

AKADEMIA GÓRNICZO-HUTNICZA
IM. STANISŁAWA STASZICA W KRAKOWIE

AGH UNIVERSITY OF SCIENCE
AND TECHNOLOGY

AGH

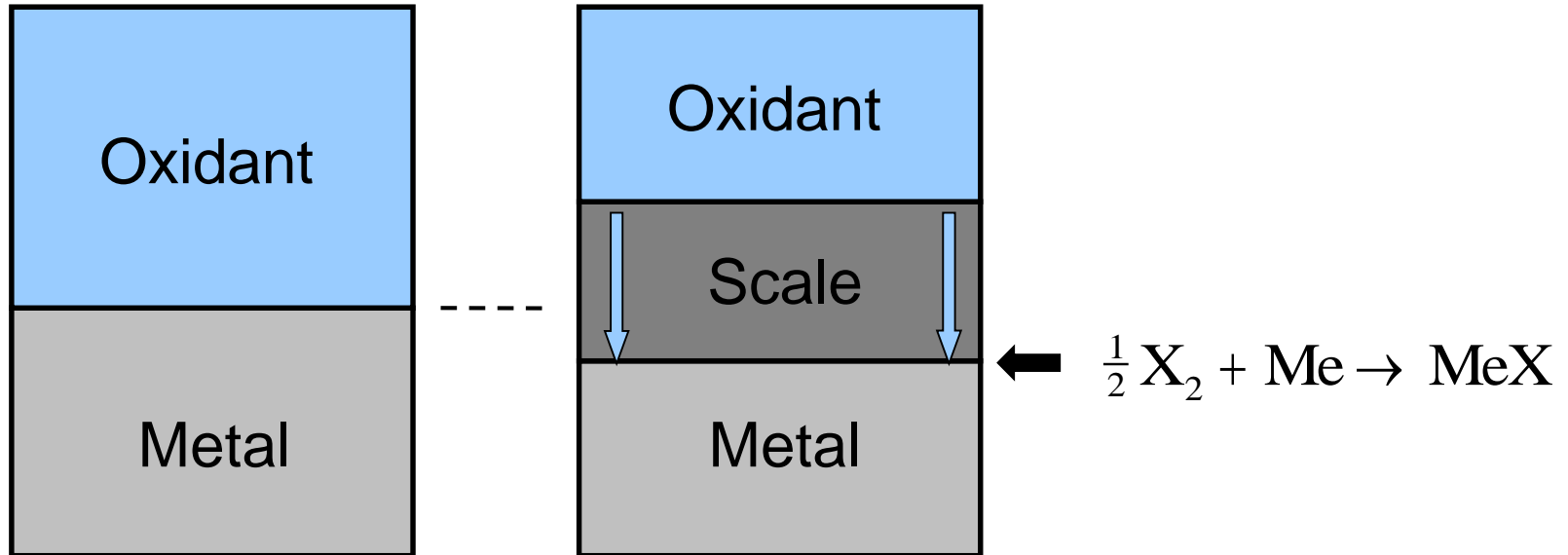
METHODS OF STUDYING THE CORROSION PROCESS MECHANISM

<http://home.agh.edu.pl/~grzesik>

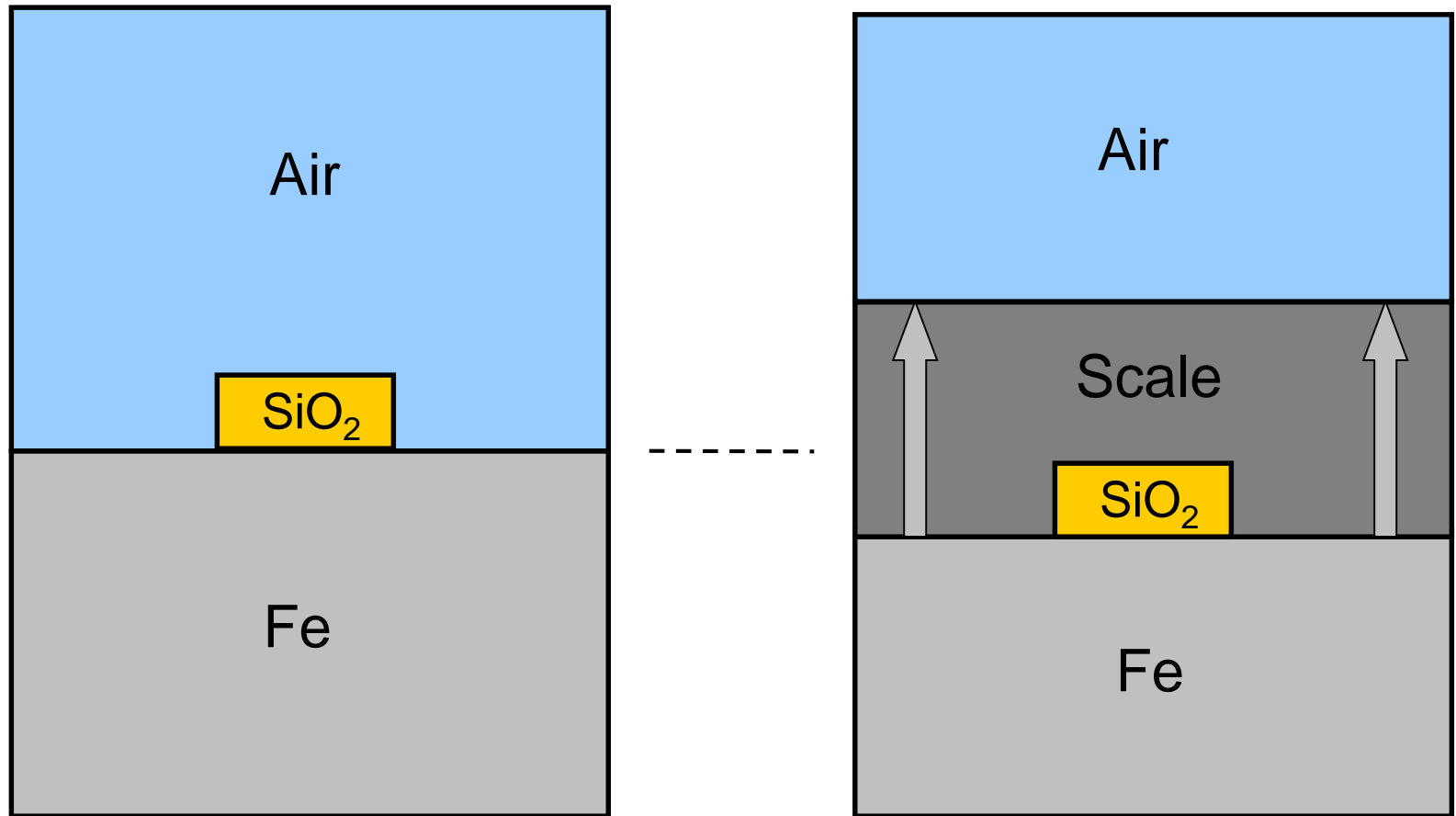
Methods of determining the contribution of individual reagents in matter transport through the scale

