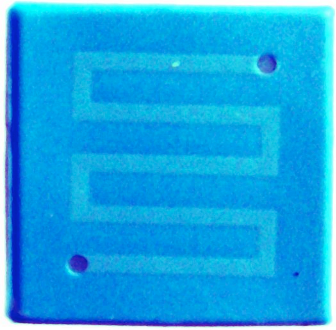


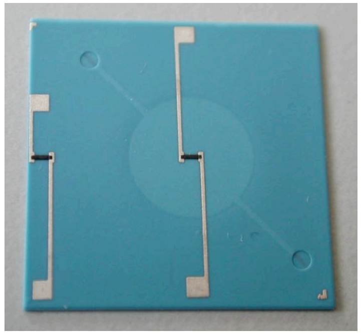

- Microreactor & flow sensor
- Inclination sensor
- Gas sensor (Golonka et al., 1998)
- Flow sensor (Gongora et al., 2001)

# LTCC fluidics

## Graphite fugitive phase

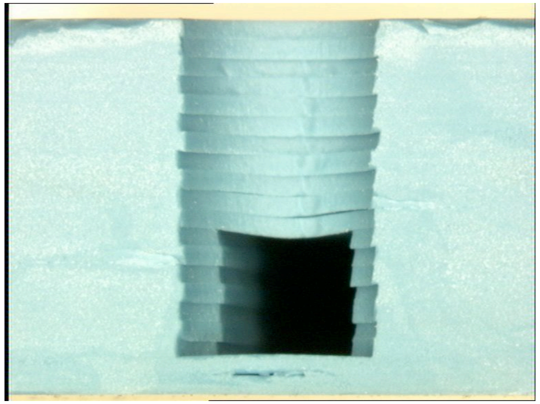
- Small height (≈ 10 µm)
- For gases essentially
- Structures defined by printing



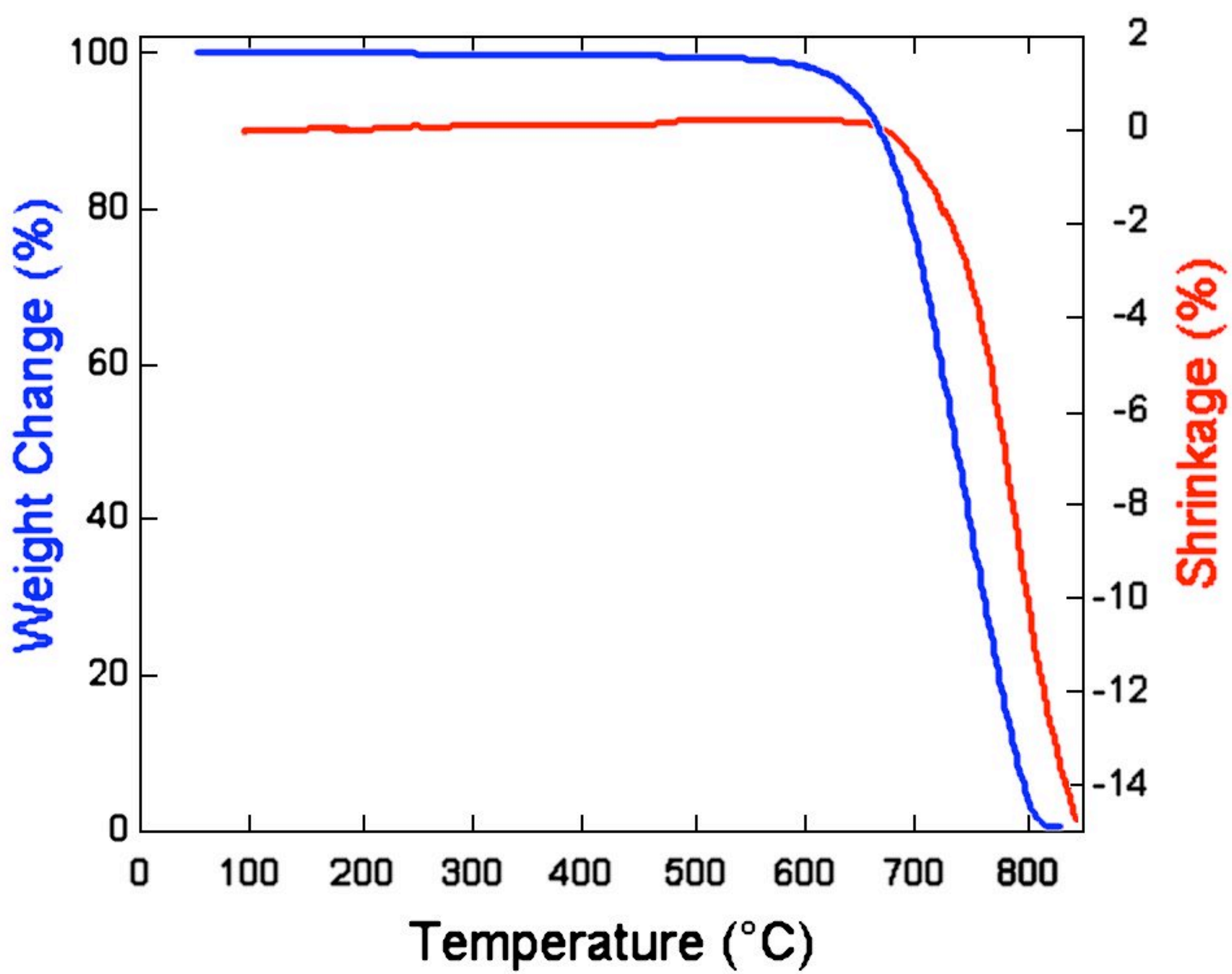


## Laser cutting

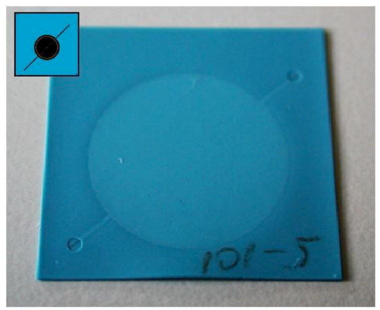
- Larger height (≈ 100 µm)
- Structures defined by cutting
- Retained solution for this project



# Cavities by graphite fugitive phase




- Graphite burns out **shortly before** LTCC densifies.
- Spacing can be controlled by **heating rate**.

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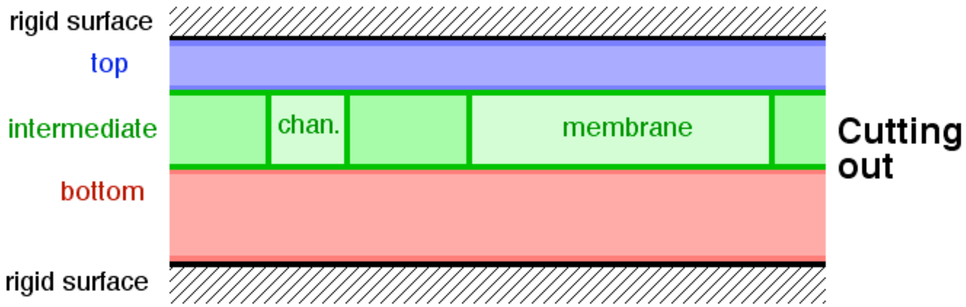
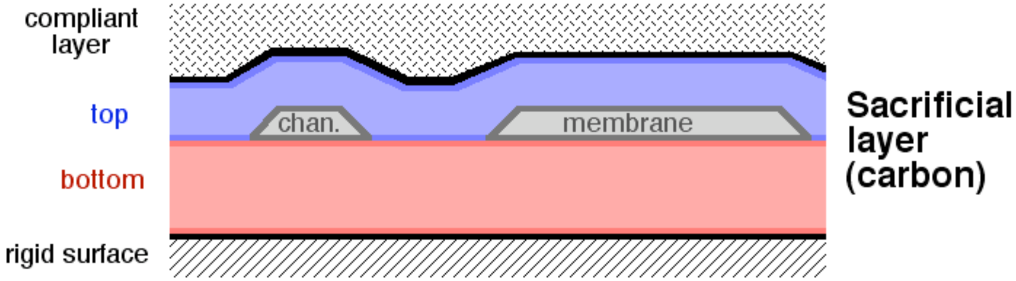
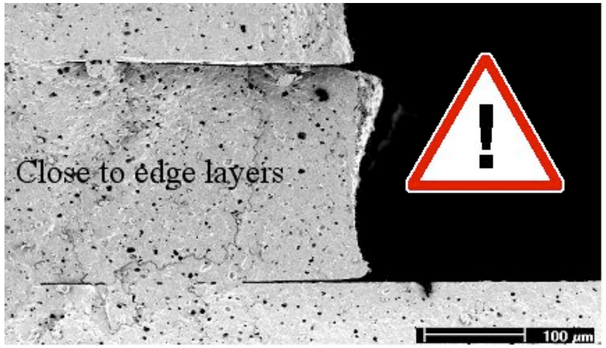
# Comparison of methods - process

