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Optimization of anodic oxidation and Cu-Cr oxide catalyst preparation on structured aluminum plates processed by electro discharge machining

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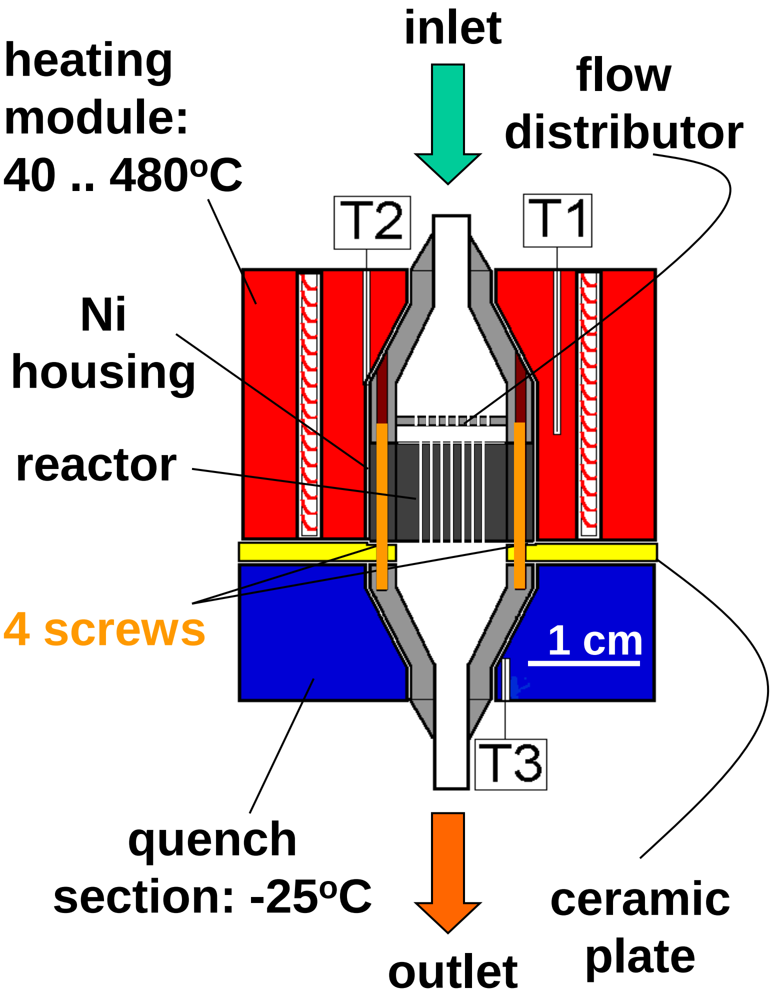
Introduction

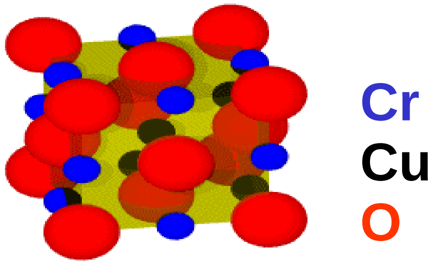


(E.V. Rebrov et al., Catal. Today 69 (2001) 183)

Microreactors: tools for both basic research and safe process development, opportunity to safely study the kinetics of catalytic total oxidation:

- small unit size
- channel diameter < 500 μm (large surface-to-volume ratio) => gas-phase reactions, including explosive ones, can be avoided
- highly exothermic reaction => efficient heat removal

- Spinel catalyst $CuCr_2O_4/\gamma\text{-}Al_2O_3$ high oxidation activity



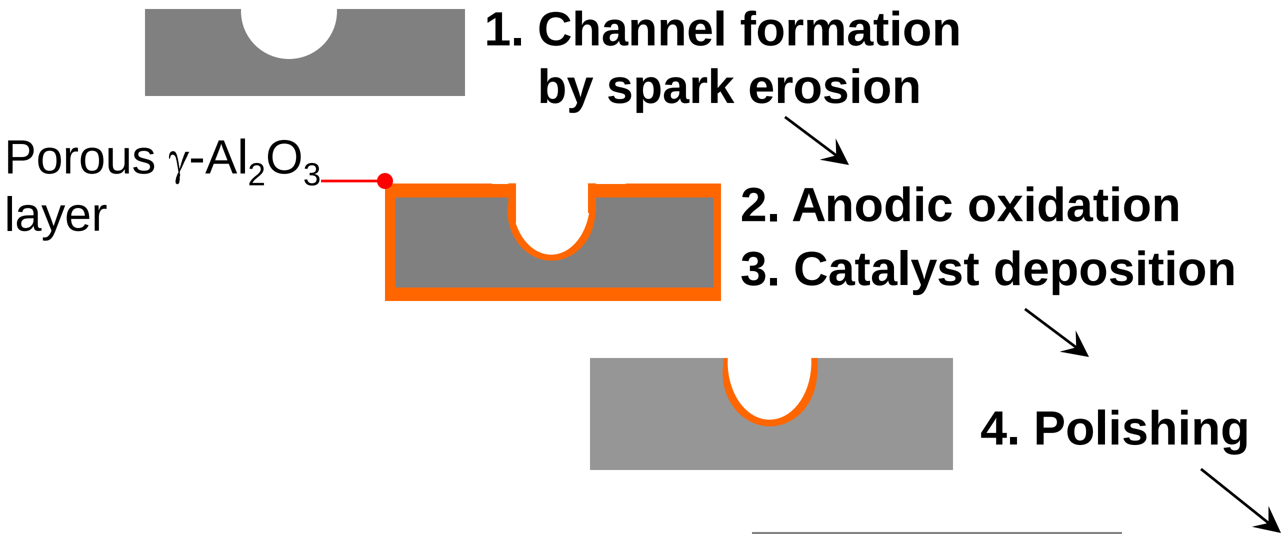
Outline

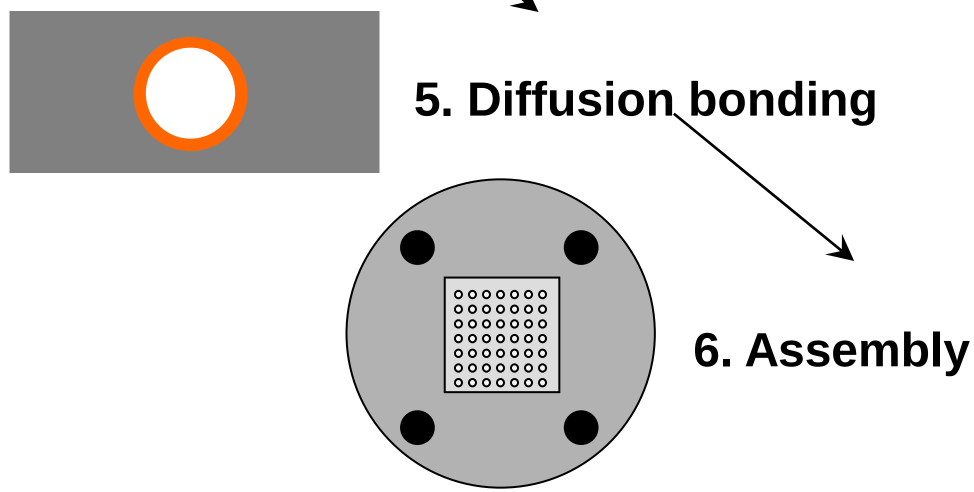
- Fabrication and characterization of microstructured plates

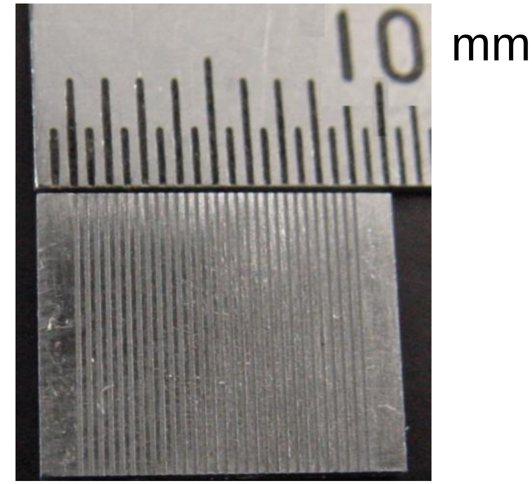
- Anodic oxidation of metal plates
  - Oxidation of flat aluminum plates
  - Adaptation of oxidation procedure with the AlMgSi1 alloy

- Development of preparation methods of catalytic coatings
  - Preparation of Cu-Cr oxide catalytic coatings on flat aluminum plates
  - Adaptation of catalysts synthesis procedure for microstructured plate

Microreactor fabrication







Microstructured Al plate

<u>Microreactor geometry</u>
<u>based on plug-flow model</u>:
channel internal diameter 400 μm,
catalyst/support layer thickness 25 μm,
76 half-plates (400 μm thick)/2 =
38 full-plates (800 μm thick),
45 channels per plate =>
assembled 26.6 mm wide, 40 mm long,
30.4 mm high, 1710 channels

Fabrication of microstructured plates

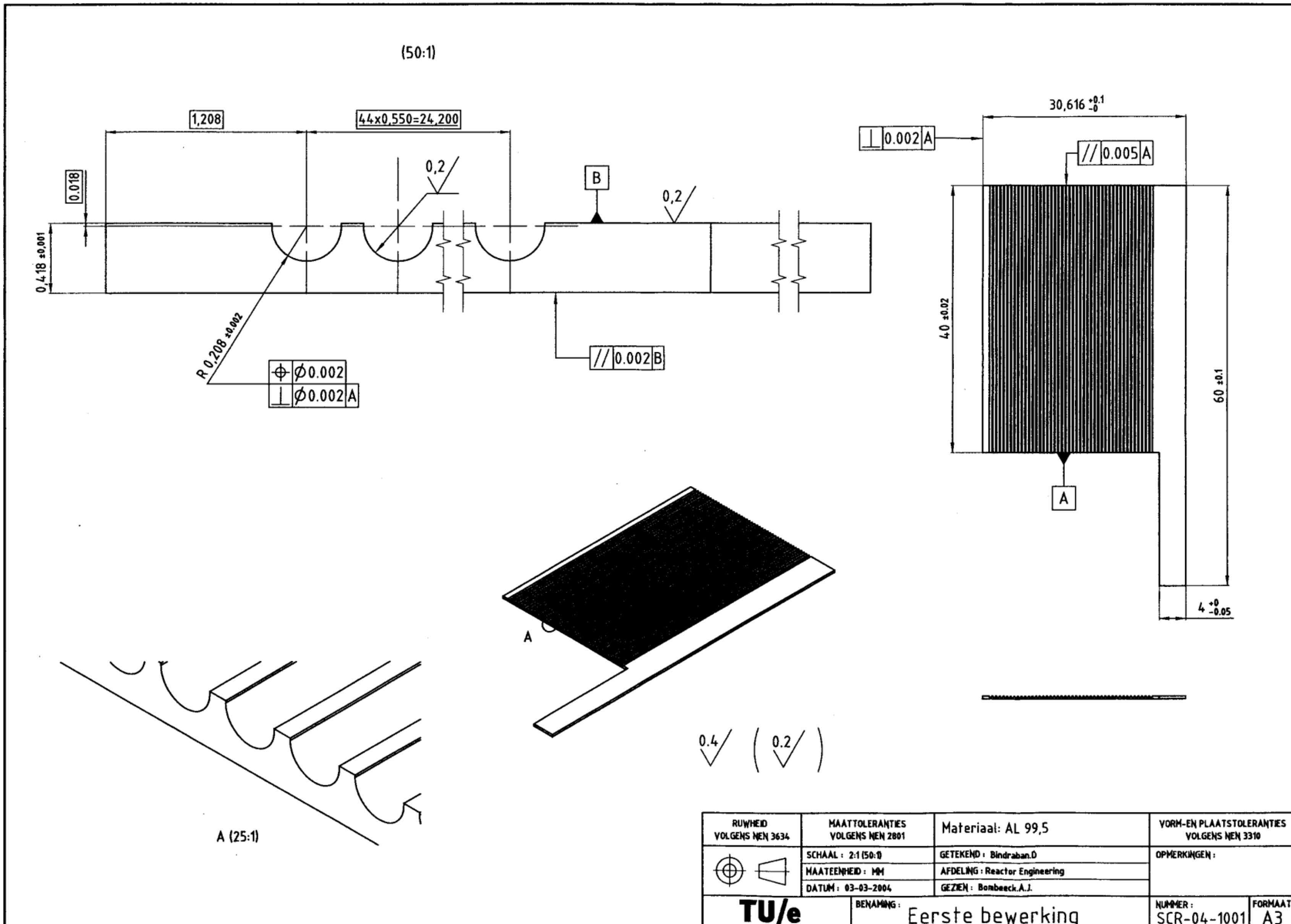
Al microreactor material:

high heat conductivity (230 W/m·K)