- Marker method
- Two-stage oxidation method
- Determining self-diffusion coefficients
- Scratch method
- Pellet method

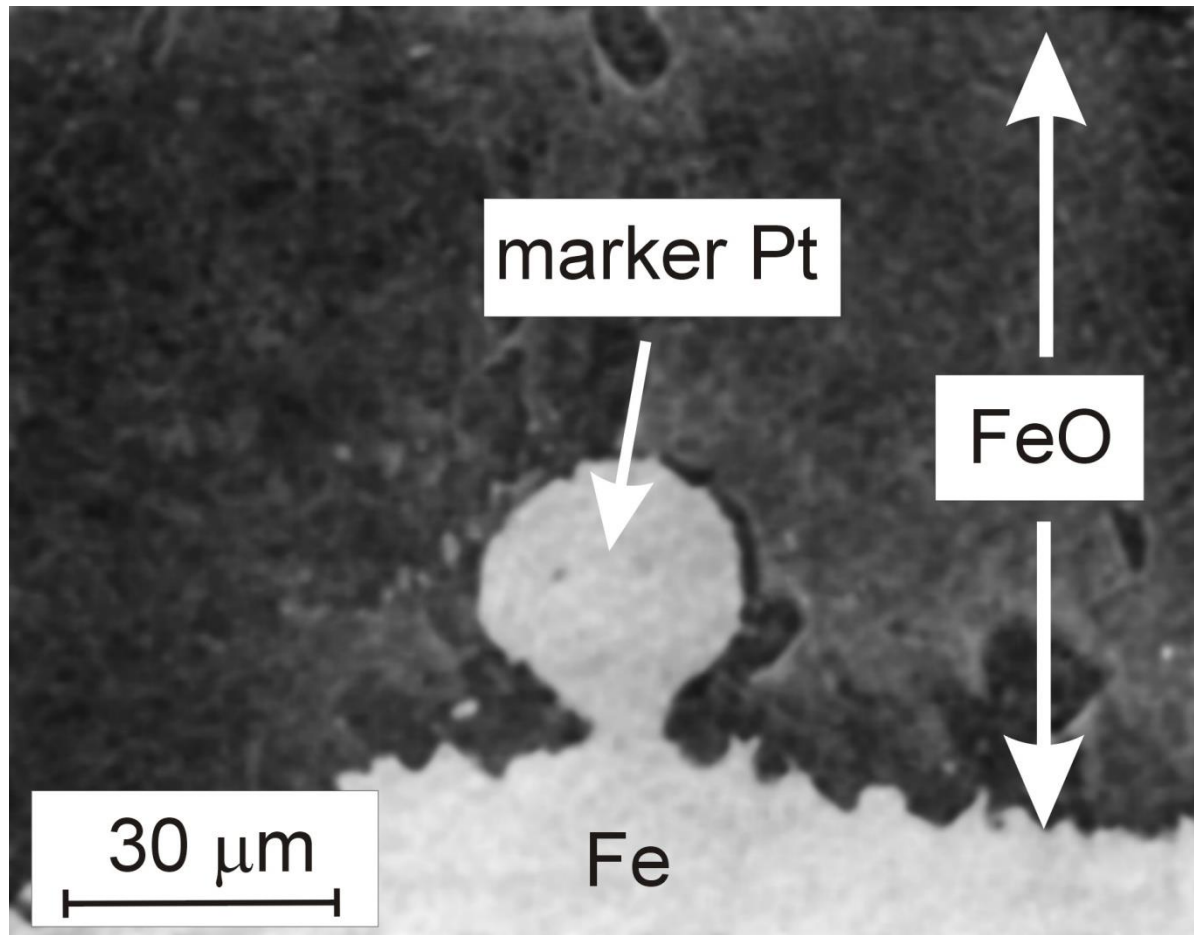
Schematic illustration of scale formation according to Tammann (1920)



