Novel methods for NEG film and vacuum chamber production:

Development of copper electroformed NEG coated vacuum chambers

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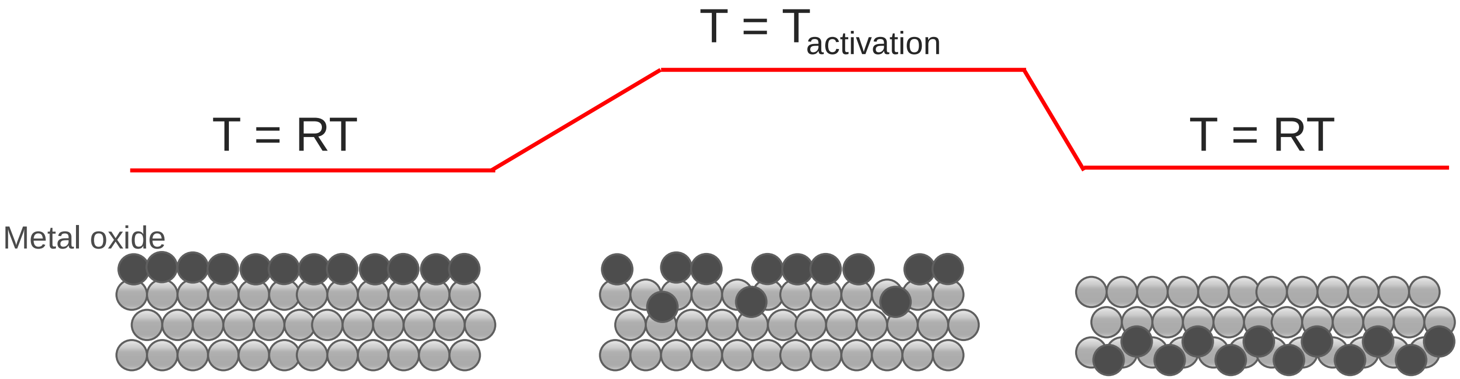
Outline

1. **Introduction**
2. Motivation
3. Reverse coating technique
4. Challenges
5. Preparation for real application
6. Conclusions & Outlook

Non evaporable getter (NEG)

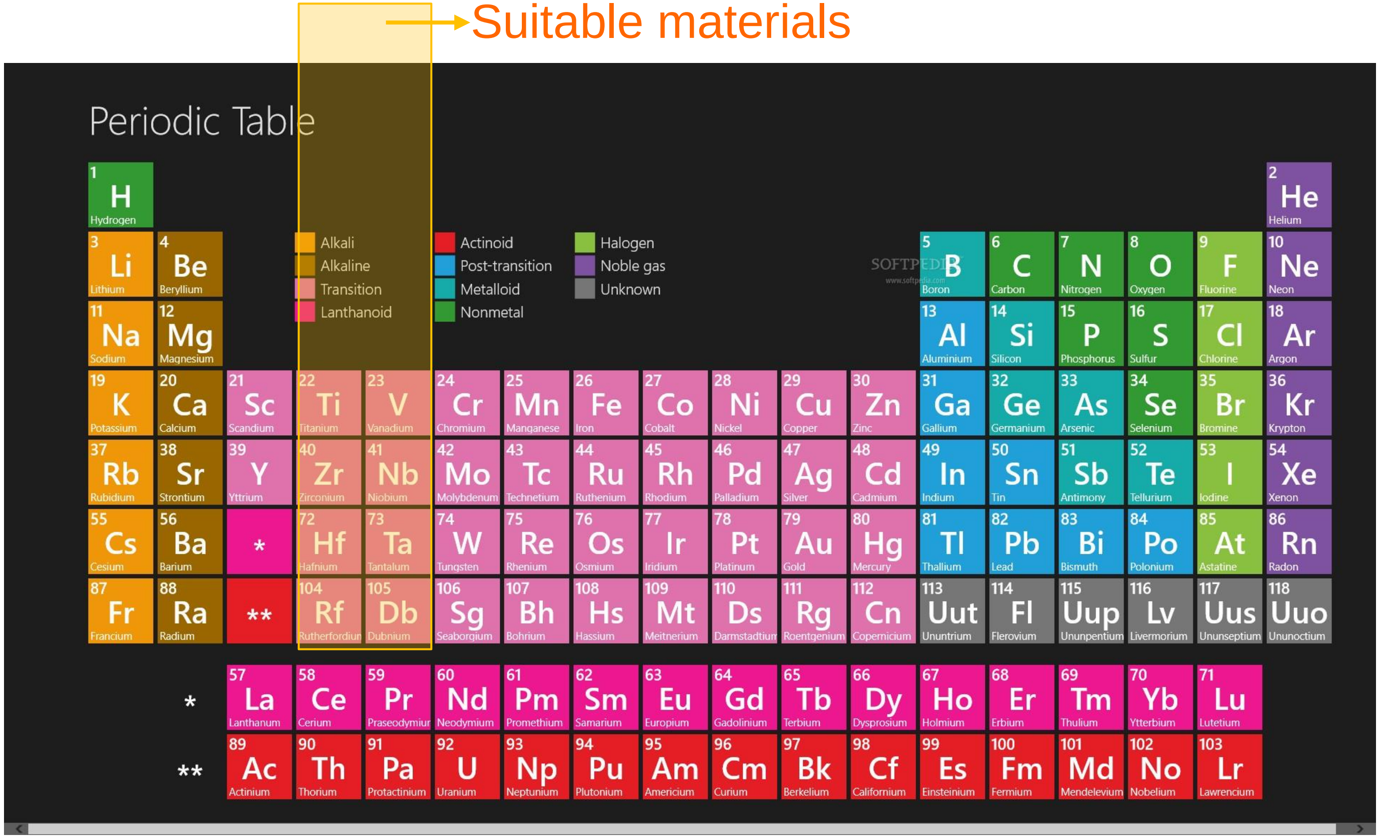
Non Evaporable Getter are materials than can pump residual gaseous molecules after thermal activation in vacuum.

During the activation, the surface oxygen diffuses inside the bulk.



Non evaporable getter (NEG)

Suitable materials: High oxygen solubility limit and oxygen diffusivity.
TiZrV alloys are used at CERN.



Suitable materials

Periodic Table

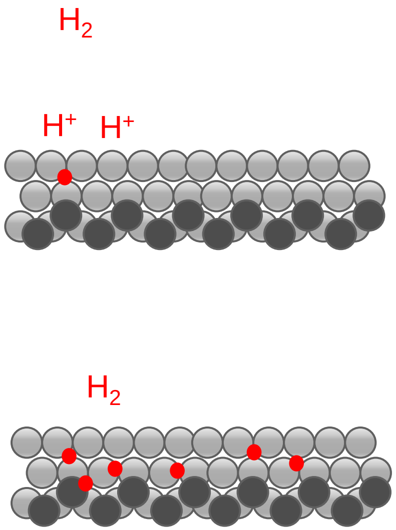
- Alkali
- Alkaline
- Transition
- Lanthanoid
- Actinoid
- Post-transition
- Metalloid
- Nonmetal
- Halogen
- Noble gas
- Unknown

1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	*	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	**	104 Rf Rutherfordiun	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtiun	111 Rg Roentgenium	112 Cn Copernicium	113 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium
	*	57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymiur	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium	
	**	89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium	

Non evaporable getter (NEG)

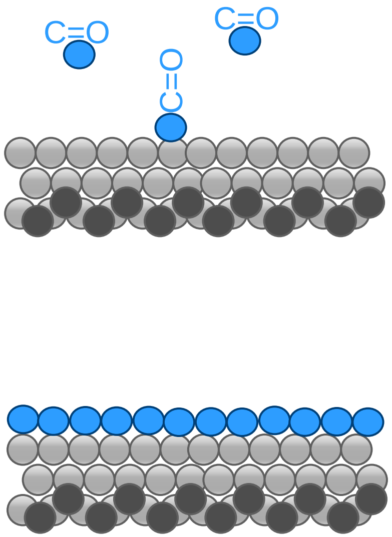
Once activated in vacuum, it can pump residual gaseous molecules (H_2, N_2, CO and CO_2). Neither CH_4 nor noble gases are pumped.

H_2 is diffused into the bulk



Saturation after 1×10^{18} molecules/cm^2

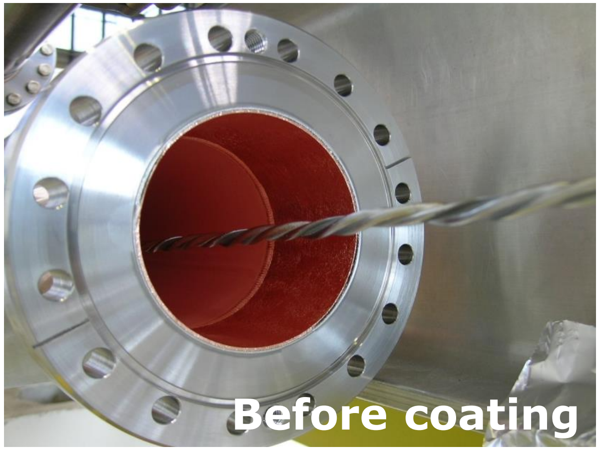
CO is adsorbed in the surface

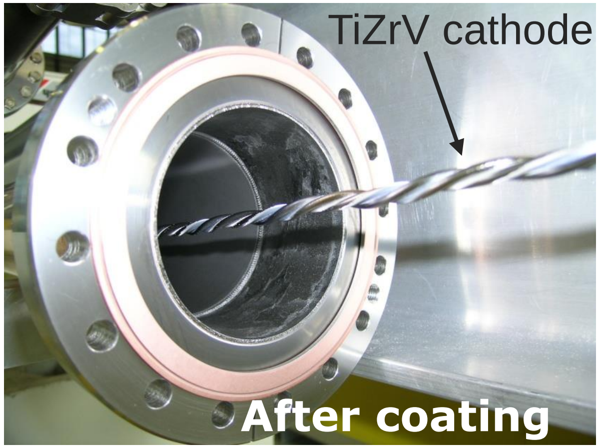


Saturation after 1×10^{15} molecules/cm^2

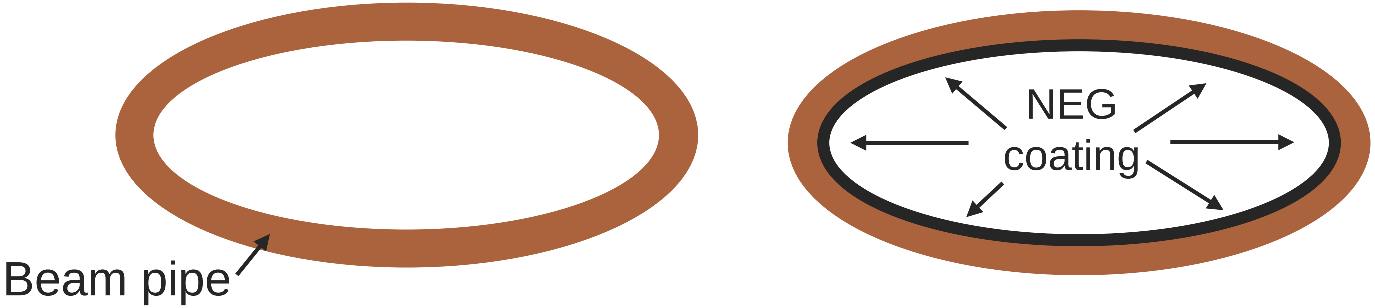
NEG thin film coating

NEG thin film coating, born at CERN, is usually done via applying DC magnetron sputtering on a twisted Ti, Zr, V wire cathode that is positioned on the centre.





NEG is deposited via DC Magnetron Sputtering



NEG thin film coating

NEG thin film coating has been extensively applied in the LHC.

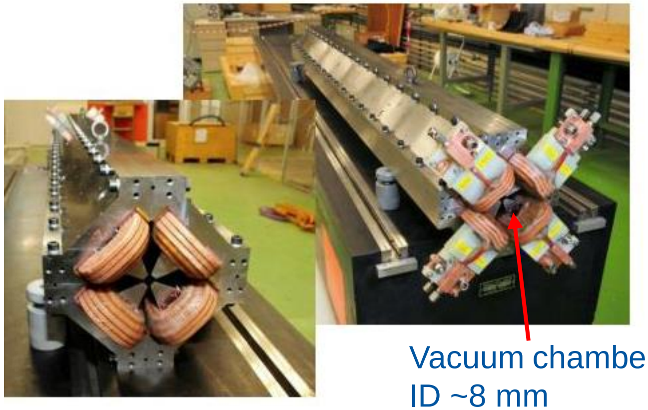
About 1200 vacuum chambers of roughly 6 Km of long straight section beam pipe have been coated at CERN.

Outline

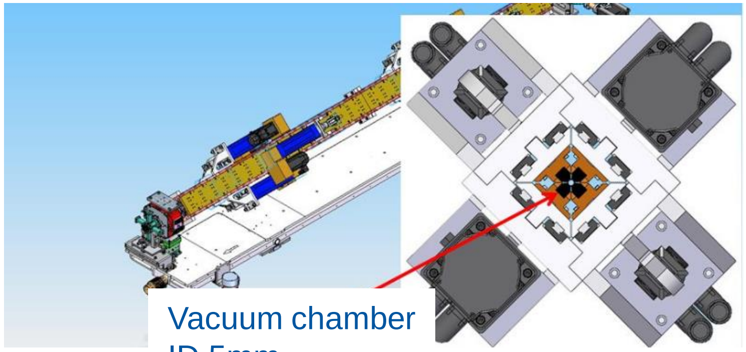
1. Introduction
2. **Motivation**
3. Reverse coating technique
4. Challenges
5. Preparation for real application
6. Conclusions & Outlook

Motivation

M. Modena et al. (2014)
CLIC MB quadrupole [1]



H. D. Nuhn et al., Presentation at FLS (2012),
Delta undulator, SLAC



New upgrades in accelerators require the use of vacuum chambers with very small apertures.

- The small vacuum chamber aperture has a big impact on the vacuum system because the conductance of the vacuum pipe is reduced.
- An approach with distributed pumping , as getter coating, is needed to keep the pressure low.

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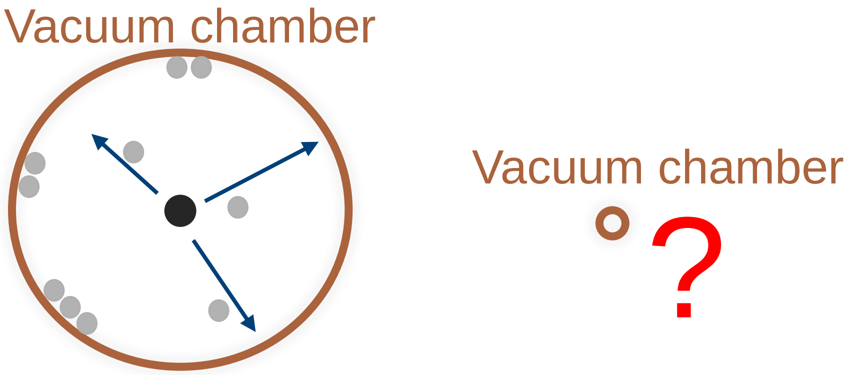
[1] http://clic-study.web.cern.ch

NEG thin film coating

Physical vapor deposition techniques are difficult to apply to indefinitely small pipe diameters (the typical limit is about 8-10 mm diameter). Lack of space for the cathode and difficulty to maintain a stable plasma.

The latter and the coating of complex shape require specific developments. A possible solution is evaluated in the present work.



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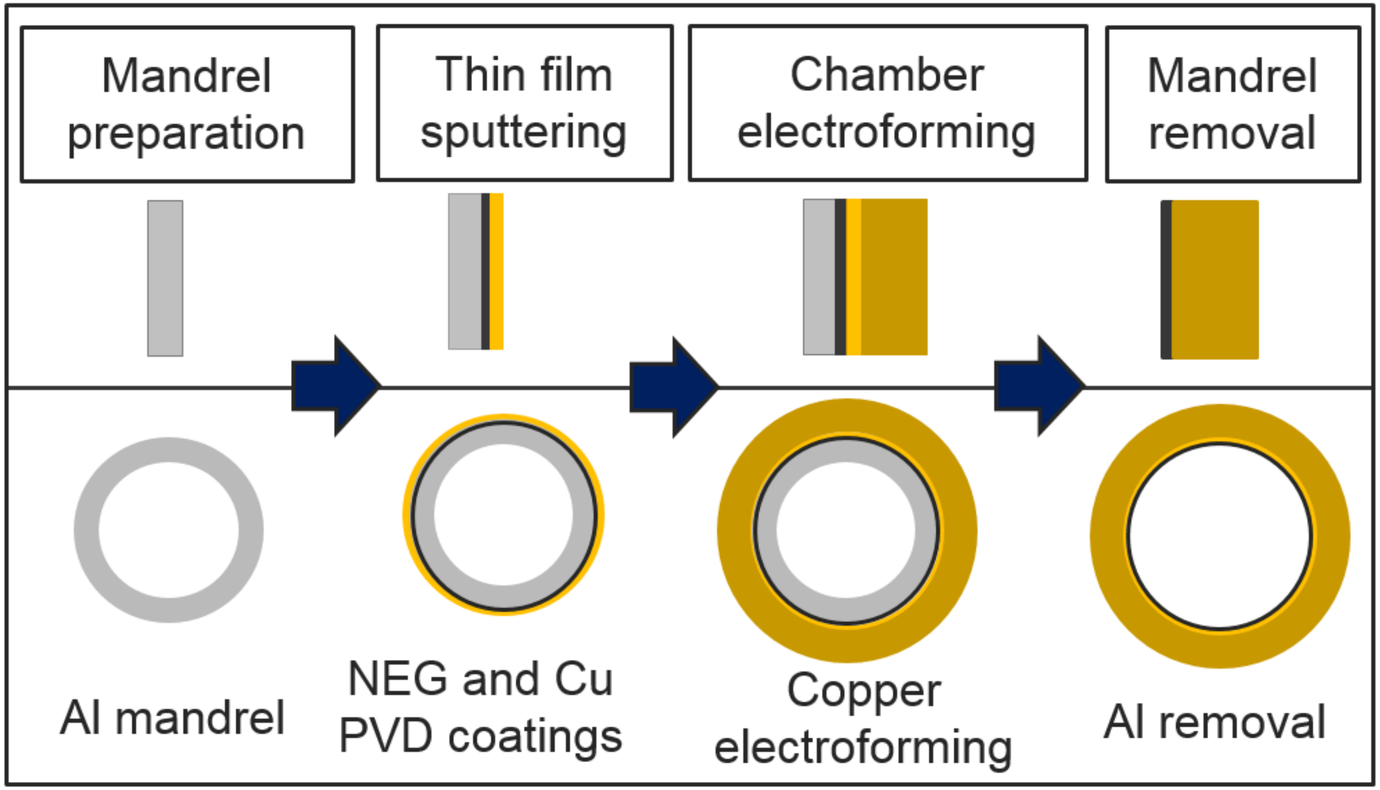
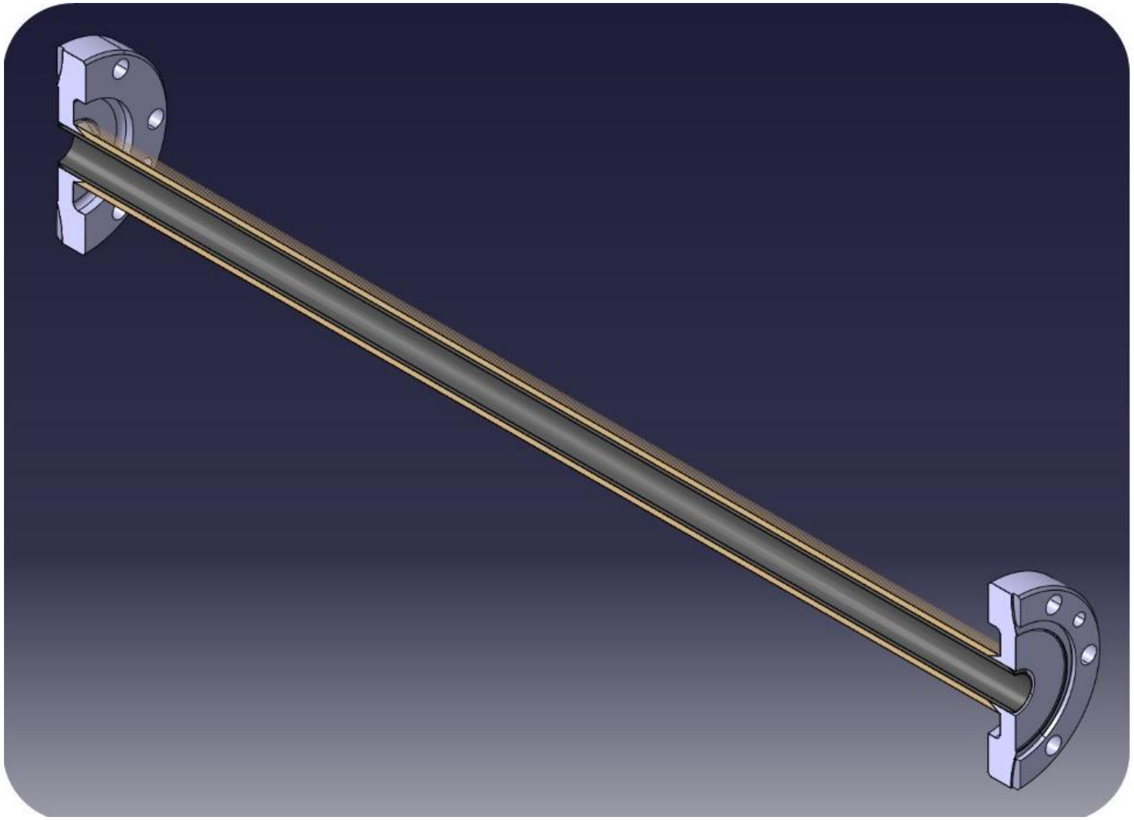
Reverse coating technique

The vacuum chamber is produced by copper electroforming around a sacrificial aluminium mandrel which is pre-coated with a NEG thin film.