- **can be used up to 450 ^oC (m.p. 660 ^oC)**
- **microchannels easily made (e.g., by spark erosion)**
- **anodic oxidation allows formation of external porous g-Al_2O_3 layer for catalyst active component deposition**

- Material
  - **Al 99.5**
  - **AlMgSi1 alloy (Al51 st)**
- EDM procedure
  - **1 incision**
  - **2 incisions**
  - **3 incisions**

Single sided plates h =0.42



Fabrication of microstructured plates

- 1st series: 21+63 microstructured plates (1 incision)

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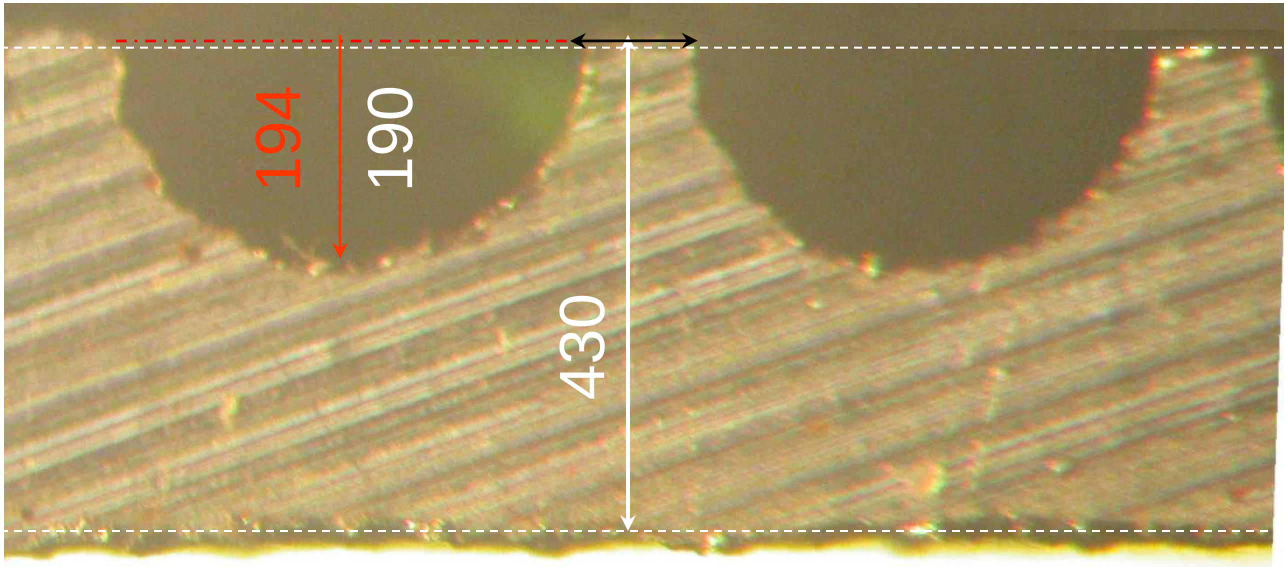
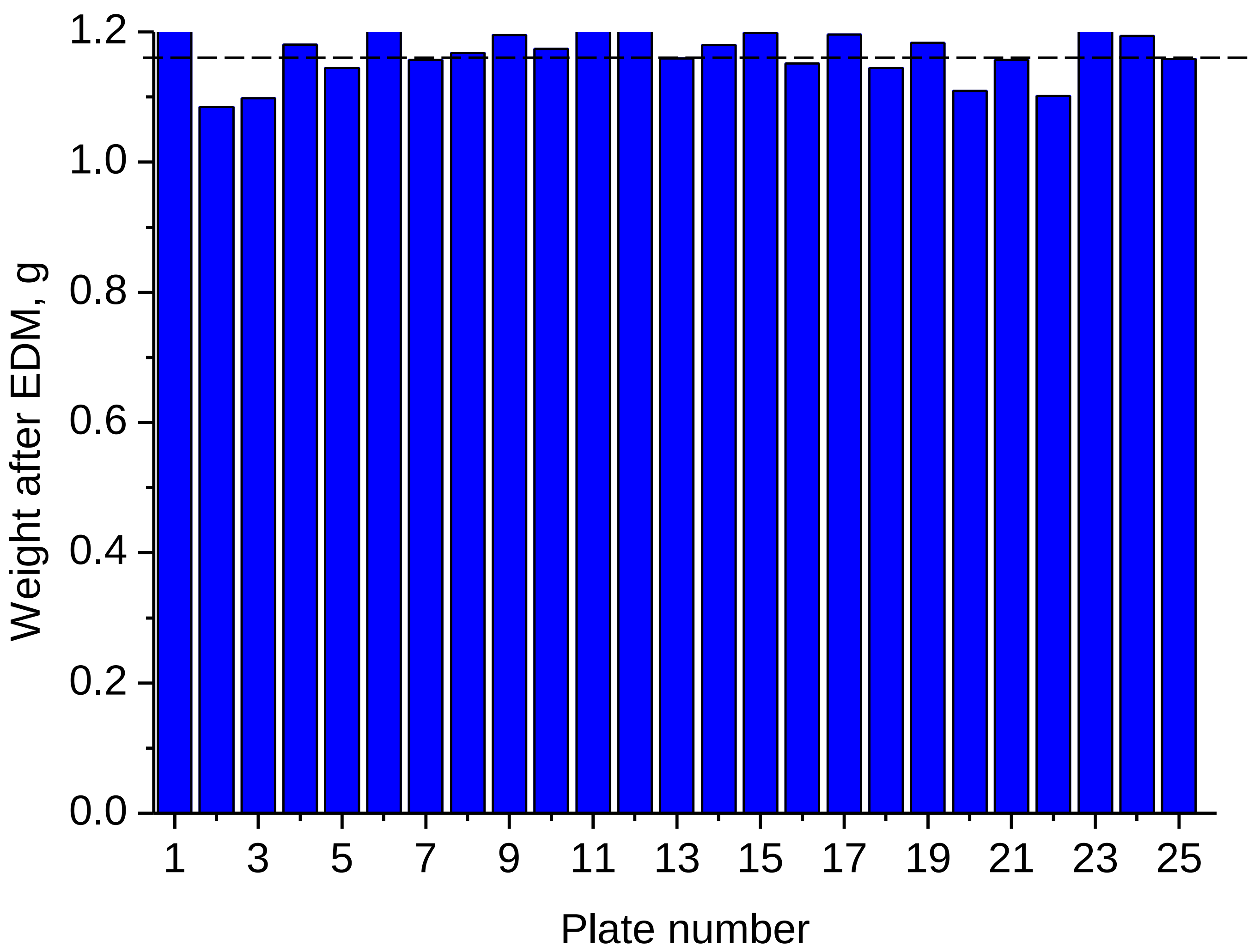


Ra >3

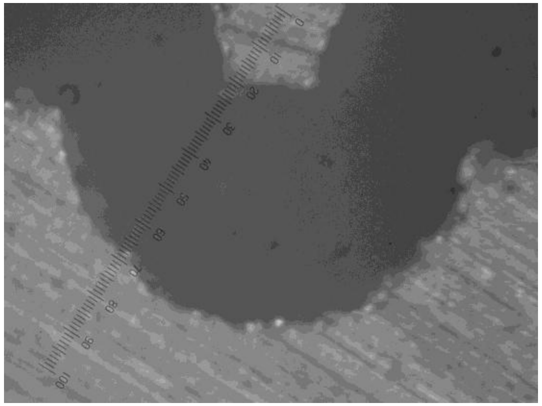
Dimensions: 45 channels with R=208 micron, L = 40 mm

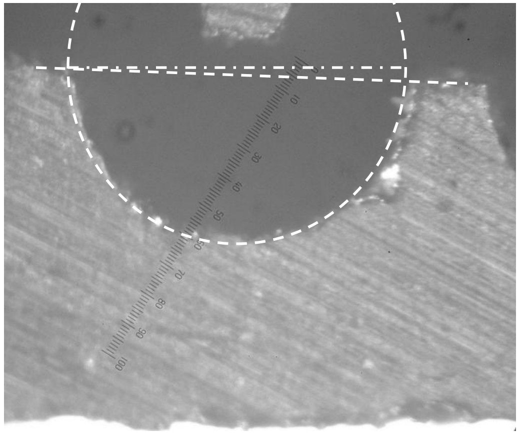
Plate weight after EDM



2nd series

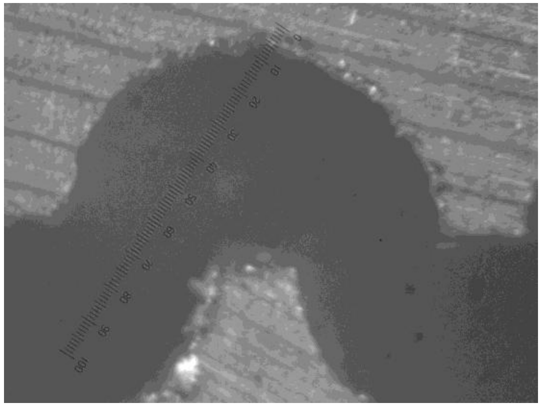
2 incisions

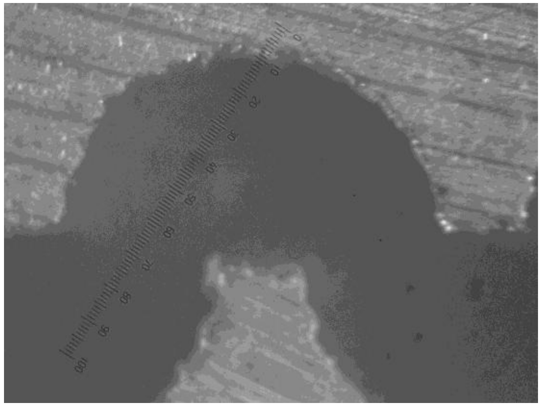




Ra =2.0

2 incisions + micro-powder jet treatment





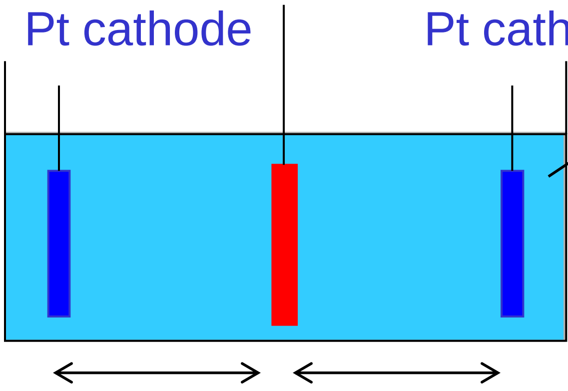
Ra =2.0

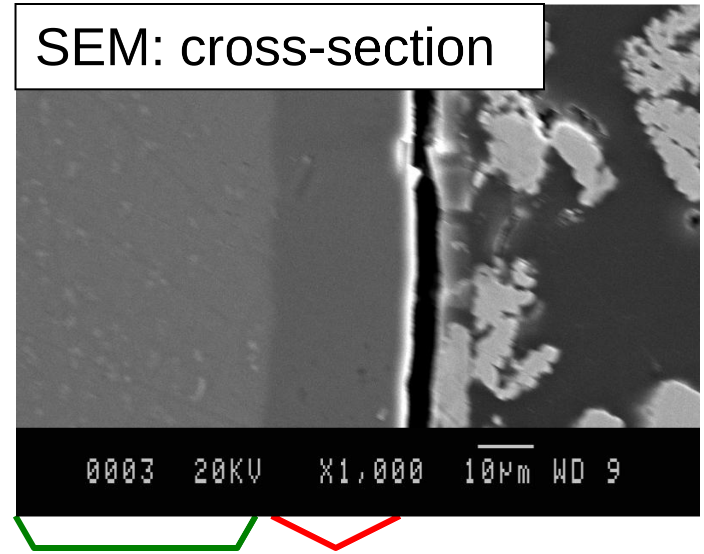
Summary

- Fabrication of long (40 mm) microchannels in Al 99.5 (code:1050A) is not possible
- Method "1 incision" gives surface roughness Ra >3.2 with the Al51st alloy
- It is possible to reach Ra=2.0 with fabrication method "2 incisions" in Al51st

