Ti-Zr-V based NEG thermal activation study

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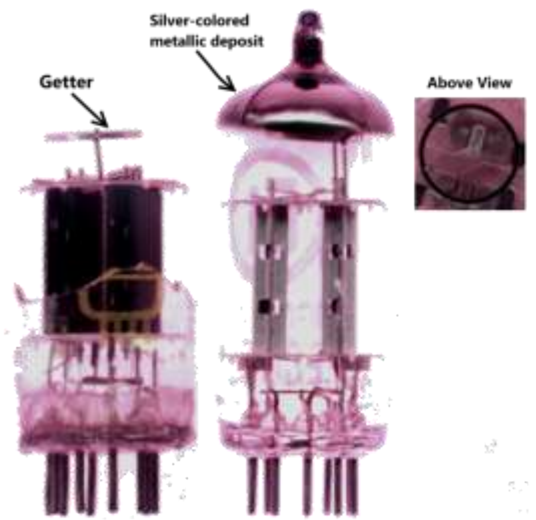
Schedule

- Getters and their use
- NEG – generations review
- Surface sensitive methods for activation studies
- Preparation of the samples
- Activation
- Results
- Conclusions

Getters

- Reactive materials that captures gas by strong bond (chemisorption)
- Works as a pump in vacuum systems
- Fresh reactive interface is usually generated by depositing new layer of the getter in the system Ti, Ba.
- Usually big active surface compared to conventional pumping
- Widely used in sealed off systems

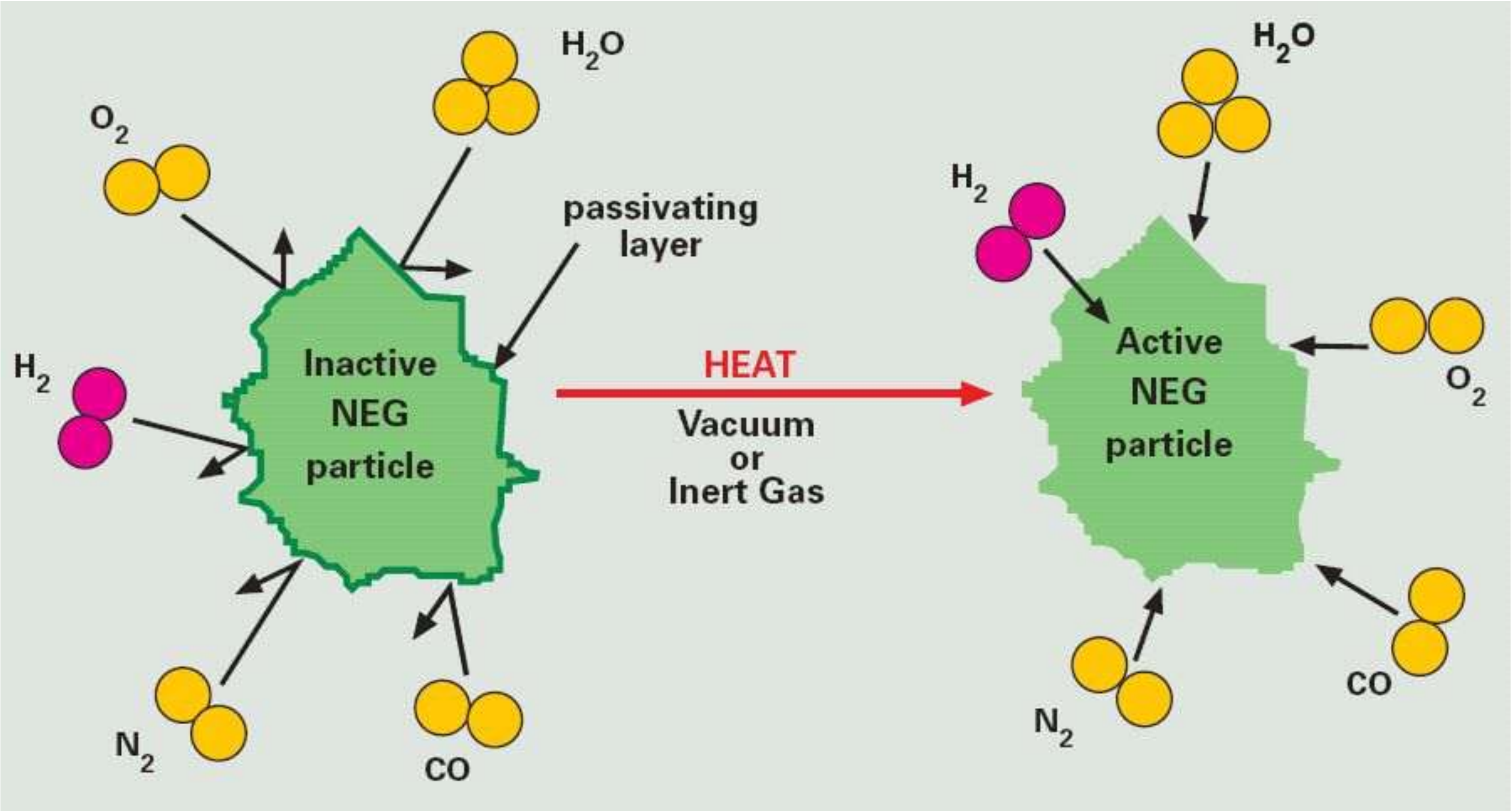


Non Evaporable Getters

- Materials repeatably generating active surface without depositing new layer of the getter.
- Activation usually by heating of the NEG to the temperatures above „activating temperature“
- Several standard NEGs:

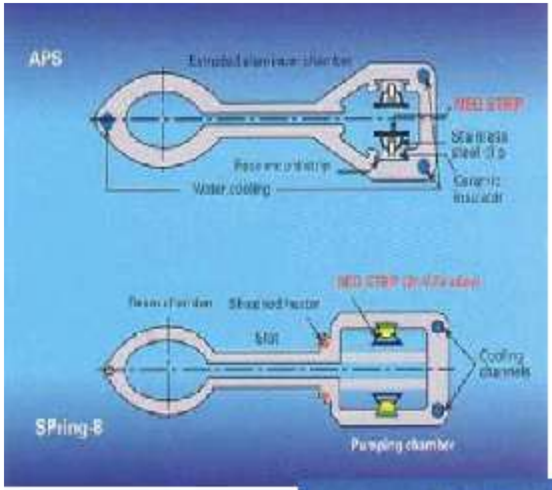
Type	Comp.	Standard shape	Activation
St 707	Zr-V-Fe	strips	450°C / 45 min.
St 172	Zr-V-Fe	Sintered discs	450°C / 45 min.
St 185	Ti-V	Sintered sheets	500°C / 45 min.
St 101	Zr-Al	Tablets, strips, ..	700°C / 45 min

Activation of the NEG



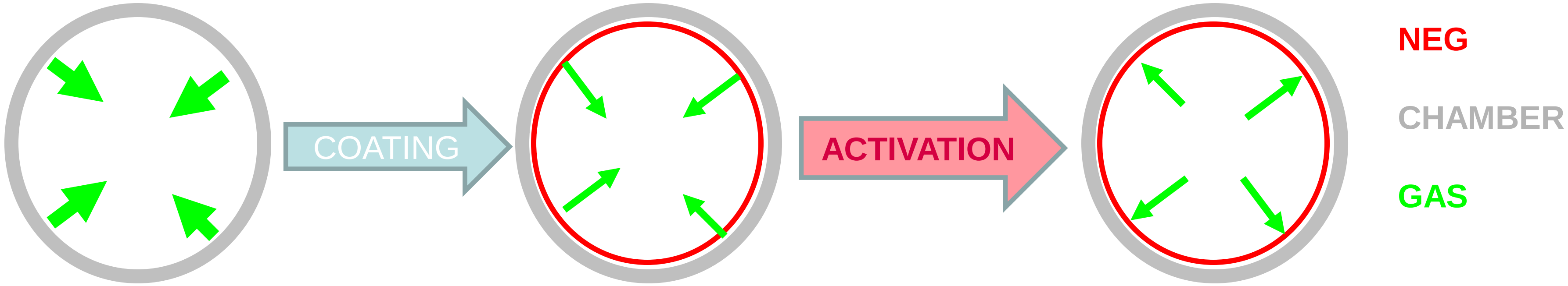
Common use of NEG

- Systems with low conductance but UHV to XHV conditions – accelerators, synchrotrons
- Standard vacuum system with enhanced vacuum needs XHV
- Noble gas purification
- Micromechanics vacuum setups



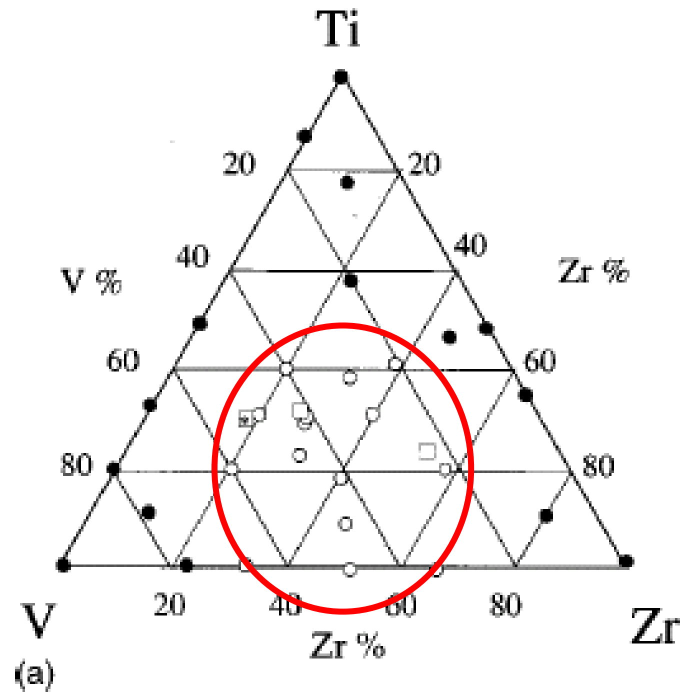
Low activation temperature NEGs

- Project of Large Hadron Colider in CERN induced further NEG developing by need of lowering activation temperature.
- Activation during baking of the system
- Large active surface – wall coating
- Good electron bombardment properties (ESD) and irradiation properties for colliders and synchrotrons
- Ti – Zr – V alloys were found as promising materials