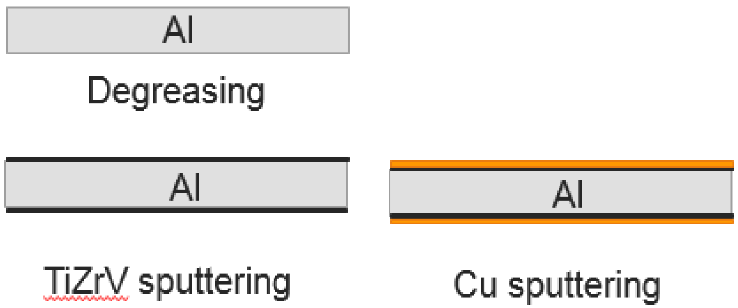
Reverse coating technique

During the electroforming, the stainless steel flanges are assembled to the chamber. Neither brazing nor EB welding are needed.

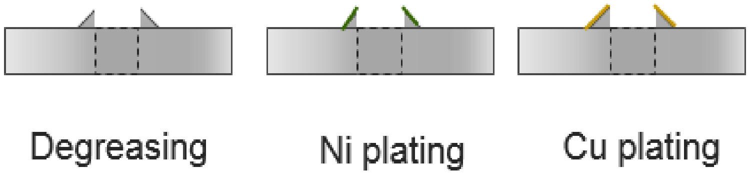


Chamber manufacturing procedure

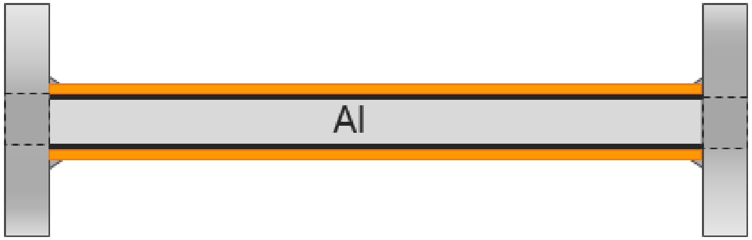
1 Mandrel preparation



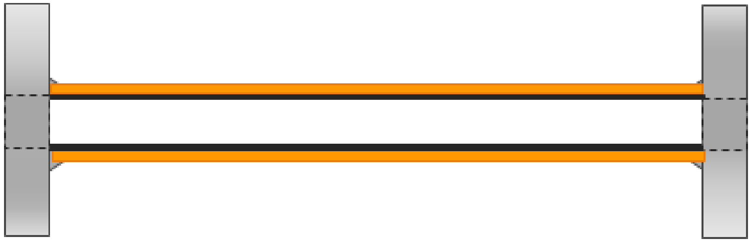
2 Flange preparation



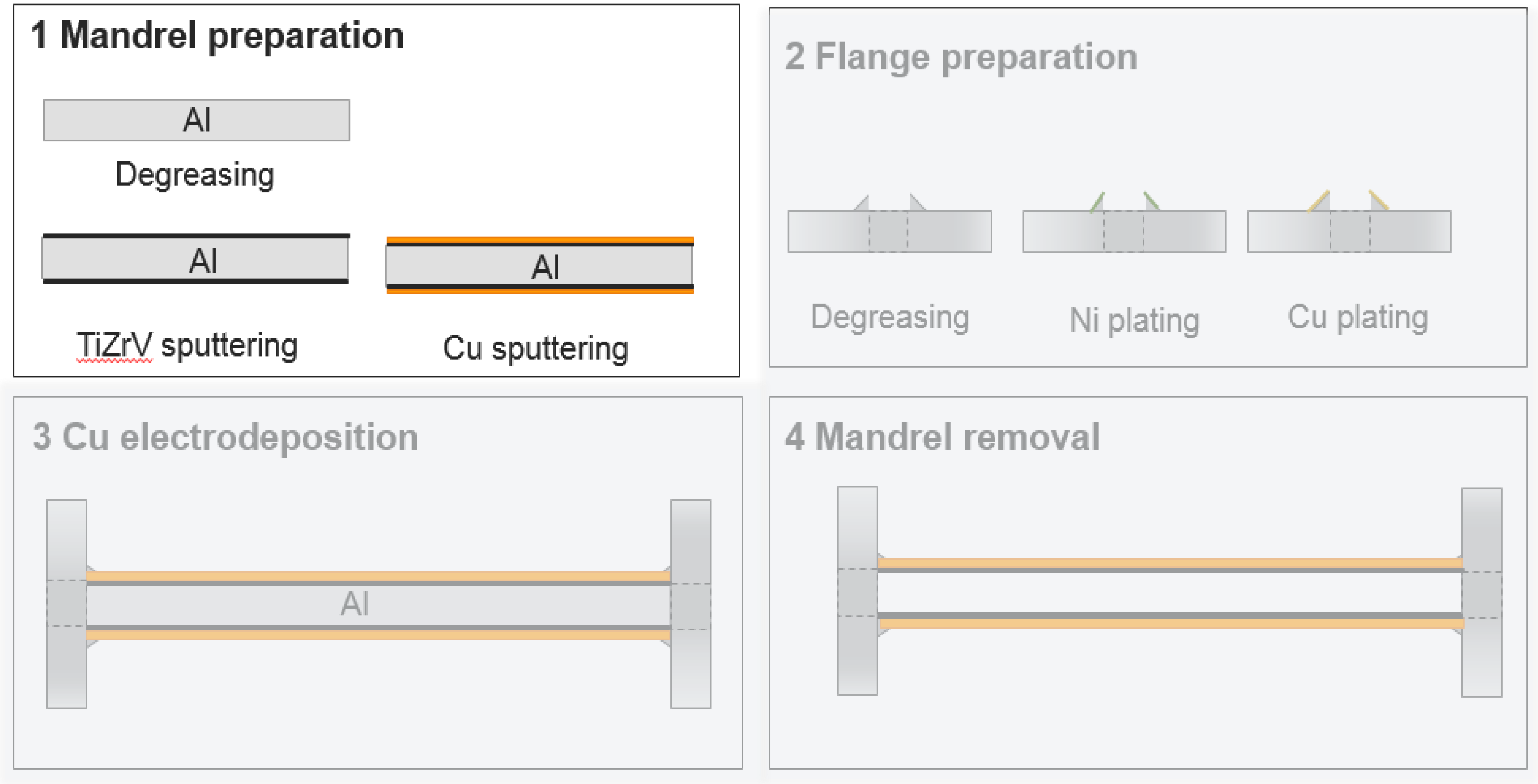
3 Cu electrodeposition



4 Mandrel removal



Chamber manufacturing procedure



1 Mandrel preparation

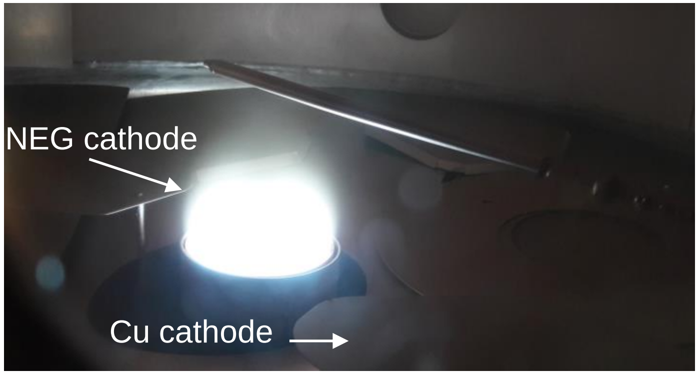
2 Flange preparation

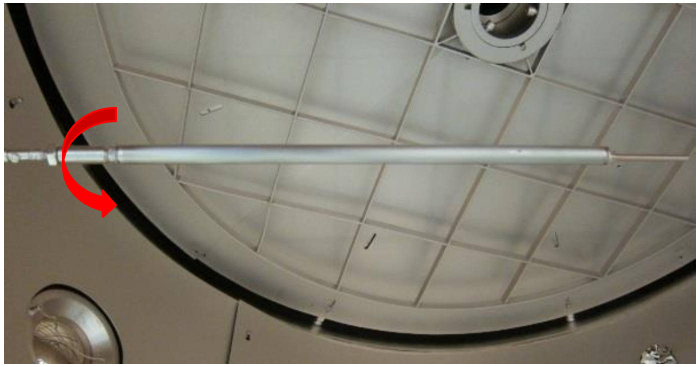
3 Cu electrodeposition

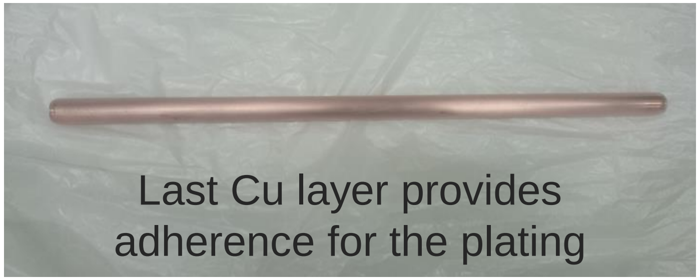
4 Mandrel removal

Mandrel thin film coating

- Aluminium mandrel tubes (series 6060)
- Degreased in alkaline solution
- Mounted in coating system equipped with TiZrV and Cu cathode
  - 1.5 µm of TiZrV coating
  - 3 µm of Cu coating



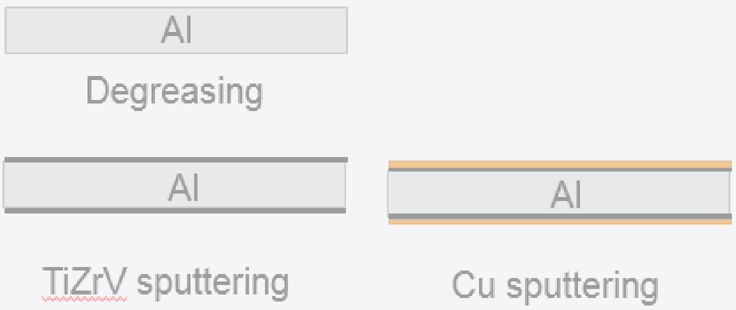




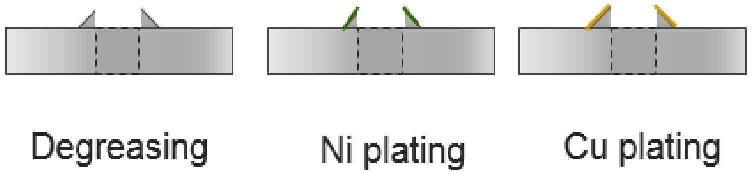
Last Cu layer provides adherence for the plating

Chamber manufacturing procedure

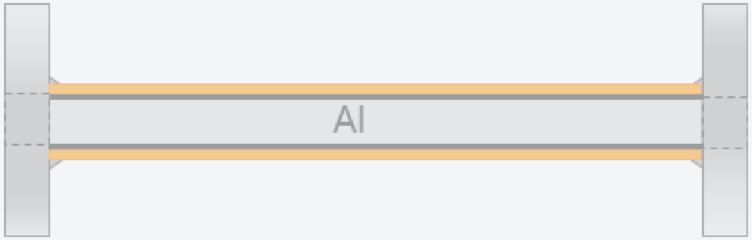
1 Mandrel preparation



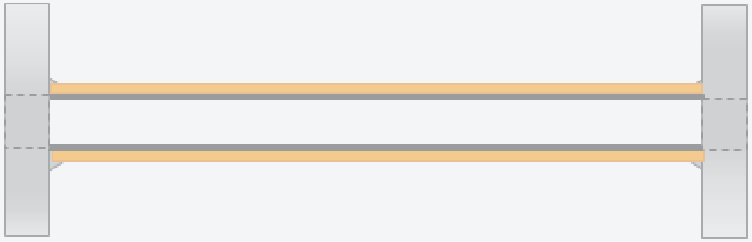
2 Flange preparation



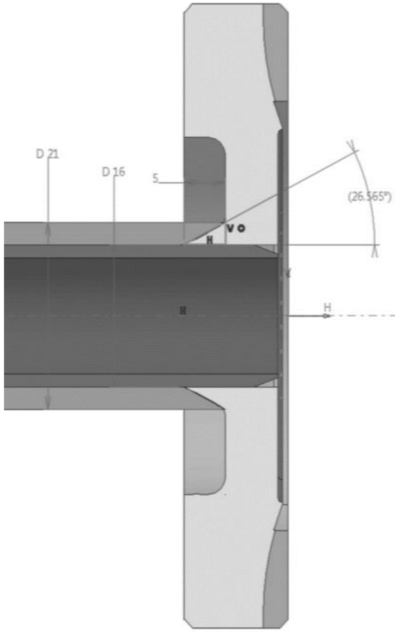
3 Cu electrodeposition



4 Mandrel removal

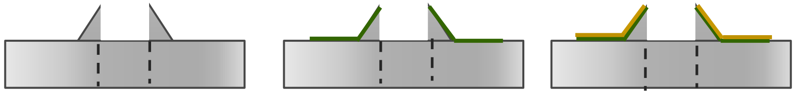


Flanges preparation



Flange is machined with a smooth transition between the SS flange and the aluminium tube

Flange preparation



Degreasing

Ni plating

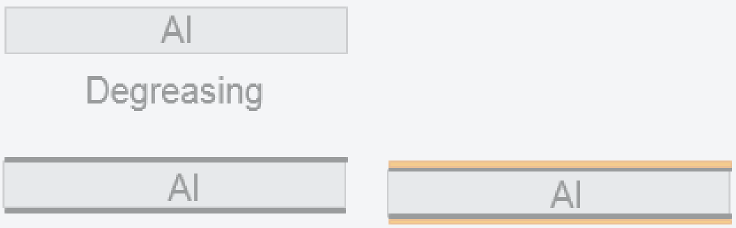
Cu plating

Cu plating is not adherent on SS. We need a Ni flash plated layer

Ni and Cu plating on stainless steel

Chamber manufacturing procedure

1 Mandrel preparation



Degreasing

TiZrV sputtering

Cu sputtering

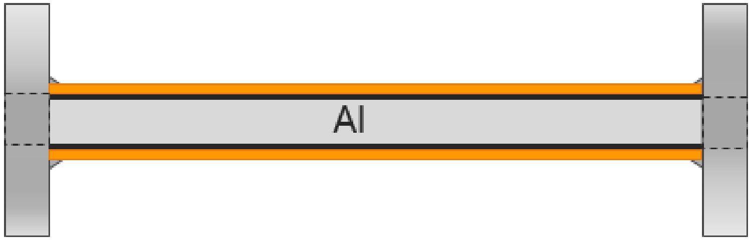
2 Flange preparation

Degreasing

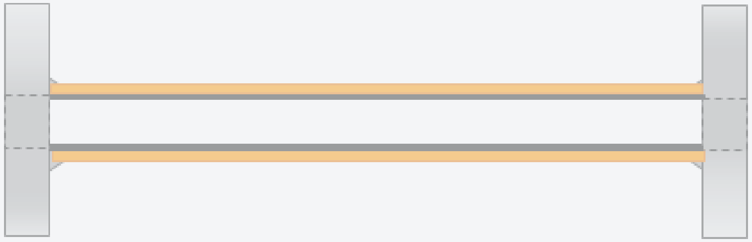
Ni plating

Cu plating

3 Cu electrodeposition



4 Mandrel removal



Copper electroforming

Cathode (reduction):

$Cu^{2+} + 2e^{-} \rightarrow Cu$

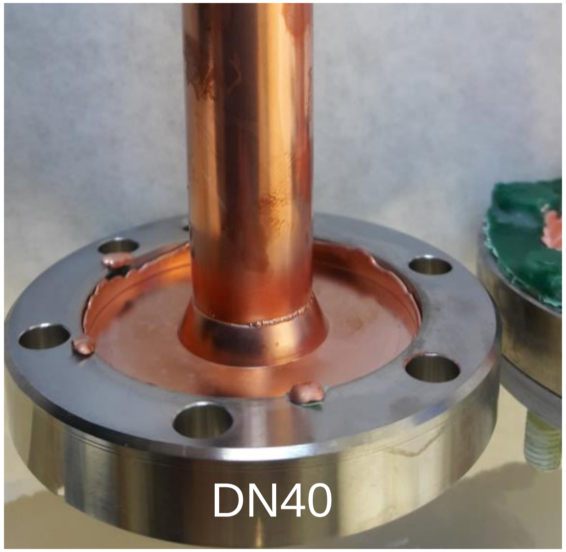
Anode (oxidation):

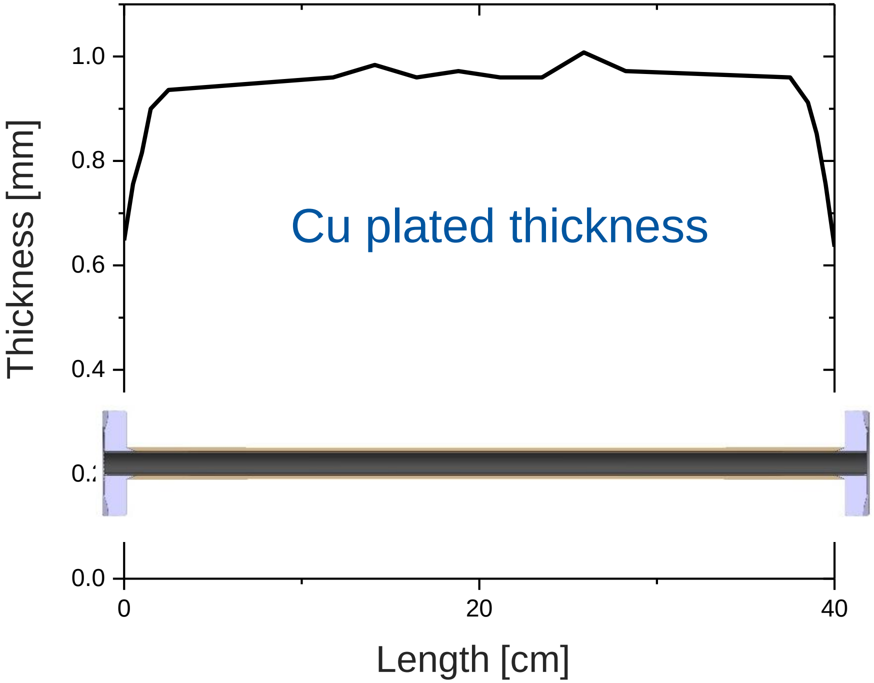
$Cu \rightarrow Cu^{2+} + 2^{e-}$

Electrodeposition of Cu, 2A/dm^2 , copper sulphate bath

- 1 mm of Cu deposited (chamber wall thickness)
- Two plating procedures: DC with brightener and AC without additives