Anodic oxidation

Anode: Al flat (or microstructured) plate





Anode:

$$2\,Al + 3\,H_2O \longrightarrow Al_2O_3 + 6\,H^+ + 6e$$

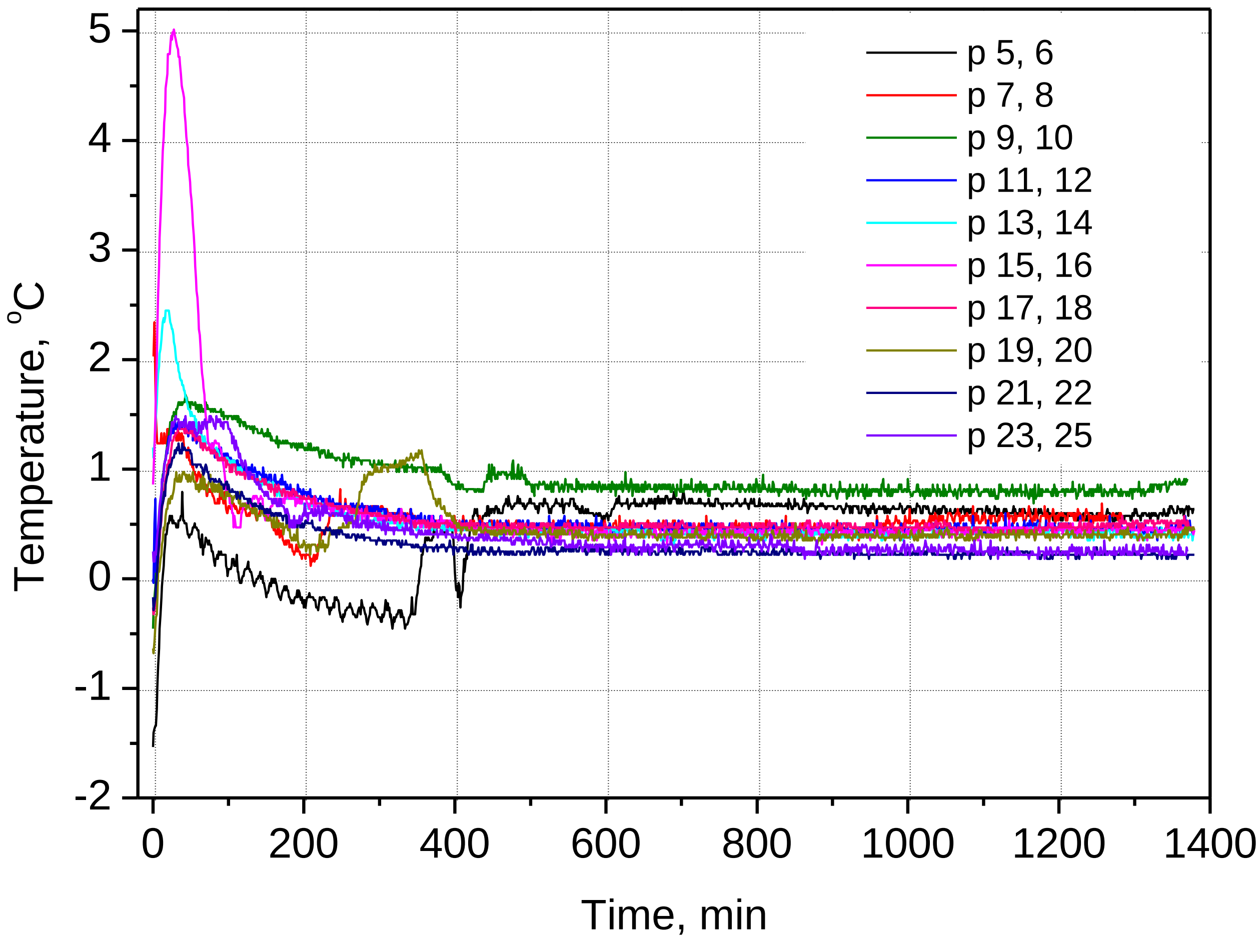
$$C_2O_4^{\,2-} \longrightarrow 2\,CO_2 + 2e$$

Cathode:

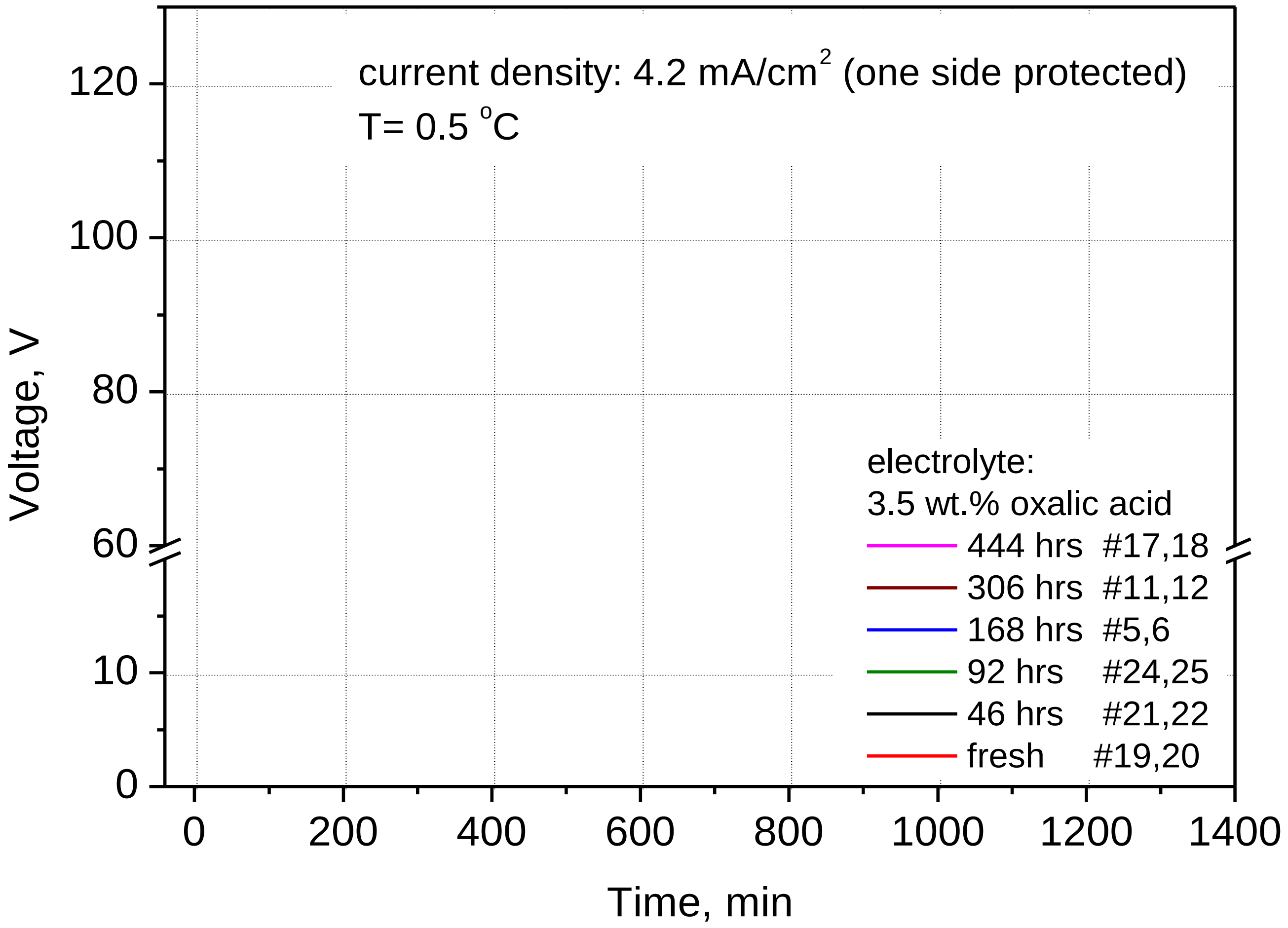
$$2\,H^+ + 2e \longrightarrow H_2$$

$$2\,Al + 3\,H_2O \longrightarrow Al_2O_3 + 3\,H_2$$

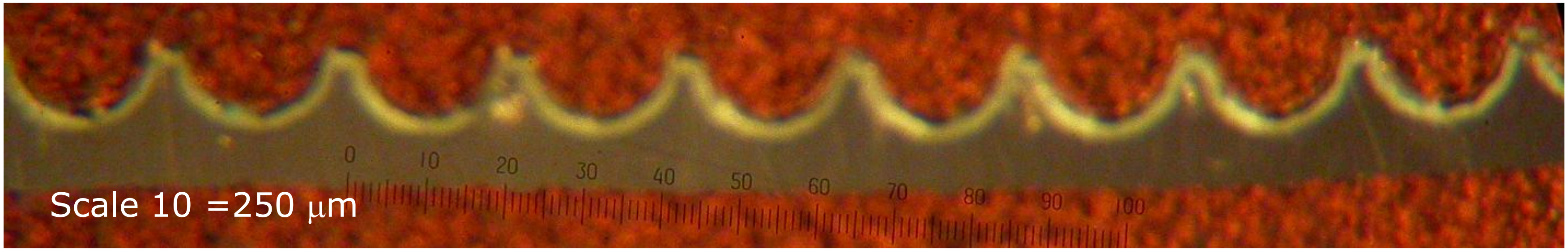
Temperature vs. time

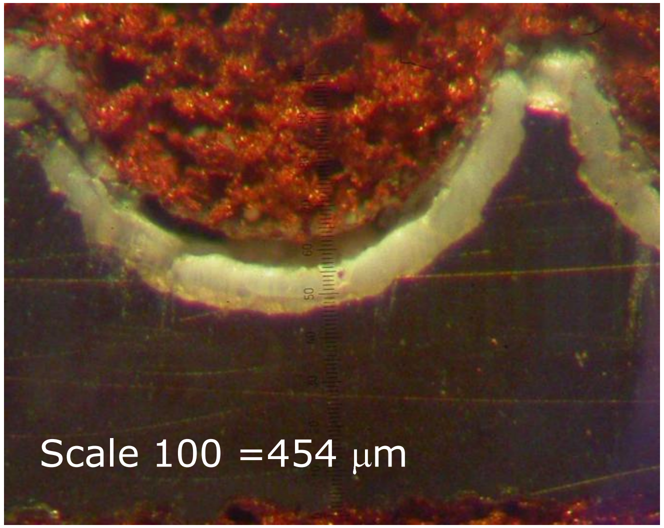


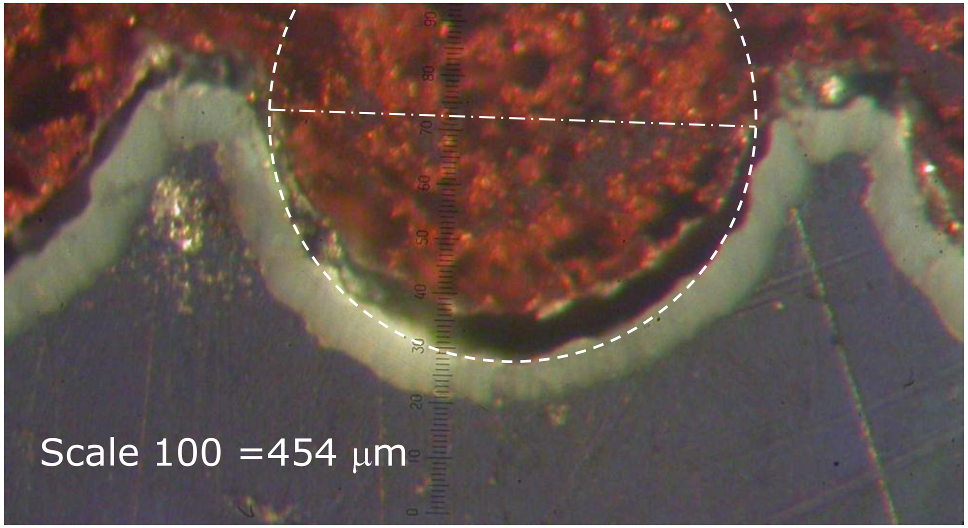
Voltage vs. time



Oxidation time 29 hrs



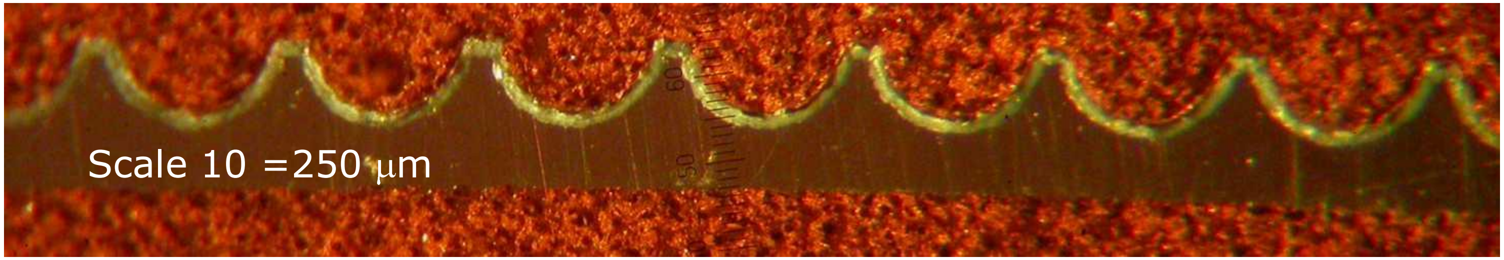


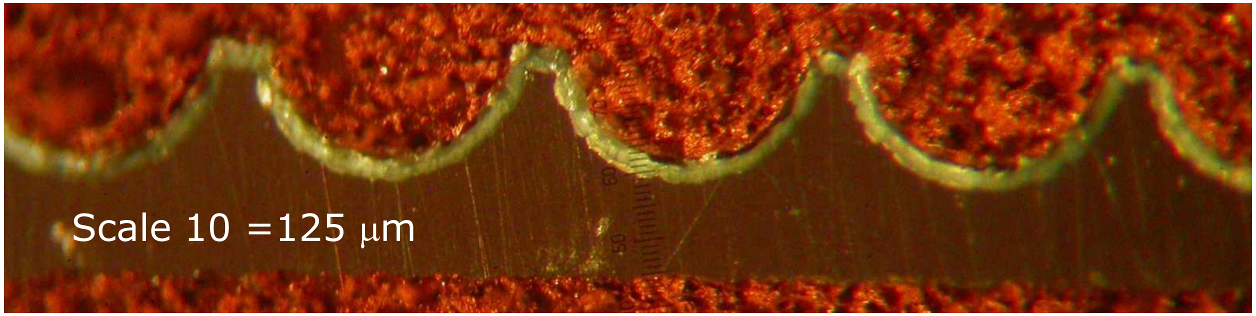


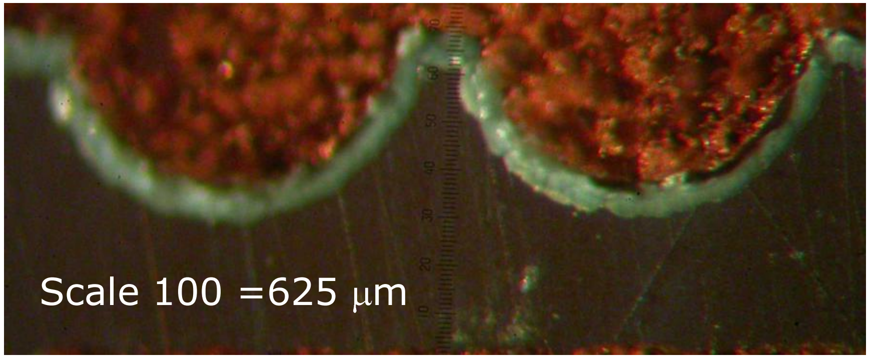
Layer thickness : 41±1 μm

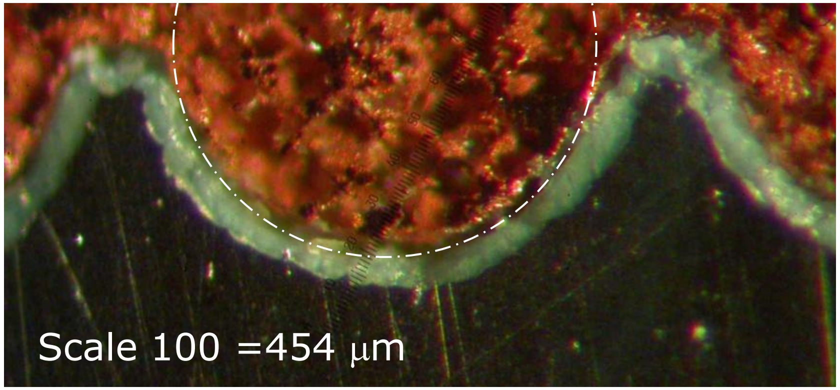
R = 408 μm

Oxidation time 23 hrs





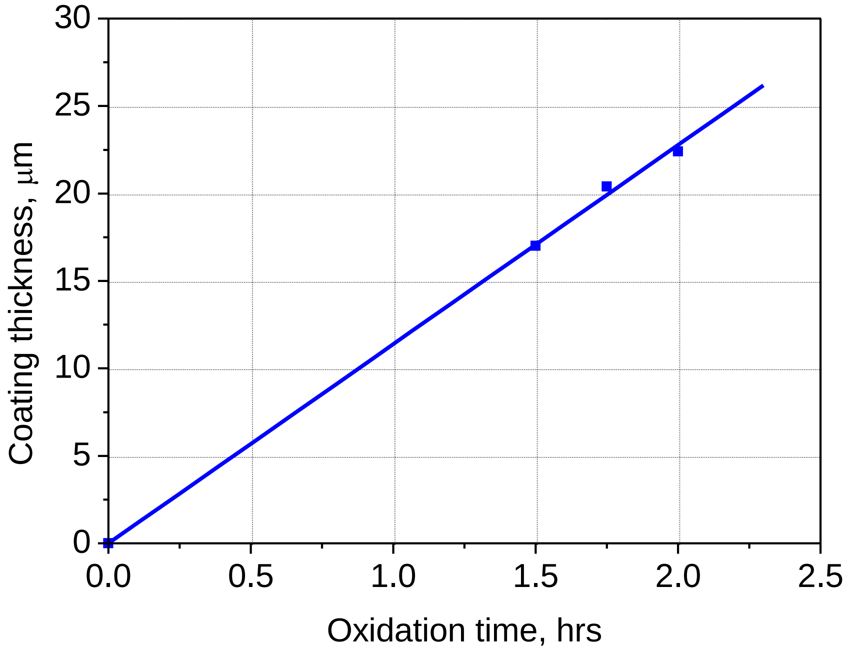




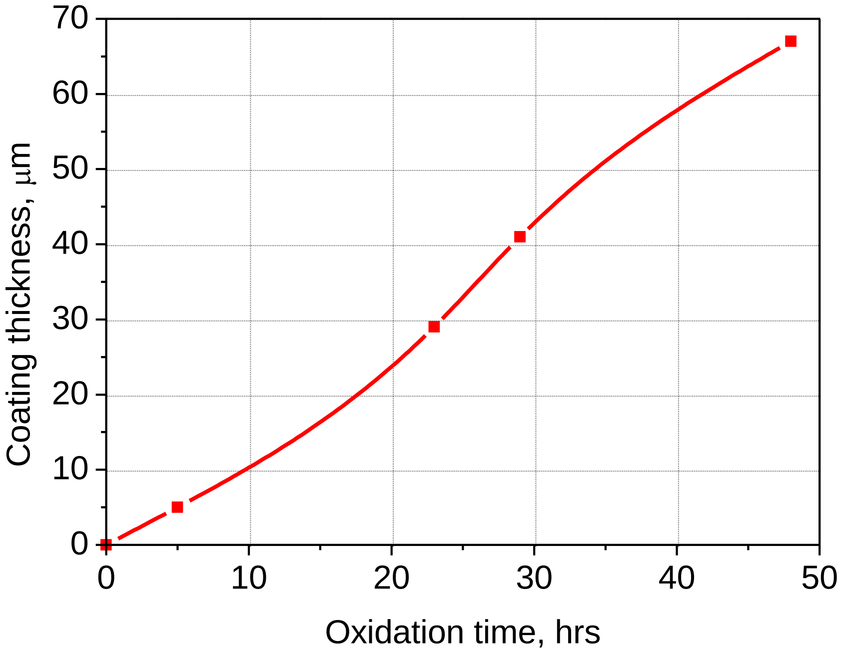
Layer thickness : 29±1 μm, R = 415 μm

Coating thickness vs. oxidation time

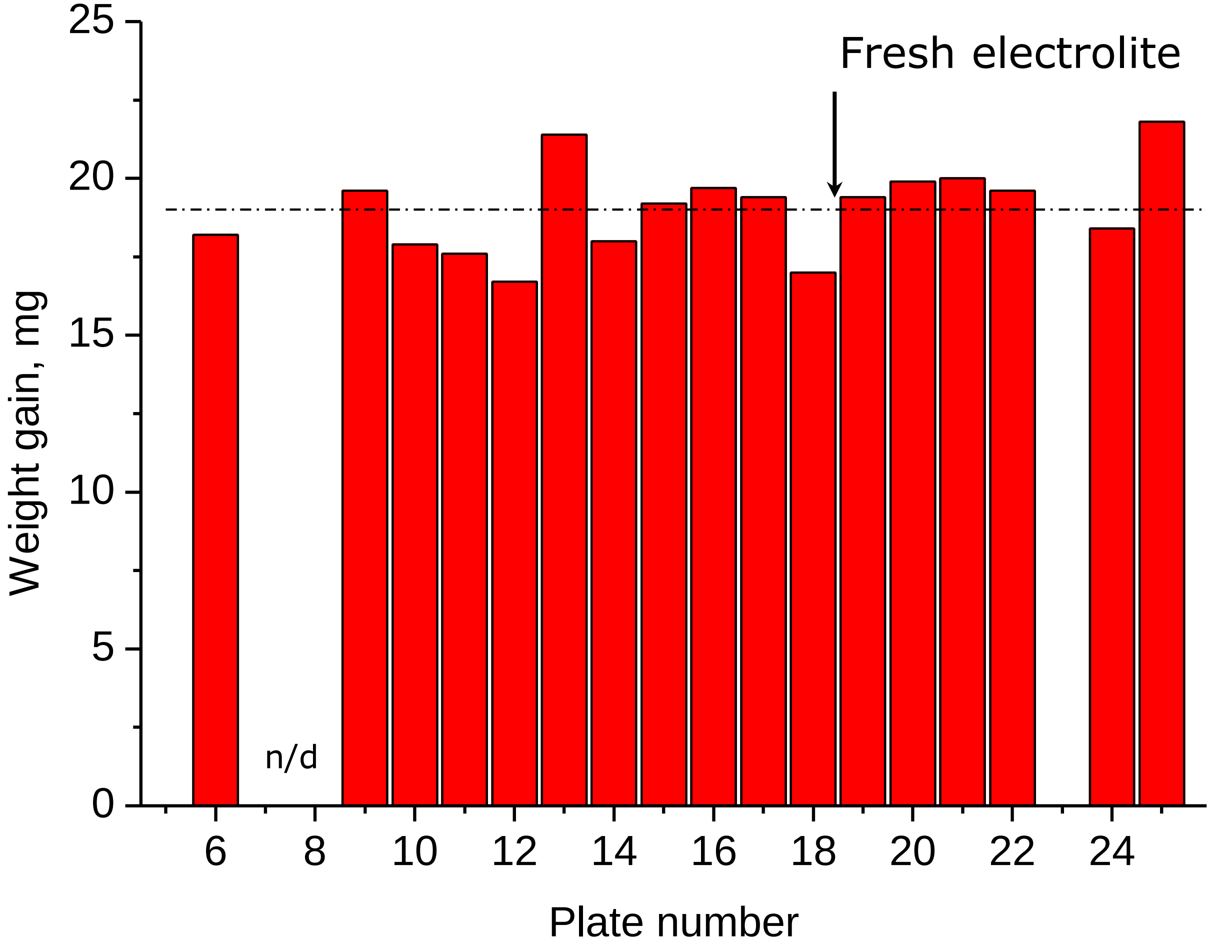
Flat plates



Microstructured plates

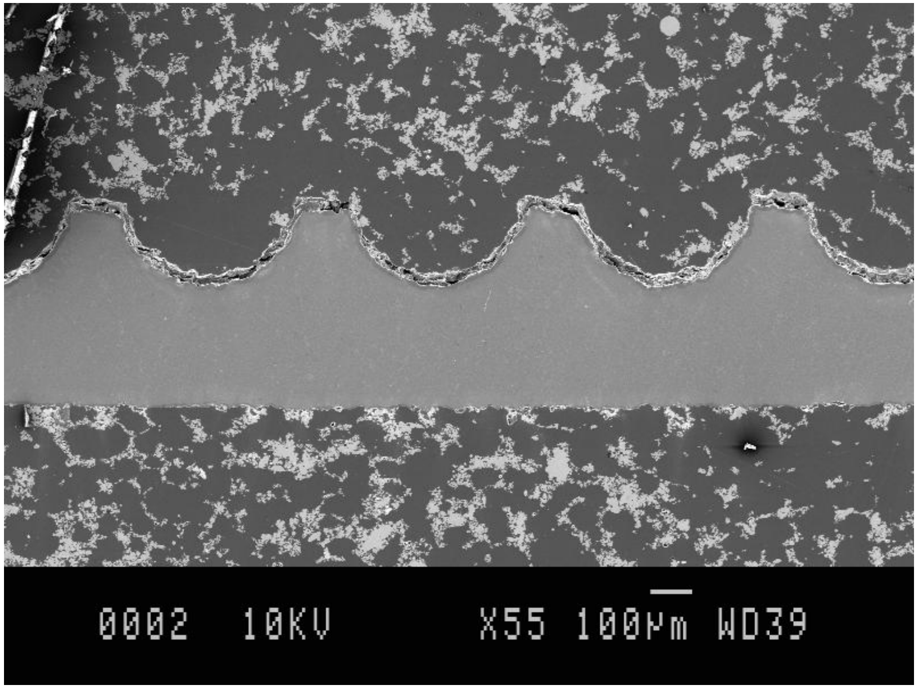


Weight gain after routine oxidation

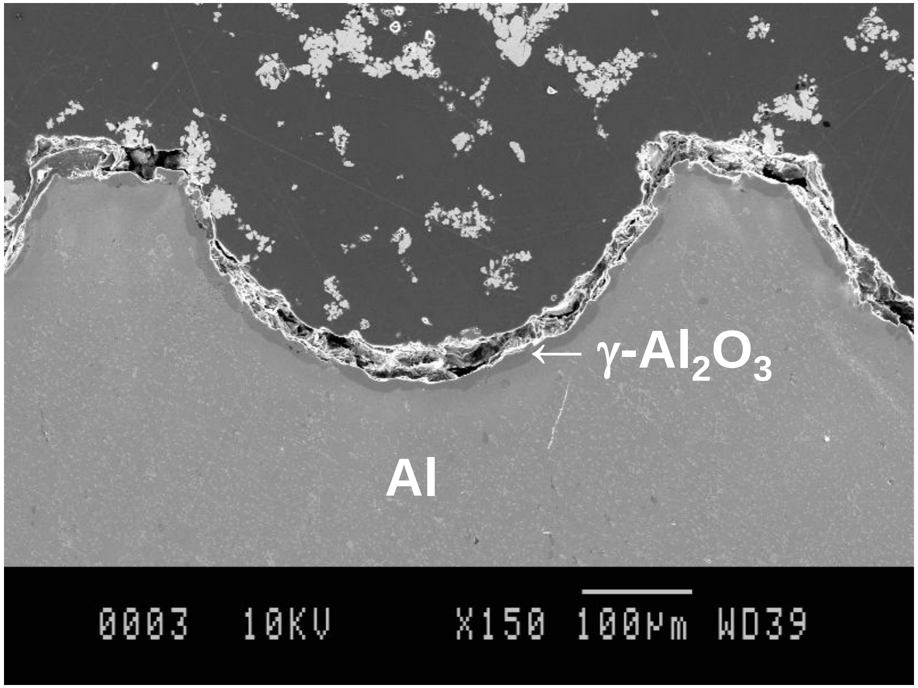


SEM: anodic oxidation of microstructured Al plates

3 microchannels

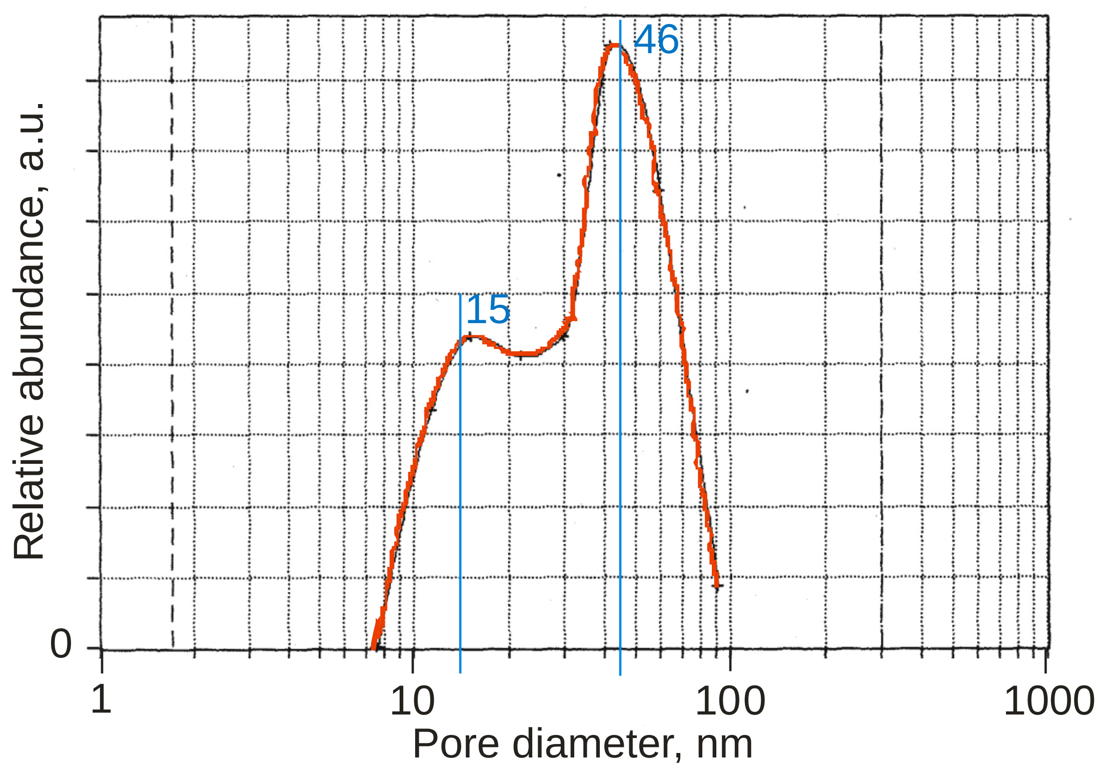