NEG study in CERN

- Benvenuti group
- Pumping properties of getter tested on real chambers.
- XHV conditions reached - 10^{-12} Pa
- Small samples testing:
  AES peaks ratios for determining quality of activation
  XPS and XRD studies
- 200 °C temp reached by Ti-Zr-V alloy
- Cooperation with other goups with detailed analyses of promising compositions



Low activation temperature

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Fields of interests for improving NEGs

- Influence of compostition to activation temperature
- Surface activity of the NEG – sticking coeficient for H, CO
- Pumping speed and capacity of the NEG thin layer
- Total capacity of NEG - ageing
- Structural changes during activation and pumping cycles
- Chemical changes of the surface during activation and pumping cycle
- Desorption under different conditions

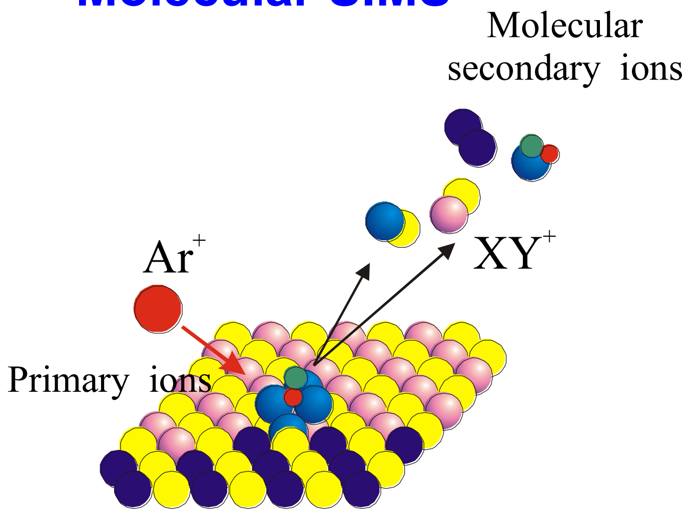
Experimental methods

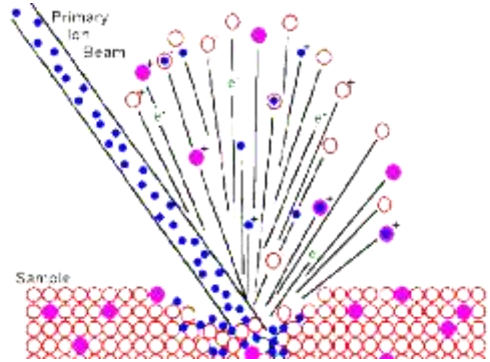
- **SIMS** - Secondary Ion Mass Spectrometry
- **XPS** - X-ray Photoelectron Spectroscopy (ESCA)
- **SRPES** - Synchrotron Radiation Electron Spectroscopy
- **AES** - Auger Electron Spectroscopy
- **LEIS** – Low Energy Ion Scattering
- **XRD** – X-Ray Difraction
- Sticking coeficient

SIMS – Secondary Ion Mass Spectrometry

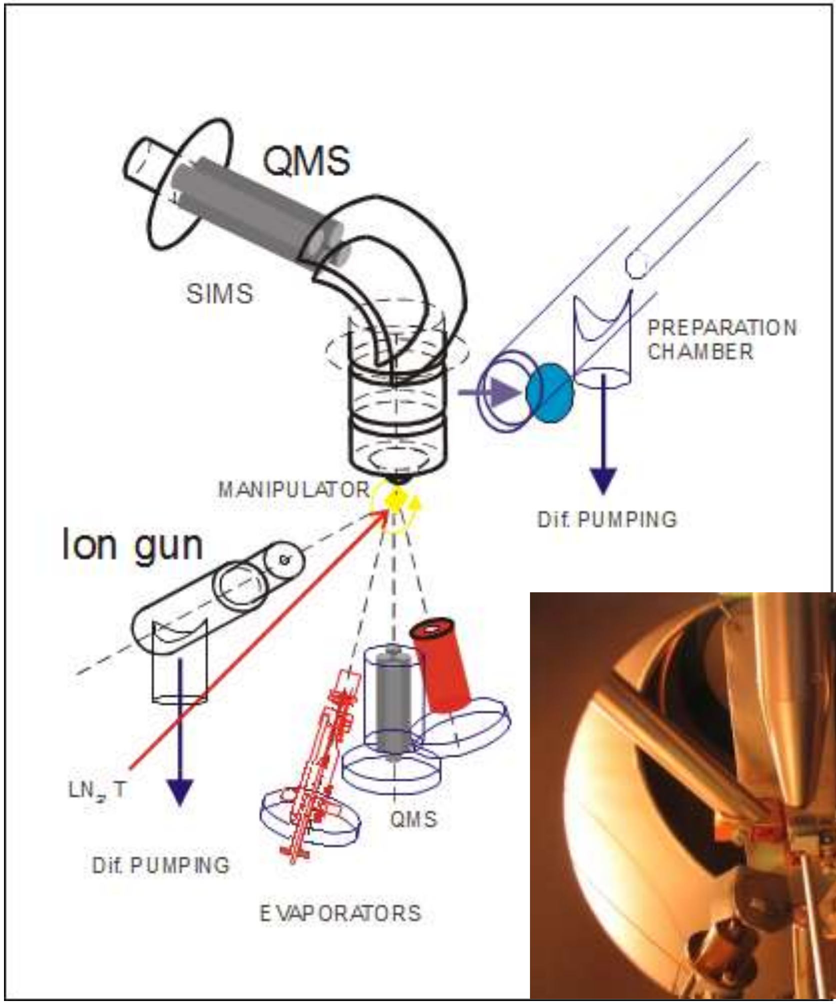
- Analysed material is sputered by primary ion beam and secondary ions are analysed by mass spectrometer.
- Very sensitive analysing method
- Strong matrix effect. Difficult quantitative analysis.
- Several modifications
  S-SIMS, D-SIMS, SNMS