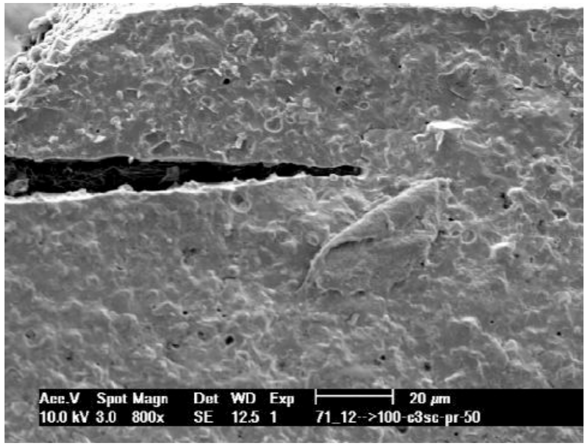
## Processing




## Properties

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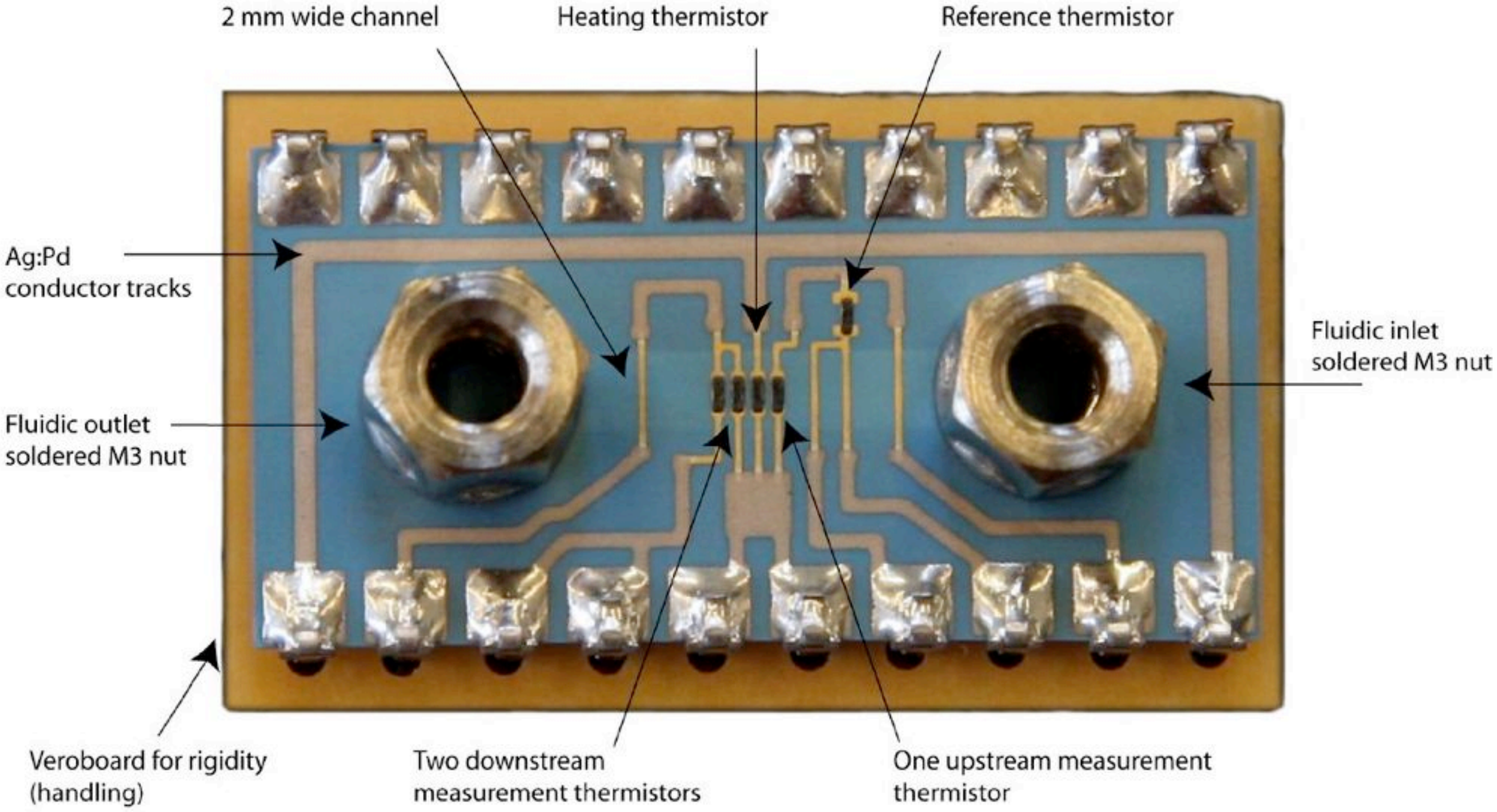
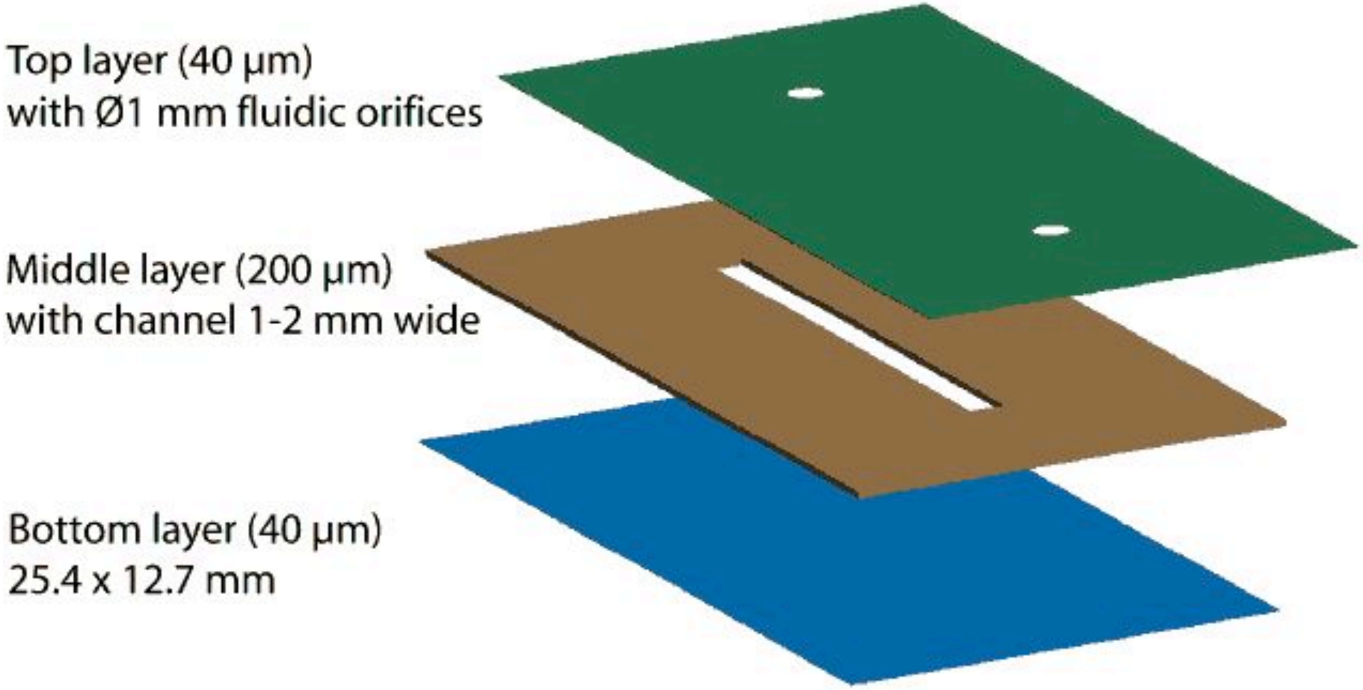
# Flowmeter

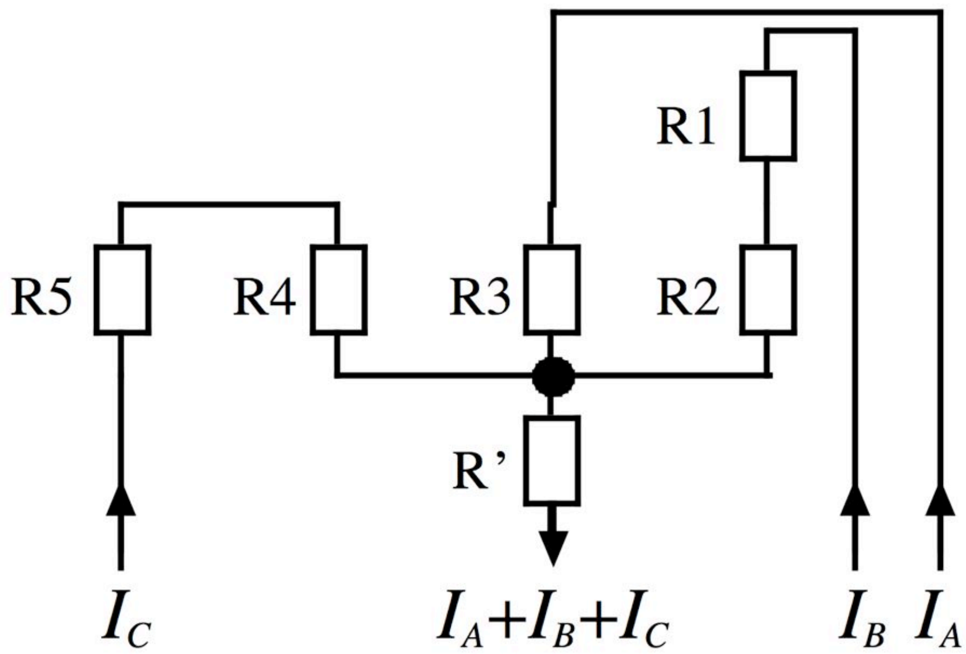

2 mm wide channel
Heating thermistor
Reference thermistor
Ag:Pd conductor tracks
Fluidic inlet soldered M3 nut
Fluidic outlet soldered M3 nut
Veroboard for rigidity (handling)
Two downstream measurement thermistors
One upstream measurement thermistor