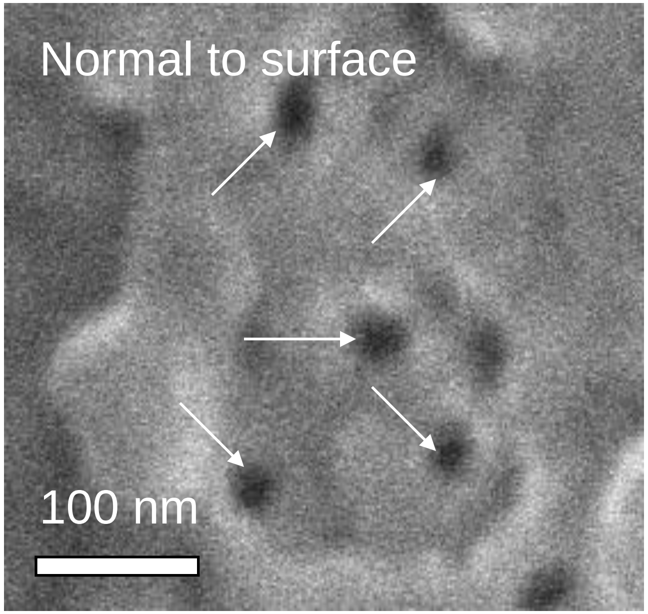
1 microchannel

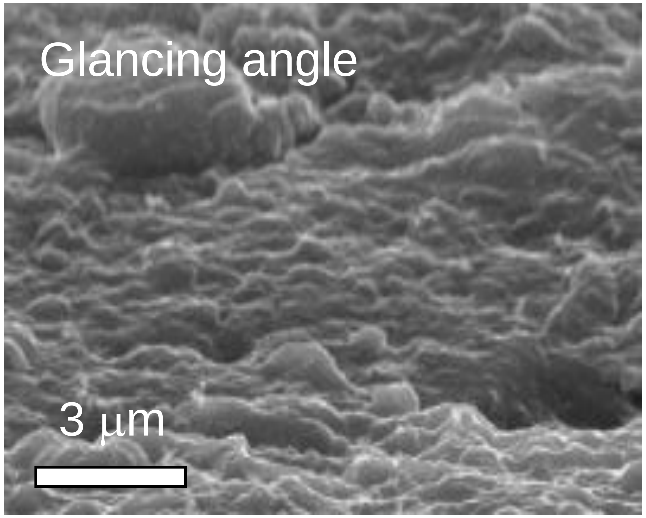


15 μm of γ-Al_2O_3 have been formed (low thickness due to the other, non-porous Al_2O_3 produced by spark erosion procedure) => anodic oxidation conditions are being optimized to form required 25 μm of γ-Al_2O_3

Anodized flat aluminum plates: S_{sp}, porosity, SEM







S_{sp} (γ-Al_2O_3/Al plate) = 95 m^2/cm^3 (30 m^2/g),
pore volume ~ 14 %, pore (cylindrical shape) distribution maxima at 15 nm and 46 nm

Result: Close to expected from literature, input data for catalyst active component deposition

Summary

- Low current density (I= 4 mA/cm2) is required for anodic oxidation of Al51 st
- Low temperature (close to the melting point of the electrolyte) is required to decrease the rate of undesirable reaction with oxalic acid
- Temperature control within ±0.5 K is crucial during oxidation to get reproducible results
- Higher voltage is required in subsequent runs due to copper deposition on the cathodes and copper dissolution in the electrolyte.