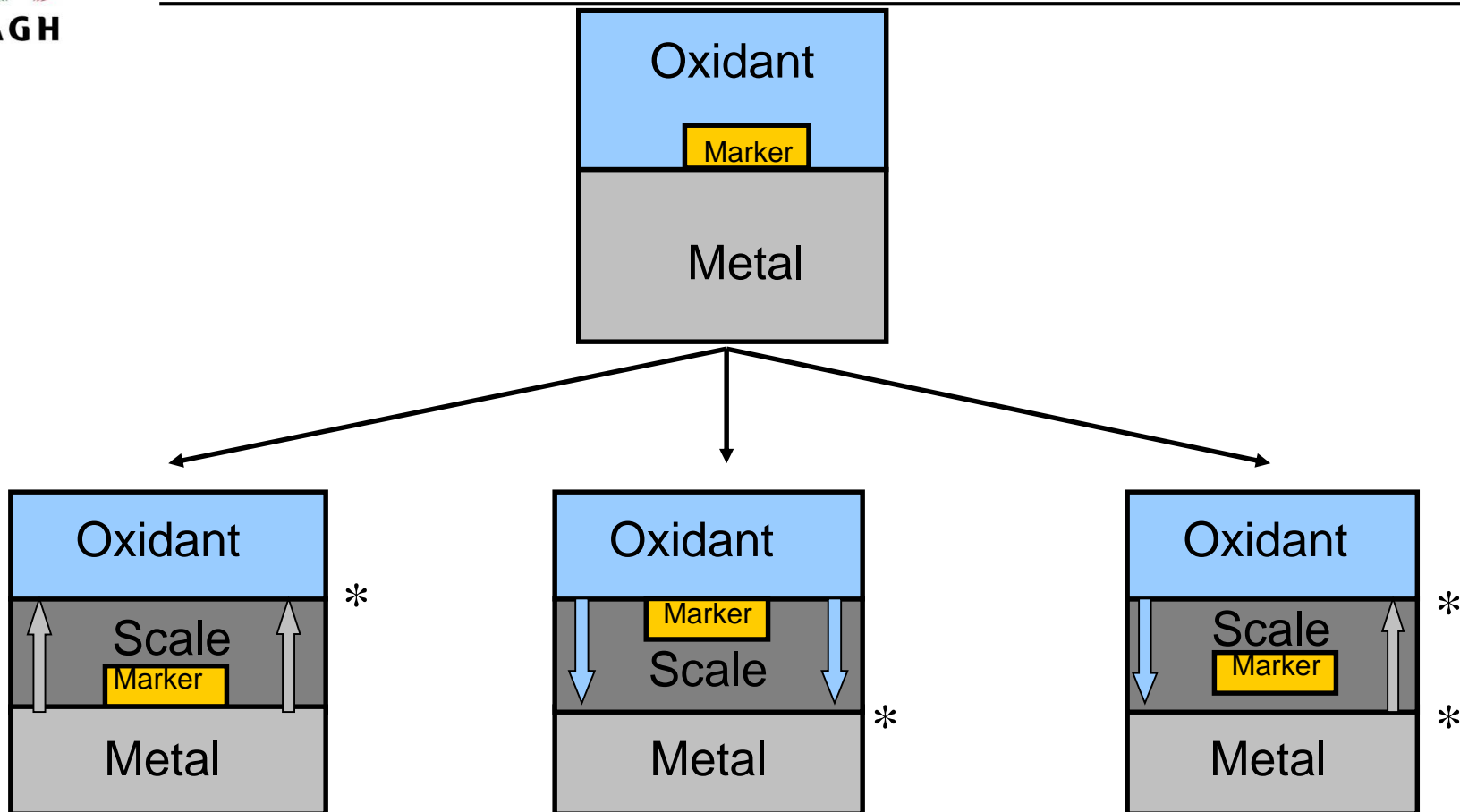
Marker method – schematic illustration of Pfeil's classic experiment (1929)