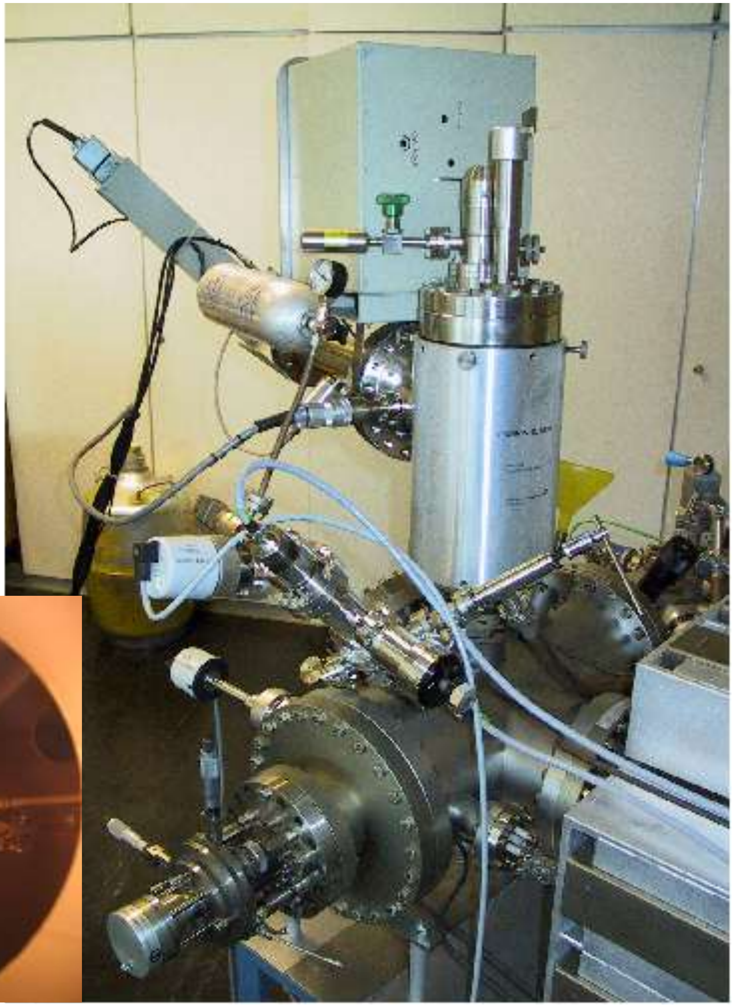
Molecular SIMS



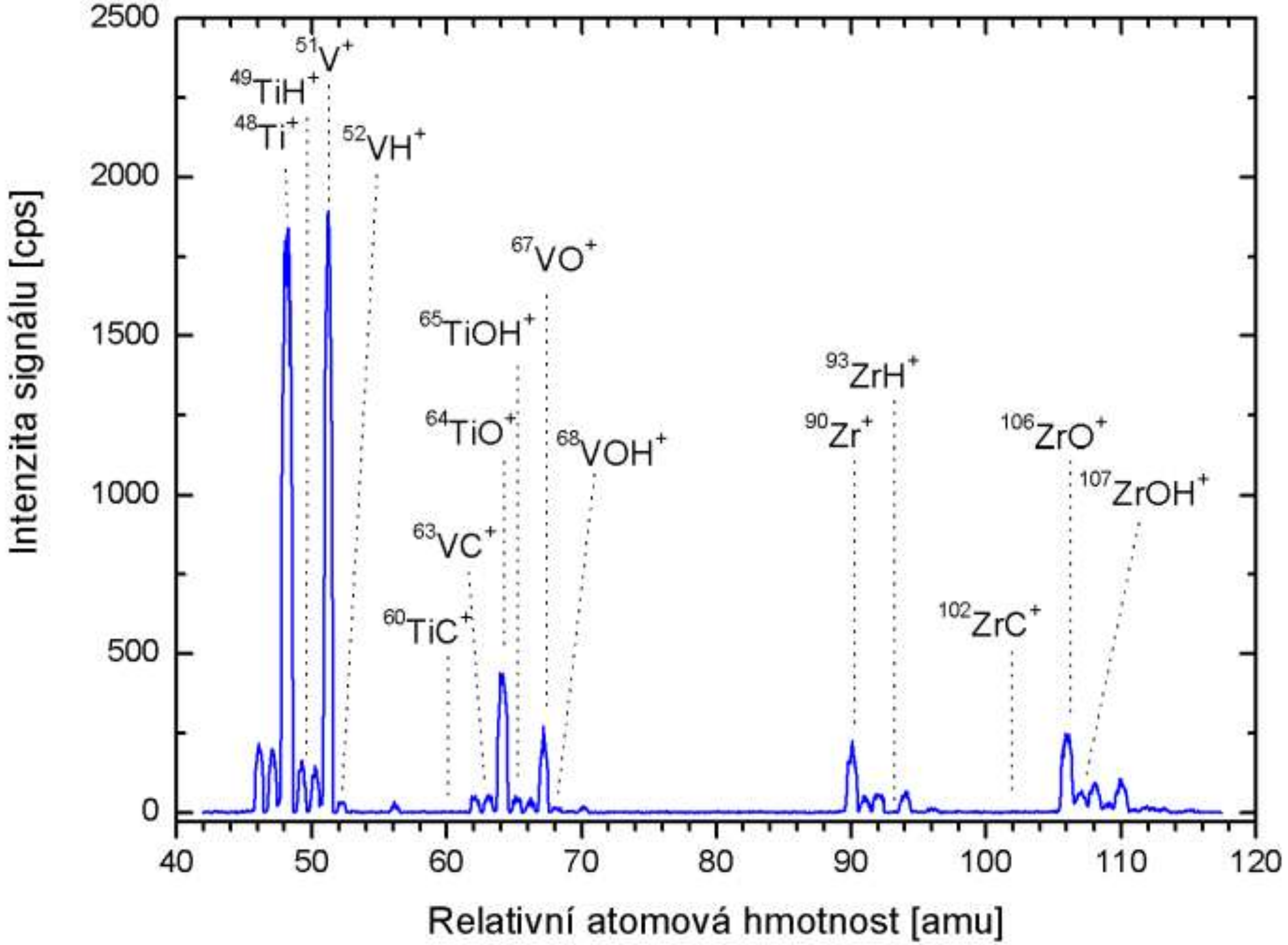


SIMS – Experimental system



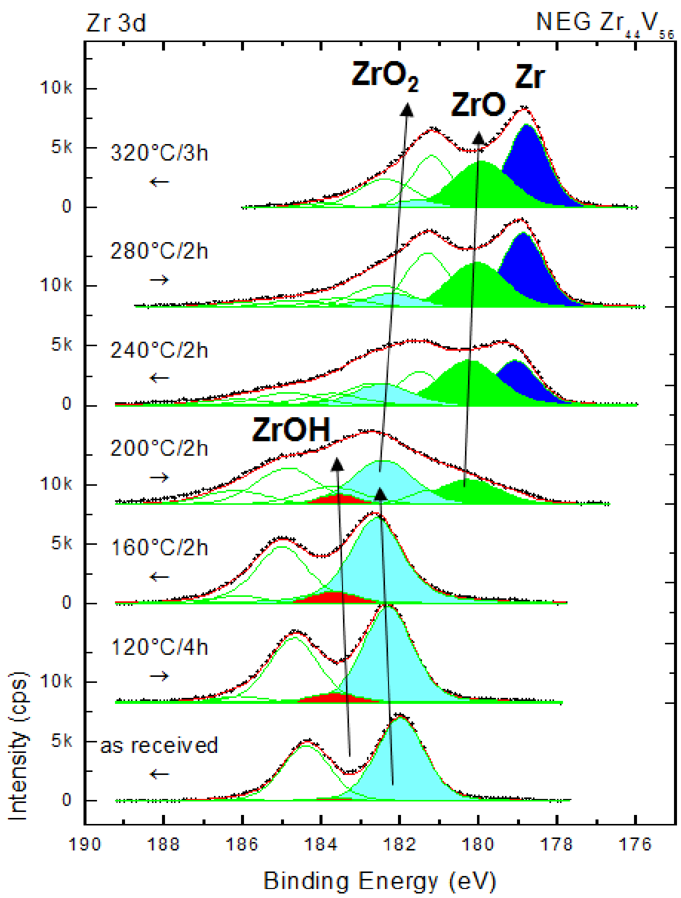


SIMS – experimental data



XPS

- Spectroscopy of secondary electrons generated by X-ray
- Info about bonds in the material
- More bulk than surface info
- Not simple decomposition of peaks
- Stoichiometry info by peak ratios
- Fixed X-ray energy

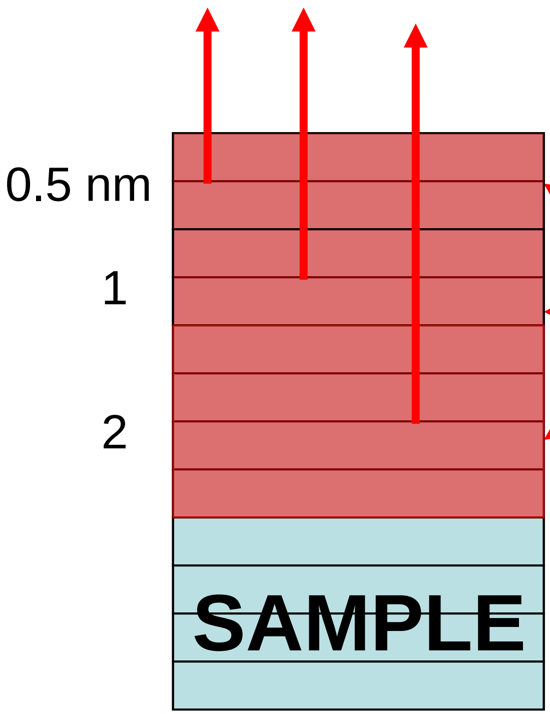


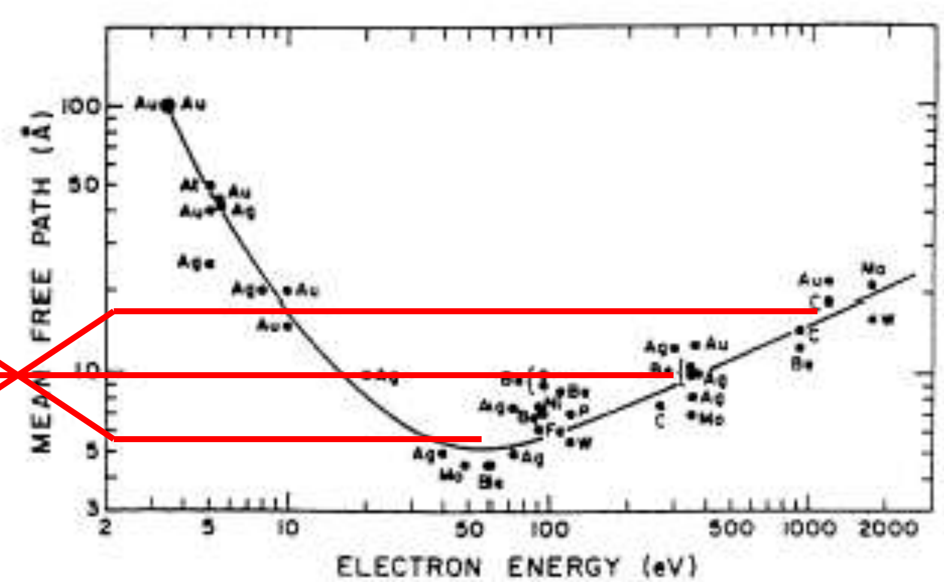
SRPES

- Tunable light source allows adjust information depth

SRPES depth profiling

Zr3d (BE = 180 eV)