Development of spinel catalyst synthesis method using Al_2O_3/Al plates

1. Finding initial synthesis conditions by testing different methodologies of catalyst active component deposition using conventional pelleted γ-Al_2O_3 supports

2. Synthesis using the flat plates, catalysts characterization (physical methods, catalytic activity), optimization of synthesis conditions

3. Synthesis using the microstructured plates

Catalyst active component deposition on pelleted γ-Al_2O_3 supports

• Limiting condition: on γ-Al_2O_3/Al plates, catalyst calcination T not to exceed 500 ^oC, because m.p. of Al is ~ 600 ^oC (especially for microstructured Al plates)

• Method tested on pelleted (1.0-1.6 mm) γ-Al_2O_3: low-T formation of $CuCr_2O_4$ spinel (impregnation with solution of copper dichromate, drying and calcination at T = 450^oC for 4 h)

• XRD, BET results: at T = 450^oC dominate low-T solid solutions based on spinel structure $(Cu,Cr,Al)[Cr,Al]_2O_4$ with lattice parameter a = 7.905-7.960 Å, particle size D < 50 Å and S_{sp} ~ 130 m^2/g

• Reference catalyst composition 26%$CuCr_2O_4$/γ-Al_2O_3

Catalyst active component deposition on γ-Al_2O_3/Al supports

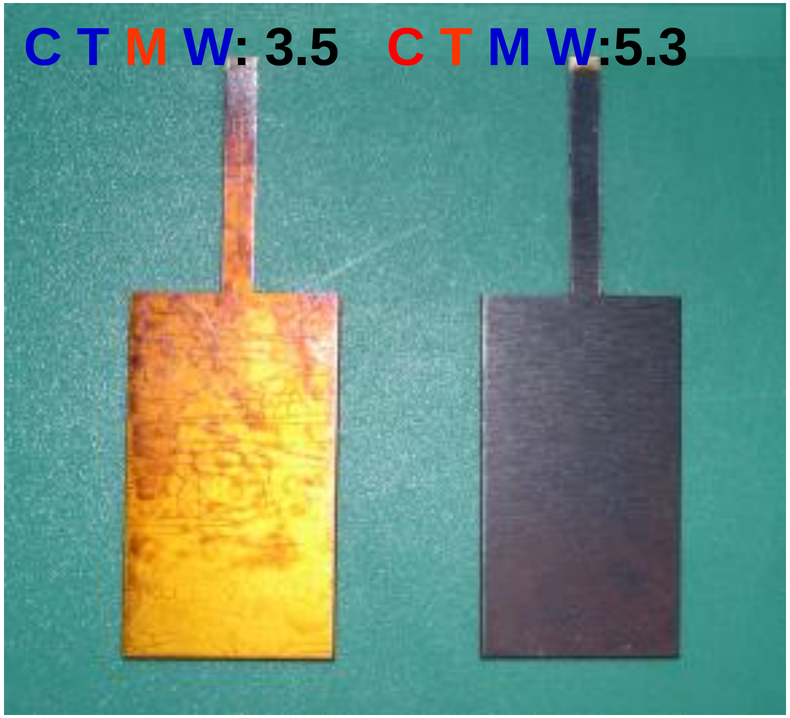
Parameter	Level of implementation	
	Low (No*)	High (Yes*)
C of impreg-nation soluti-on, g/l	**C** (250)	**C** (500)
Time of im-pregnation, h	**T** (0.25)	**T** (1.0)
Multiplicity of impregnati-ons *	**M**	**M**
Washing off excess soluti-on *	**W**	**W**

Examples (with resulting wt.% of a.c.):

C T M W: 0.4

C T M W: 2.5

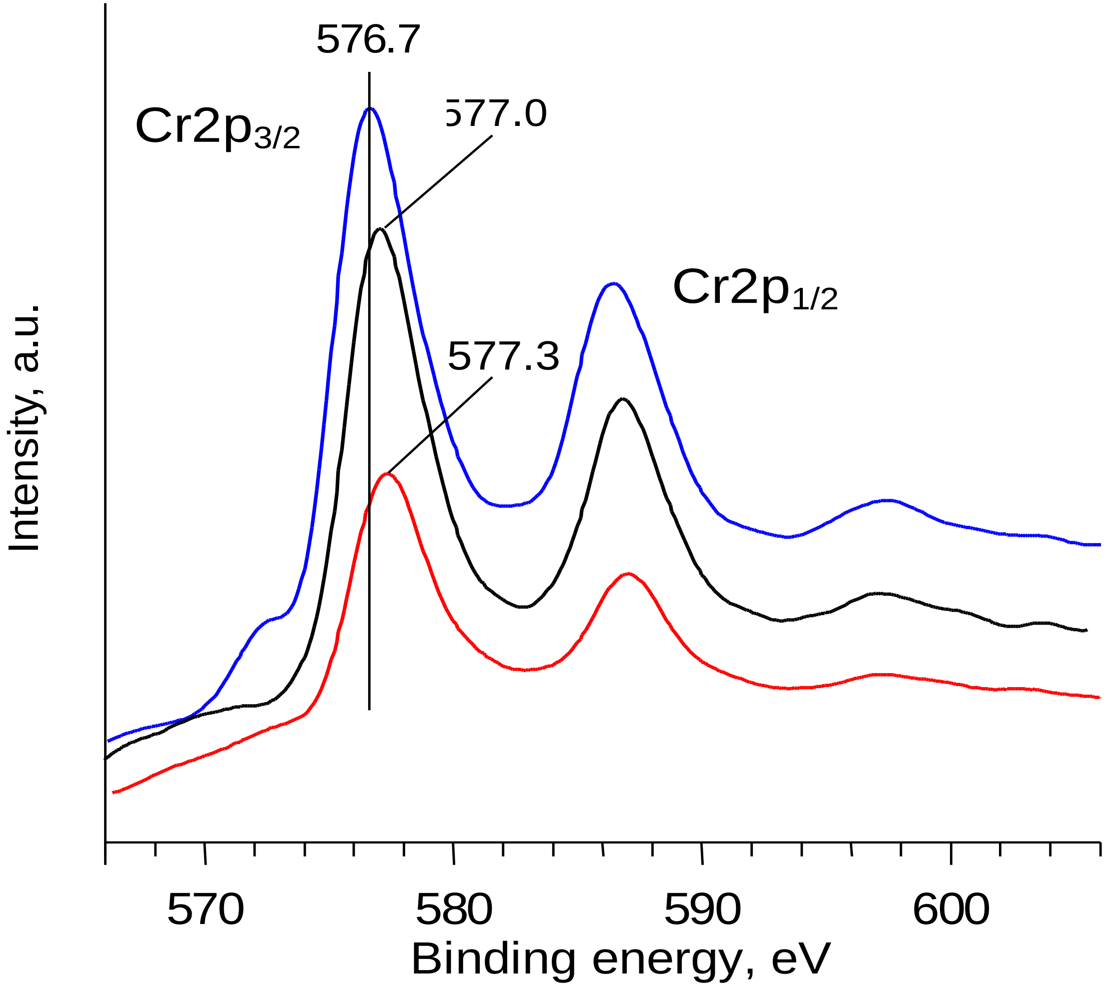
C T M W: 5.3



Results:

- Washing removes most of active component (a.c.)
- Concentrated solution – excess a.c. on surface (confirmed by XRD)
- Low concentrations deposit a.c. mostly in pores of γ-Al_2O_3

XPS and UV-Vis: Cr cations



Normal spinels: XY_2O_4
(X(Cu^{2+}, T_d coordination),
Y(Cr^{3+}, O_h coordination),
face-centered cubic unit cell
(formed by close-packed O^{2-})

Resulting wt.% of a.c.:

C T M W: 5.3

C T M W: 3.5

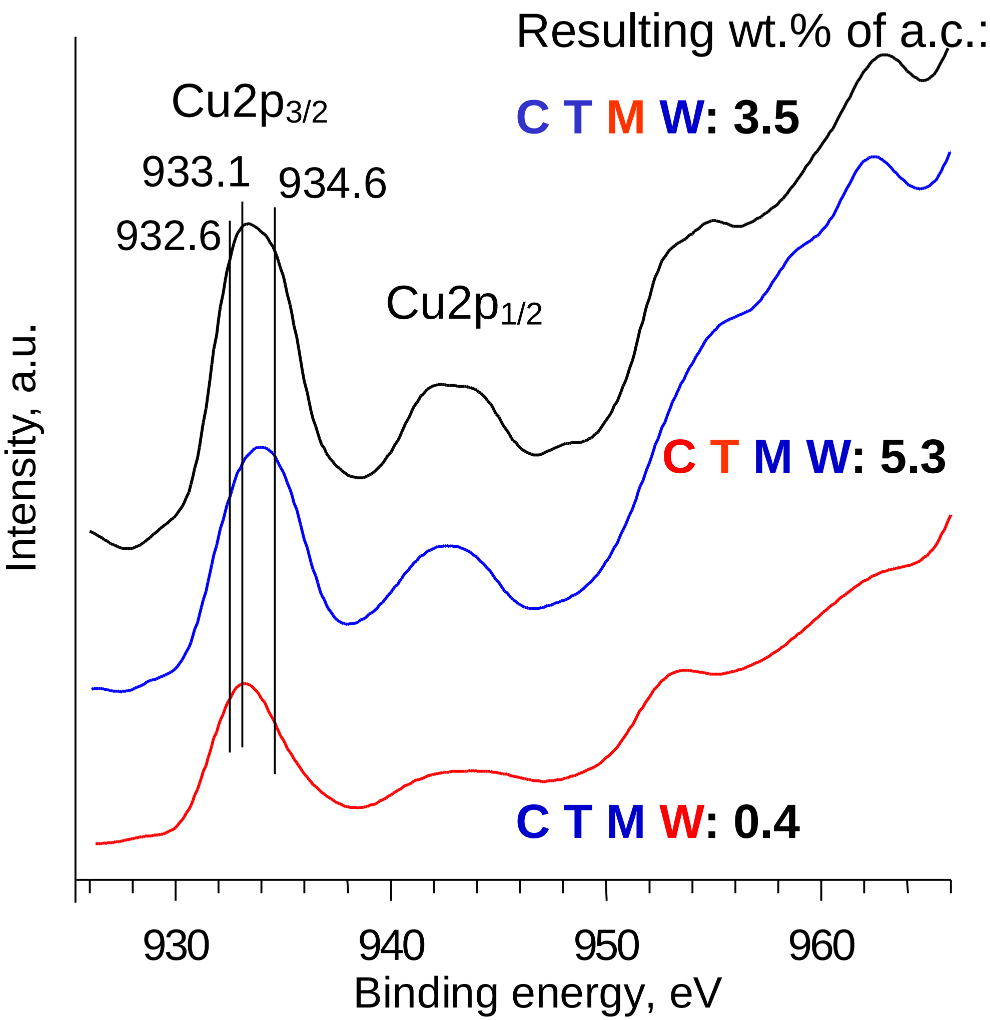
C T M W: 0.4

Shift to lower BE with increase of active component (a.c.) loading => possibly, interaction with γ-Al_2O_3 support is stronger, than within a.c. particles themselves

$Cr2p_{3/2}$ of Cr^{3+}: 576.5-577.5 eV (577.1 eV for $CuCr_2O_4$)

UV-Vis: O_h Cr^{3+} ~ 17000 cm^{-1} and ~ 22000 cm^{-1} (d-d transitions)

XPS and UV-Vis: Cu cations

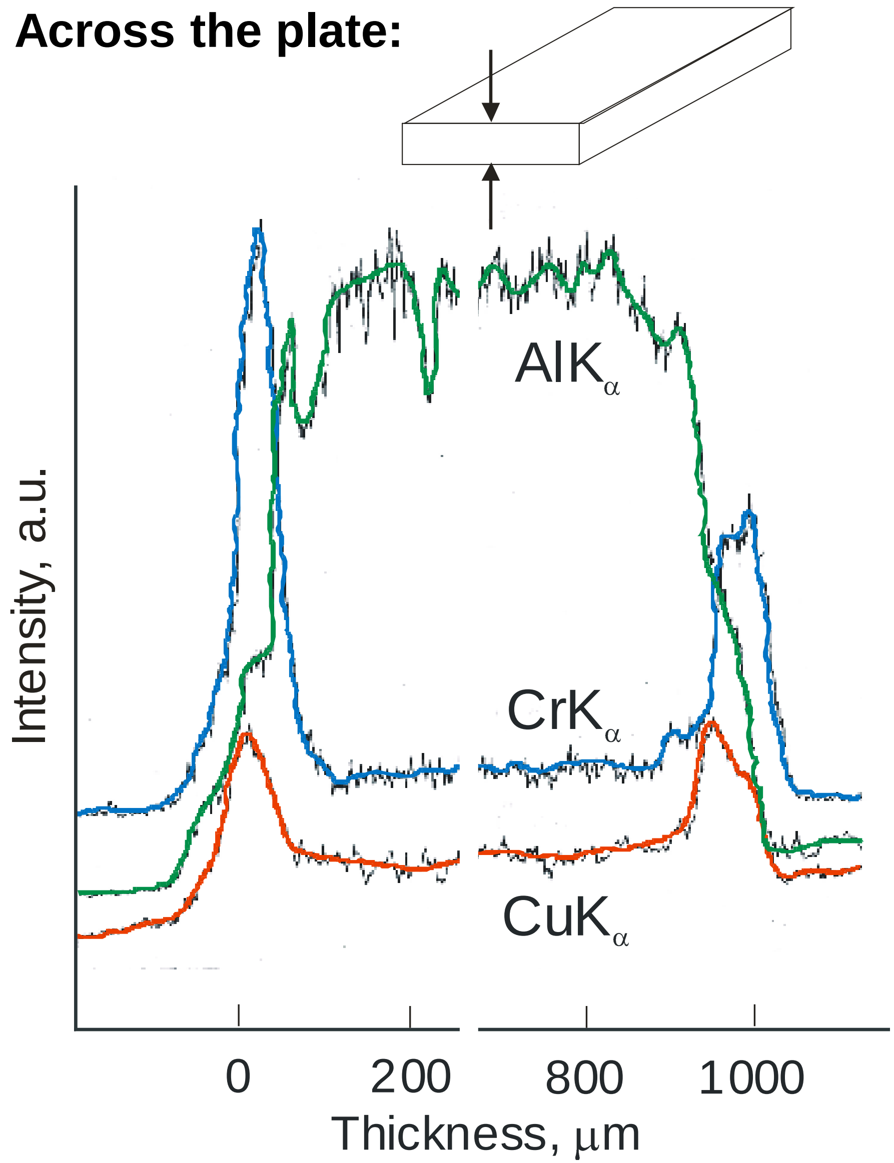


- For sample with low a.c. loading, the $CuCO_3$ signal overlaps with $CuCr_2O_4$ signal, looking as 1 peak at 933.1 eV. With higher a.c. loadings, $CuCO_3$ signal becomes more pronounced
- Maximum of Cu^{2+} content is observed for medium a.c. loading catalyst (XPS is surface-sensitive). Cu^{2+} is considered the most active part of spinel catalyst => probably, better a.c. dispersion and Cu^{2+} localization for this catalyst
- Shift to higher BE with increase of a.c. loading – opposite to Cr^{3+}