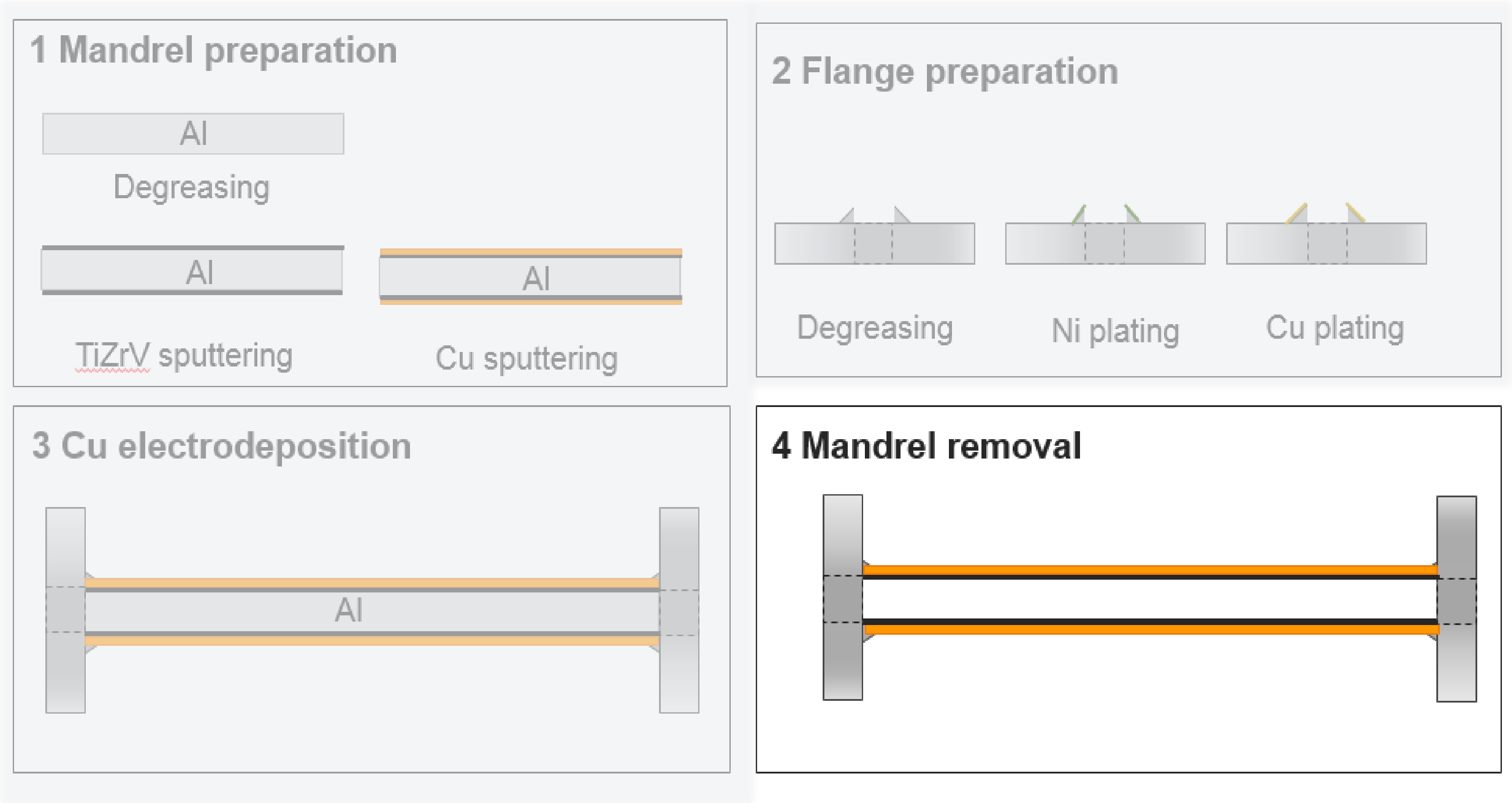
Cu chamber thickness profile





Leak-tight joining with flanges

Chamber manufacturing procedure

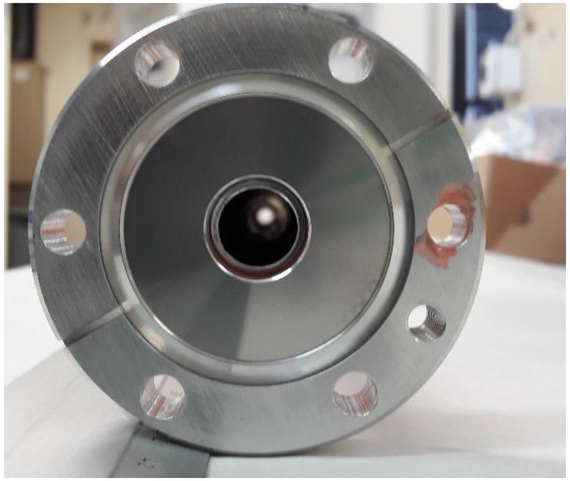

1 Mandrel preparation

2 Flange preparation

3 Cu electrodeposition

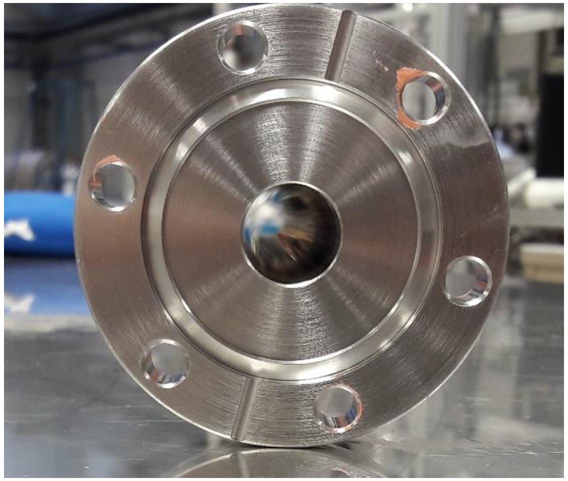
4 Mandrel removal

Mandrel removal



Al removal by NaOH chemical etching

$2Al + 2NaOH + 6H_2O \rightarrow 2Na + 3H_2 + 2Al(OH)_3$



Acidic rinsing in ammonium persulfate to clean residues from mandrel.

TiZrV coating is visible on the inner surface of the chamber.

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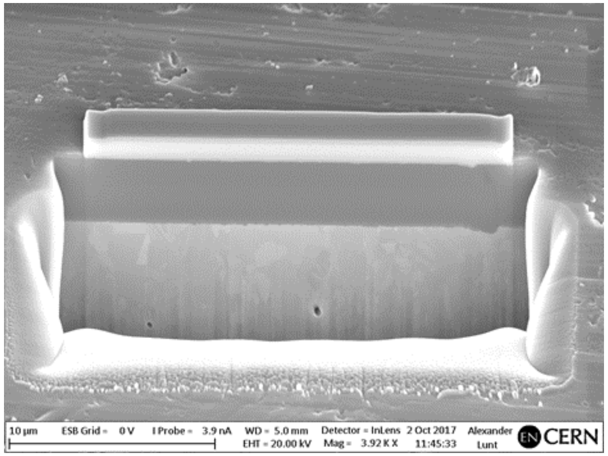
Challenges

- **Removal of the aluminium mandrel without damaging the NEG thin film**

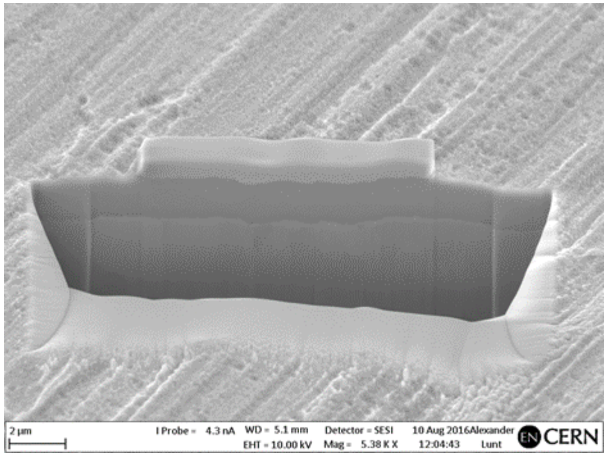
TiZrV coating characterization: FIB cross section

Two different coating recipes are tested.

Recipe 1



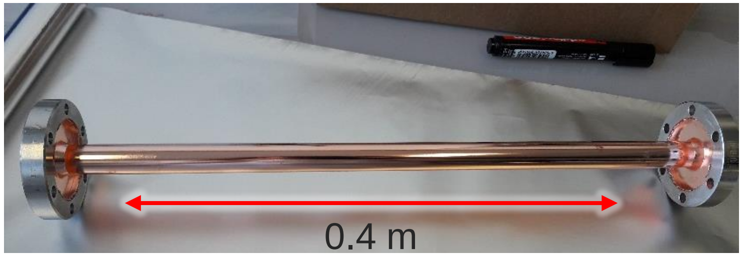
Recipe 2



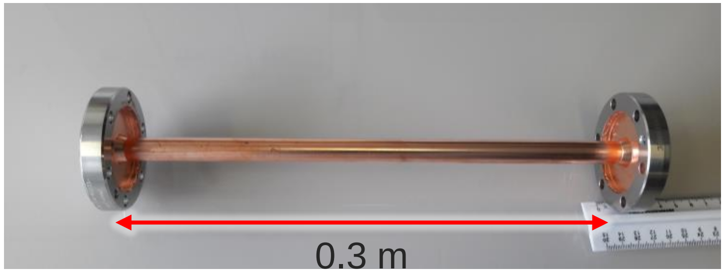
NEG coating follows the topography of the mandrel

Coating thickness profile on chambers produced

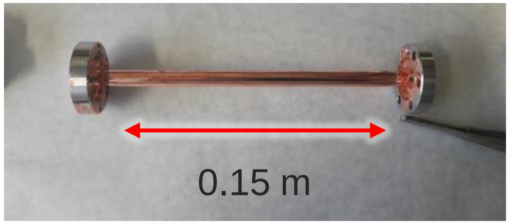
Chamber 16 mm diameter



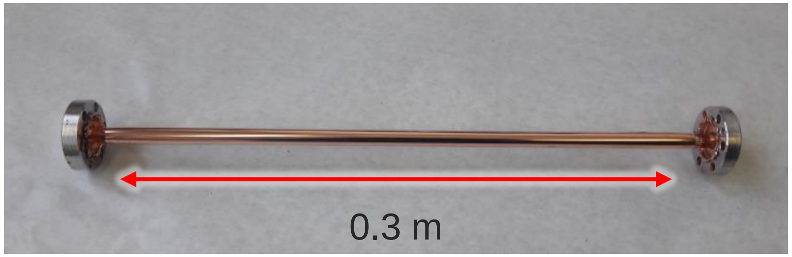
Chamber 12 mm diameter



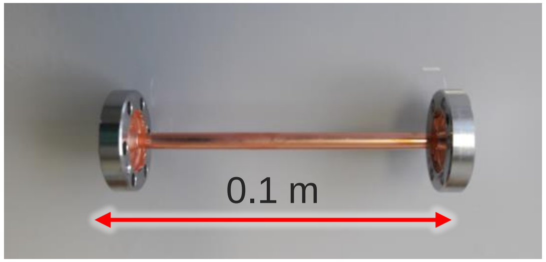
Chamber 6 mm diameter



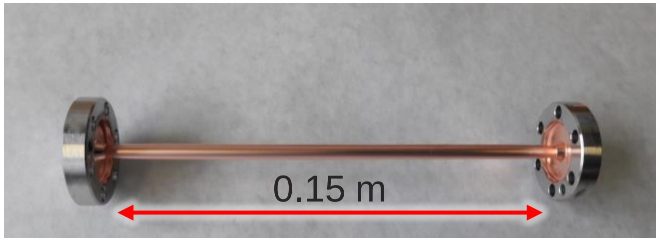
Chamber 5 mm diameter



Chamber 4 mm diameter

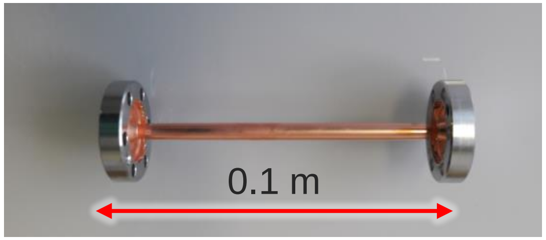


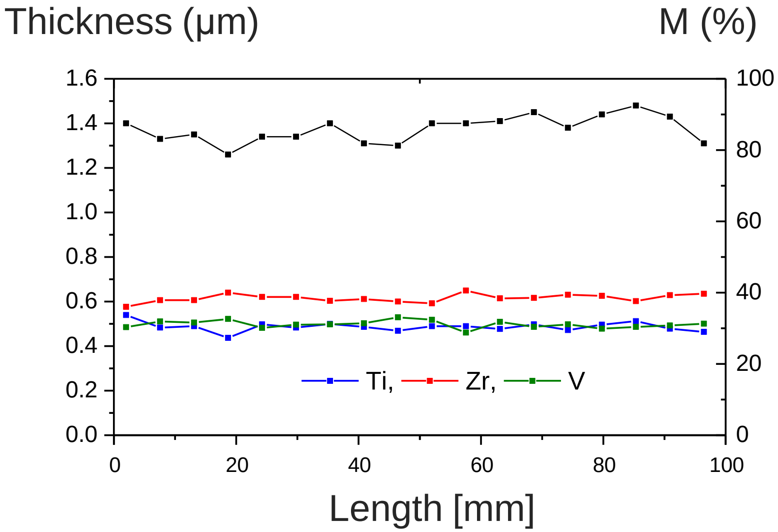
Chamber 3 mm diameter



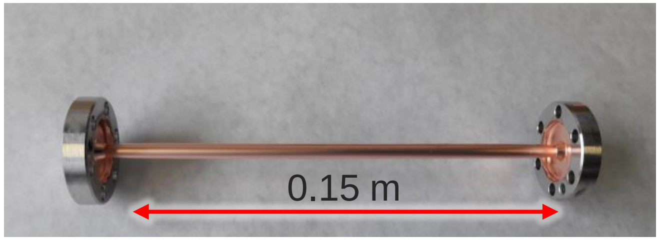
Coating thickness profile (NEG on Cu) with XRF analysis

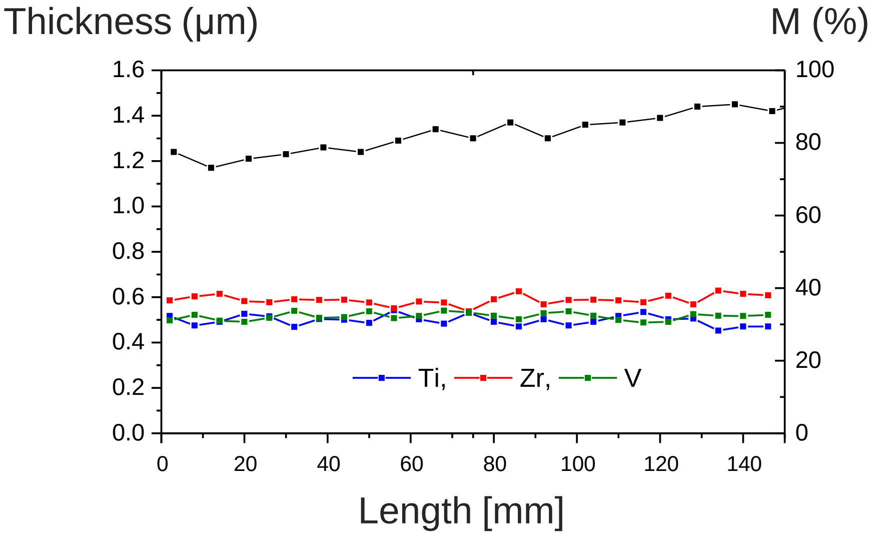
Chamber 4 mm diameter





Chamber 3 mm diameter

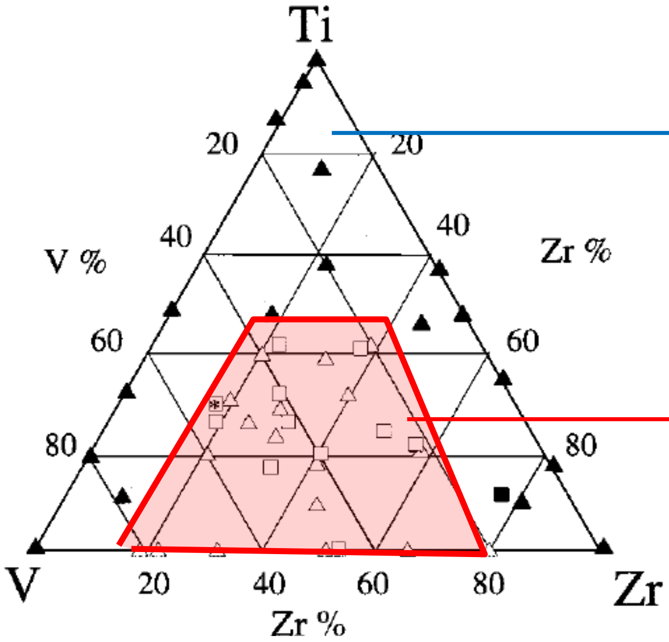




Homogeneous TiZrV composition, Thickness variation < 15%

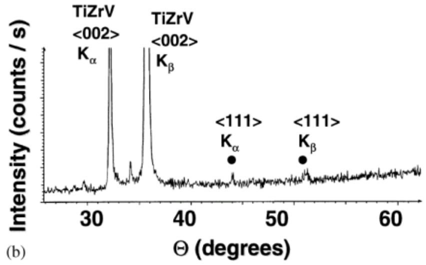
TiZrV coating characterization: X-Ray diffraction analysis

Structure composition map of TiZrV films based on the crystal grain size.

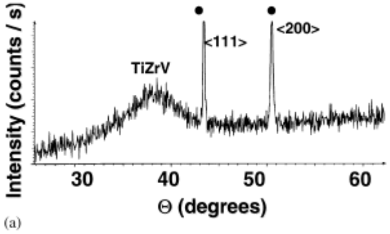


A. E. Prodromides et al. Vacuum 60 (2001) 35, 41

Grain size above 100 nm.