# Flowmeter - structure



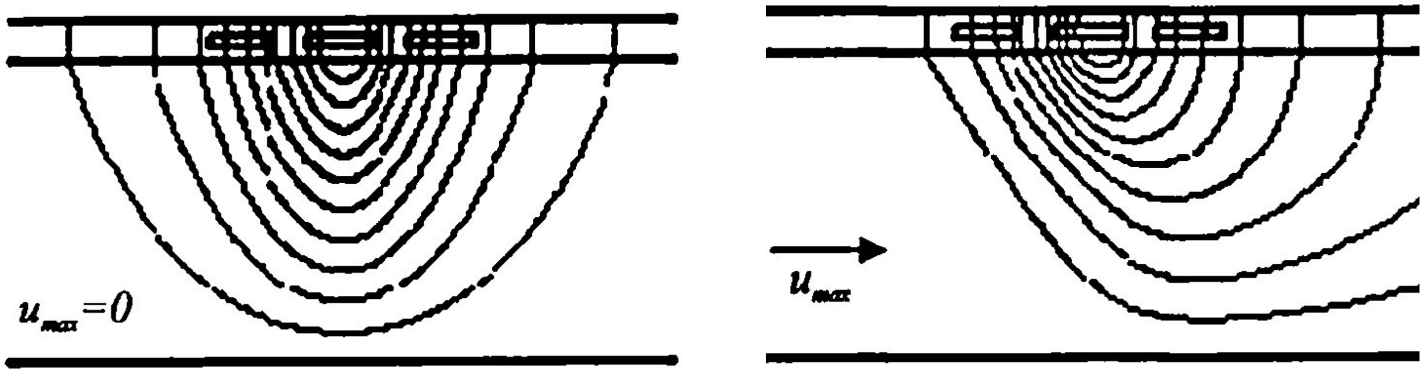

- Simplest structure
- Good start for LTCC processing

# Flowmeter - electrical




- All resistors are thick-film PTC thermistors
- Here, resistors are *post*-fired (process comptability)

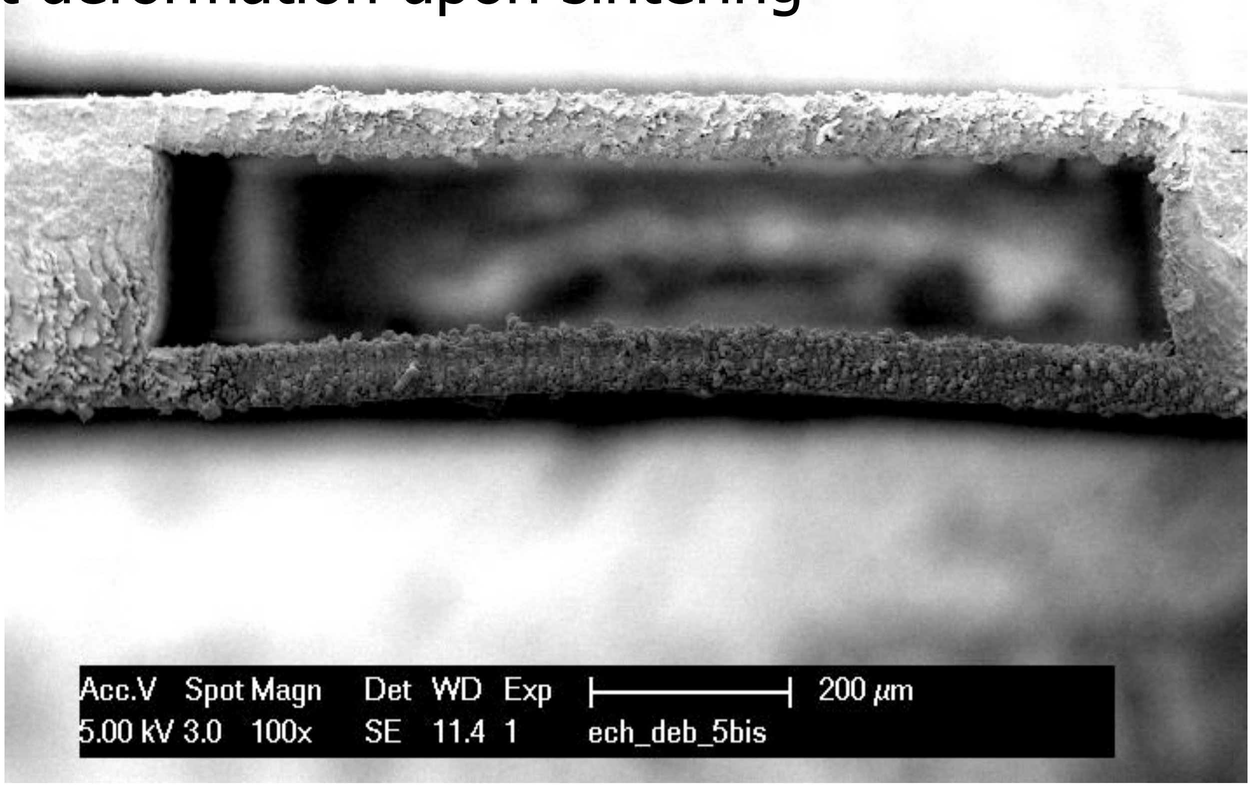
# Flowmeter - principle




- Flow = 0: symmetrical temperature profile
- Flow ≠ 0: downstream resistor hotter than upstream
- Very large flow: use heat loss

# Flowmeter - channel

- Good integrity
- Slight deformation upon sintering

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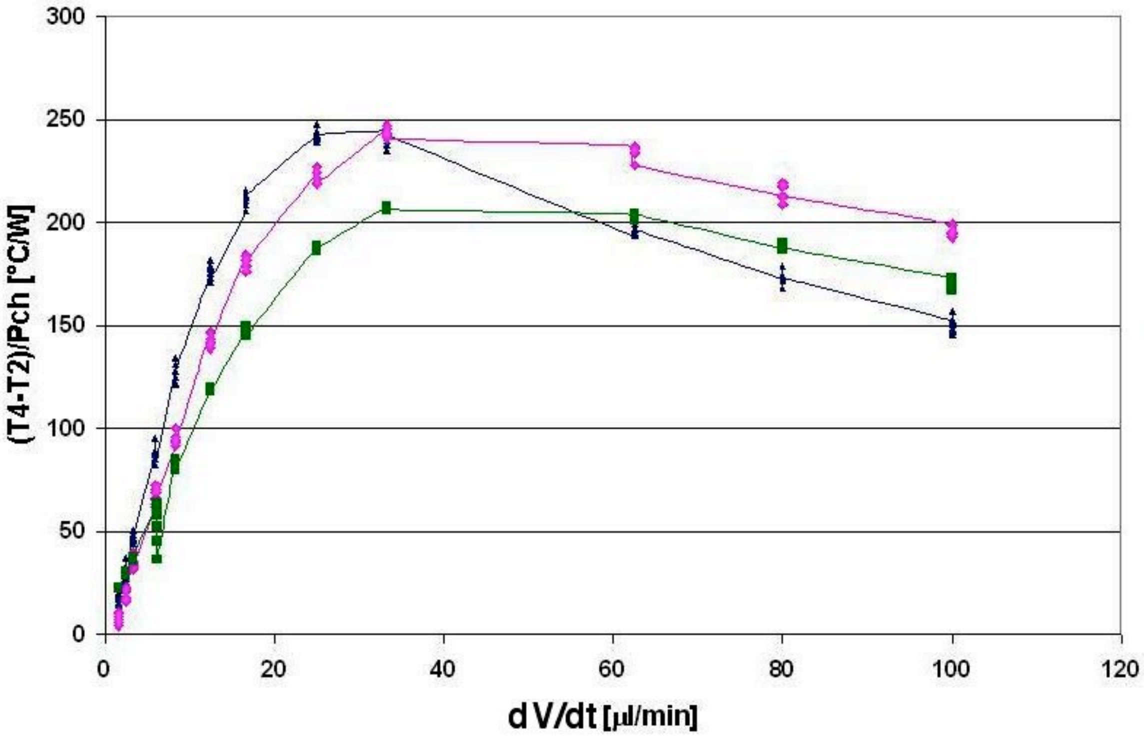
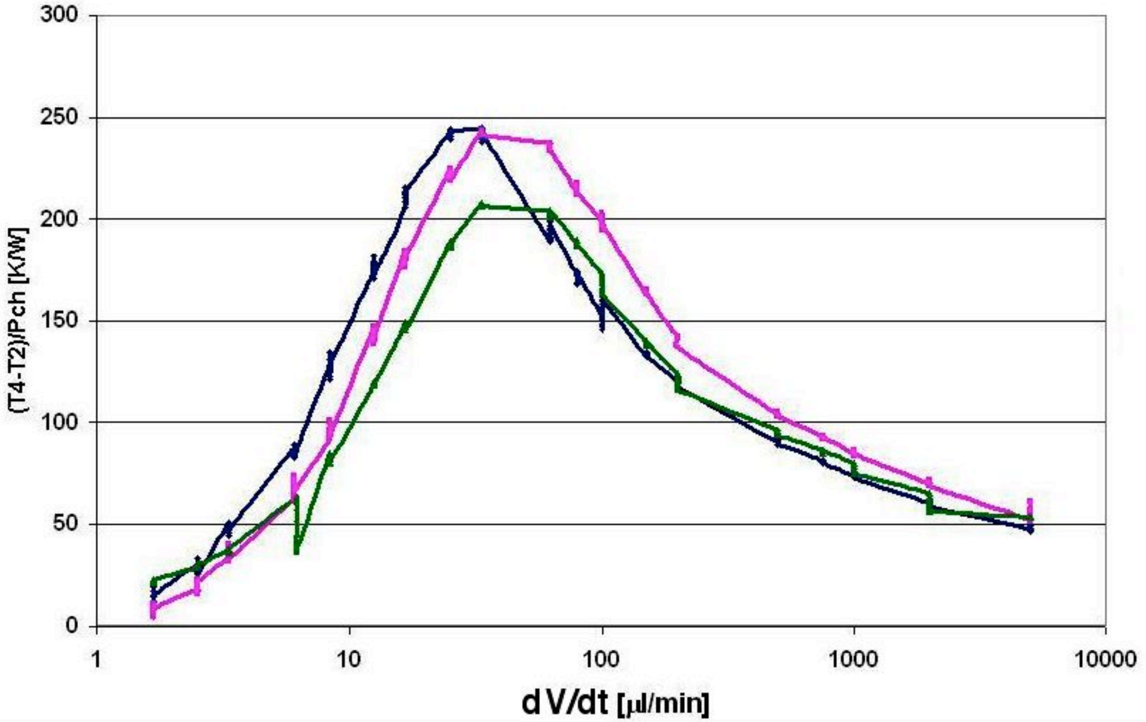
# Flowmeter - results @ low flow