65 = 250 - 180 – 5

415 = 600 - 180 – 5

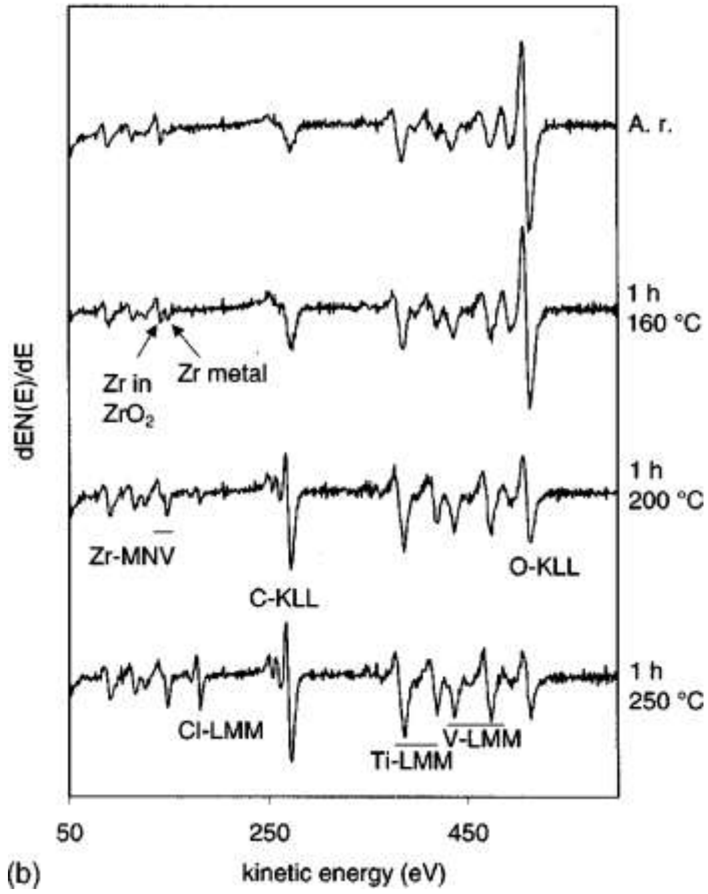
1068 = 1253 - 180 – 5

$$E_c = h\nu - BE - \Phi_s$$

AES – Auger Electron Spectroscopy

Used for quality of activation analysis by metal / oxidic peak ratio

Good spatial resolution due to precise focusing of primary electrons



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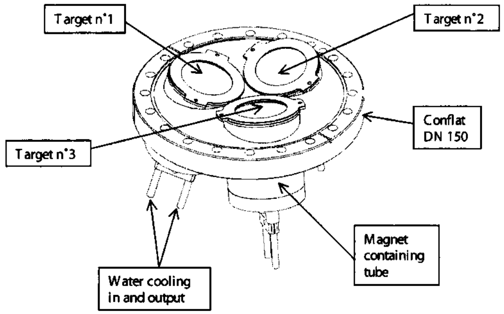
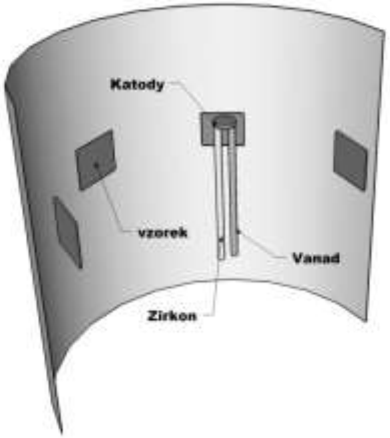
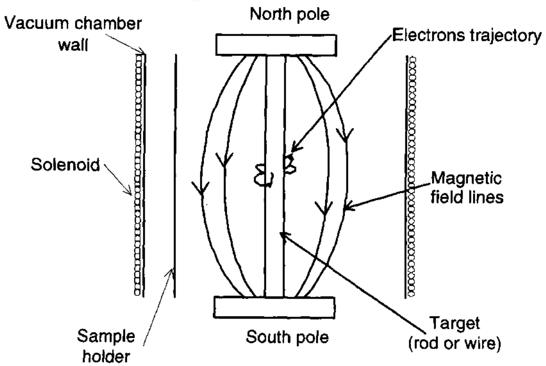
Preparation of the NEG layer

Magnetron sputtering

- Combination of planar magnetrons for precise control of sample stoichiometry.
- Double coaxial magnetron for tesing samples preparation.
- Coaxial magnetron for vacuum tubes coating for testing pumping properties of the NEG layer







SIMS analysis method

- **SSIMS** – static condidtions
- Ratio MX^+/M^+ is lineary corelated with surface coverage of MX and indeúendent to local work function

Relevant ratios for Ti-Zr-V getters

$^{49}(TiH^+)/^{48}Ti^+$

$^{64}(TiO^+)/^{48}Ti^+$

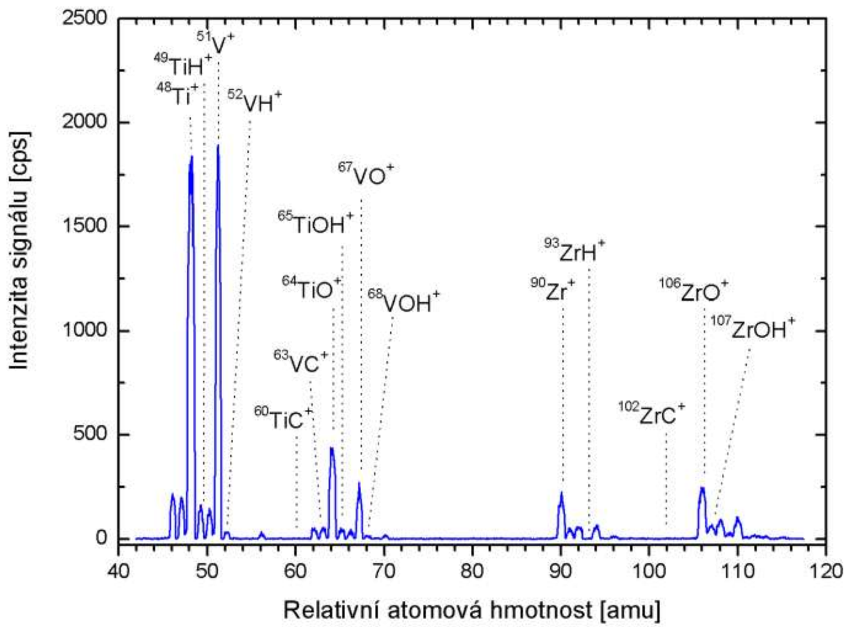
$^{93}(ZrH^+)/^{90}Zr^+$

$^{106}(ZrO^+)/^{90}Zr^+$

$^{52}(VH^+)/^{51}V^+$

$^{67}(VO^+)/^{51}V^+$

Peak surface instead of peak height have been used to improve S/N ratio



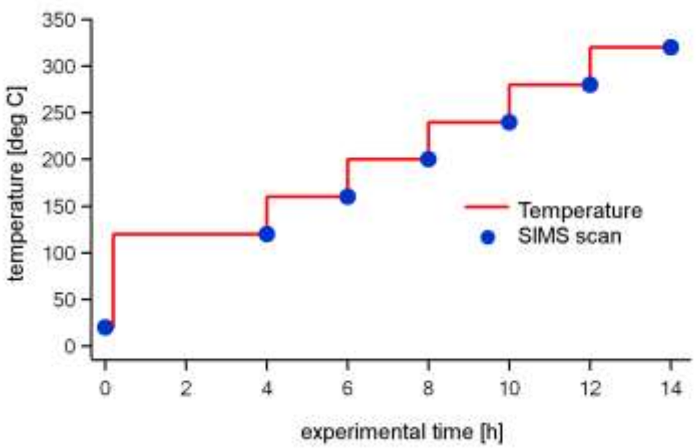
- **DSIMS** – depth profiling, apllyied for several samples only to check the under surface region. Compared to SRPES results.

Samples

Sample No	composition(%)	substrate	type of experiment	sample source
220A	Zr (100)	Cu	step activation	CERN
221A	Ti (100)	Cu	step activation	CERN
222A	V (100)	Cu	step activation	CERN
223A	TiZrV (30:30:40)	Cu	2x step activation	CERN
224A	ZrV (50:50)	Cu	step activation	CERN
225A	TiZr (50:50)	Cu	step activation	CERN
ZrV_03	ZrV (44:56)	nerez	step activation	KEVF
PN01_02	ZrV (64:36)	nerez	continuous activation	KEVF
PN04_03	TiZrV (25:50:25)	nerez	step and cont. activation	KEVF

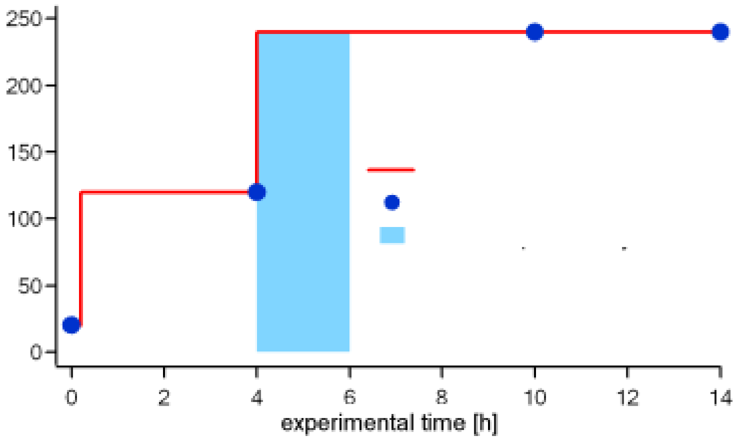
Activation processes

Step activation



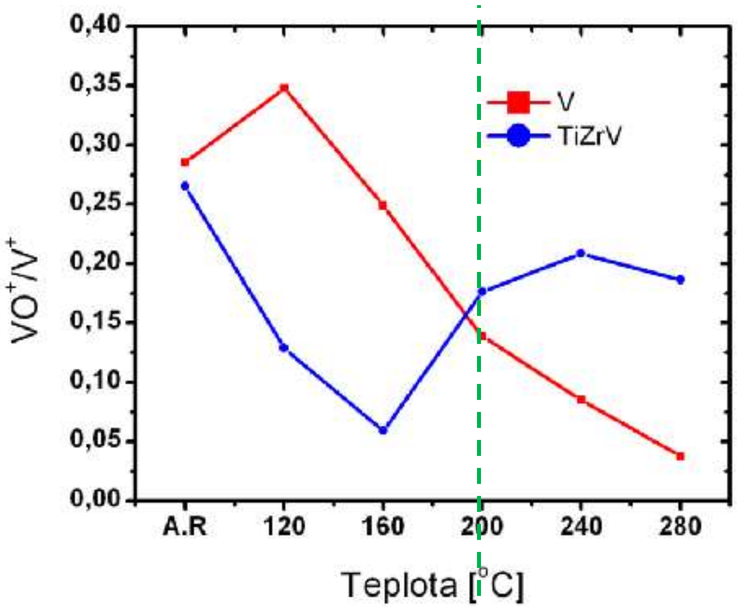
- Degas at 120 °C for 4 h
- 40°C / 2h steps
- SSIMS scan at relevant points
- DSIMS profile in some cases