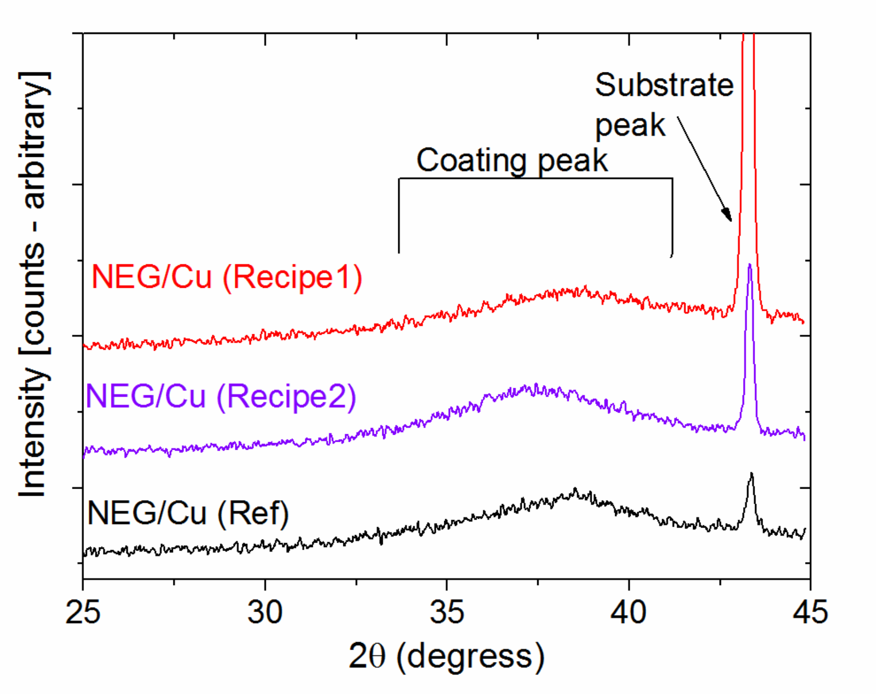


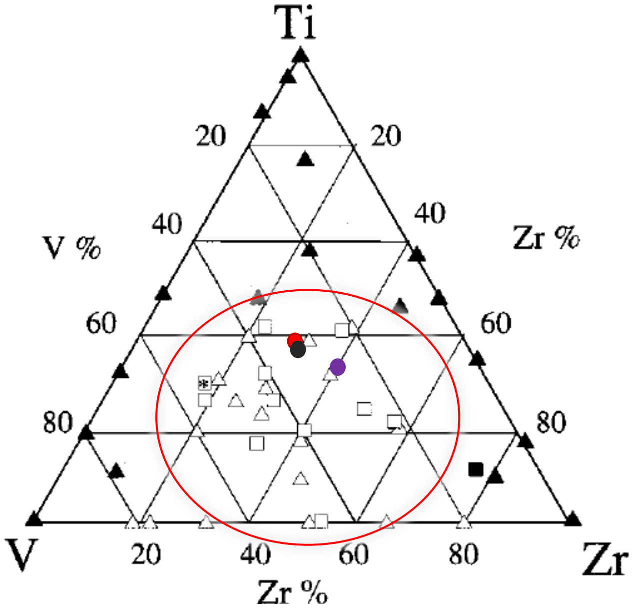
Grain size below 5 nm.



Best activation region

TiZrV coating characterization: X-Ray diffraction analysis





For all samples the crystallite size is very small, < 5nm, around 3 nm.

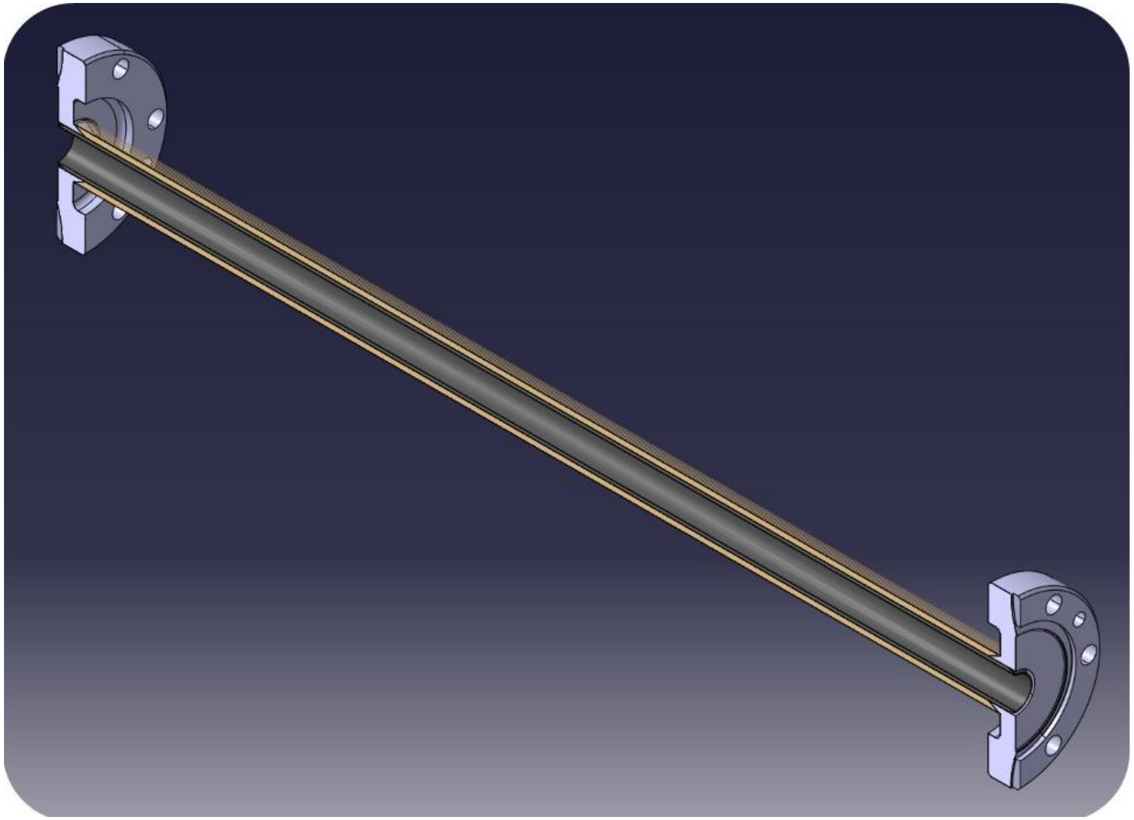
Challenges

- Removal of the aluminium mandrel without damaging the NEG thin film

- **Leak-tight and robust assembly without brazing or EB welding step**

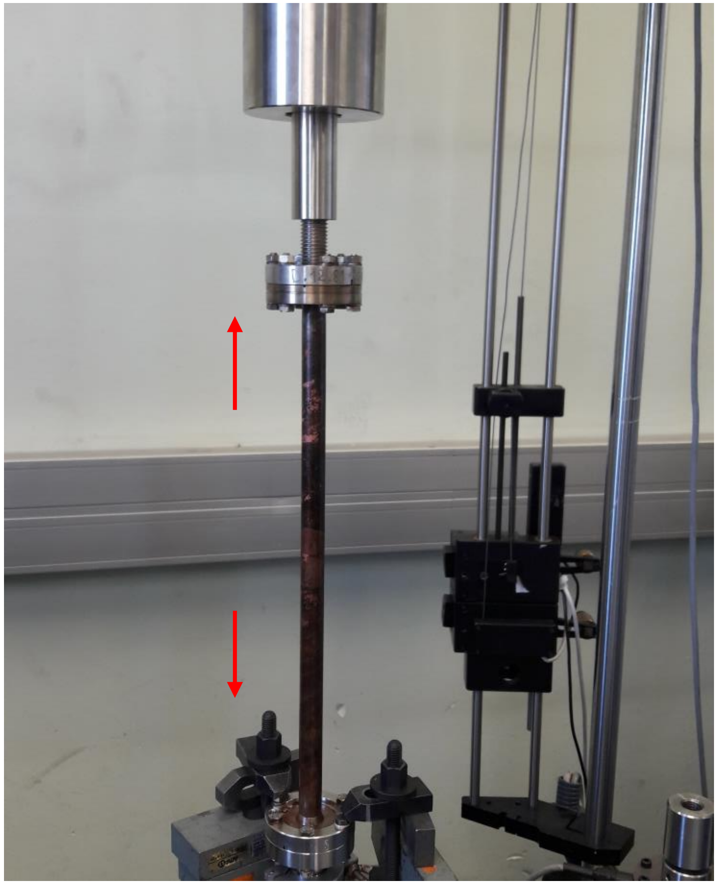
Reverse coating technique

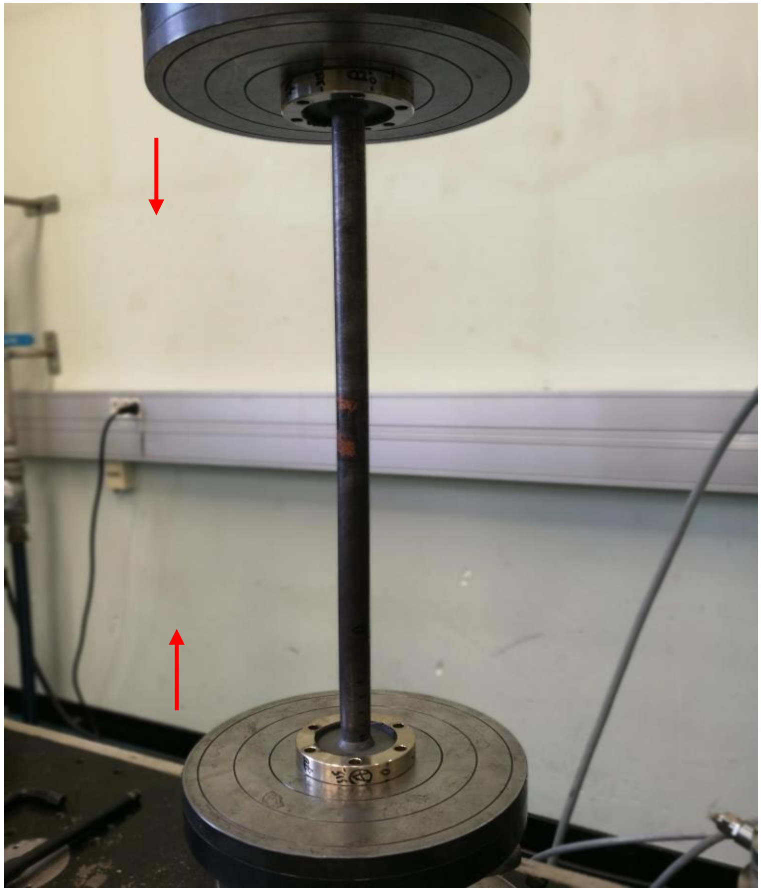
During the electroforming, the stainless steel flanges are assembled to the chamber. Neither brazing nor EB welding are needed.



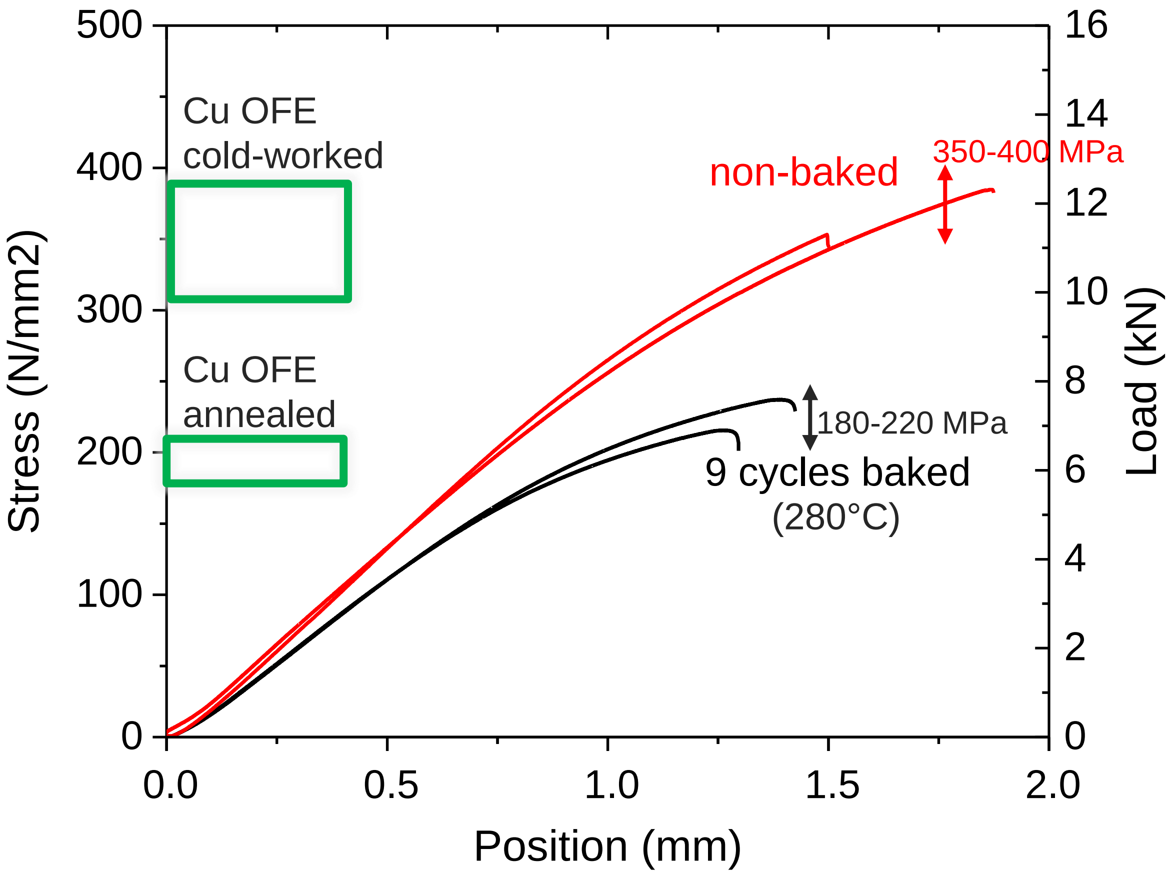
Mechanical performance

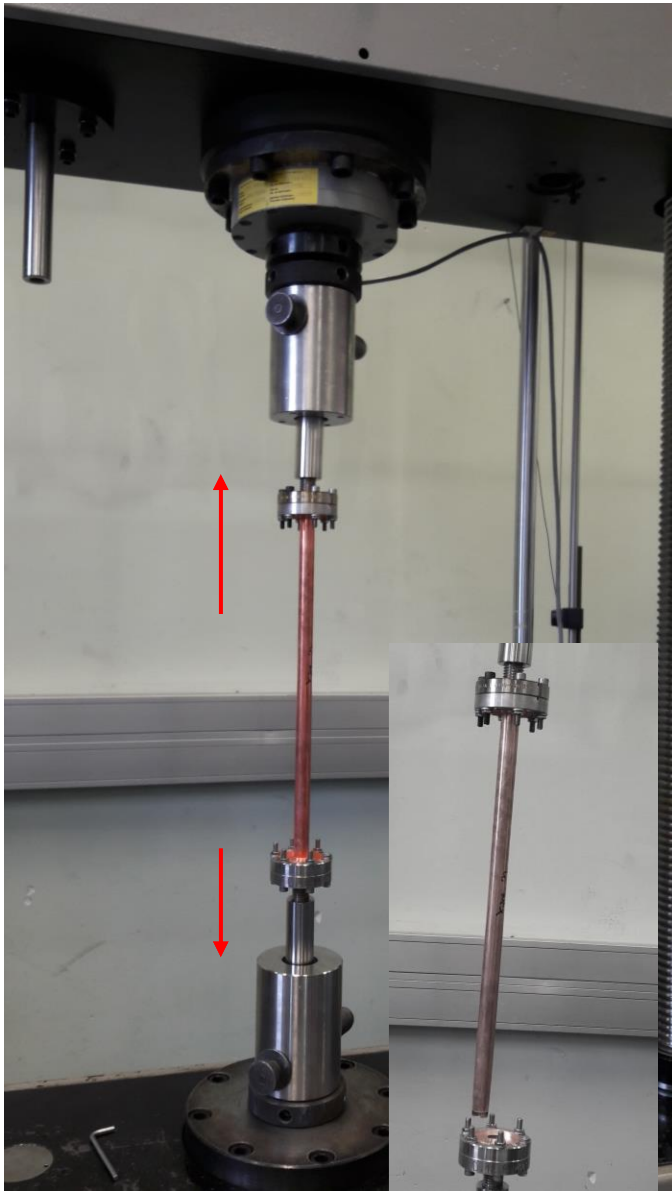
Robustness of the assembly? Tensile and compression tests





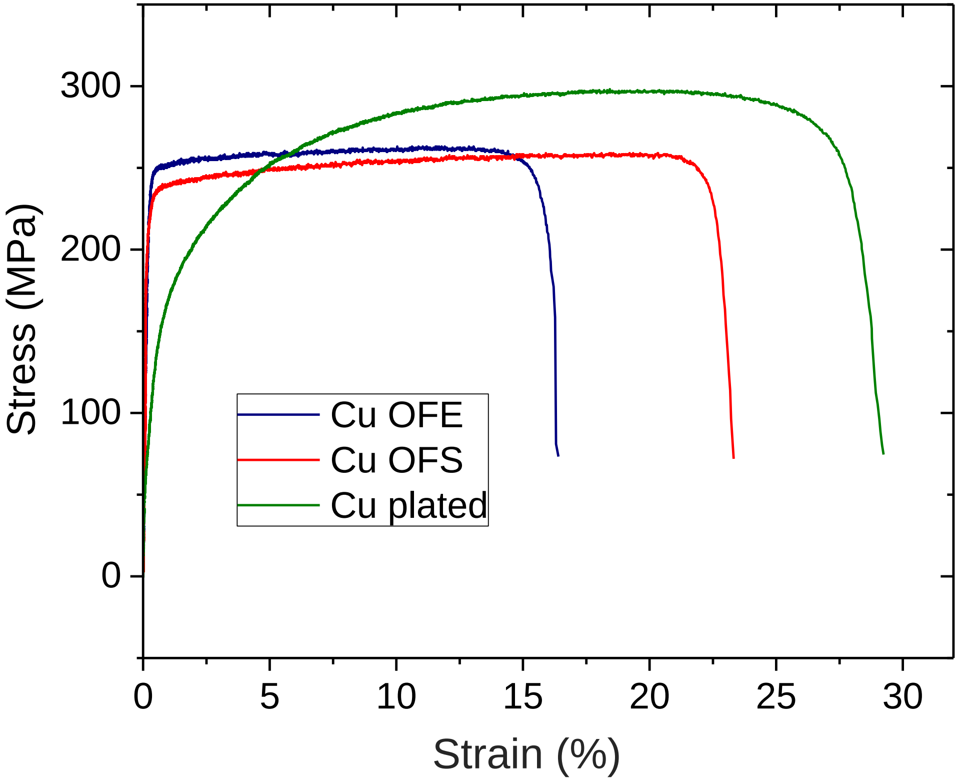
Mechanical performance

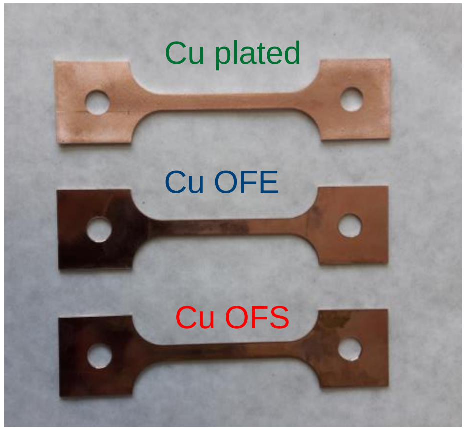




Chambers before and after bake-out exhibit a tensile strength comparable to Cu OFE