- **Low flows**: increase in dissymetry with flow
- **Large flows**: decrease of signal due to heat loss

# Flowmeter - results @ high flow




- **Low flows**: increase in dissymetry with flow
- **Large flows**: decrease of signal due to heat loss

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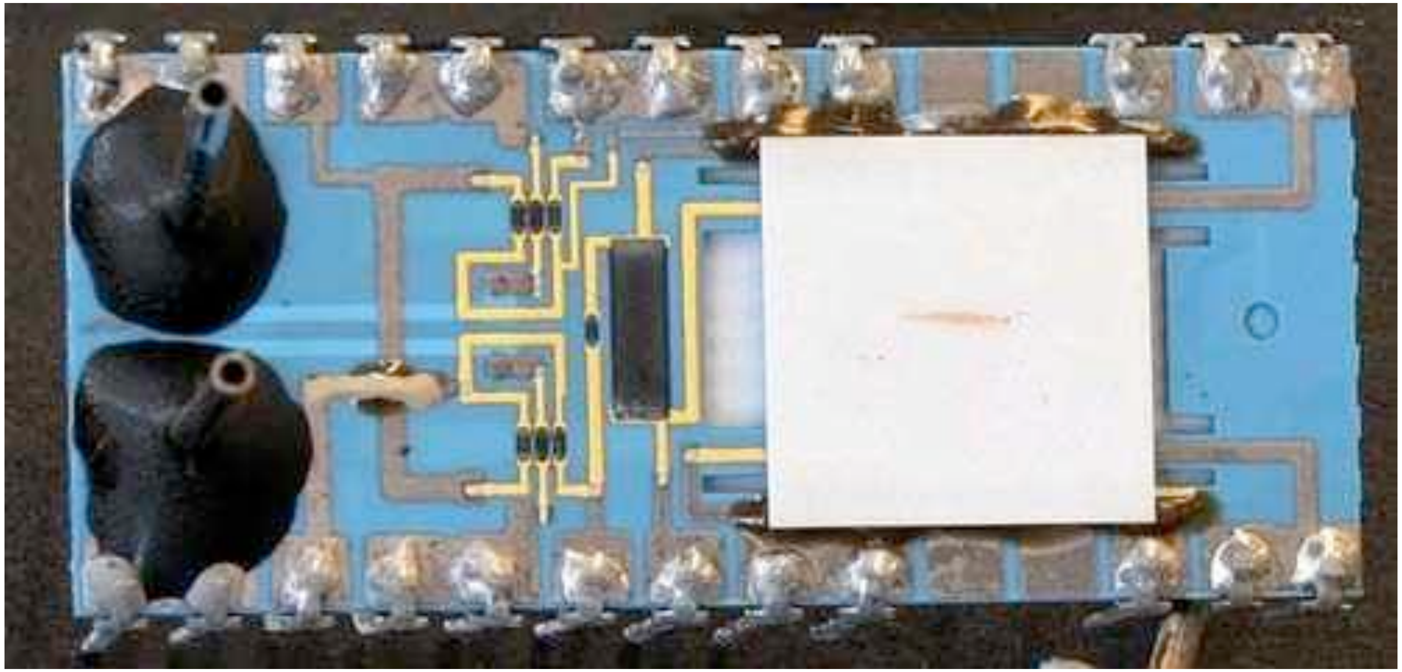
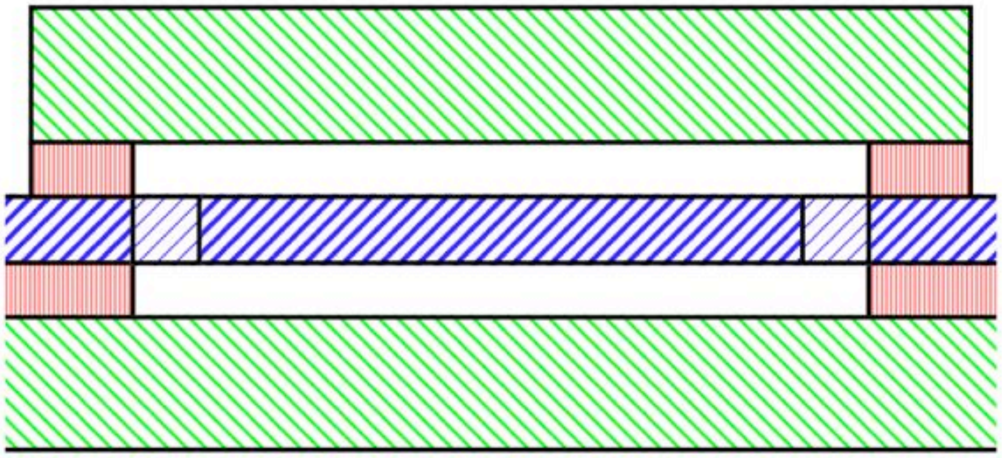
# Microreactor / calorimeter



- 2 flowmeters (similar design), one for each reactant
- Control of temperature
- Measurement of heat of reaction

# Microreactor - design (1)




- Isolated & enclosed reaction zone
- Well-defined thermal resistance to enclosure
- Steady state heat power = $\Delta T / R_{th}$
- Calibration of $R_{th}$ by calibration heating resistor

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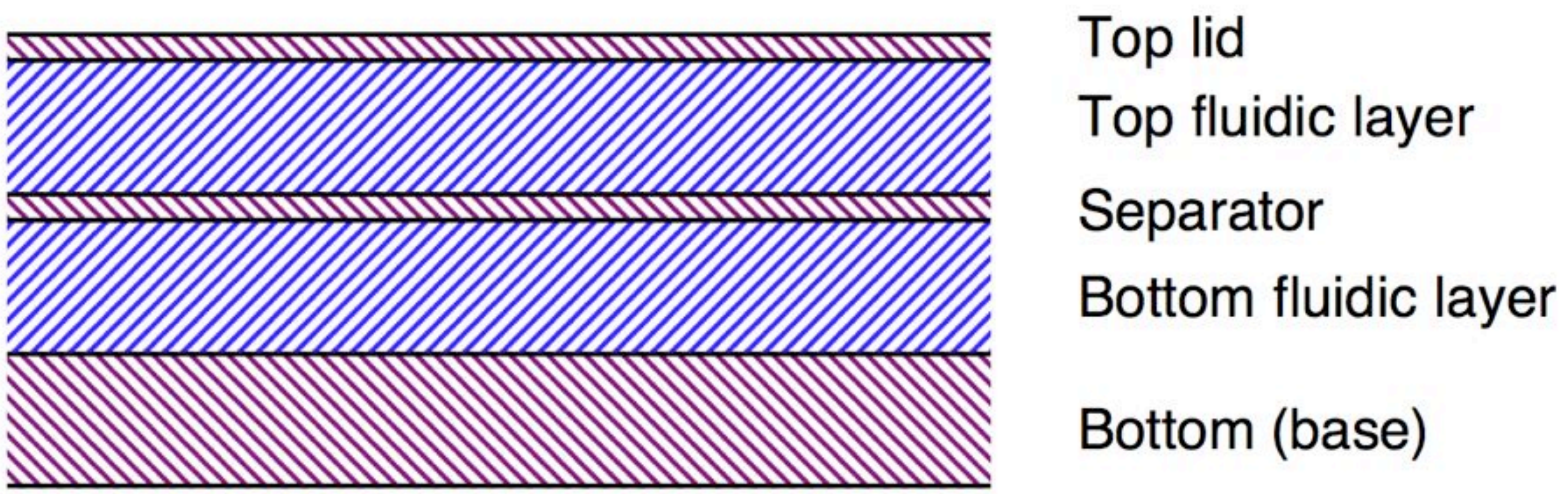
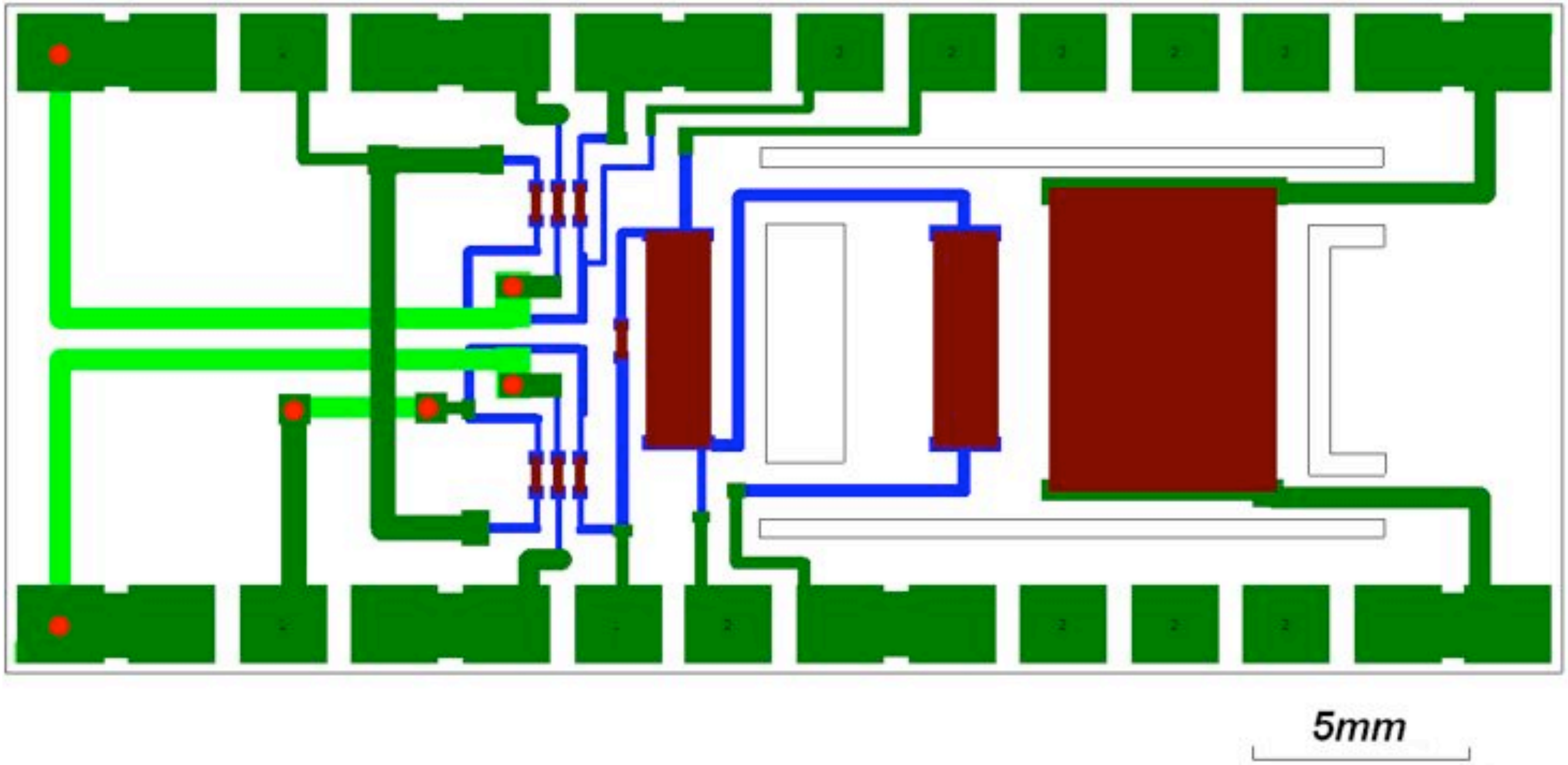
# Microreactor - design (2)