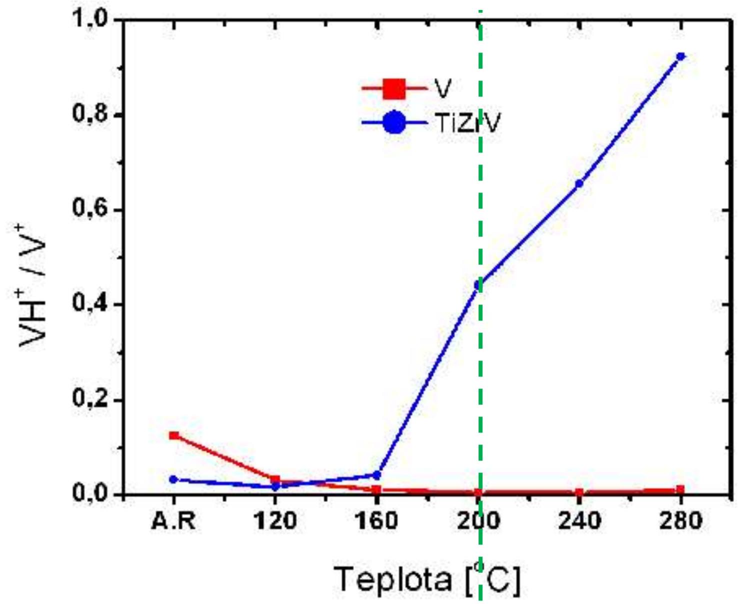
Continuous activation

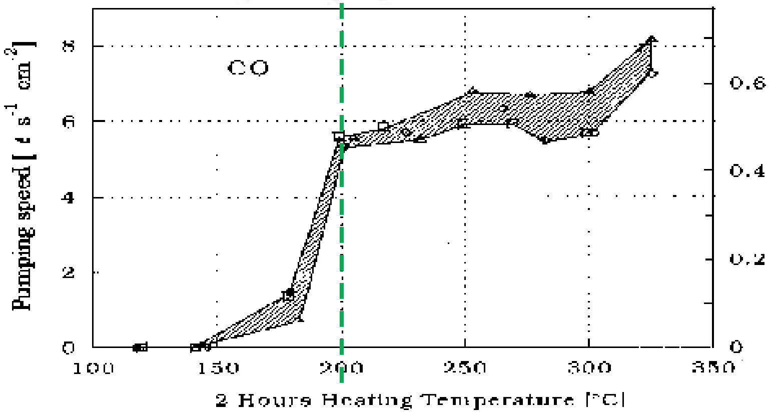


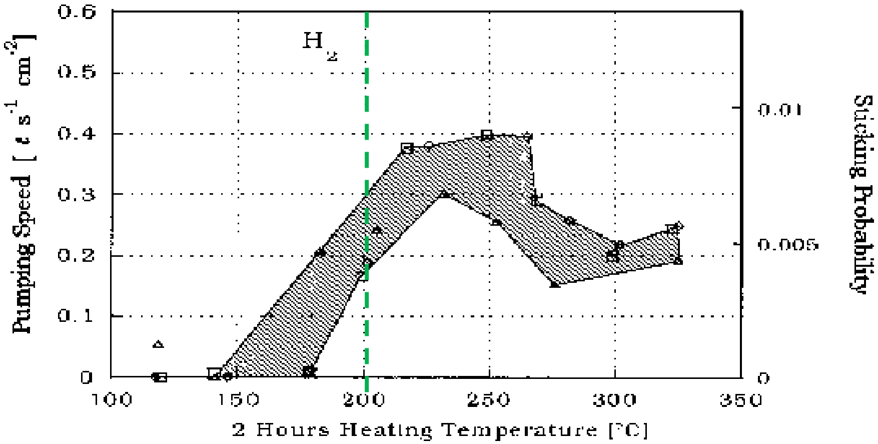
- Degas at 120 °C for 4 h
- Activation at 240°C
- SSIMS scan at relevant points
- SSIMS record after activation starts
- DSIMS profile in some cases

Vanadium and its properties



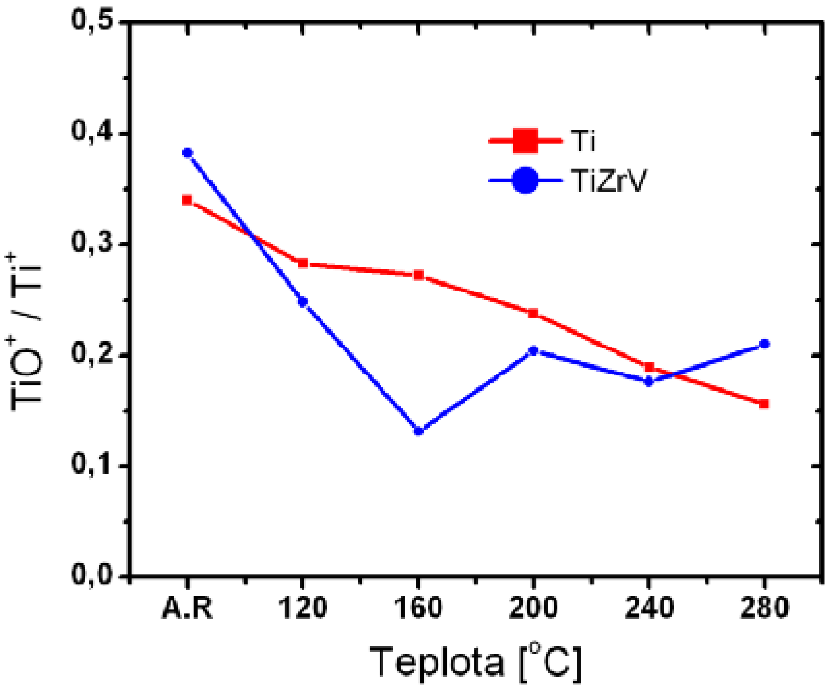




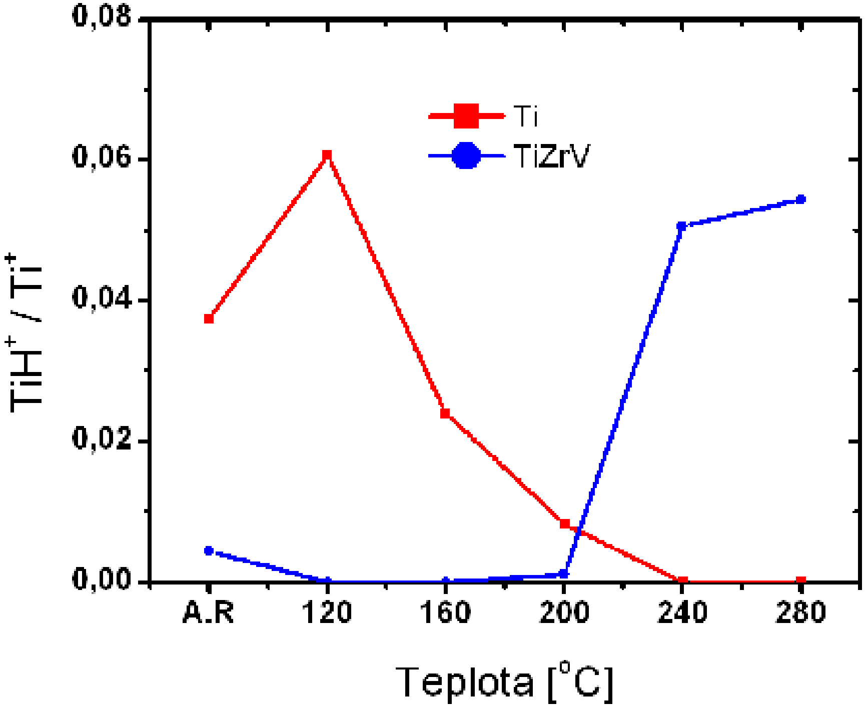


Převzato z Ruzinov V., Scheuerlein C., Taborelli M. Benvenuti C., Chiggiato P., Mongelluzzo, A., Prodromides A. Journal of Vacuum Science and Technology A, 19:2925, 2001.

Titanium

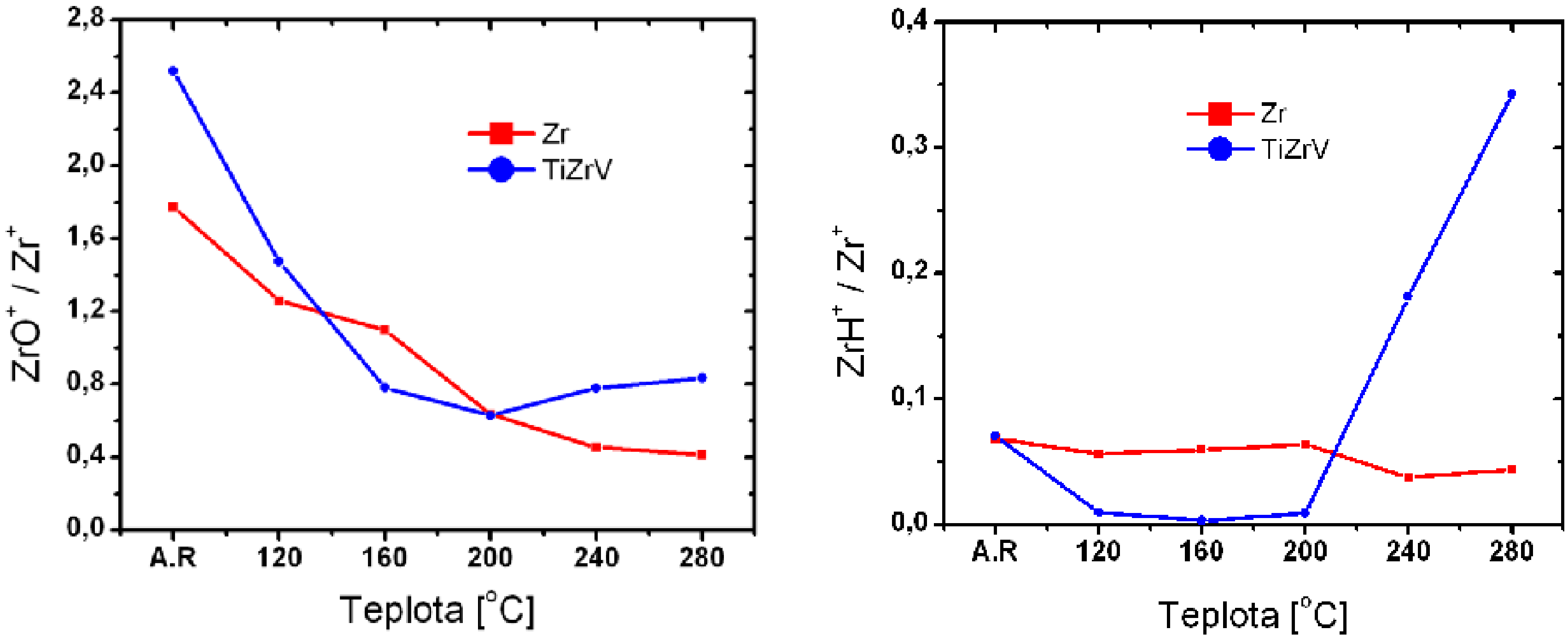


0,5
0,4
0,3
0,2
0,1
0,0
TiO^+ / Ti^+
Ti
TiZrV
A.R
120
160
200
240
280
Teplota [°C]