Marker experiment in a Fe-O system



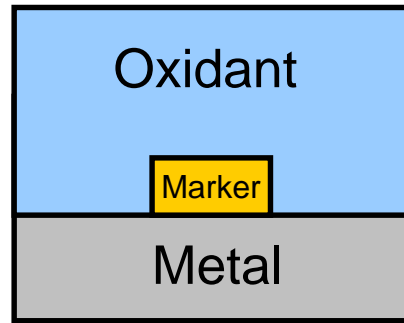
Marker method – interpreting results



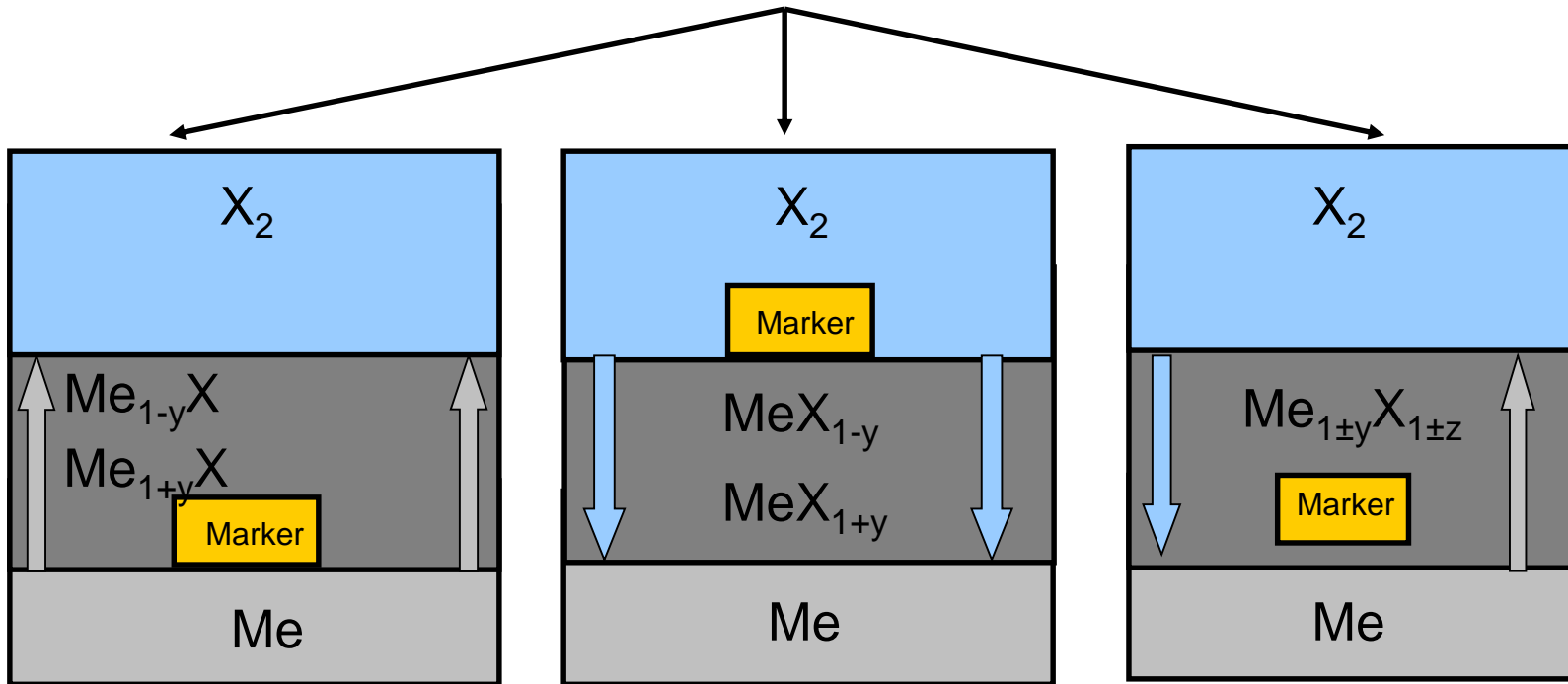
* reaction location:



Marker method – interpreting results in the case of predominant lattice diffusion



For temperatures above Tammann's temperature



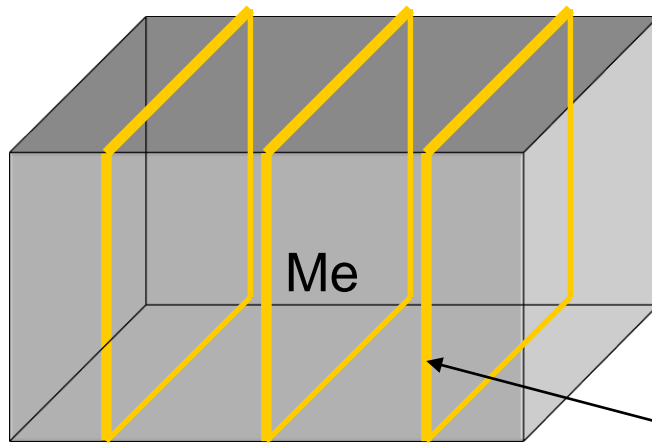
Conditions for the correct procedure of a marker experiment

- the surface of the examined metal or alloy is smooth
- the marker does not react with the metallic substrate, oxidant, or with substances that are compounds constituting the scale
- before beginning the oxidation process, contact between the marker and surface of examined material is maintained
- the formed scale is compact, single-phase and strictly adheres to the metallic core
- oxidation time is selected so that the thickness of the scale will be at least one order of magnitude larger than the marker

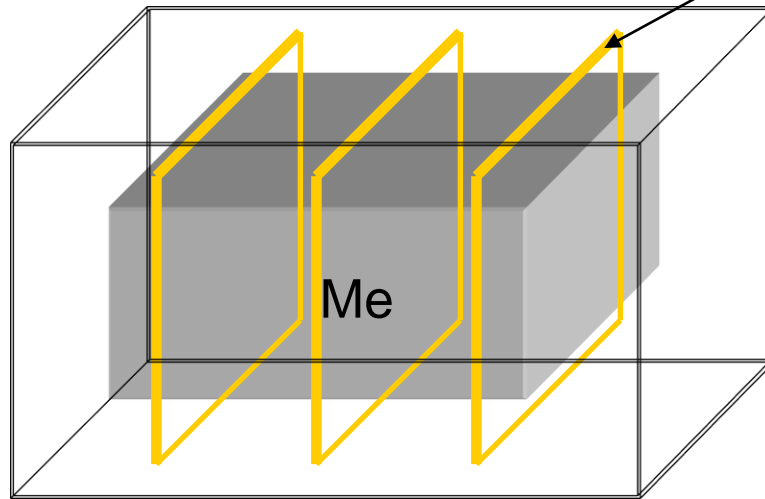
Methods of depositing markers on metallic substrate surfaces