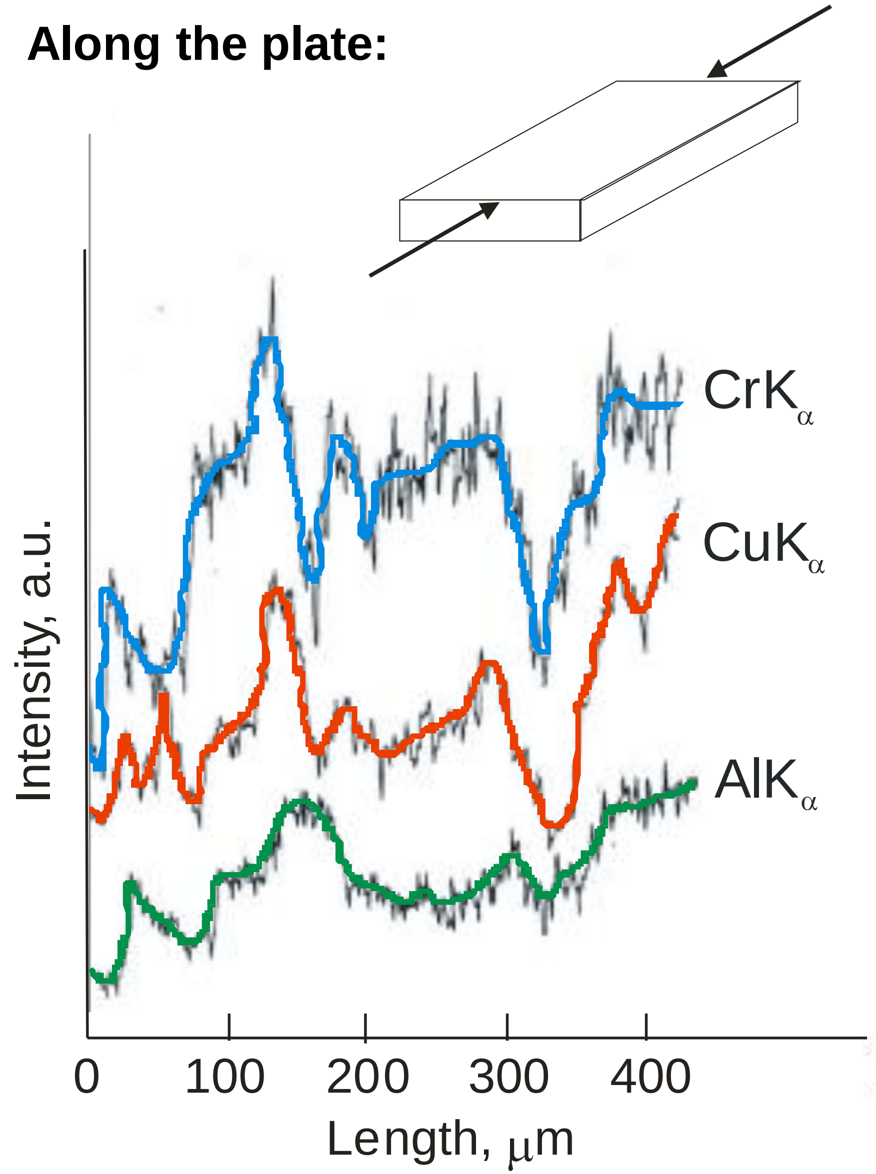
$Cu2p_{3/2}$ of Cu^{2+}: ~ 933 eV for $CuCr_2O_4$, ~ 935 eV for $CuCO_3$
UV-Vis: T_d Cu^{2+} ~ 13000 cm^{-1} (d-d transitions)

XMA: Cu, Cr, Al distributions (sample C T M W: 3.5%$CuCr_2O_4$)

Across the plate:



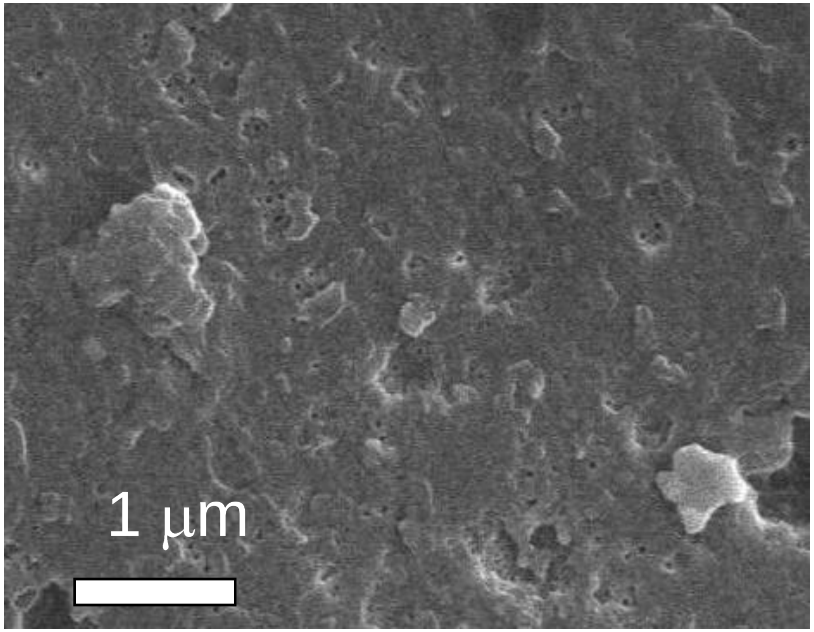
Along the plate:

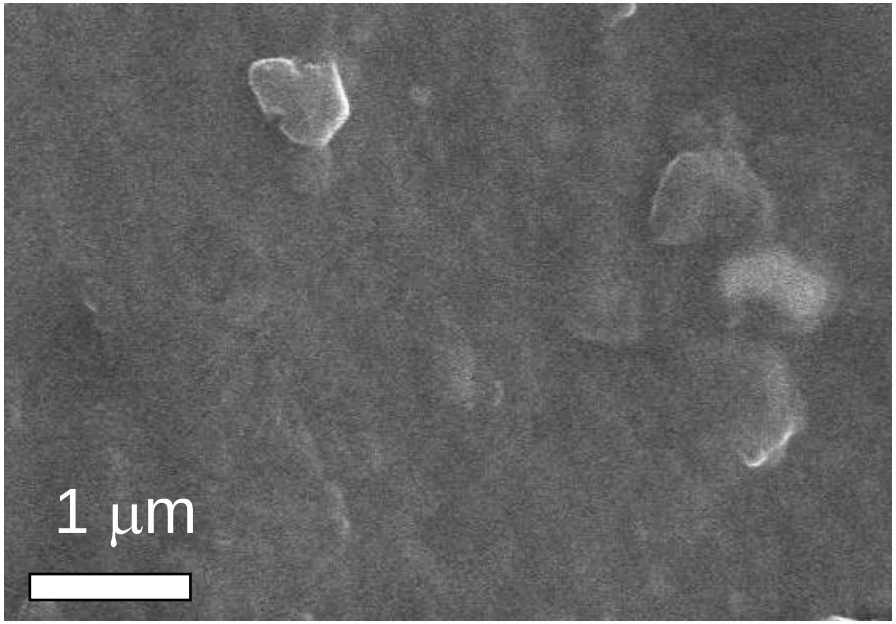


SEM: γ-Al_2O_3 surface before and after impregnation with $CuCr_2O_7$

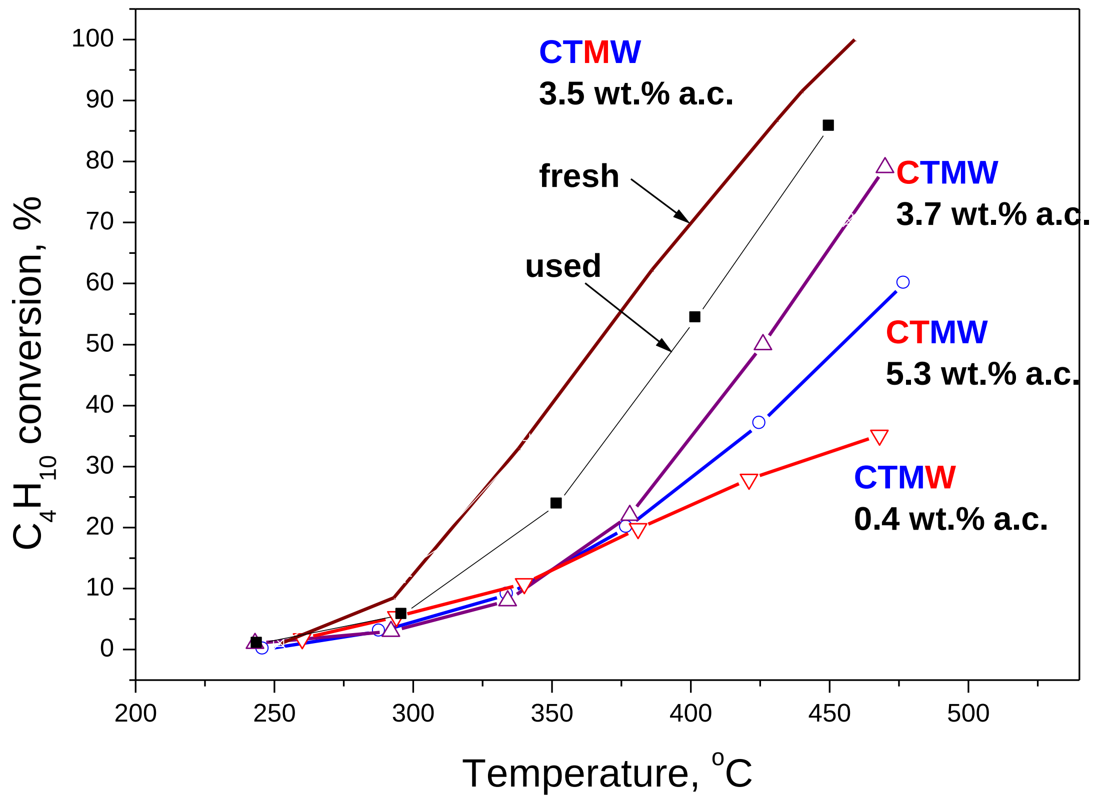
Before:
cylindrical pores are clearly visible