Mechanical performance

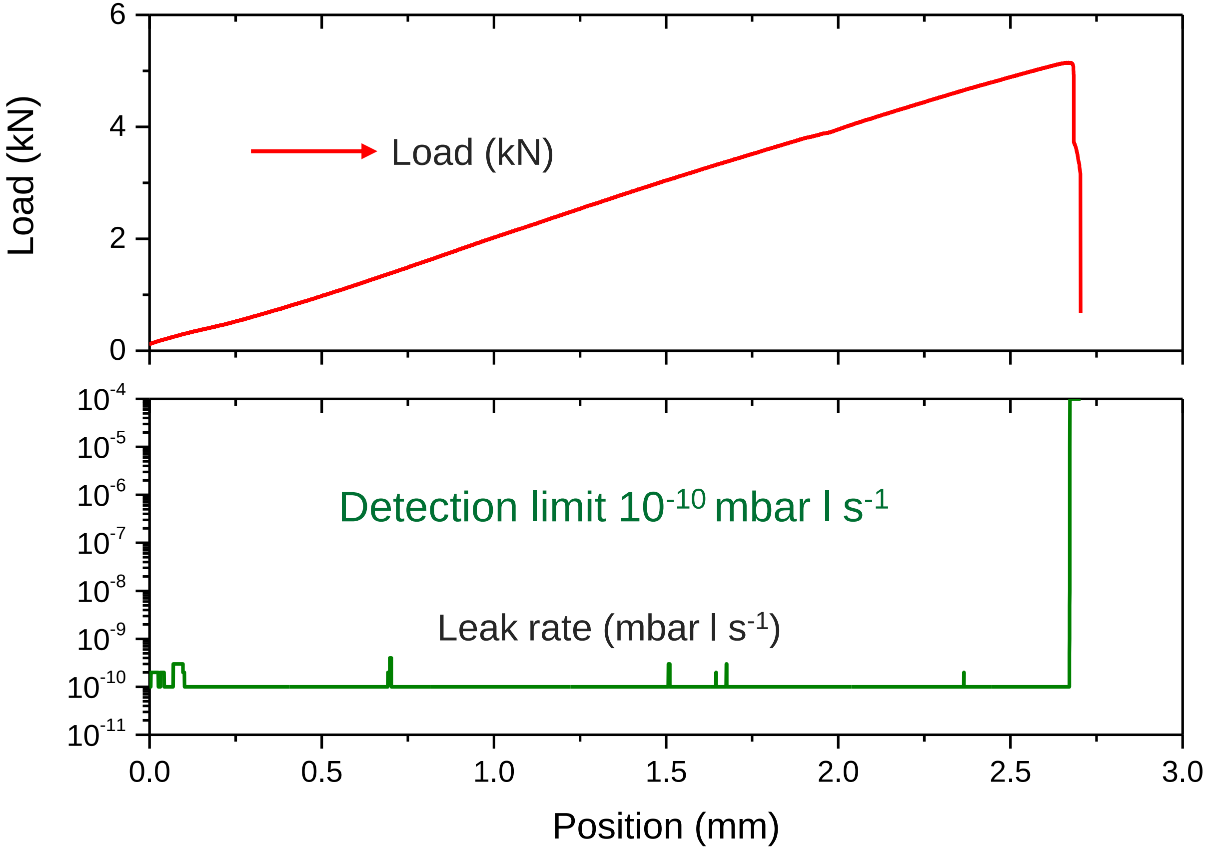




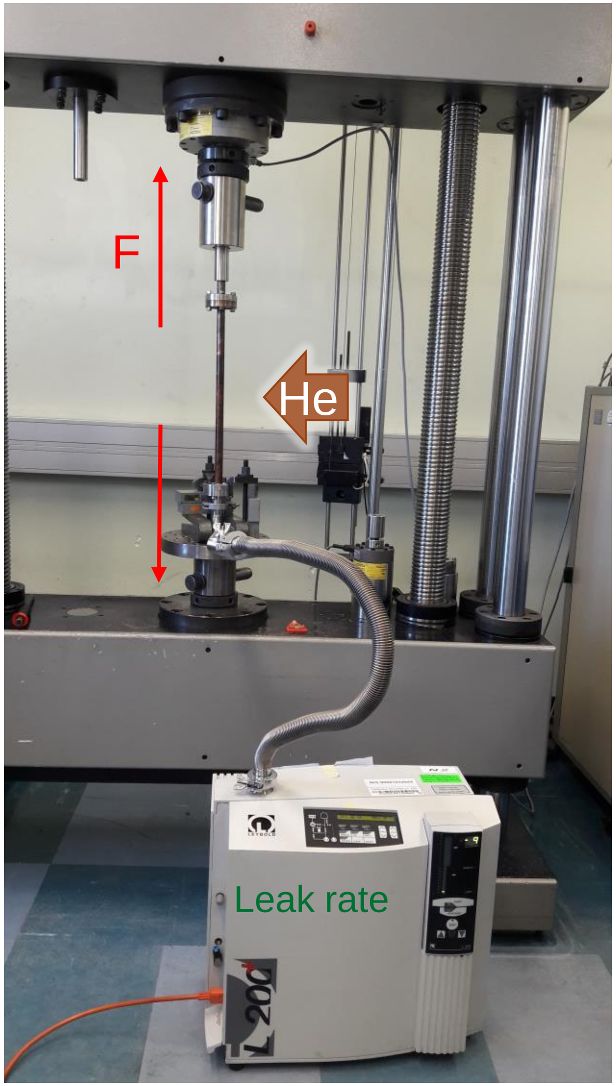
Specimens	UTS (Mpa)	YS (Mpa)	Elongation (%)	E (Gpa)
Cu OFE	263	243	16	114
Cu OFS	268	237	24	114
Cu plated	285	117	30	112

Mechanical and tightness performance

Chamber is leak-tight until rupture



Detection limit 10^{-10} mbar l s^{-1}



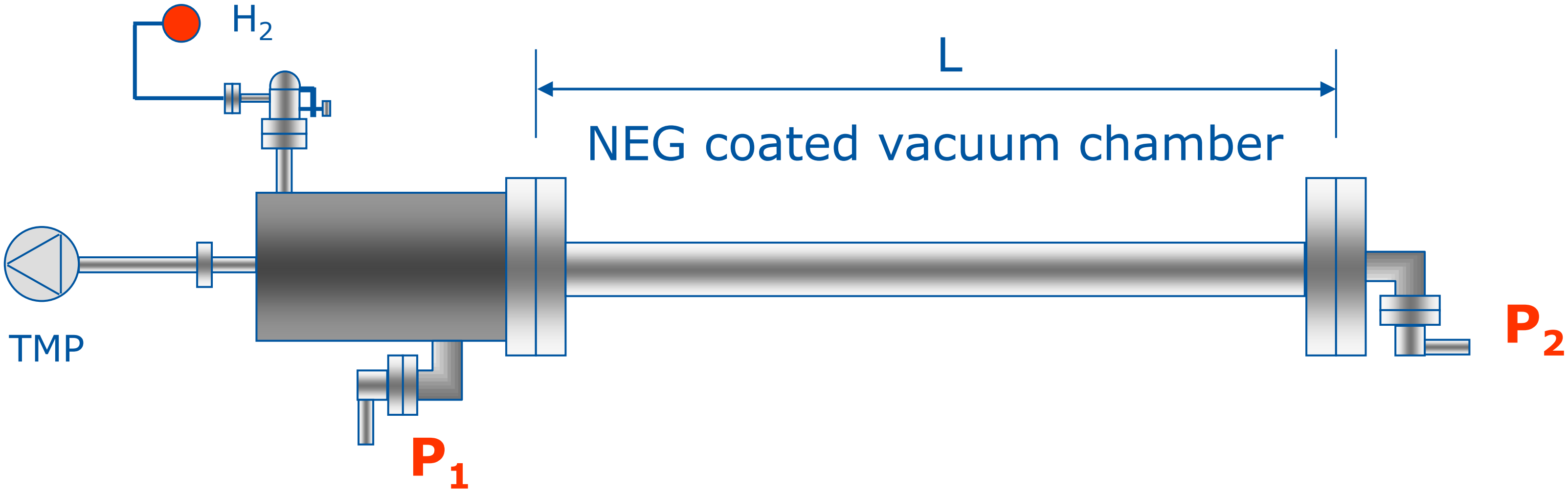
Challenges

- Removal of the aluminium mandrel without damaging the NEG thin film

- Leak-tight and robust assembly without brazing or EB welding step

- **Preserve the NEG film from process related impurities**

Pumping speed measurement via Transmission tests



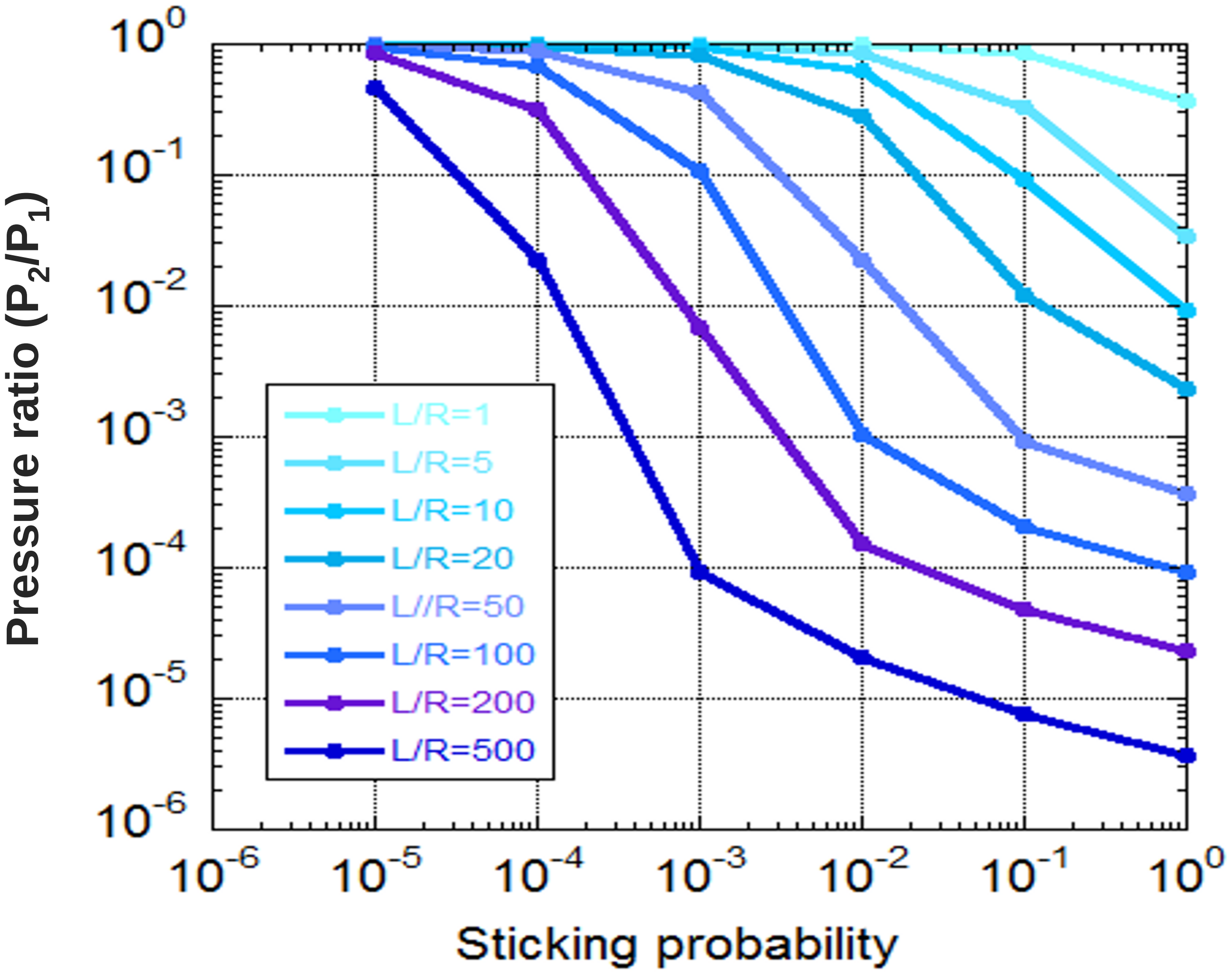
$$\text{Pressure ratio} = \frac{\Delta P_2}{\Delta P_1}$$

With a Monte Carlo simulation we calculate the sticking probability of H_2 from ΔP2/ΔP1

Sticking probability (probability of a molecule to stick to the surface and be pumped)

Pumping speed measurement via Transmission tests

Monte Carlo simulation

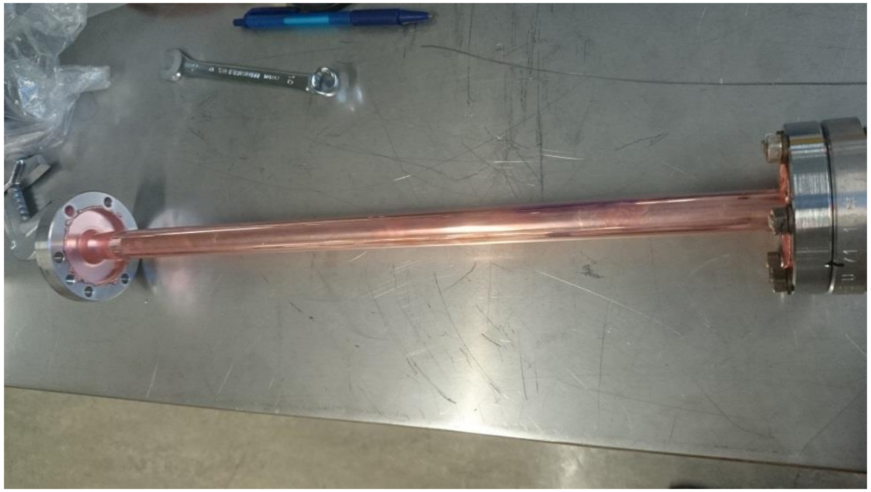


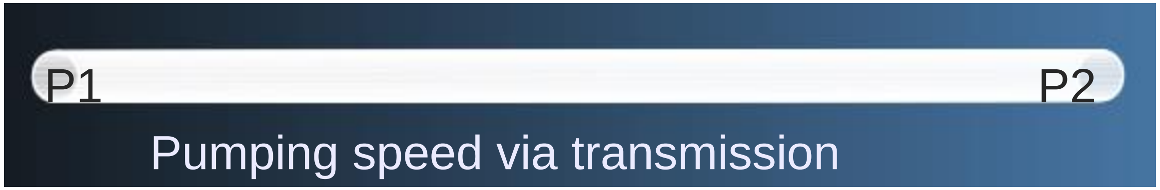
Pumping speed measurement via Transmission tests

Case of study:

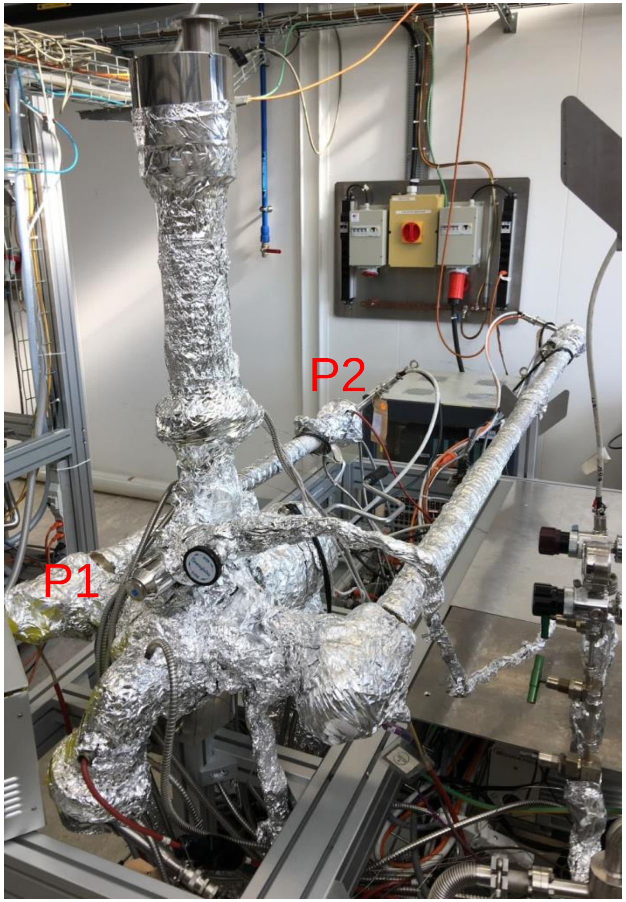
Chamber 16mm diameter, 0.4m long

L/R=50



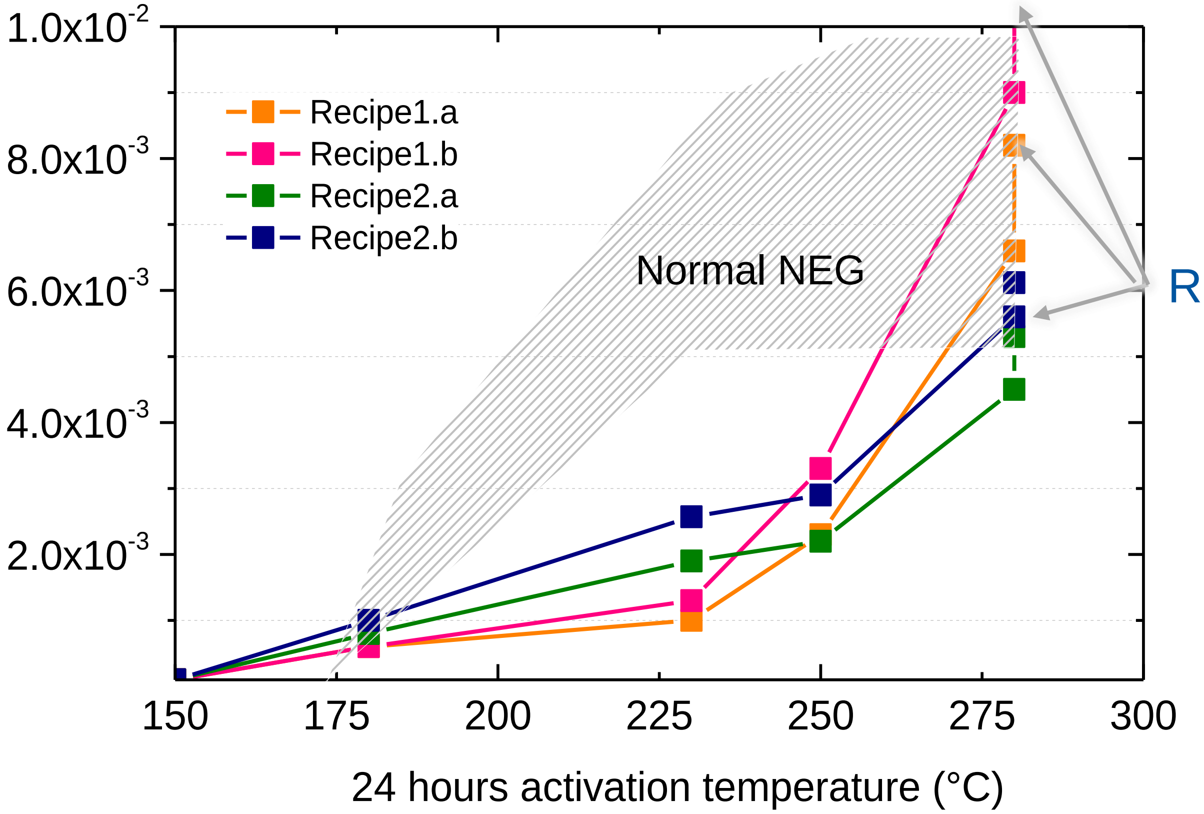


Pumping speed via transmission



Pumping performance via Transmission tests

H_2 sticking probability



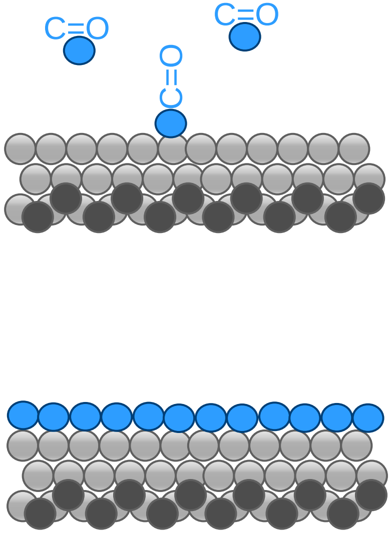
Removing CH_4 effect

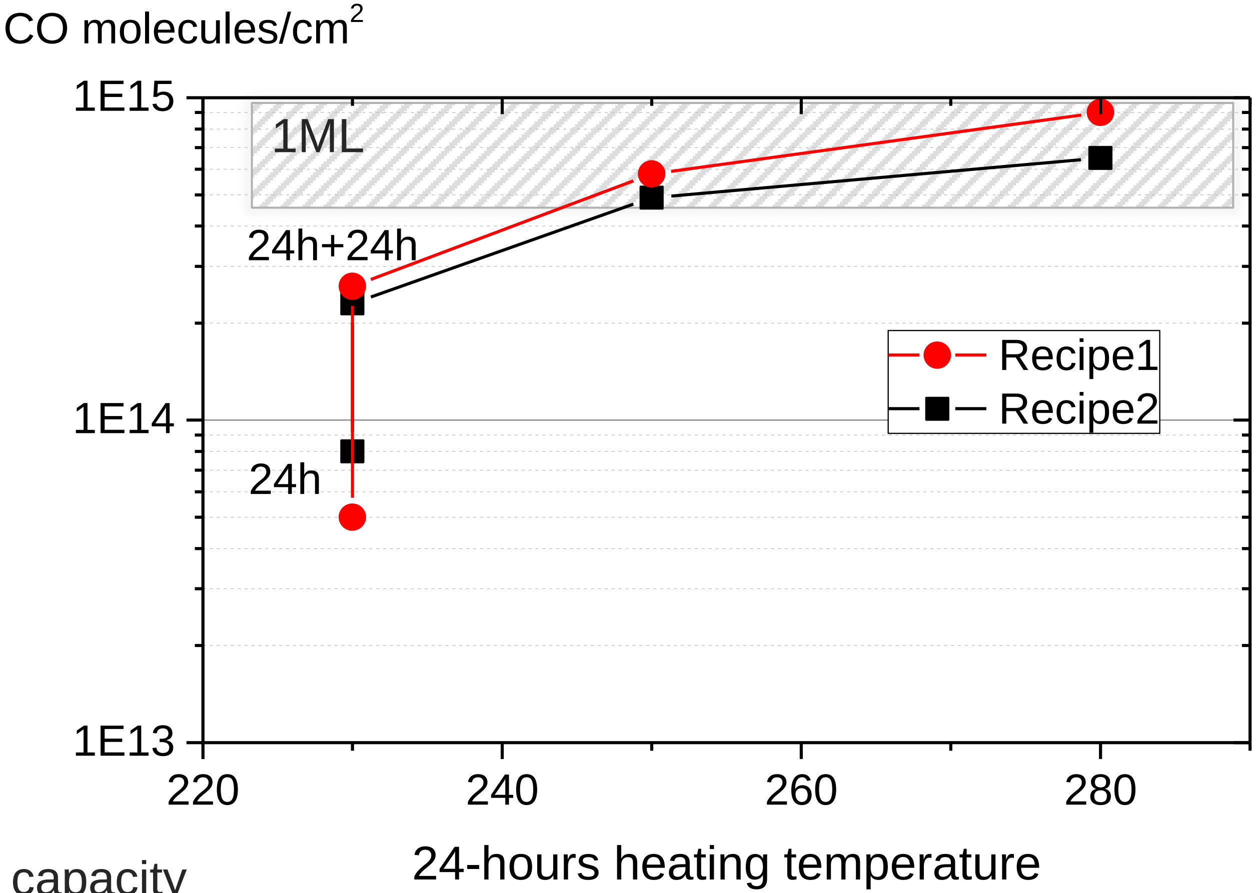
H_2 sticking factor comes close to $1x10^{-2}$, but there is a delay in activation temperature

Pumping performance via Transmission tests

CO saturation measurement: 1 Monolayer ML CO ($5x10^{14}$ -$1x10^{15}$)

CO is adsorbed in the surface





The results show a good capacity when activated 250°C for 24 hours

Open questions

Why a delay in activation temperature?

NEG composition	OK
NEG microstructure	OK

Impurities in the NEG film might affect this process and limit the pumping speed.

Possible sources:

- Impurities in the electroformed copper migrating to the NEG film
- Impurities transfer during mandrel etching

Challenges

- Removal of the aluminium mandrel without damaging the NEG thin film
- Leak-tight and robust assembly without brazing or EB welding step
- Preserve the NEG film from process related impurities
  - **Limit the transfer of impurities from electroformed copper to the NEG film**

Measurement of impurities on electroformed copper

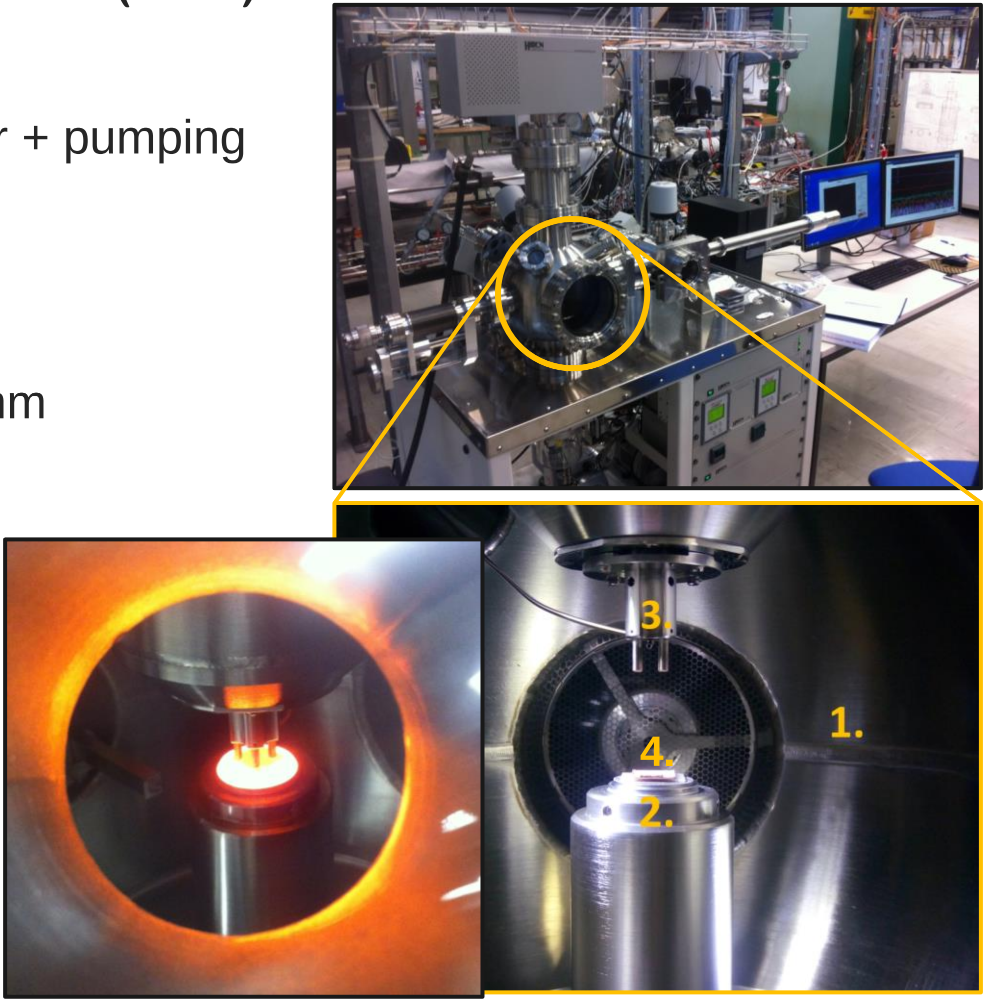
Thermal Desorption Spectrometer (TDS)

How does it work?

1. UHV system: Vacuum chamber + pumping system
2. Heater
3. Residual Gas Analyser (RGA)
4. Sample: 10 mm x 10 mm x 1 mm

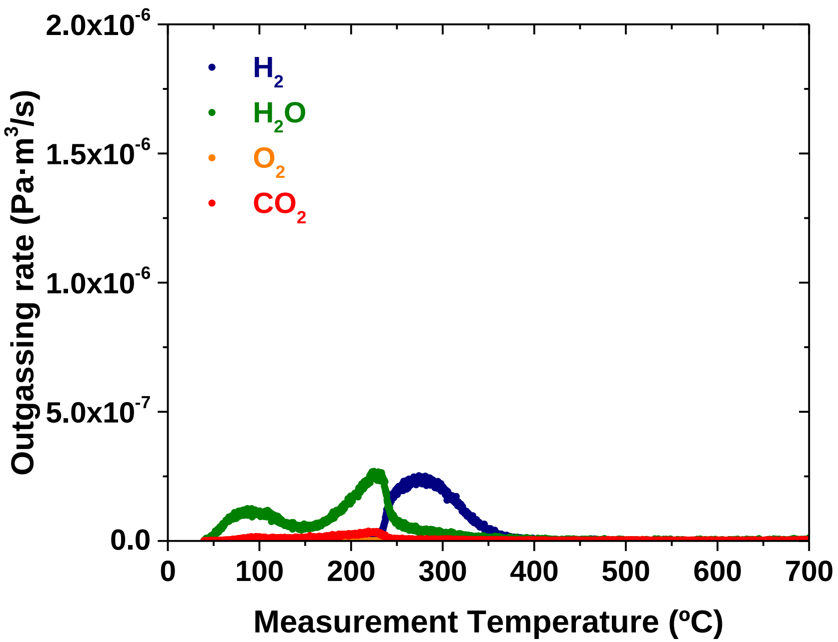
Measurement of gases desorbed as a function of temperature for different electroplating parameters

TDS System

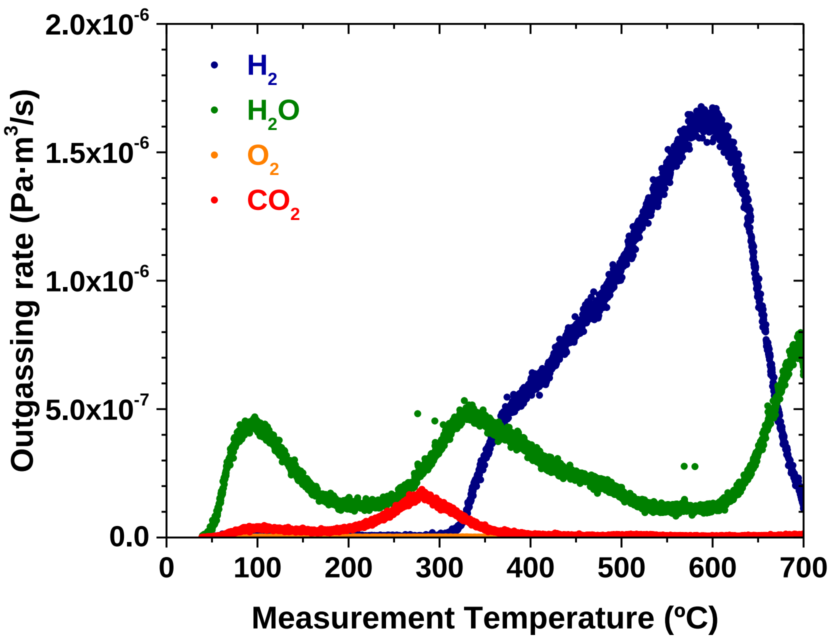


Copper electroformed outgassing

Cu OFE
1mm thickness



Electroformed Cu
1mm thickness



Copper electroformed outgassing

Two plating procedures: DC with brightener and AC without additives

DC plating with brightener
(organic additive)

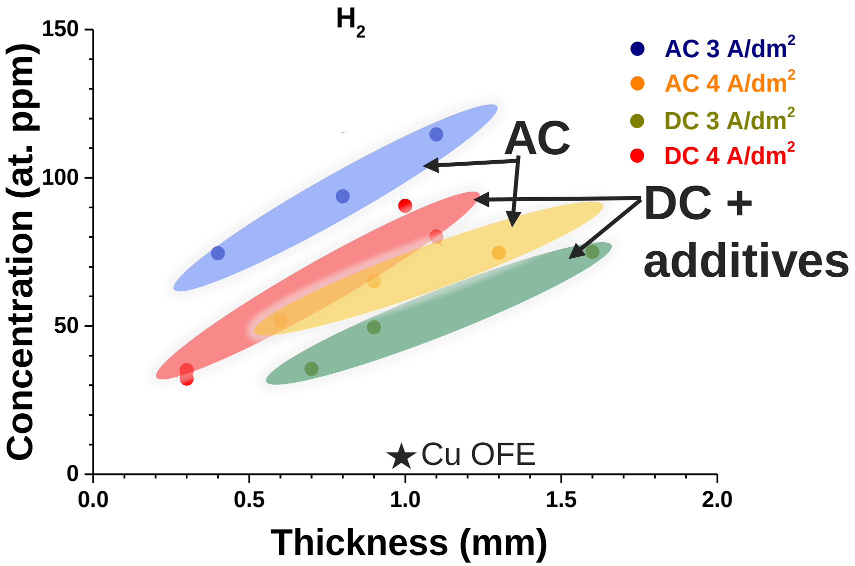
Grain refinement

AC plating bath without additives

Columnar growth

Copper electroformed outgassing

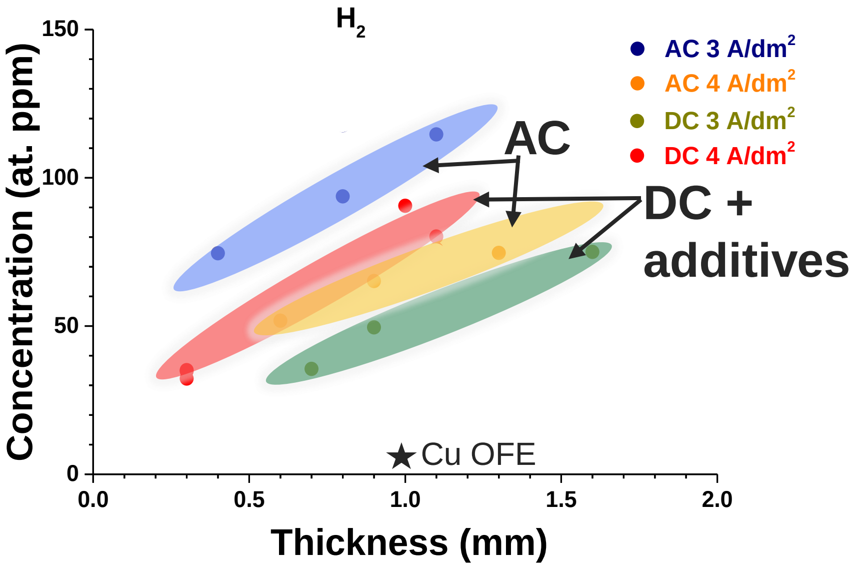
H_2 concentration ppm



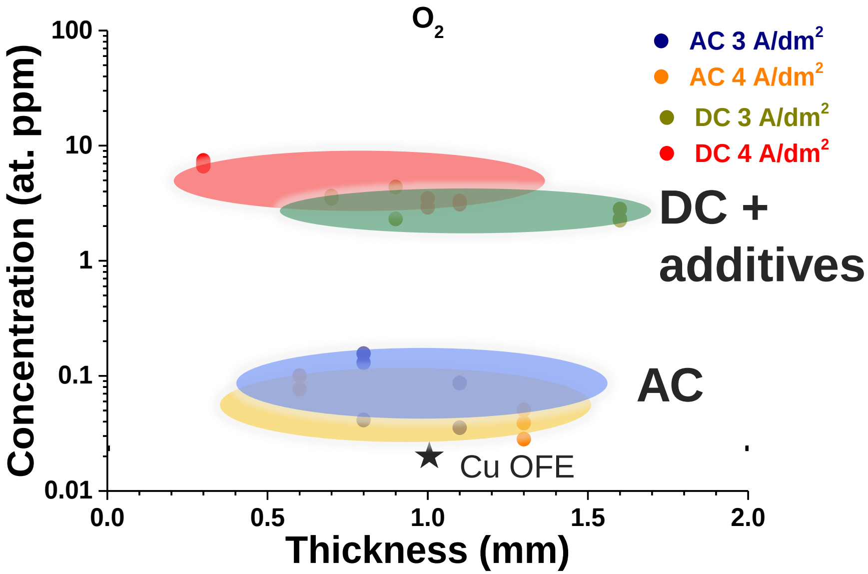
H_2: concentration of H_2 increases with thickness (bath drift). Keep the lowest thickness possible

Copper electroformed outgassing

H_2 concentration ppm



O_2 concentration ppm



H_2: concentration of H_2 increases with thickness (bath drift). Keep the lowest thickness possible

O_2 : Reduce the presence the oxygen by avoiding organic additives

Challenges

- Removal of the aluminium mandrel without damaging the NEG thin film

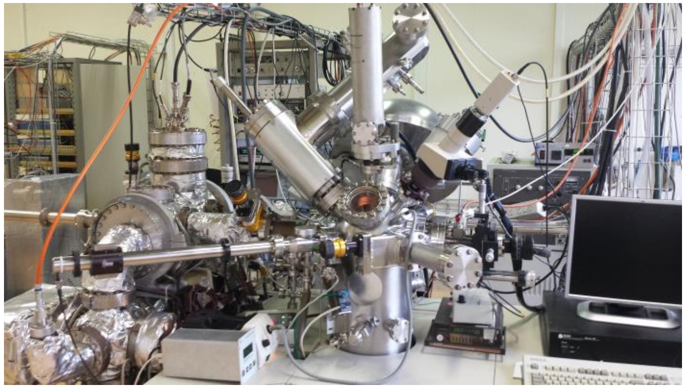
- Leak-tight and robust assembly without brazing or EB welding step

- Preserve the NEG film from process related impurities

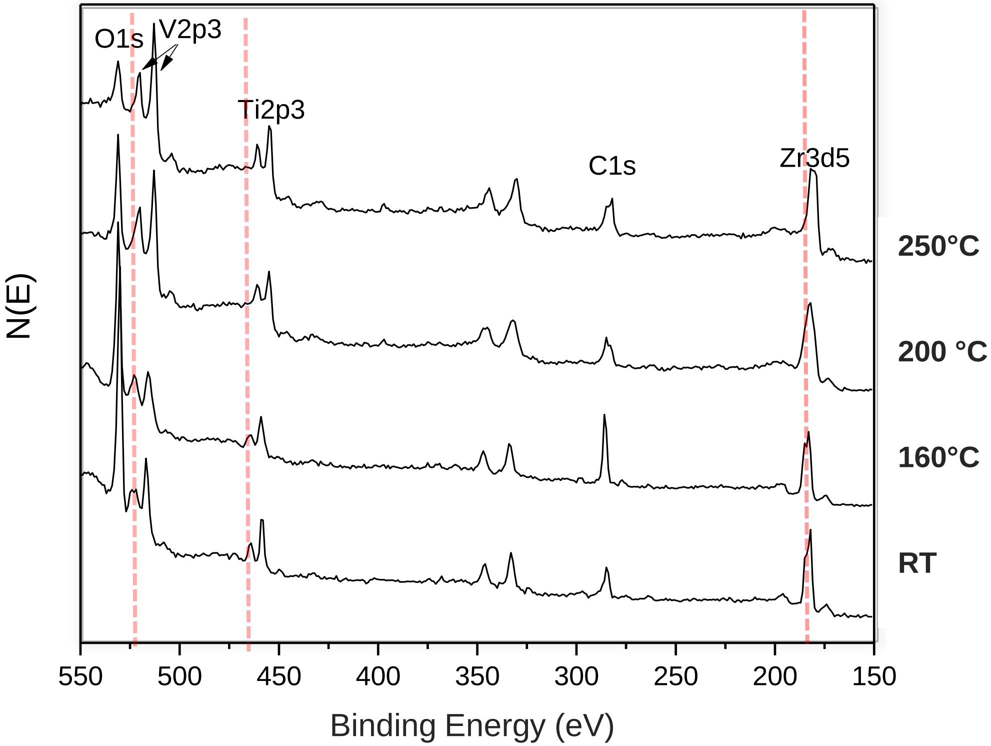
  - Limit the transfer of impurities from electroformed copper to the NEG film
  - Avoid to introduce impurities from the mandrel or etching solution

XPS surface analysis

X-ray Photoemission Spectroscopy:



XPS activation evolution and detection of impurities



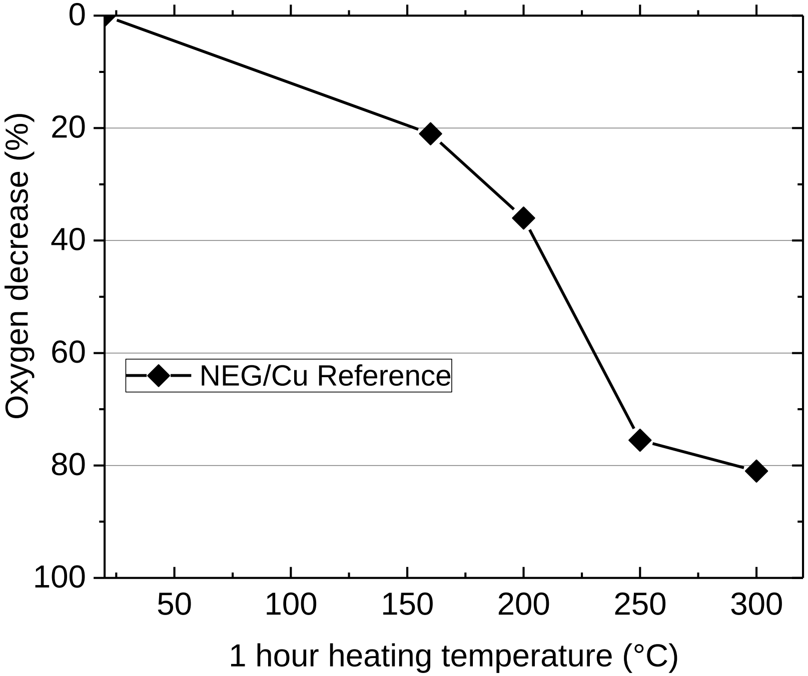
XPS surface activation

1.5 mm thickness mandrel: 24 hours etching

0.5 mm thickness mandrel: 7 hours etching

1.5mm thickness 0.5mm thickness

Oxygen decrease (%) surface to bulk



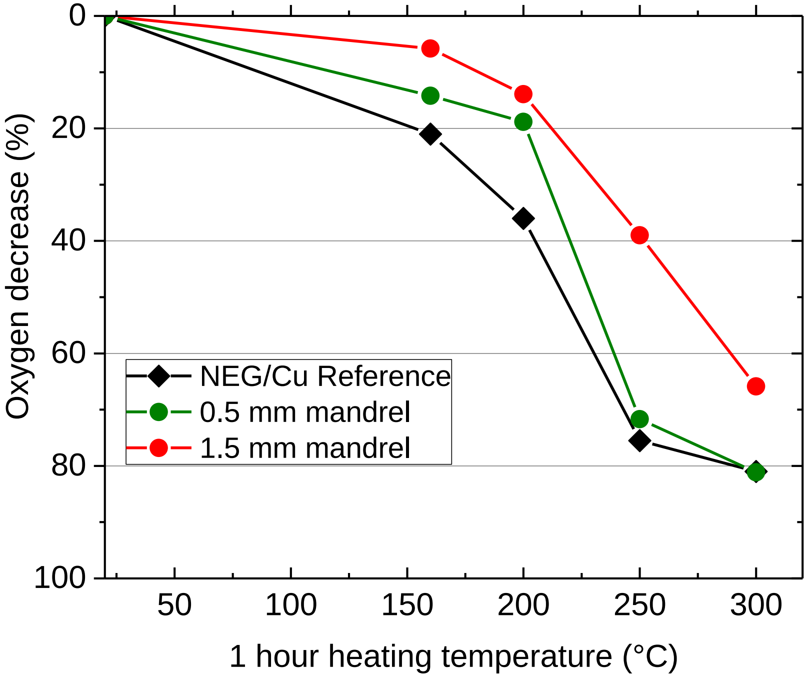
XPS surface activation

1.5 mm thickness mandrel: 24 hours etching

0.5 mm thickness mandrel: 7 hours etching

1.5mm thickness 0.5mm thickness

Oxygen decrease (%) surface to bulk



Oxygen decrease is delayed in temperature with increasing etching time

Outline

1. Motivation
2. Usual NEG sputtering technique
3. Reverse coating technique
4. Challenges
5. **Preparation for real application**
6. Conclusions & Outlook

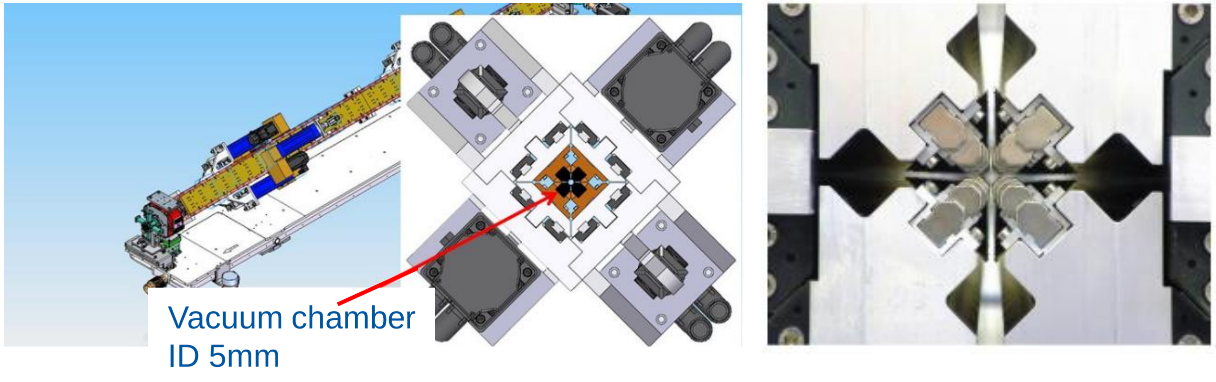
Preparation for real application

No diameter constraint is found. Real case scenario precises long chambers (magnets are usually 2m long).

In our facilities, we comissioned a bath of 3m height to produce up to 2.5m length vacuum chambers.

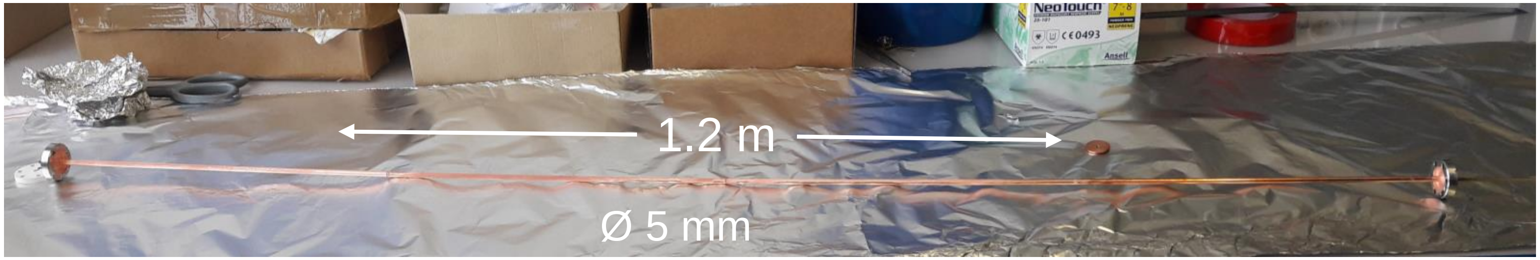
The coating system is limited to 0.5 m length so the assembly of several tubes will be needed to produce a chamber.

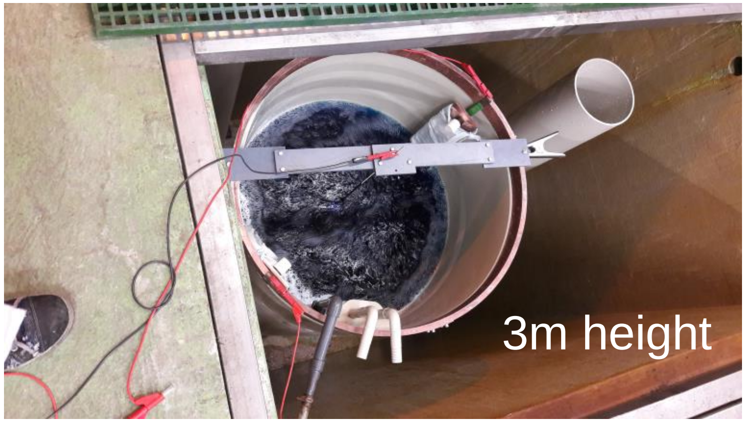
H. D. Nuhn et. al, Proceedings of FEL2015
Presentation at FLS 2012, Delta undulator, SLAC



Longer lengths: 1.2 meters

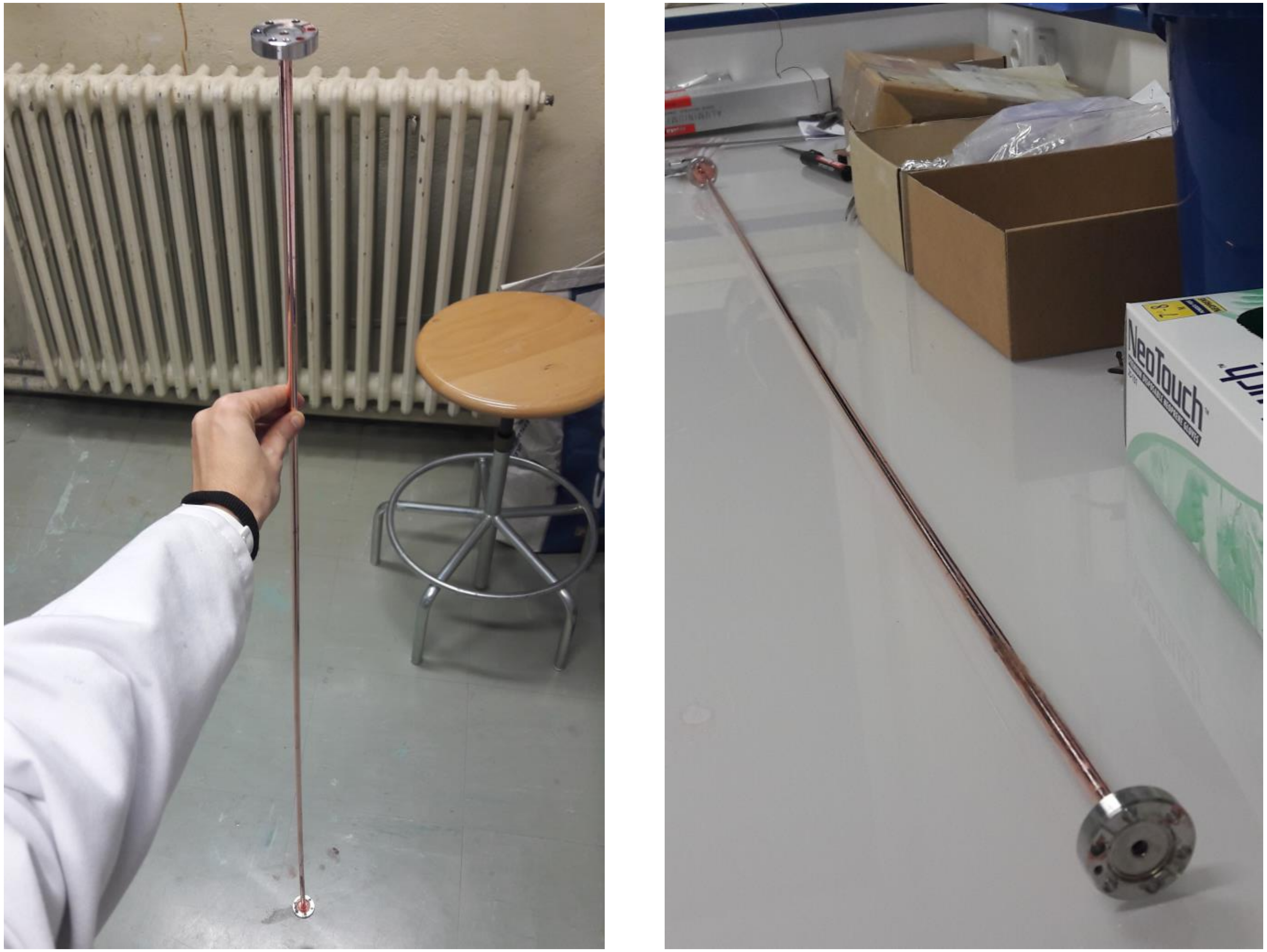
Chamber: 1.2 m length, 5 mm diameter chamber





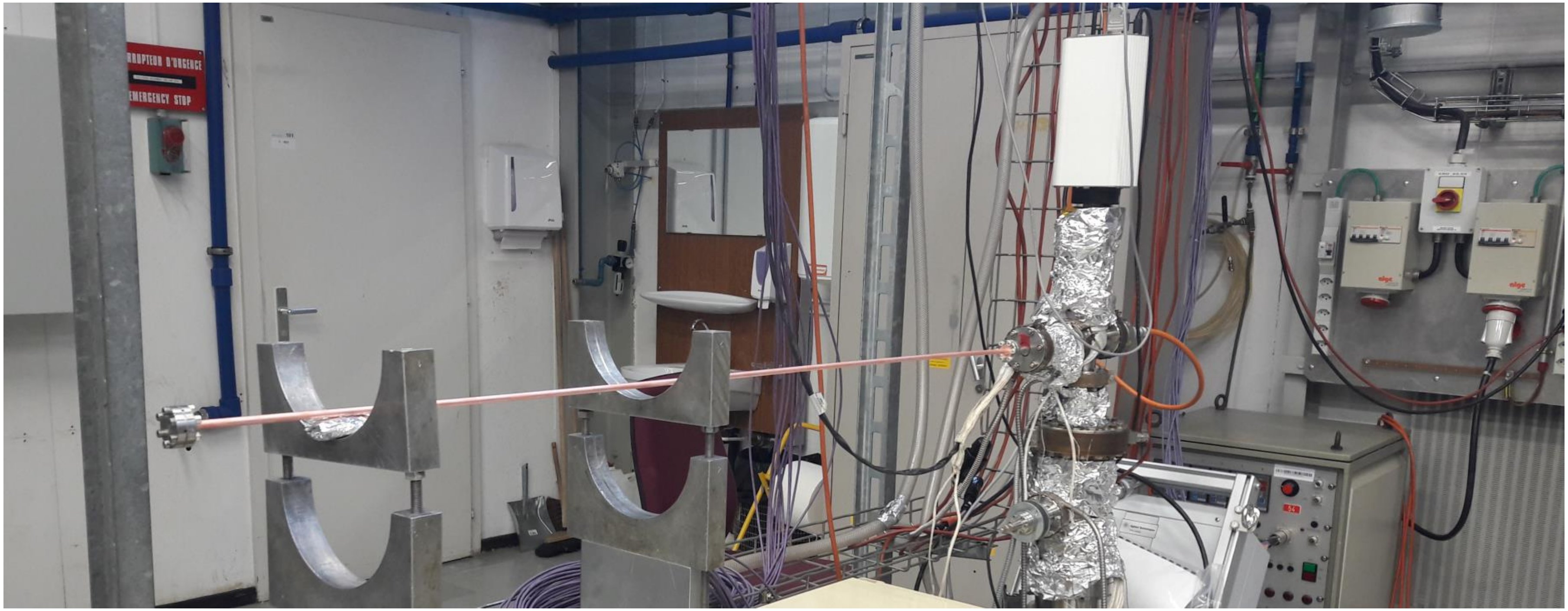
Copper plating 2A/dm^2, 1 mm thickness

After etching of aluminum mandrel

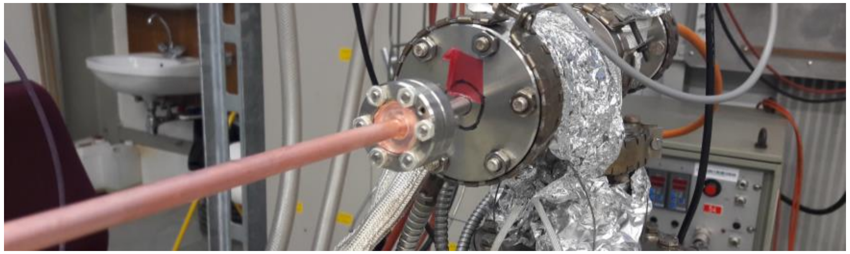


No difficulties encountered at the present stage

Longer lengths: 1.2 meters

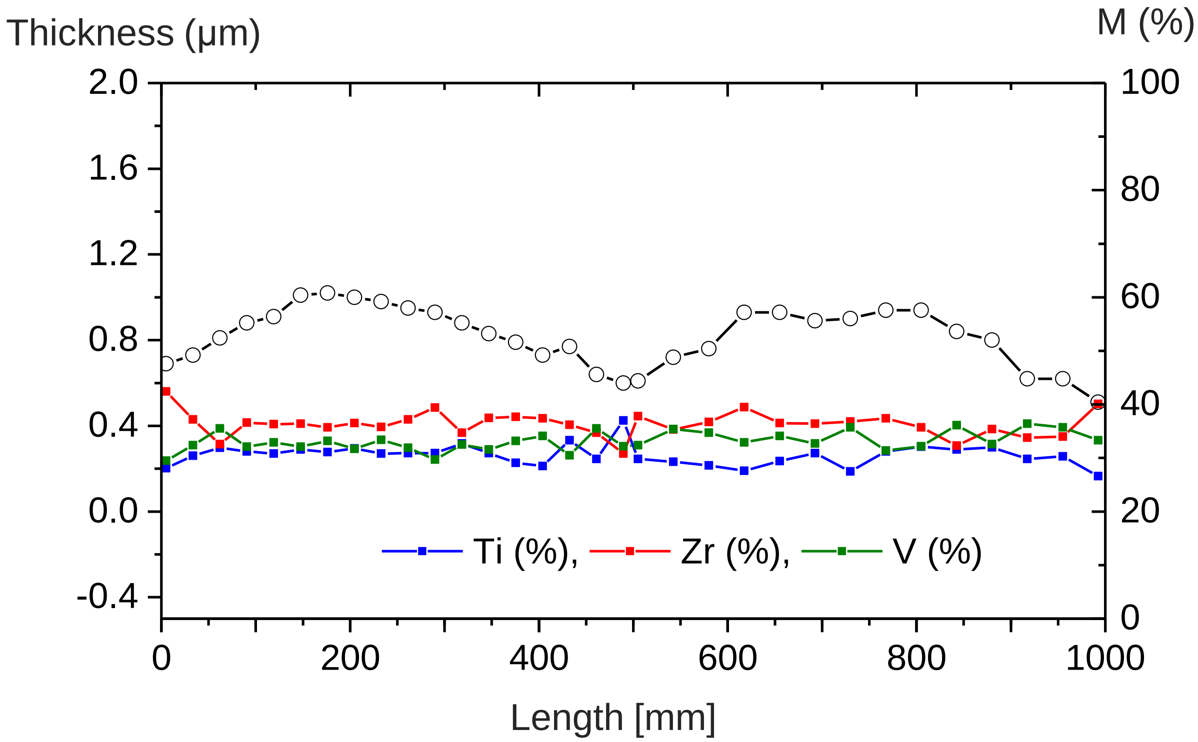


It is leak-tight



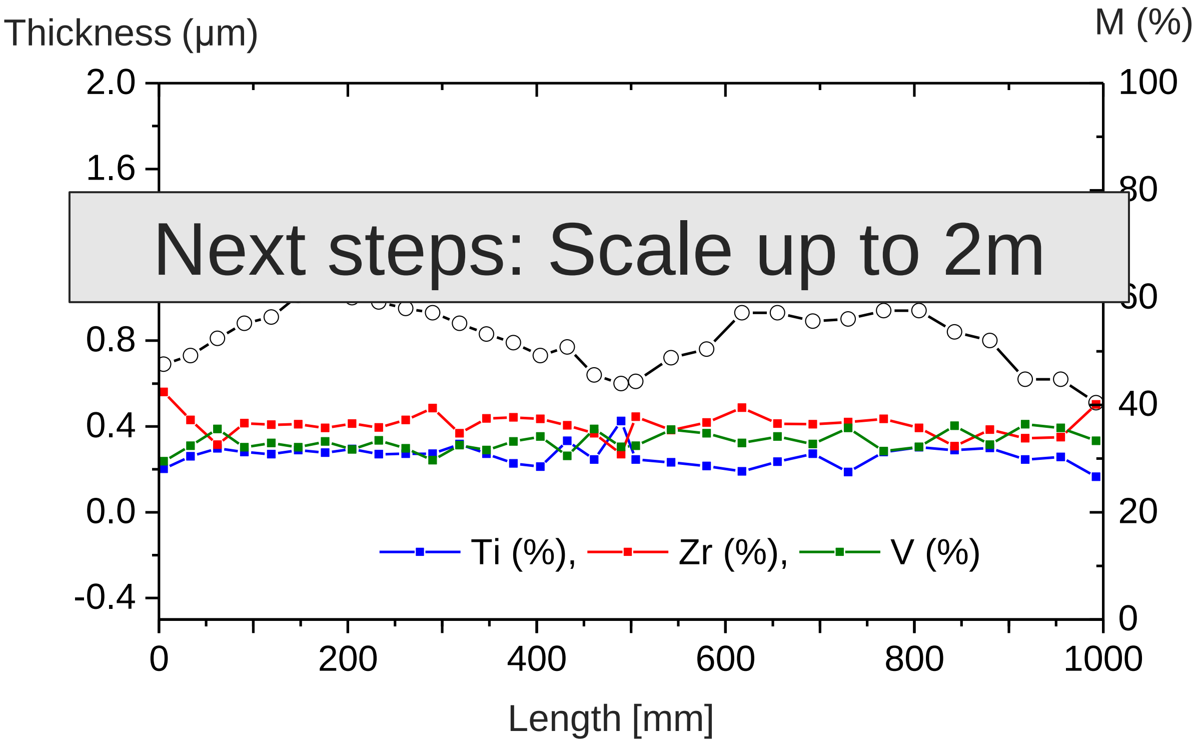
Examples of chambers produced

3mm internal diameter, 1 m length TiZrV coated chamber



Examples of chambers produced

3mm internal diameter, 1 m length TiZrV coated chamber



Next steps: Scale up to 2m

Outline

1. Motivation
2. Usual NEG sputtering technique
3. Reverse coating technique
4. Challenges
5. Preparation for real application
6. **Conclusions & Outlook**

Conclusions & Outlook

The electroformed pre-coated chambers can be successfully assembled and the overall assembly procedure was validated from the point of view of mechanical strength and vacuum tightness.