- even distribution of marker grains (Al_2O_3 , SiO_2 , etc.)
- even distribution of a thin ($10\ \mu\text{m}$) wire (Pt, Au) with around 1 mm length
- welding a thin wire constituting a marker
- Depositing a marker (Pt, Au) through an appropriate mesh (Cu – SEM; Al)
- electrolytic deposition of a marker layer
- decomposition of a noble metal salt, placed on the sample surface
- photolytic method
- Covering the sample surface with diluted platinum paste

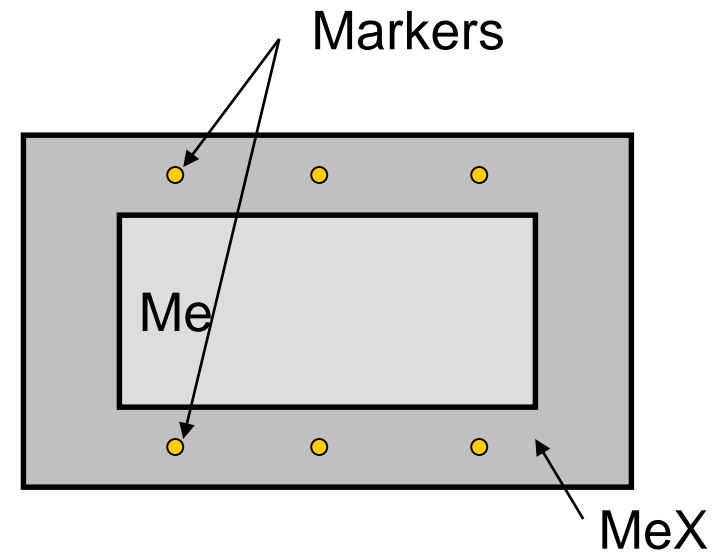
Examples of incorrectly using the marker method using a non-elastic wire around the metal