After (sample C T M W: 5.3%$CuCr_2O_4$):
surface is covered with $CuCr_2O_7$





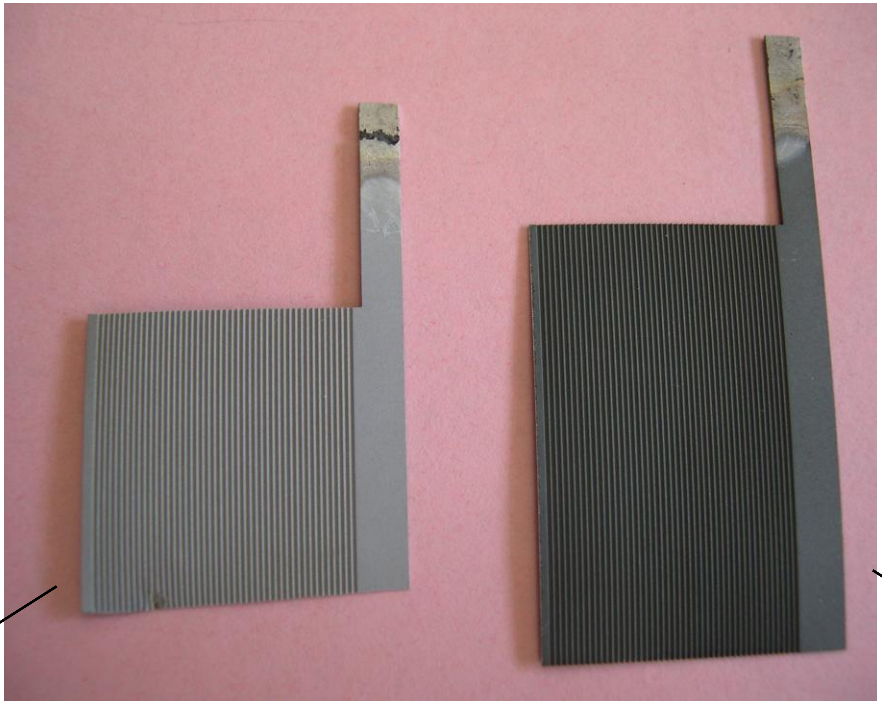
Catalytic activity: deep oxidation of C_4H_{10} on flat plate supported catalyst



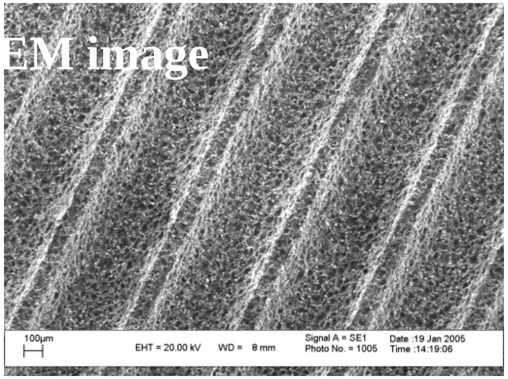
initilal C(C_4H_{10}) = 2000 ppm in air, GHSV = 120000 h^{-1} with respect to volume of catalytic coating

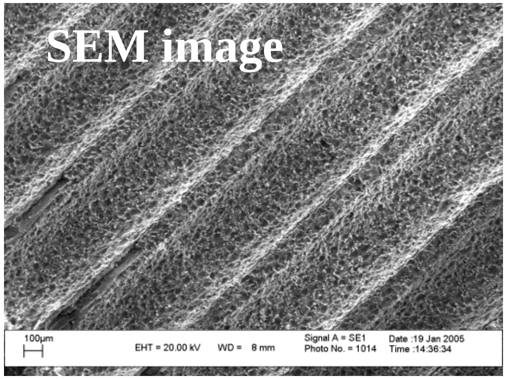
Catalyst active component deposition on microstructured plates

anodized AlMgSiCu-alloy plate without catalytic coating

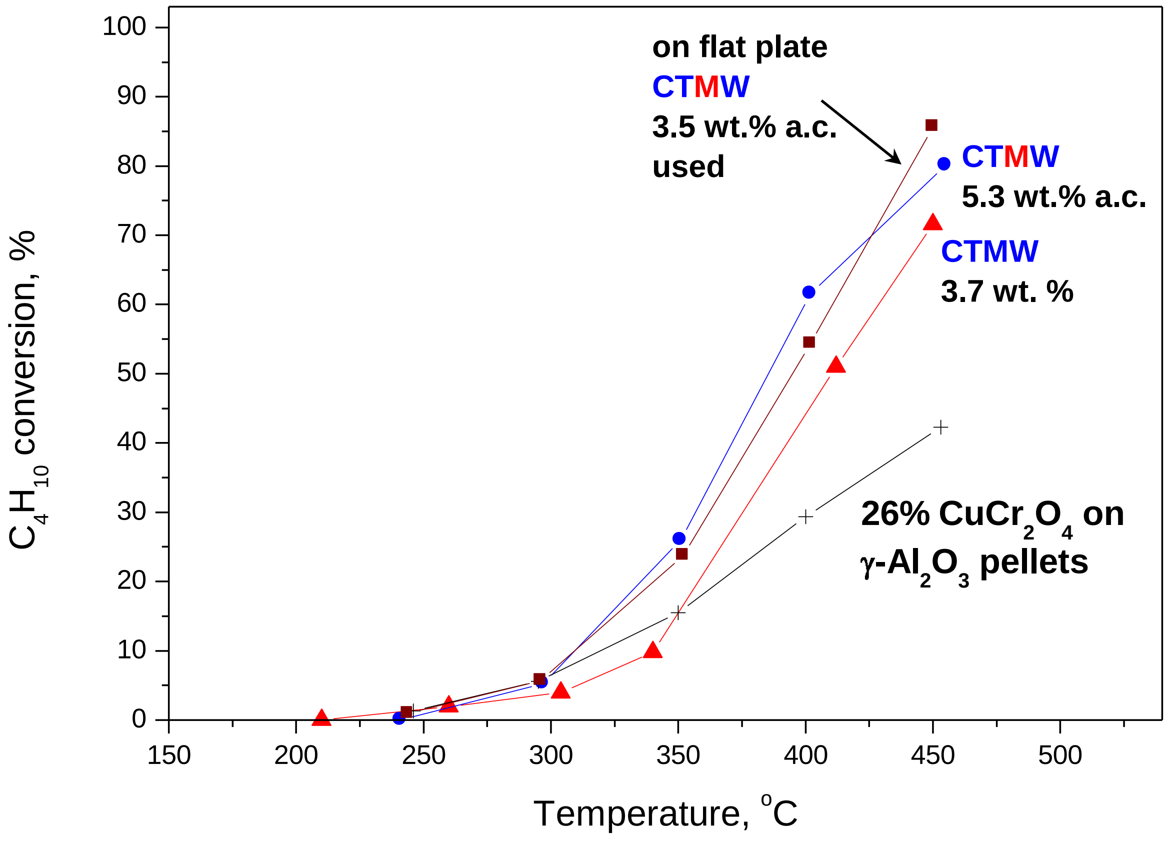


CTMW
3.7 wt. %
$CuCr_2O_4$



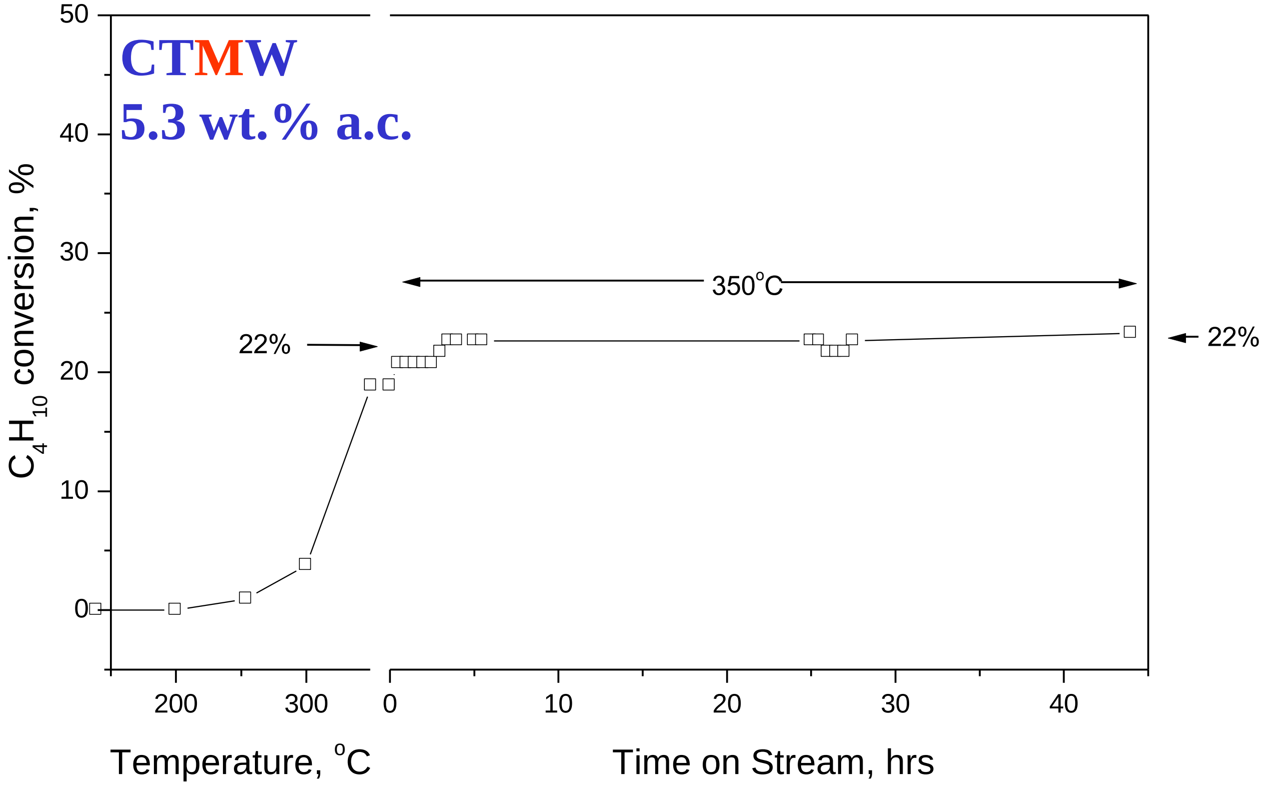


Catalytic activity: deep oxidation of C_4H_{10} on microstructured plate supported catalyst



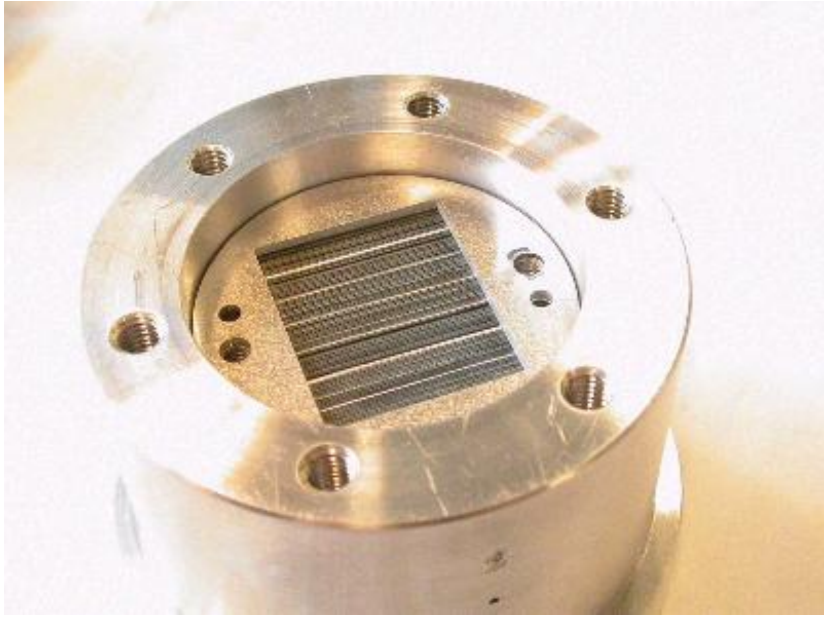
$C(C_4H_{10})$ = 2000 ppm in air, GHSV = 120000 h^{-1} with respect to volume of catalytic coating

Catalytic activity: deep oxidation of C_4H_{10} on microstructured plate supported catalyst



initilal $C(C_4H_{10})$ = 2000 ppm, GHSV = 120000 h^{-1} vs. γ-Al_2O_3 with respect to volume of catalytic coating

Catalytic microreactor for total oxidation reactions



Conclusions

1. **The alumina-supported Cu, Cr oxide catalysts for reactions of total oxidation in a microreactor were synthesized using flat and microstructured anodized Al plates and characterized**

2. **The formation of $CuCr_2O_4$ active component on γ-Al_2O_3/Al plates produced by anodic oxidation was confirmed by XPS, UV-Vis, XRD, XMA and SEM**

3. **The best catalyst synthesis method is via double impregnation for 15 min with a diluted aqueous solution of copper dichromate**

4. **The C_4H_{10} oxidation activities of coatings even at much less cotent of active component are superior to that of the reference pelleted catalyst**

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