- Total 5 LTCC layers

# Microreactor - electrical circuit

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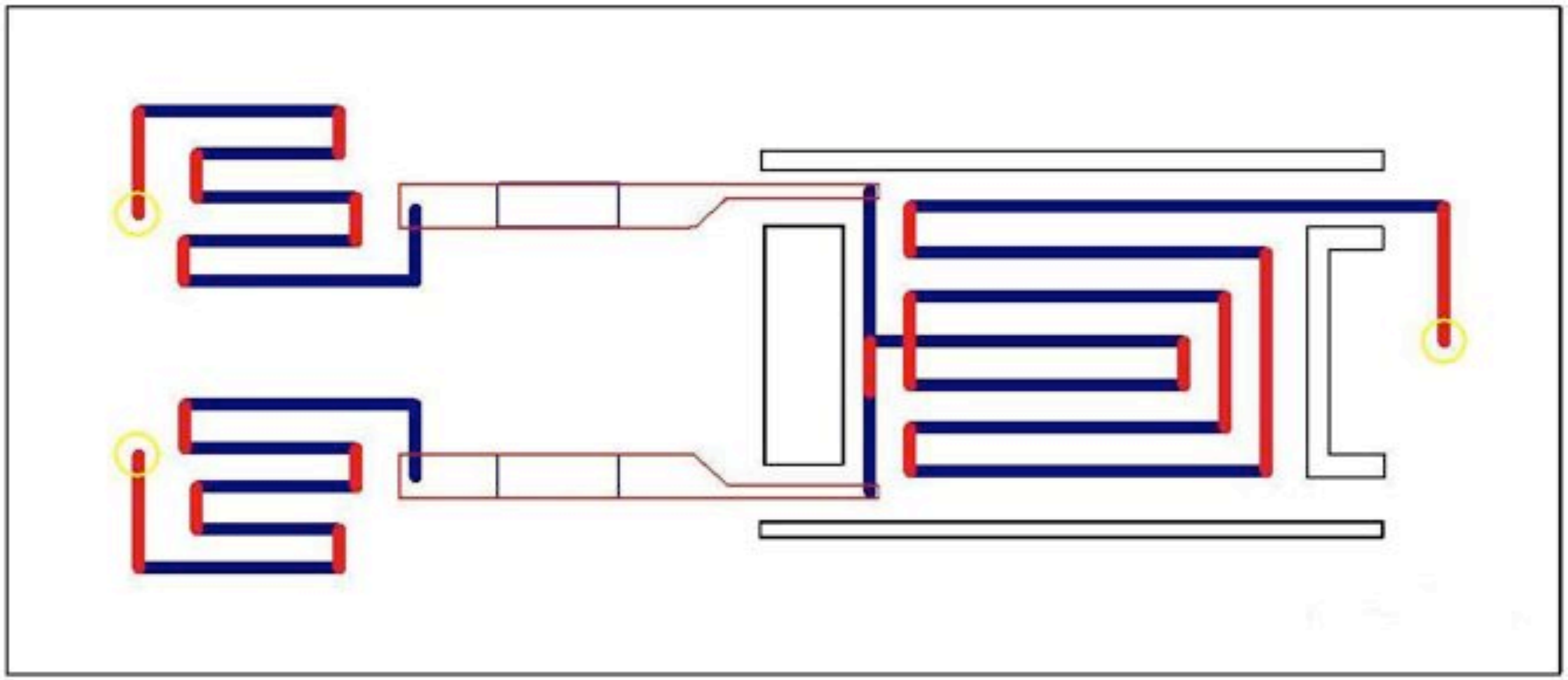
# Microreactor - fluidic circuit



Dimensions : 35.55*15.25mm

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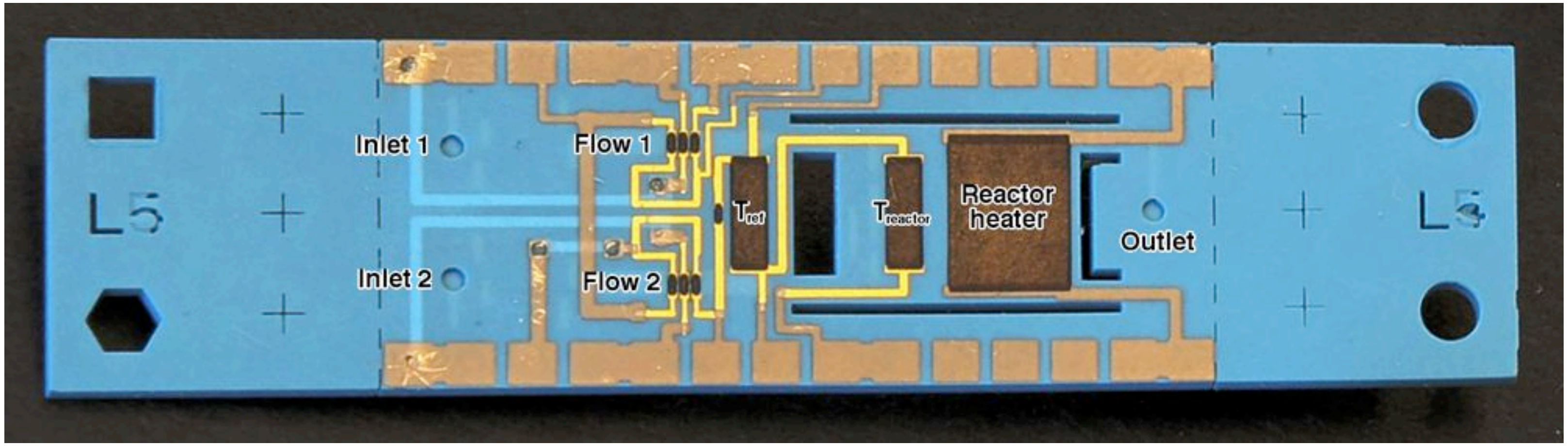
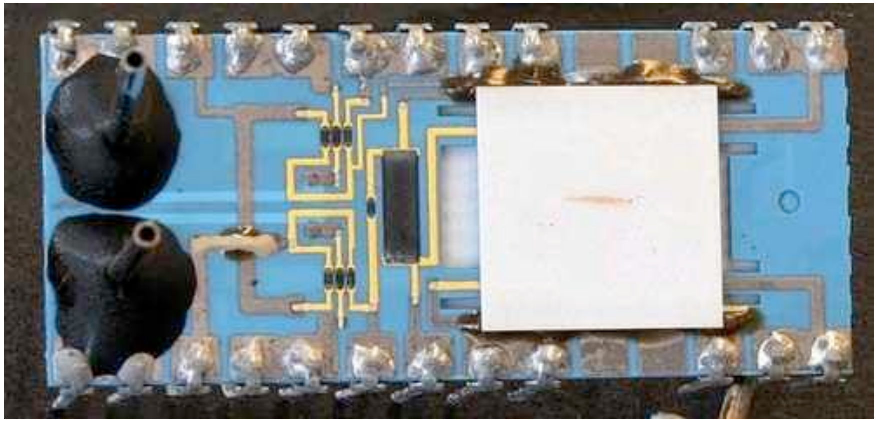
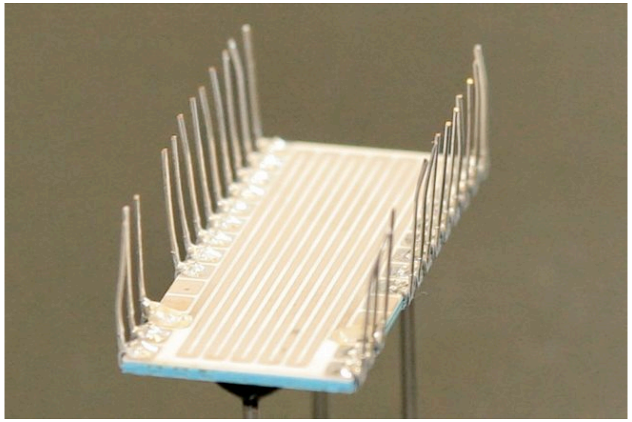
# Microreactor - LTCC (1)