The aluminium mandrel suits well as it is easy to procure, and to machine; it’s compatible with PVD coating systems; it guarantees mechanical stiffness during the all process.

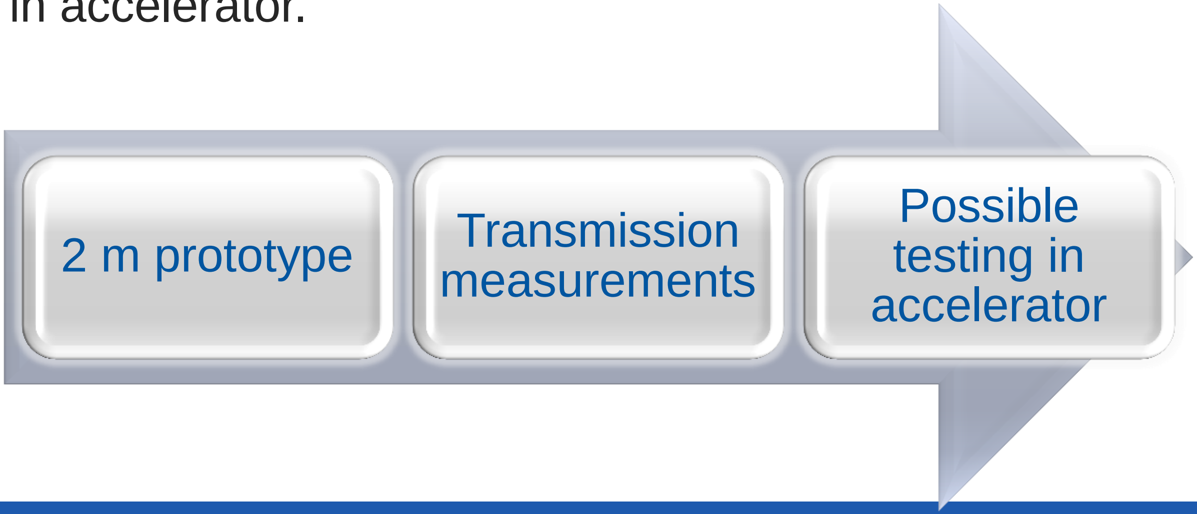
The chambers exhibited a good H_2 pumping speed performance when activated at more than 250˚C. CO pumping starts already at low activation temperatures.

Conclusions & Outlook

Studies still ongoing: Influence of type of aluminium mandrel on activation behaviour and copper plating parameters optimization.

The next step will focus in the validation of the procedure for long chambers (2 m) and measurements in transmission.

We are looking for real case applications in order to specify tolerances and possible testing in accelerator.



2 m prototype

Transmission measurements

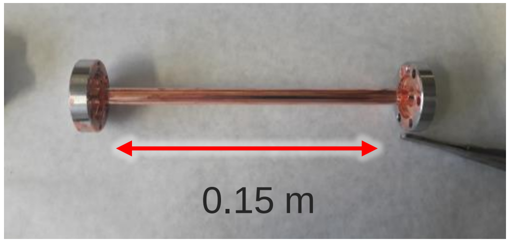
Possible testing in accelerator

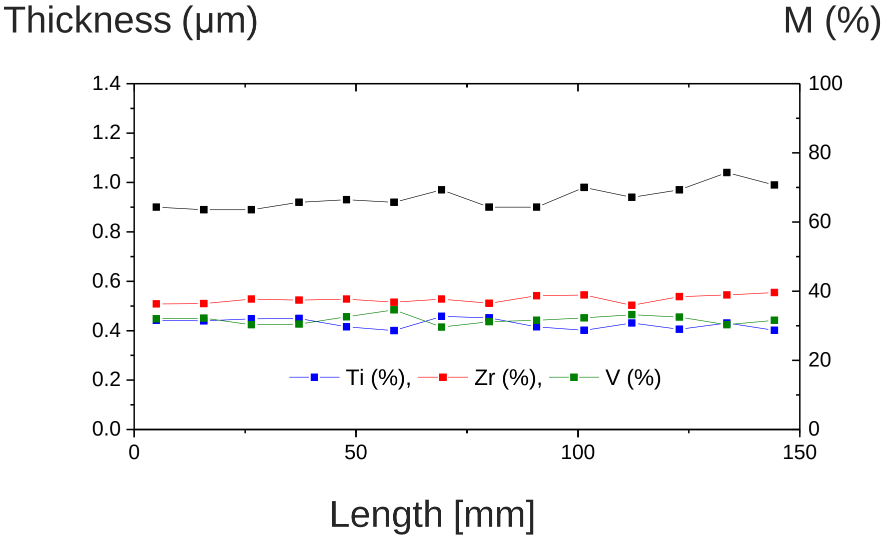
Thank you for your attention!

Acknowledgements to: TE-VSC-SCC section

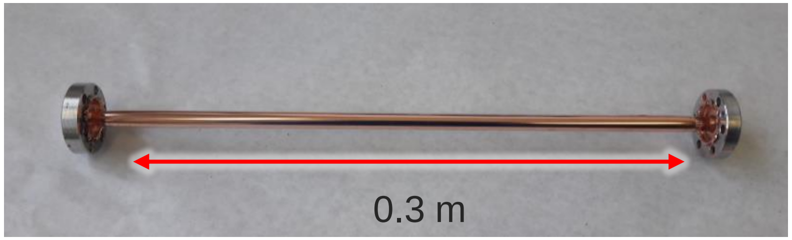
Coating thickness profile (NEG on Cu)

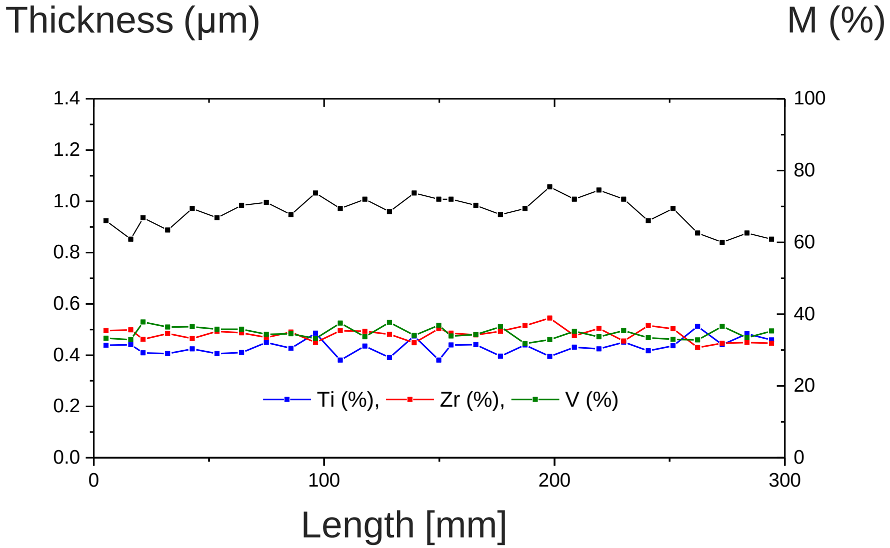
Chamber 6 mm diameter





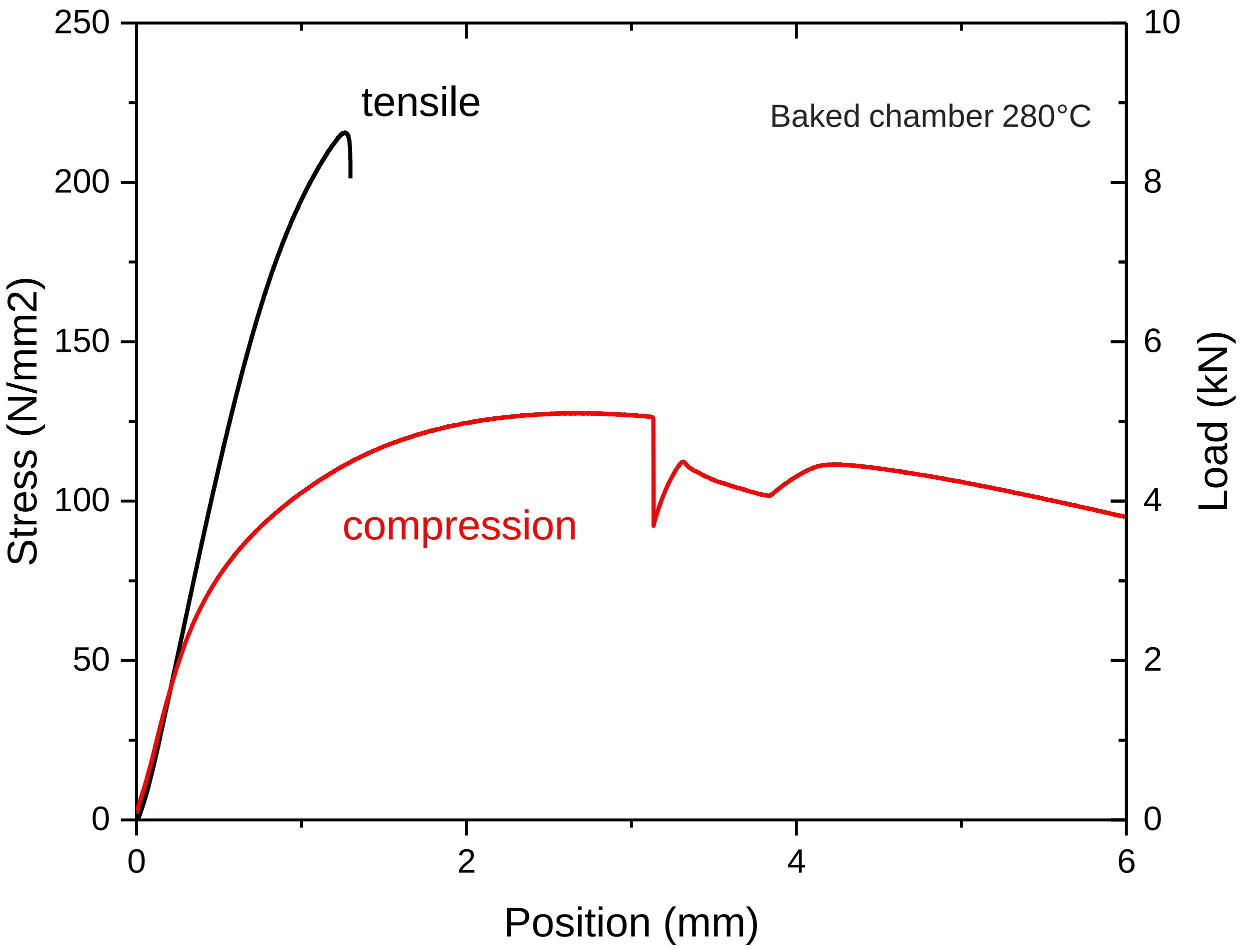
Chamber 5 mm diameter





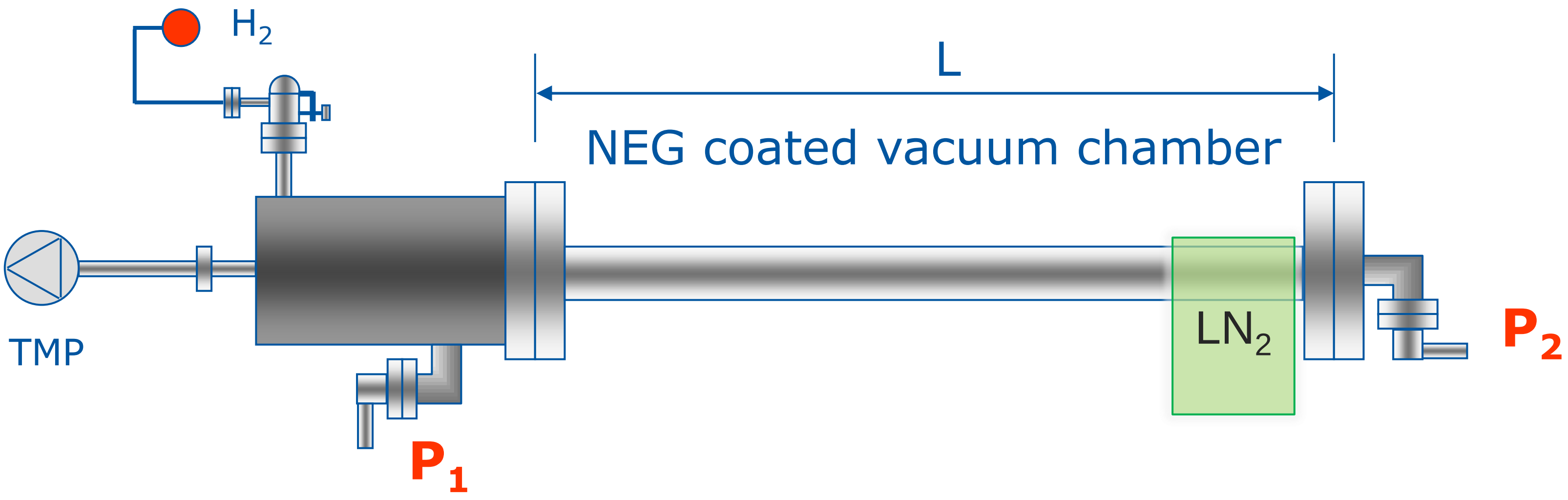
Homogeneous TiZrV composition, Thickness variation < 20%

Mechanical performance



Pumping speed measurement via Transmission tests

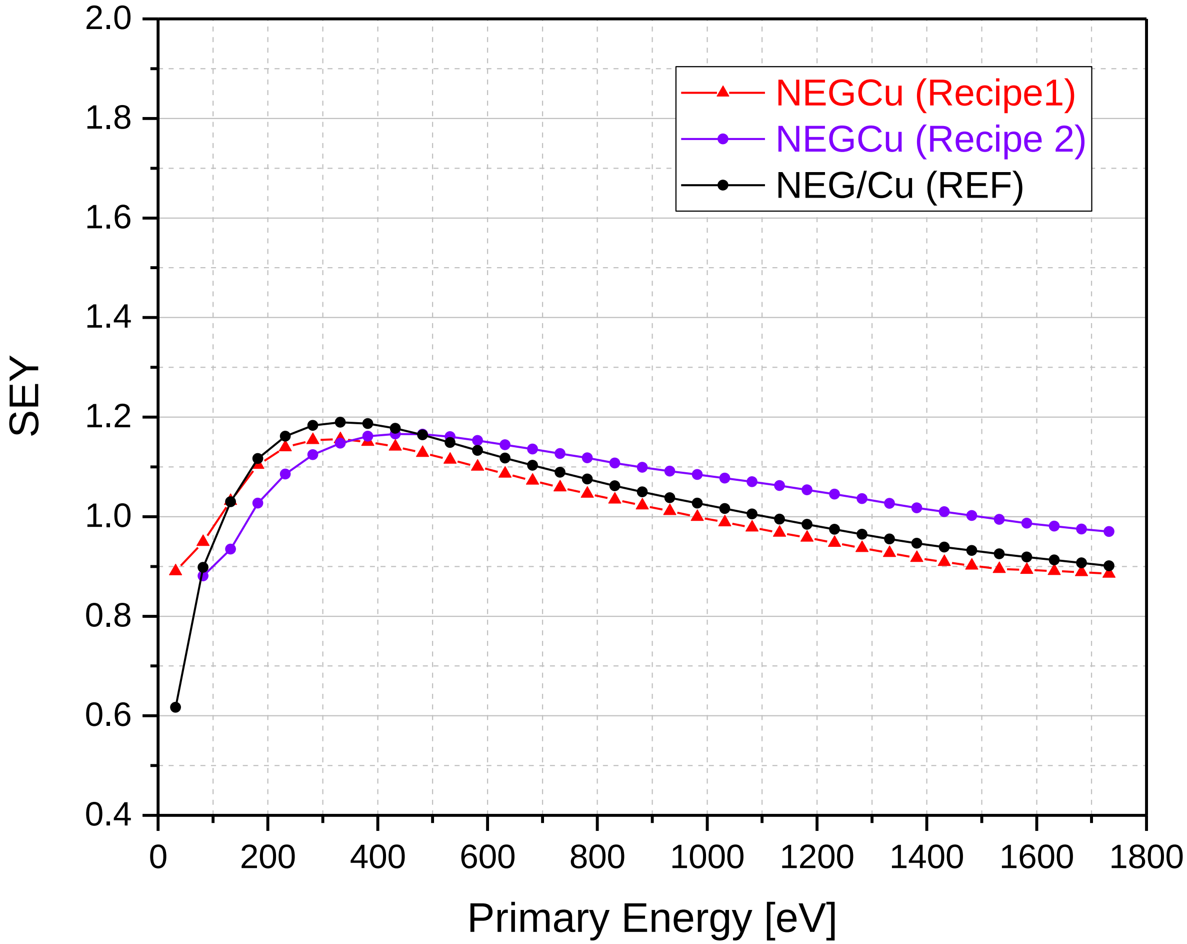
Removing CH_4 cracking from gauge: LN_2 trap



$$\text{Pressure ratio} = \frac{\Delta P_2}{\Delta P_1}$$

With a Monte Carlo simulation we calculate the sticking probability of H_2 from $\Delta P2/\Delta P1$

SEY after activation 1h at 250°C



Examples of chambers produced

5mm internal diameter, 1.2 m length, TiZrV coated chamber