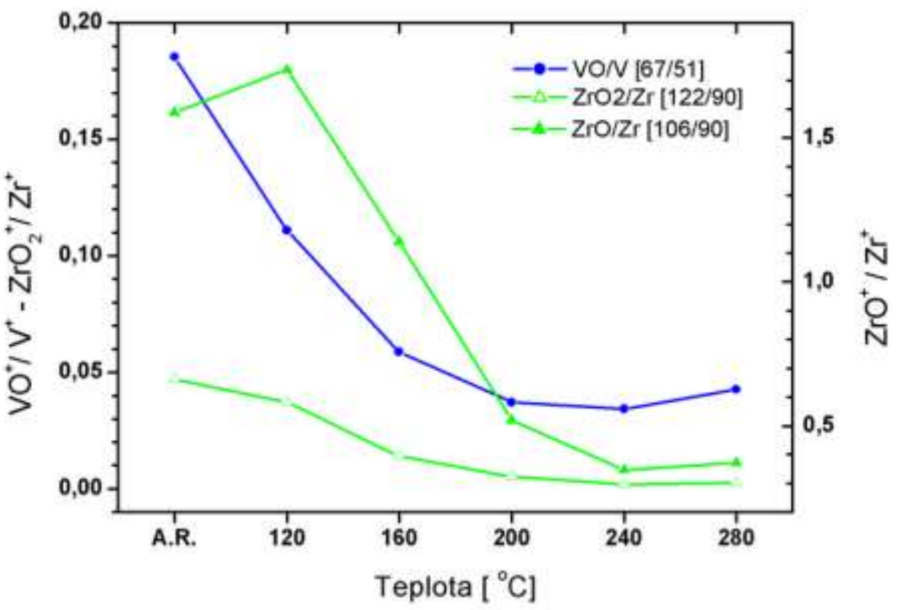


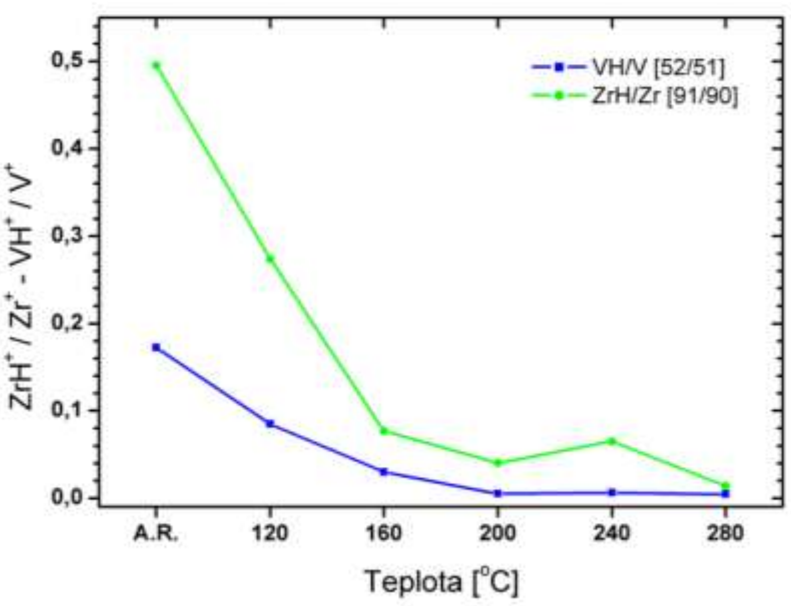
0,08
0,06
0,04
0,02
0,00
TiH^+ / Ti^+
Ti
TiZrV
A.R
120
160
200
240
280
Teplota [°C]

Zirconium

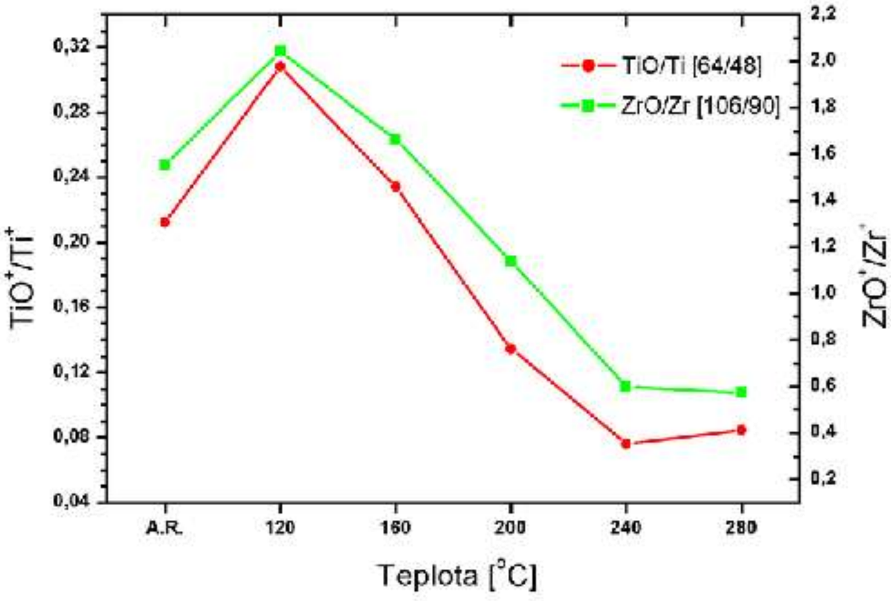

2,8
2,4
2,0
1,6
1,2
0,8
0,4
0,0
ZrO+ / Zr+
Zr
TiZrV
A.R
120
160
200
240
280
Teplota [°C]
0,4
0,3
0,2
0,1
0,0
ZrH+ / Zr+
Zr
TiZrV
A.R
120
160
200
240
280
Teplota [°C]

ZrV (50/50)


0,20
0,15
0,10
0,05
0,00
VO+/ V+ - ZrO2+/ Zr+
1,5
1,0
0,5
ZrO+ / Zr+
VO/V [67/51]
ZrO2/Zr [122/90]
ZrO/Zr [106/90]
A.R.
120
160
200
240
280
Teplota [°C]


0,5
0,4
0,3
0,2
0,1
0,0
ZrH+ / Zr+ - VH+ / V+
VH/V [52/51]
ZrH/Zr [91/90]
A.R.
120
160
200
240
280
Teplota [°C]

TiZr (50/50)


TiO/Ti [64/48]
ZrO/Zr [106/90]
TiO+/Ti+
ZrO+/Zr+
0,32
0,28
0,24
0,20
0,16
0,12
0,08
0,04
2,2
2,0
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
A.R.
120
160
200
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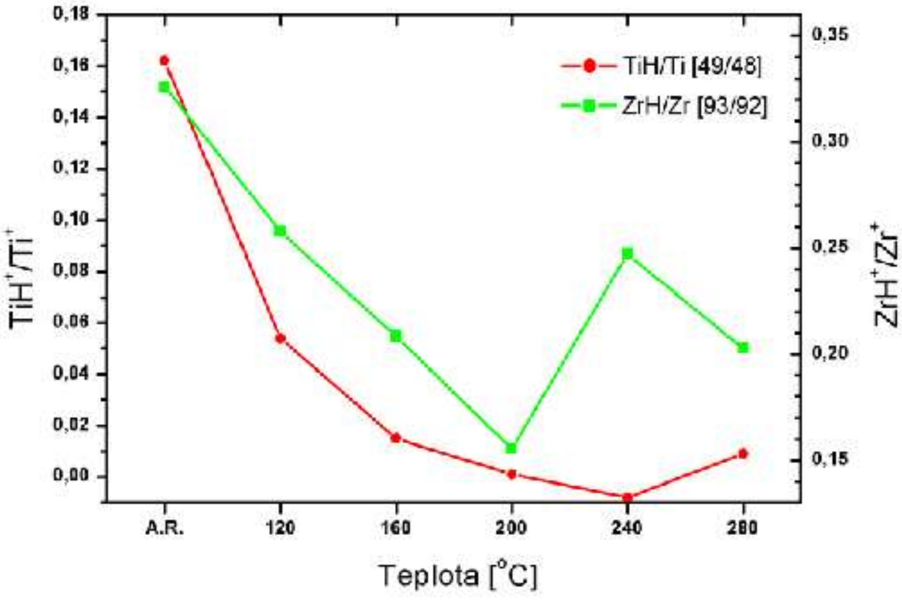
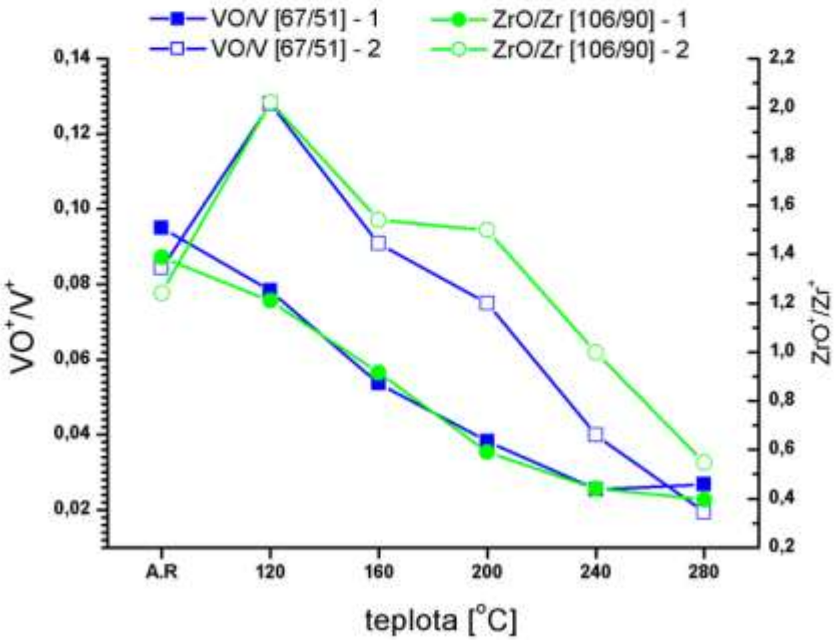
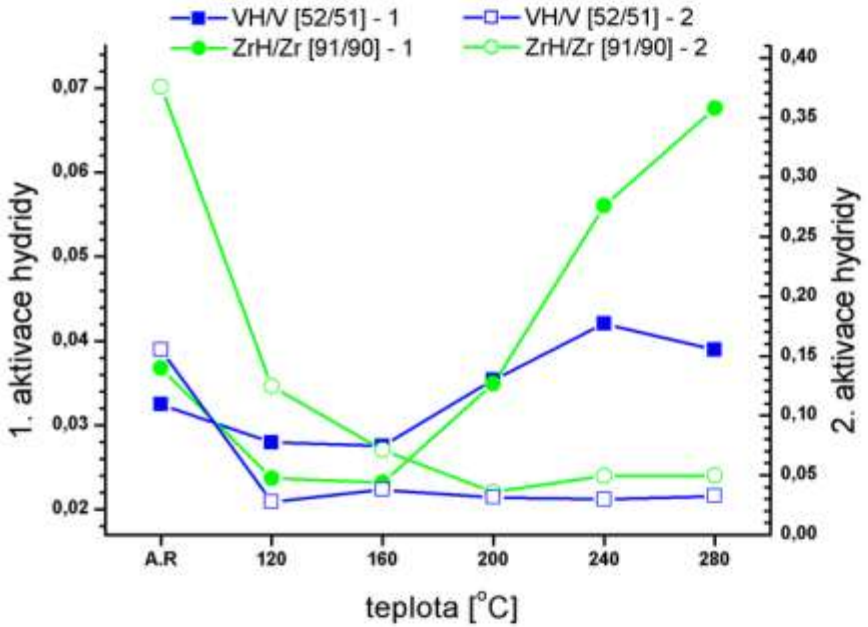
Teplota [°C]