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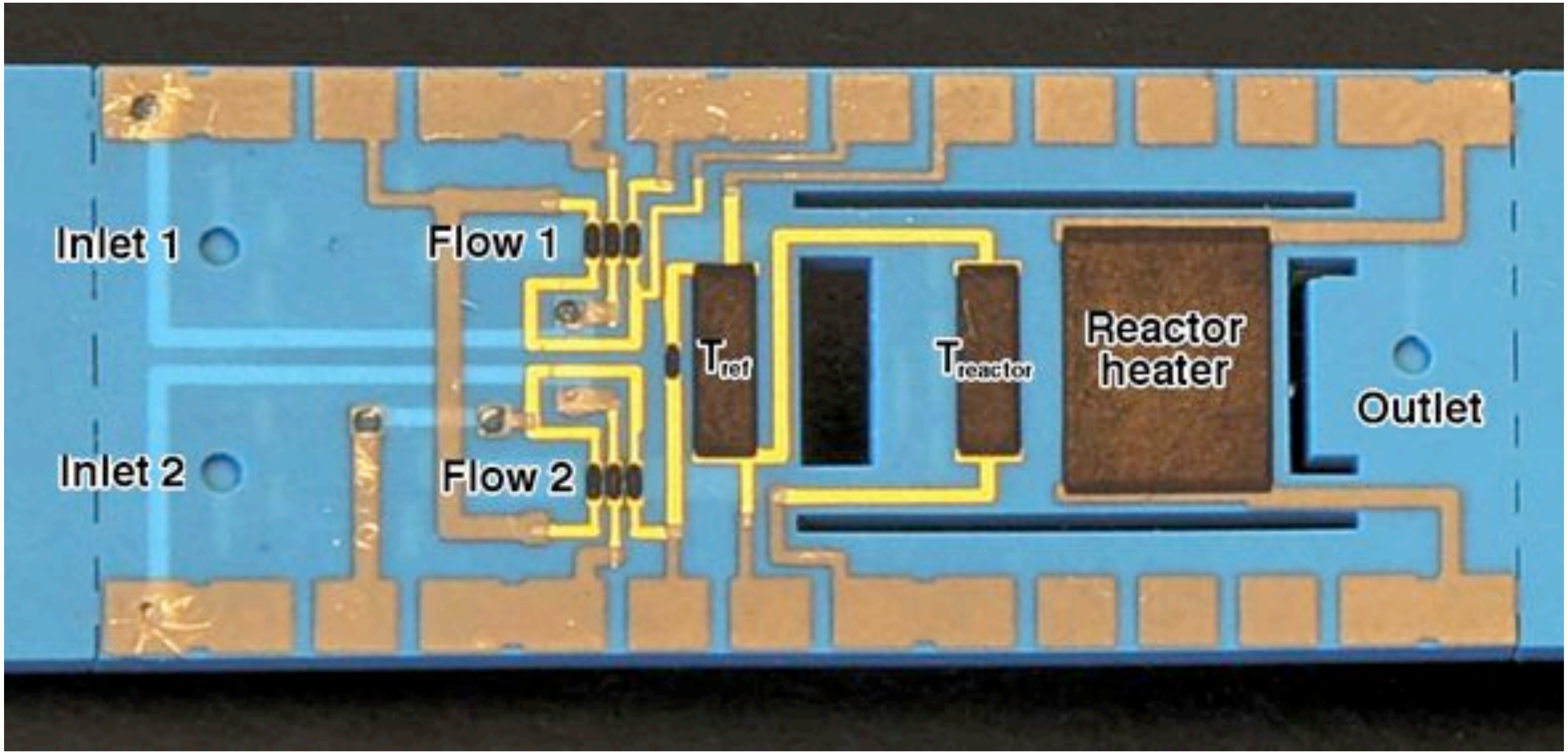
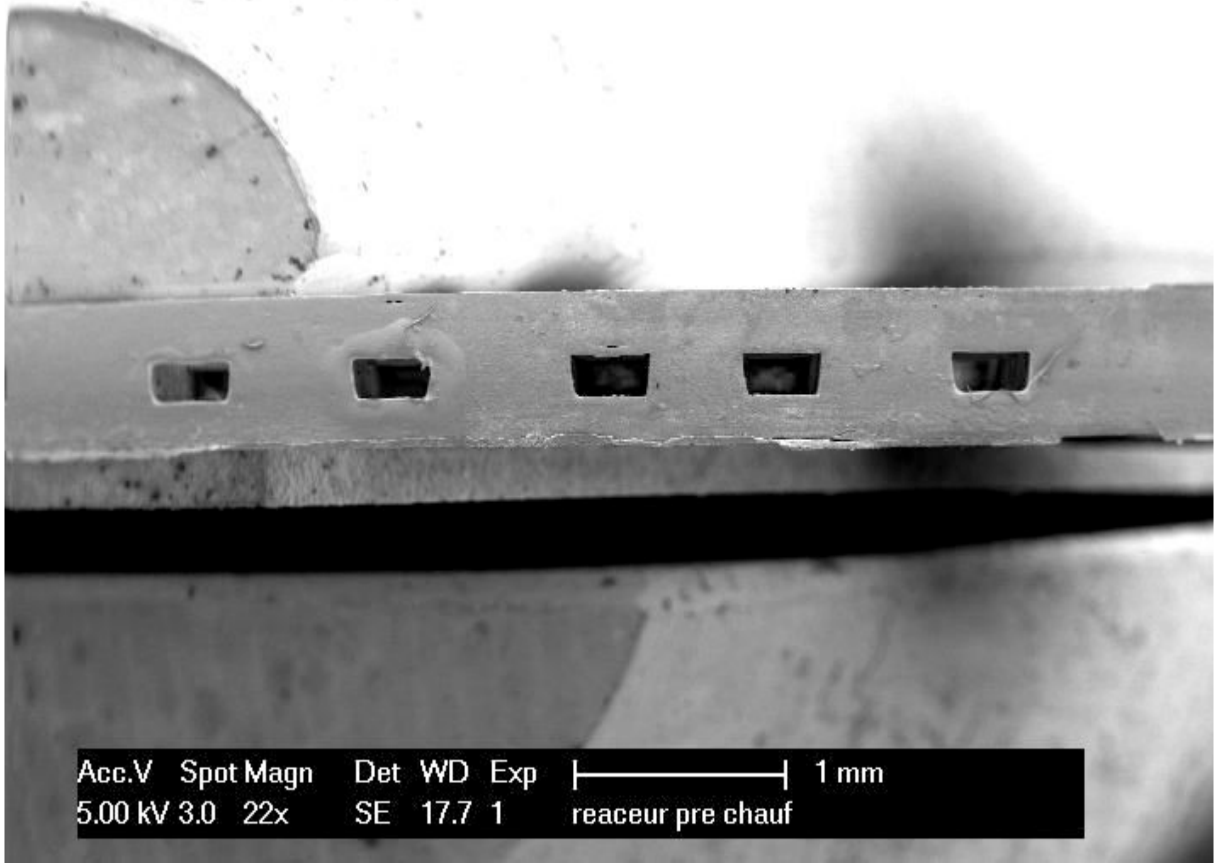
# Microreactor - LTCC (2)