Markers



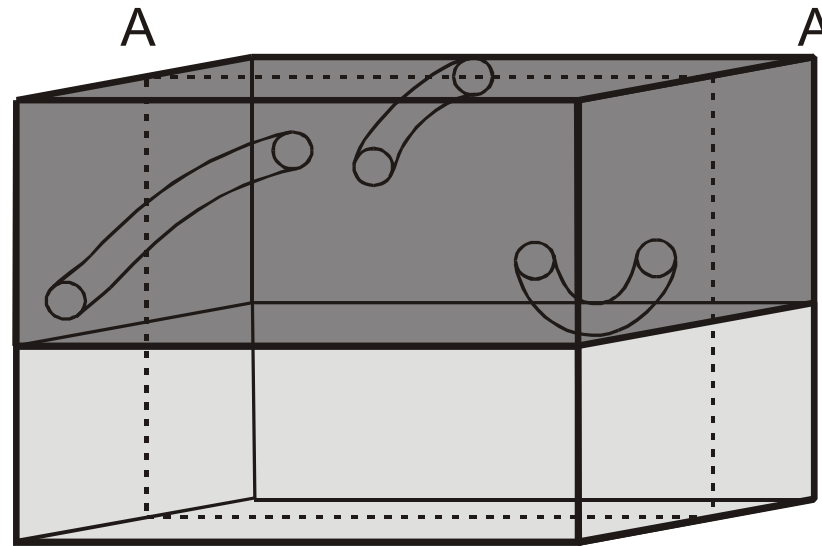
MeX



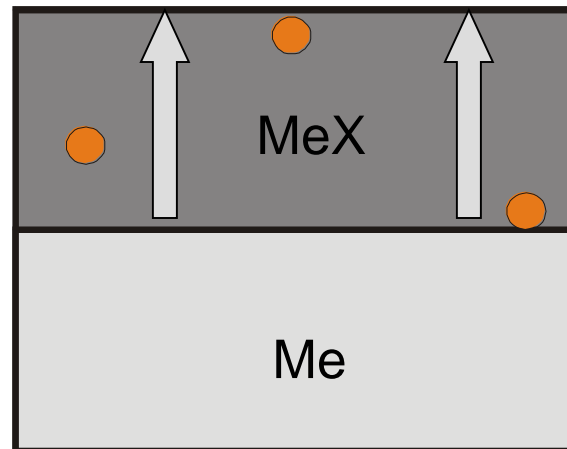
Markers

MeX

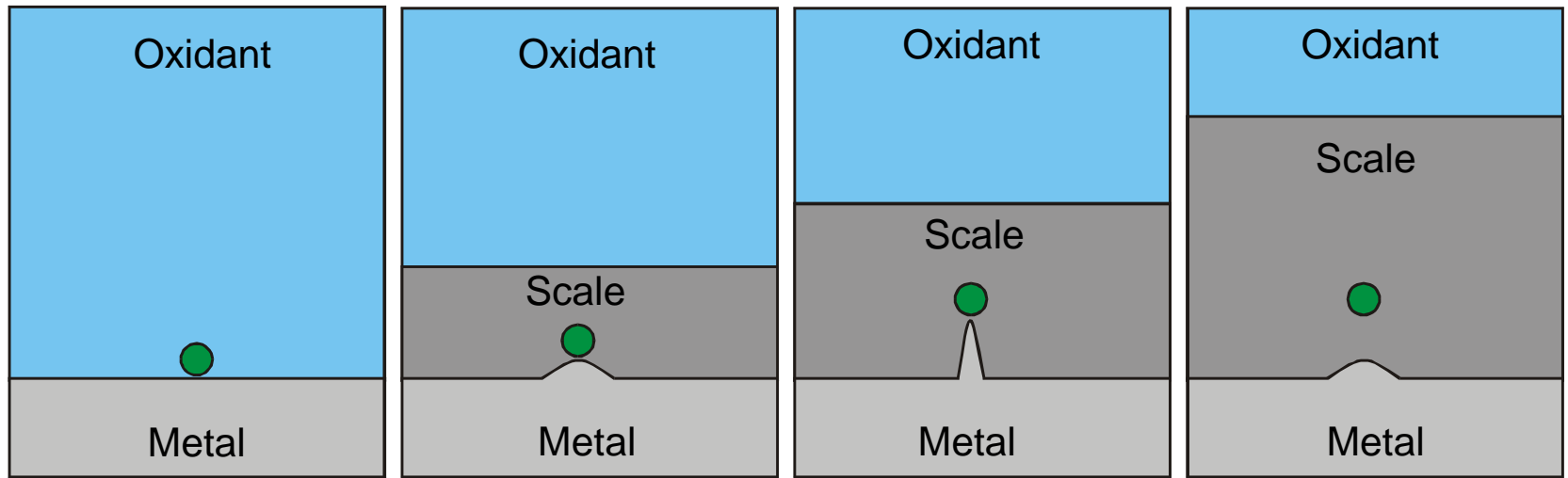
Examples of incorrectly using the marker method marker does not adhere to the metal after deposition



Cross-section A-A

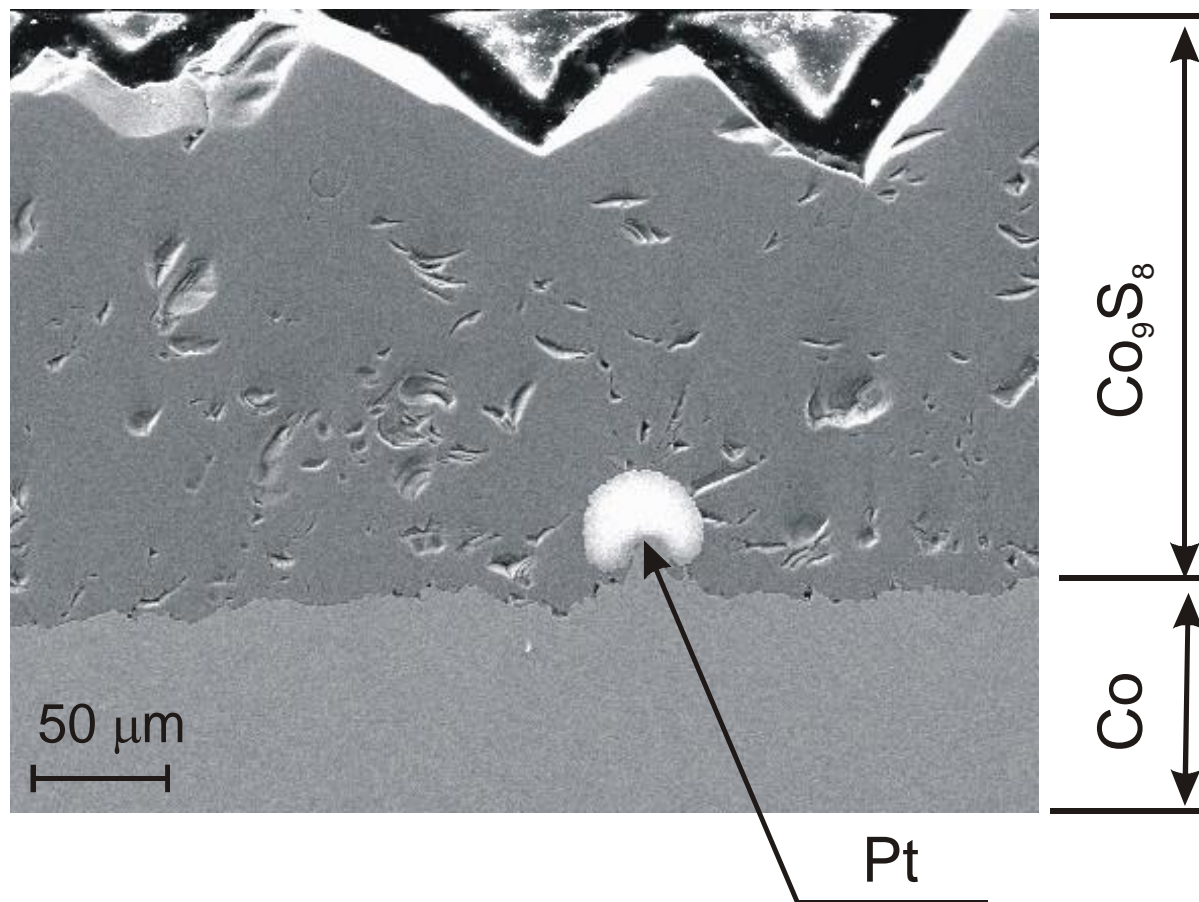


Example of how a marker experiment can be incorrectly interpreted due to the undercutting mechanism