TiH/Ti [49/48]
ZrH/Zr [93/92]
TiH+/Ti+
ZrH+/Zr+
0,18
0,16
0,14
0,12
0,10
0,08
0,06
0,04
0,02
0,00
0,35
0,30
0,25
0,20
0,15
A.R.
120
160
200
240
280
Teplota [°C]

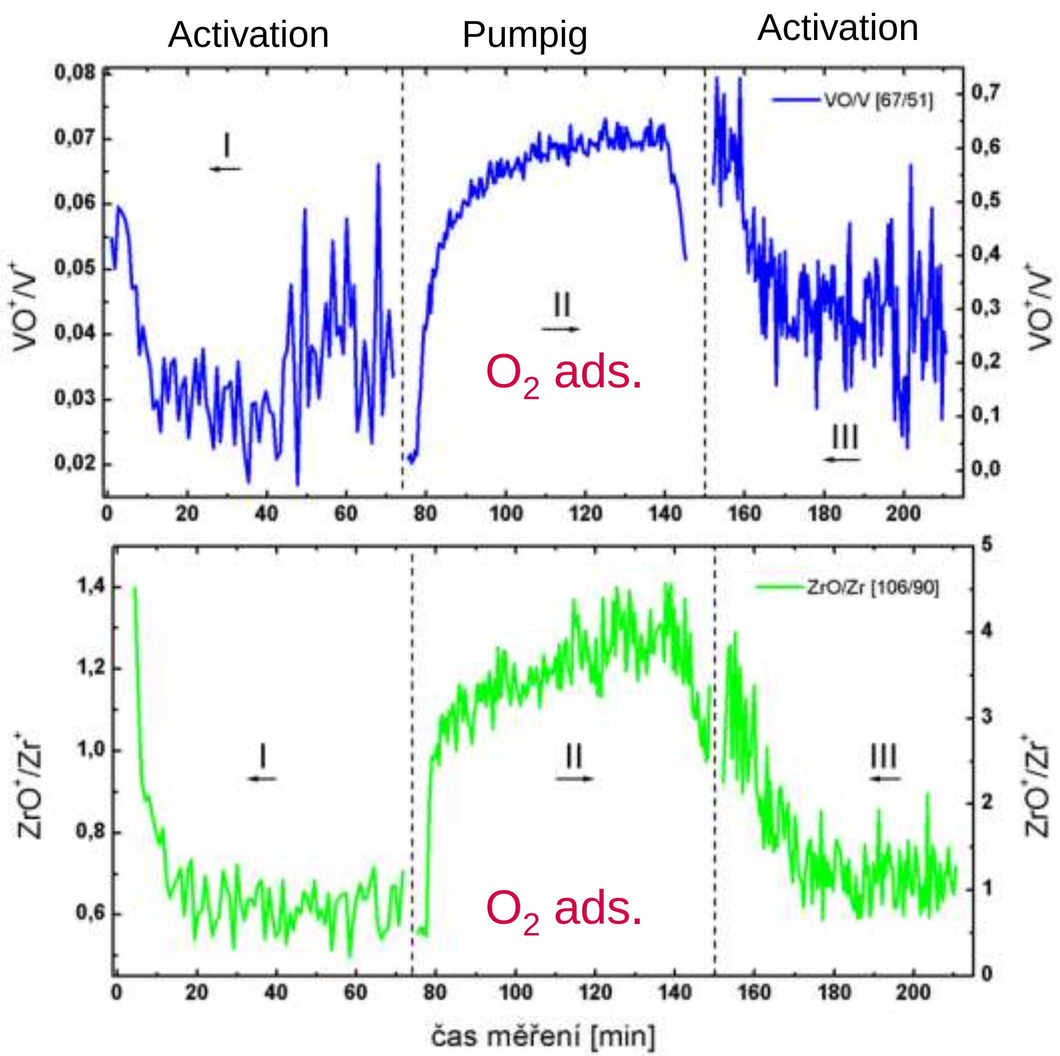
ZrV – 1st and 2nd activation





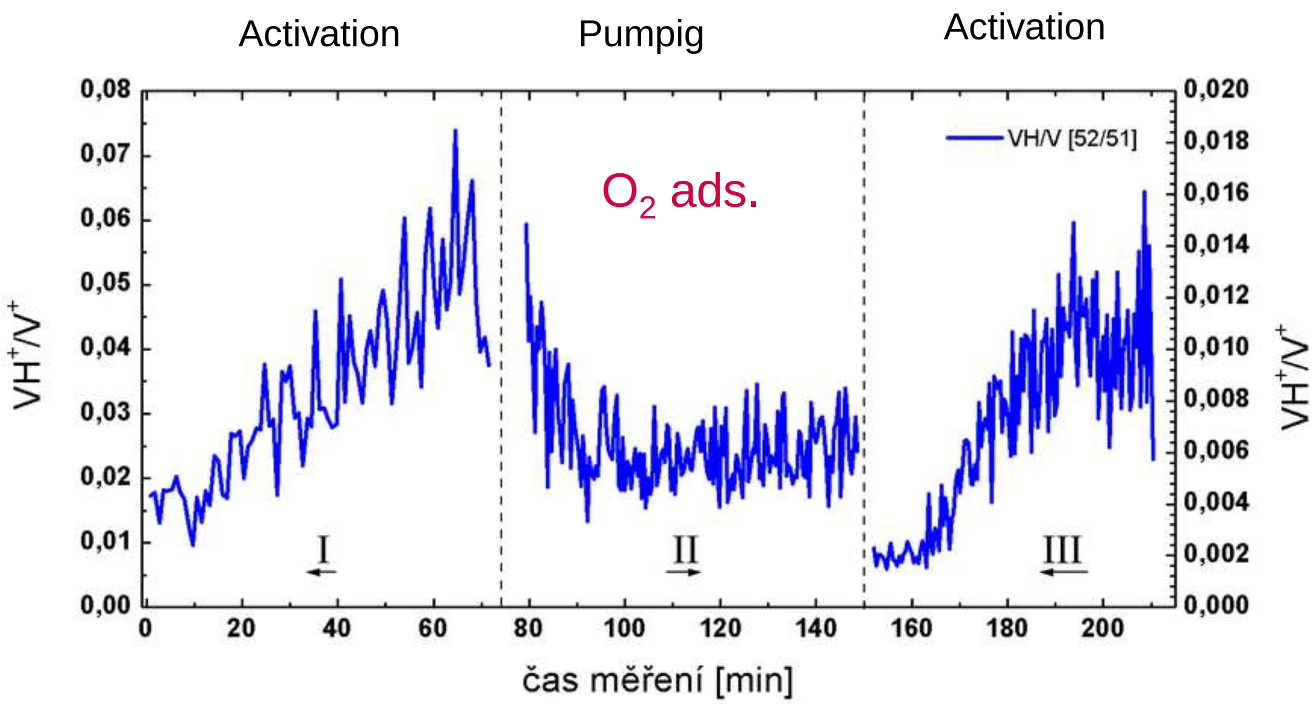
Activation – Pumping – Reactivation process

ZrV sample



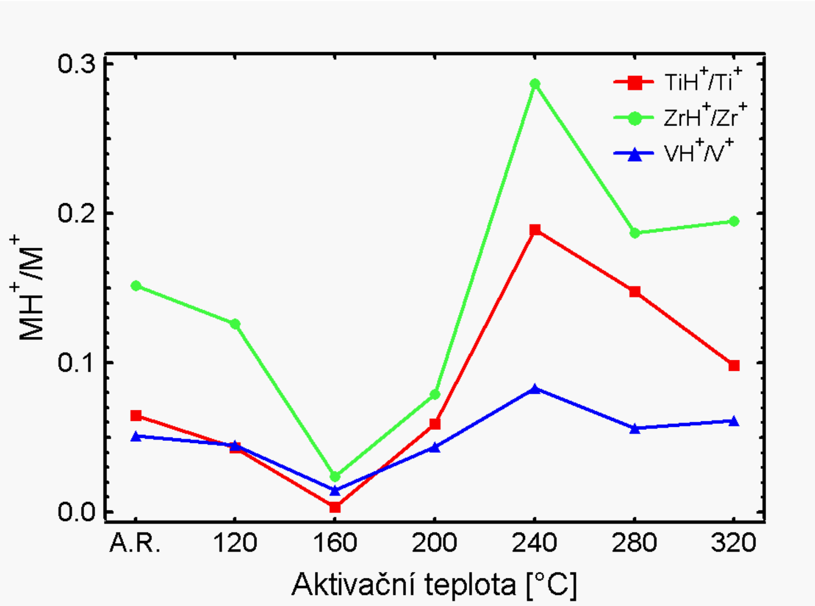
Activation – Pumping – Reactivation process