# Microreactor - microscopy (1)

- Meanders in pre-heating zones

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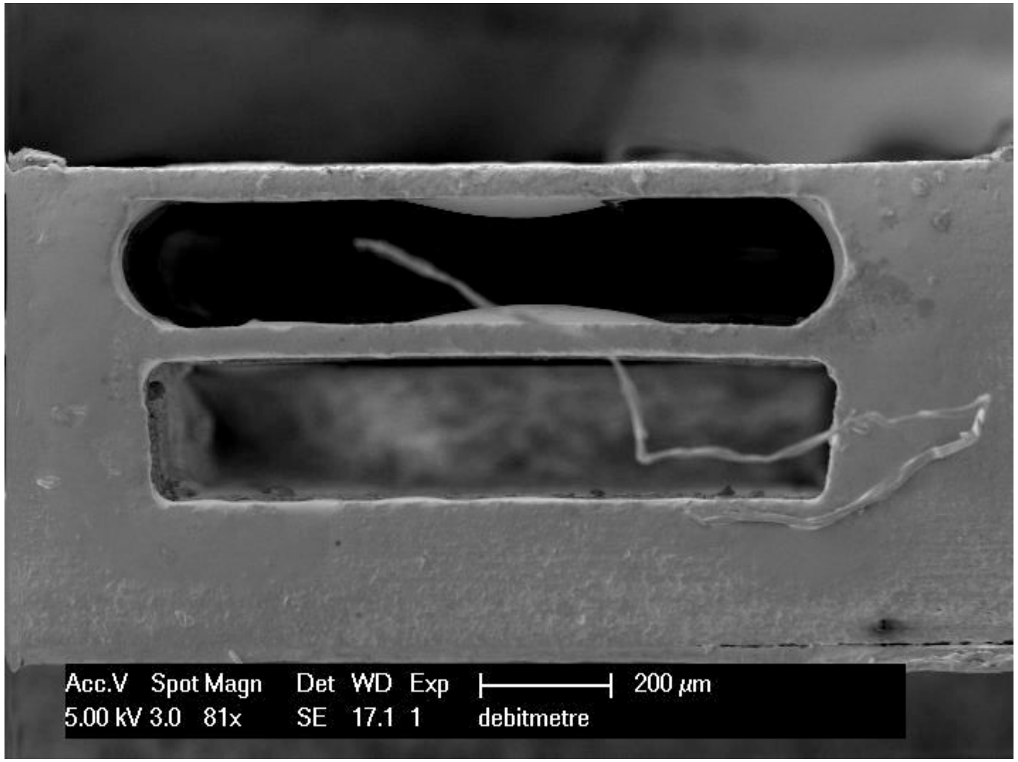
# Microreactor - microscopy (2)




- Top cavity: flowmeter channel
- Bottom cavity: thermal insulation

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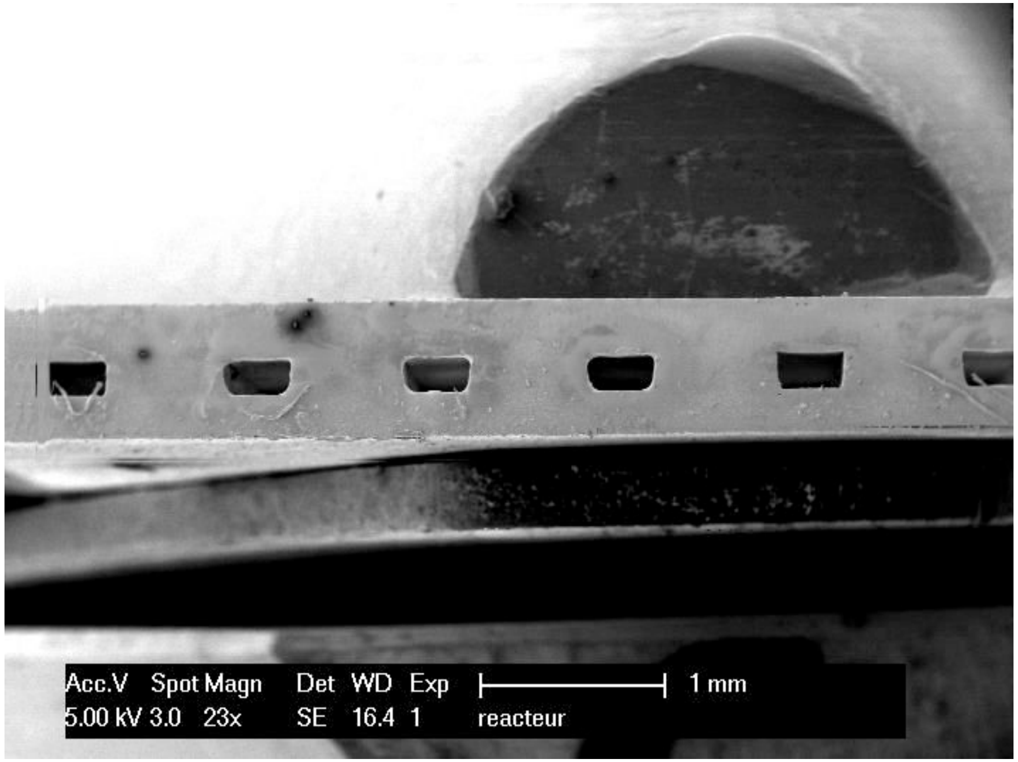
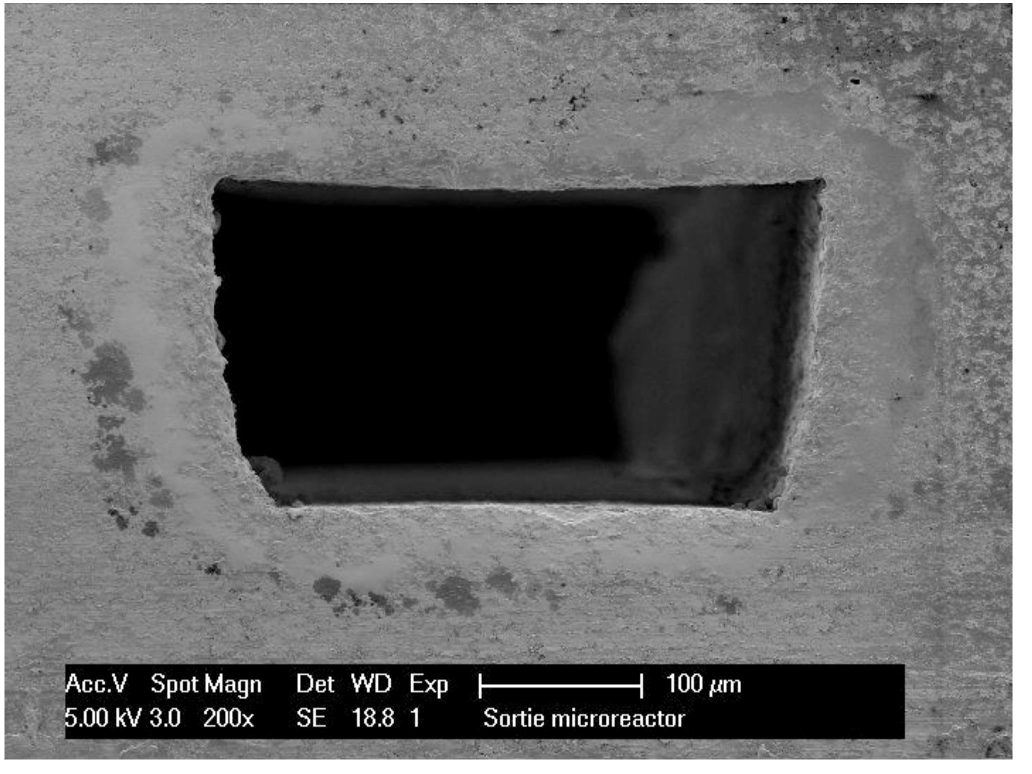
# Microreactor - microscopy (3)