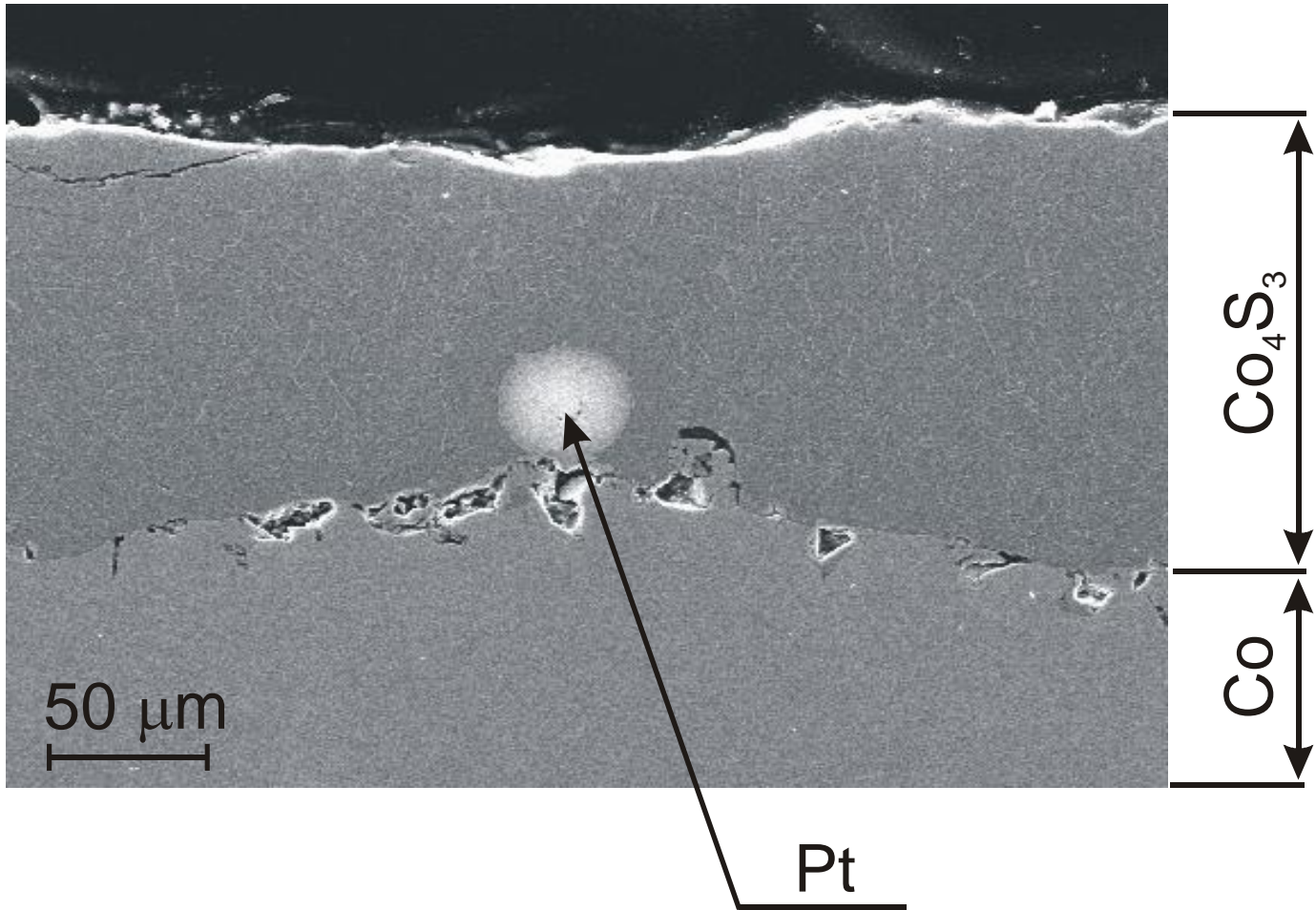
● Marker

Cross-section of a sulfide scale formed on cobalt with an indicated marker location



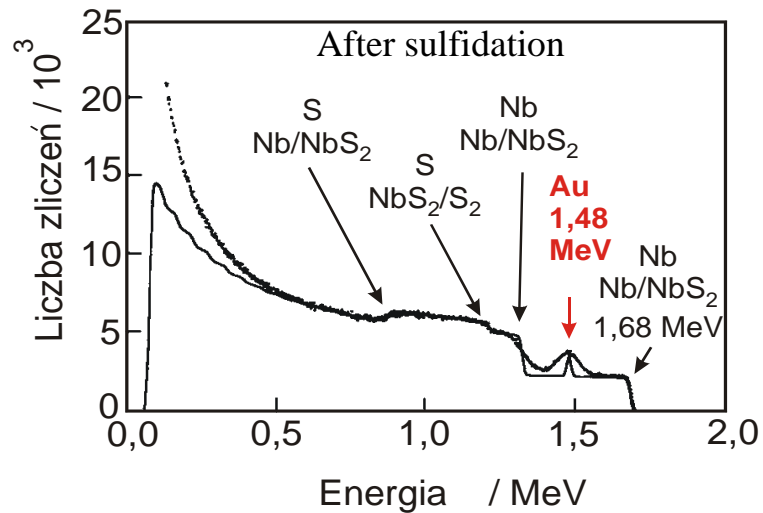
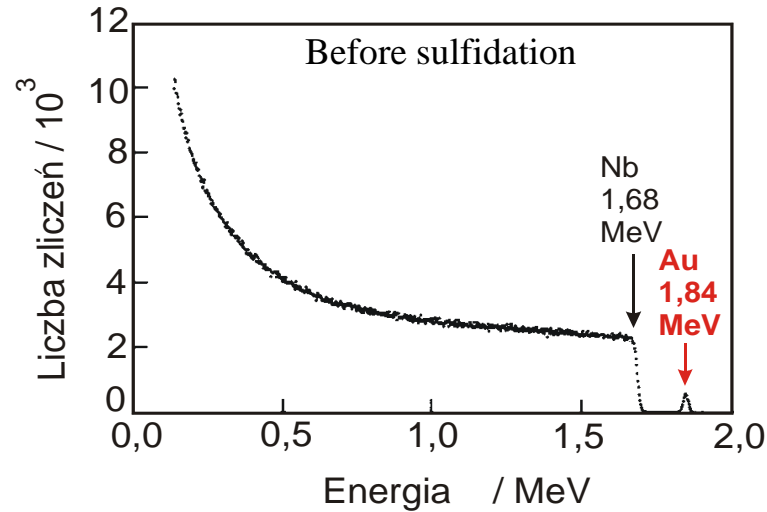
$T = 700 \text{ }^\circ\text{C}$, $p(\text{S}_2) = 10^{-2} \text{ Pa}$