ZrV sample

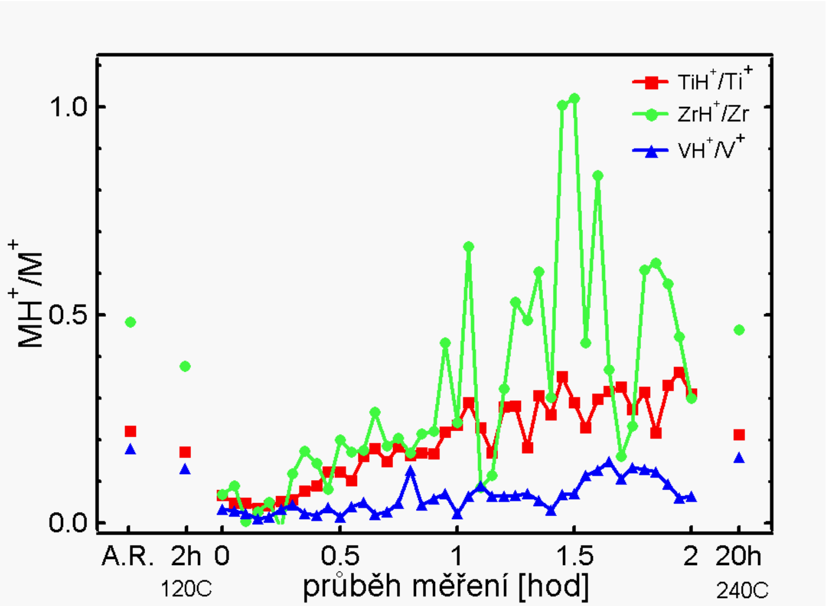


TiZrV – activation compare

Step activation



Continuous activation



 • Jiri Drbohlav, 22.11.2011

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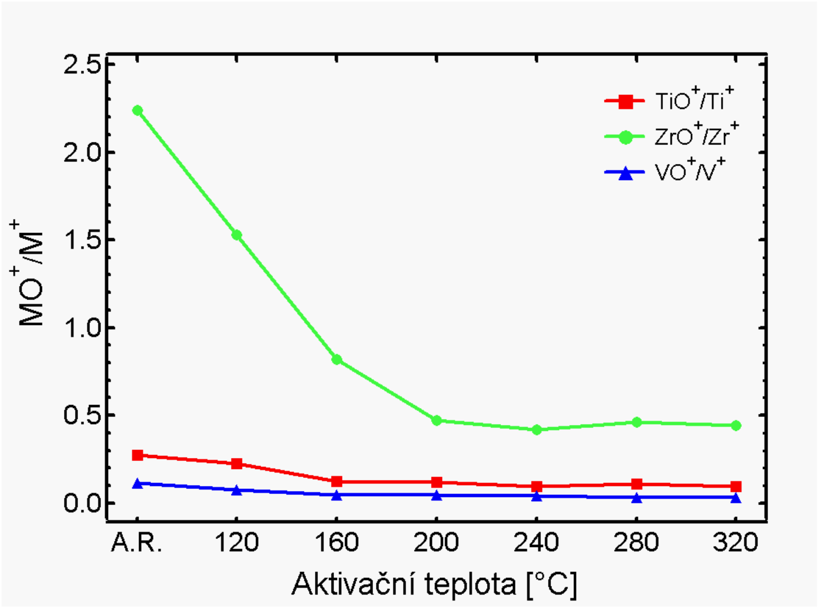
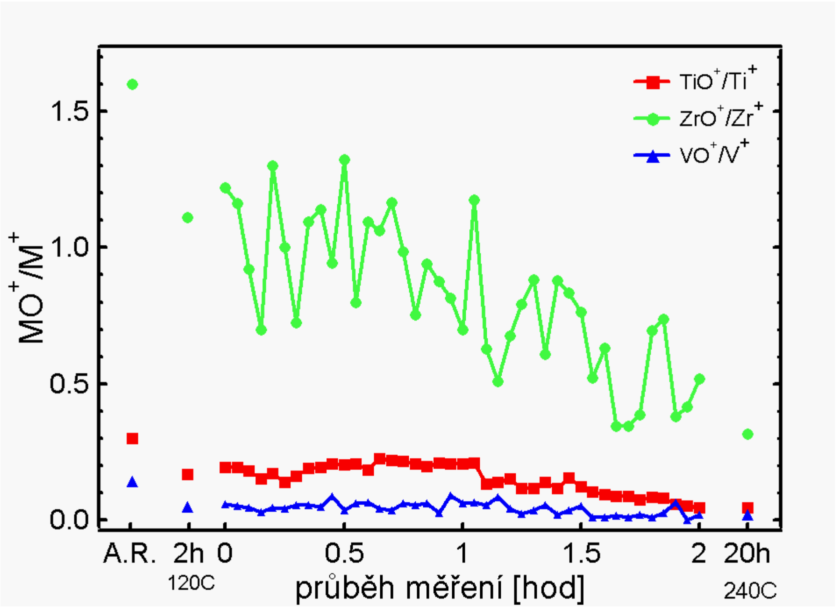
TiZrV – activation compare

Step activation



Continuous activation



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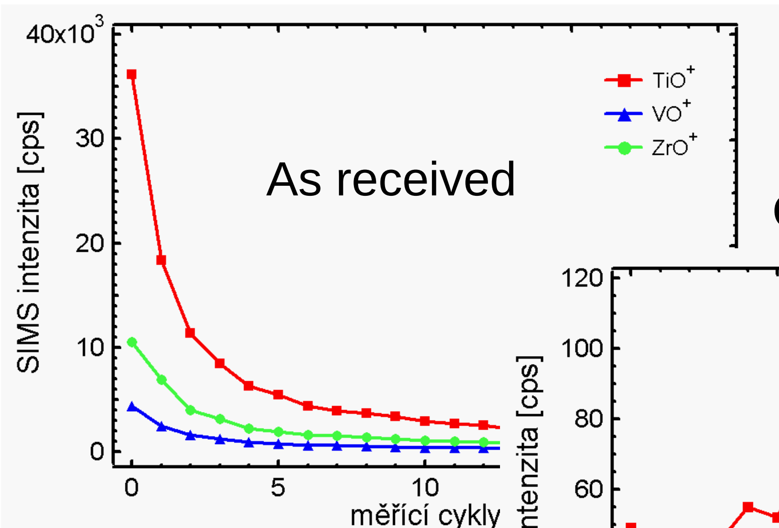
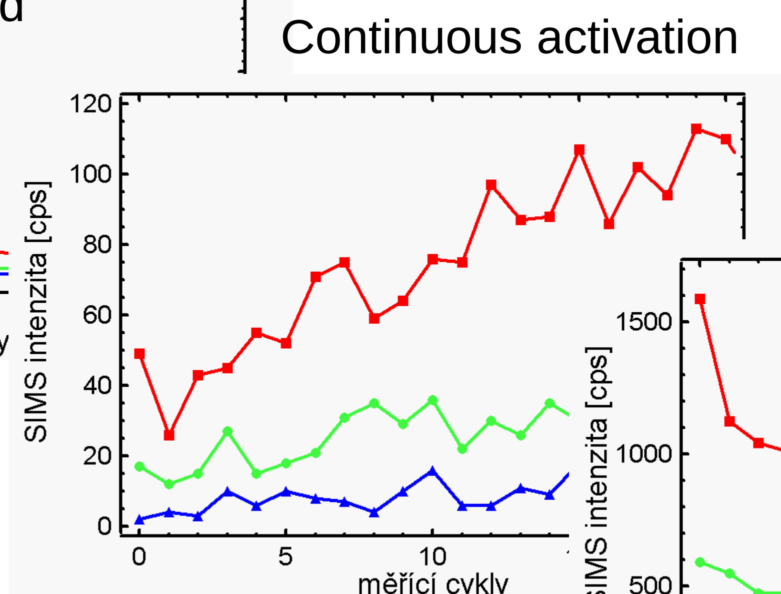
TiZrV - DSIMS depth profiles

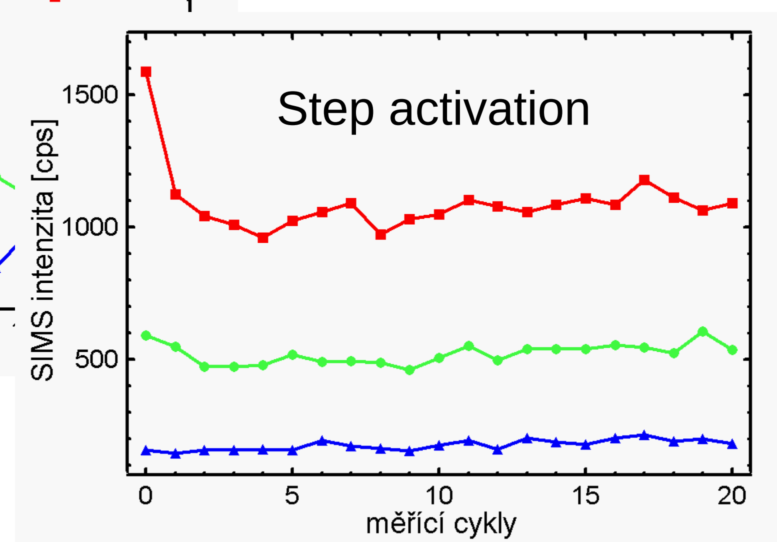
DSIMS depth profile

I_p=500nA, E_p=3 keV

S=2 mm^2, d=6 nm







Conclusions

- SSIMS and DSIMS are very good tools for studies of NEG activation process
- SIMS experimental data are consistent with other experimental techniques (SRPES) results
- NEGs are materials suitable to generate XHV environment in rarely venting systems.
- Vacuum pumps based on NEGs are nicely complementally to conventional pumps
- NEG based on TiZrV alloys decreases desorption rates from coated surfaces of the vacuum chamber

Coworkers

- Prof. Vladimír Matolín – team leader
- Doc. Karel Mašek
- Dr. František Šutara
- Doc. Iva Matolínová

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THANK YOU !