- Meanders in reaction zone
- 2nd meander in other fluidics layer

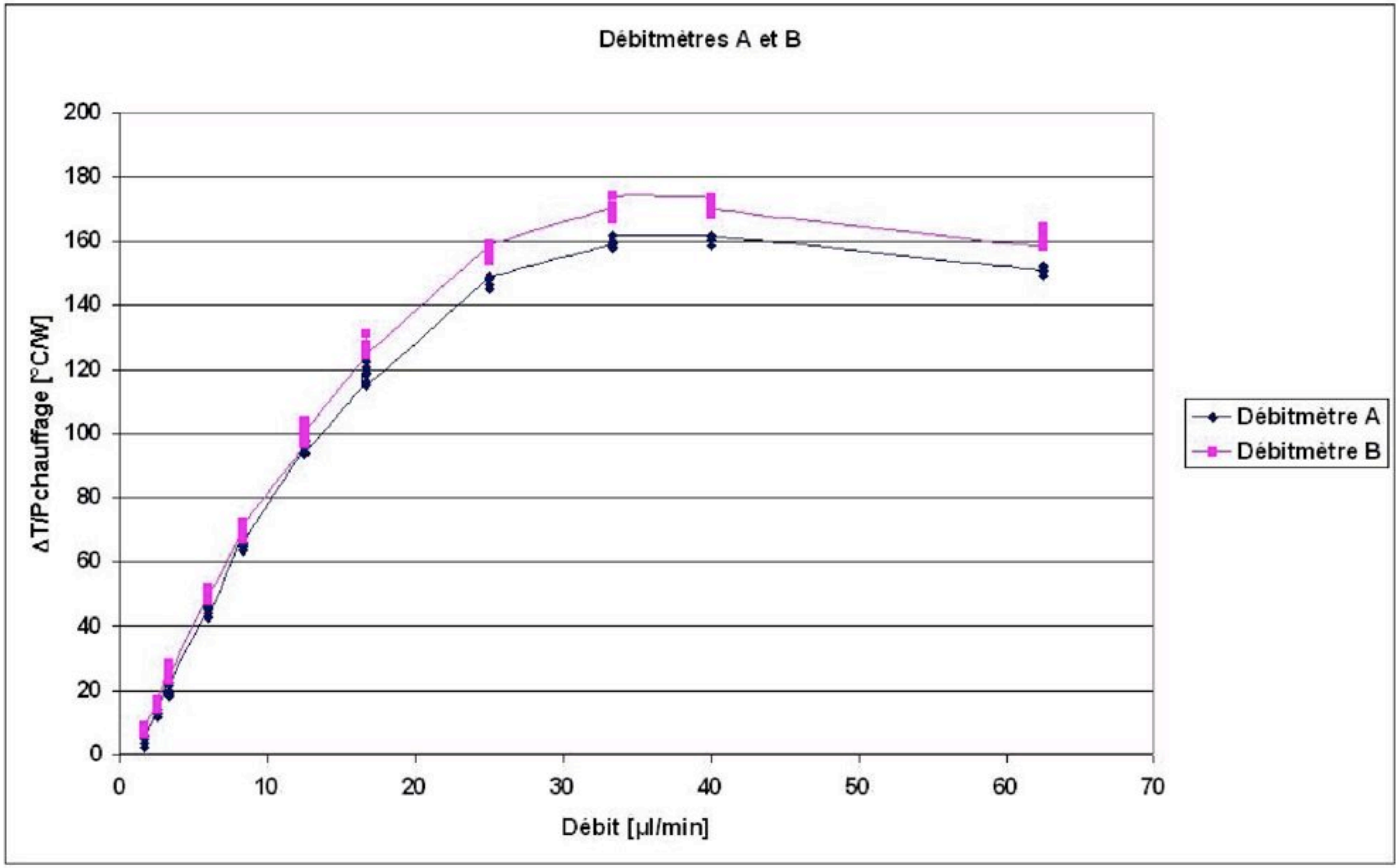


# Microreactor - microscopy (4)

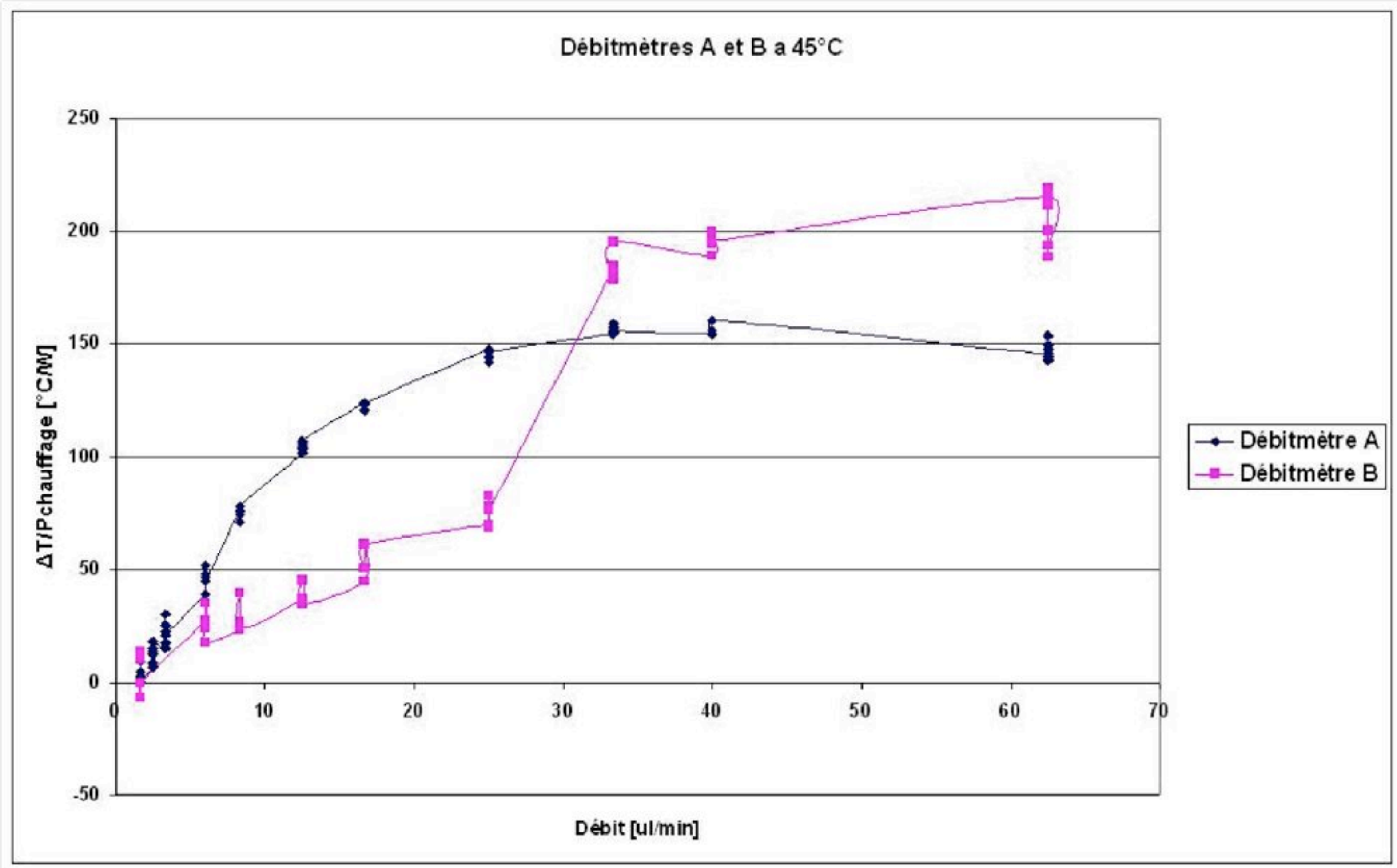
- Outlet channel + bridge



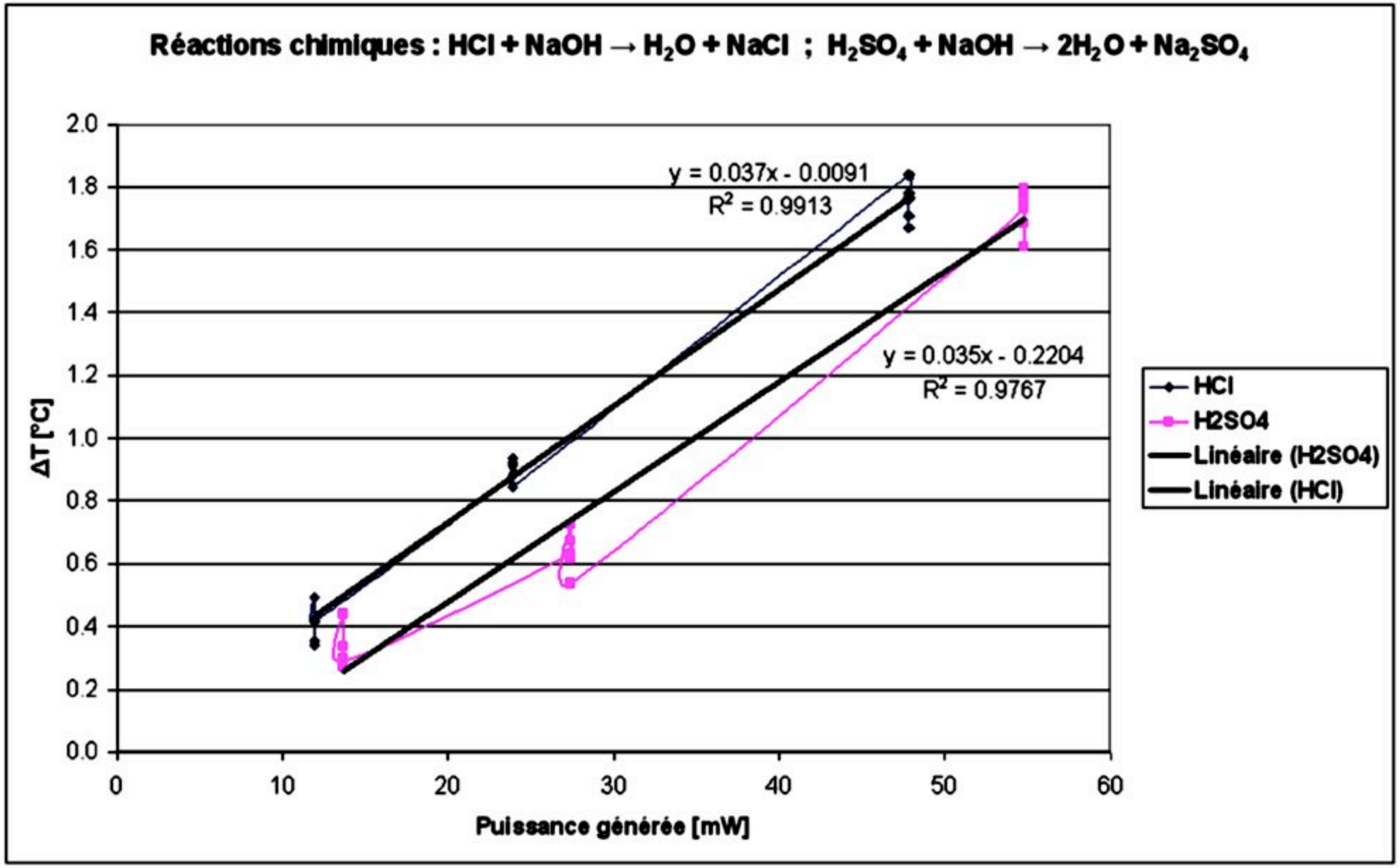
# Characterisation - flowmeters @ RT



# Characterisation - flowmeters @ 45°C



# Characterisation - acid-base reactions

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# Conclusions

- Simple integrated device
- Low manufacturing cost
- Good stability
- Very flexible technology
- Suitable for both liquids & gases
- Boundary conditions not yet optimal

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# Outlook

## Thermal design

- Use better heat spreaders: Ag, AlN
- Improve reactor boundary conditions
- Active preheat zones

## Electronics & software

- Better adjustments
- More precise measurements

# Acknowledgements


- Raphaël Willigens
- Yannick Fournier
- Hansu Birol
- Giancarlo Corradini
- Matthias Garcin


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# Merci / Danke / Grazie

THANK

YOU !