Cross-section of a sulfide scale formed on cobalt with an indicated marker location

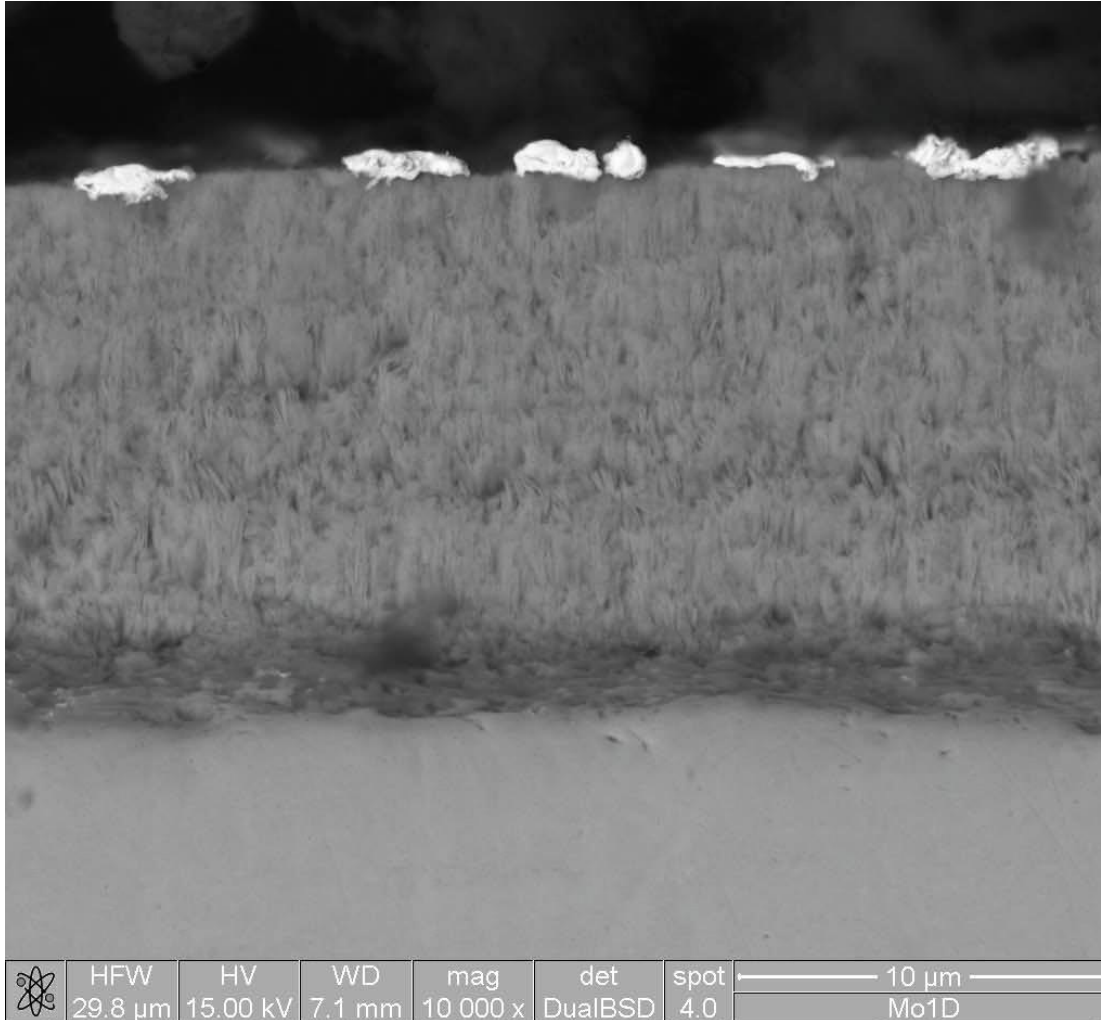


$T = 860\ \text{°C}$, $p(\text{S}_2) = 10^{-1}\ \text{Pa}$

RBS spectrum (^4He - 2 MeV) of an Nb sample marked with Au, before and after sulphidation

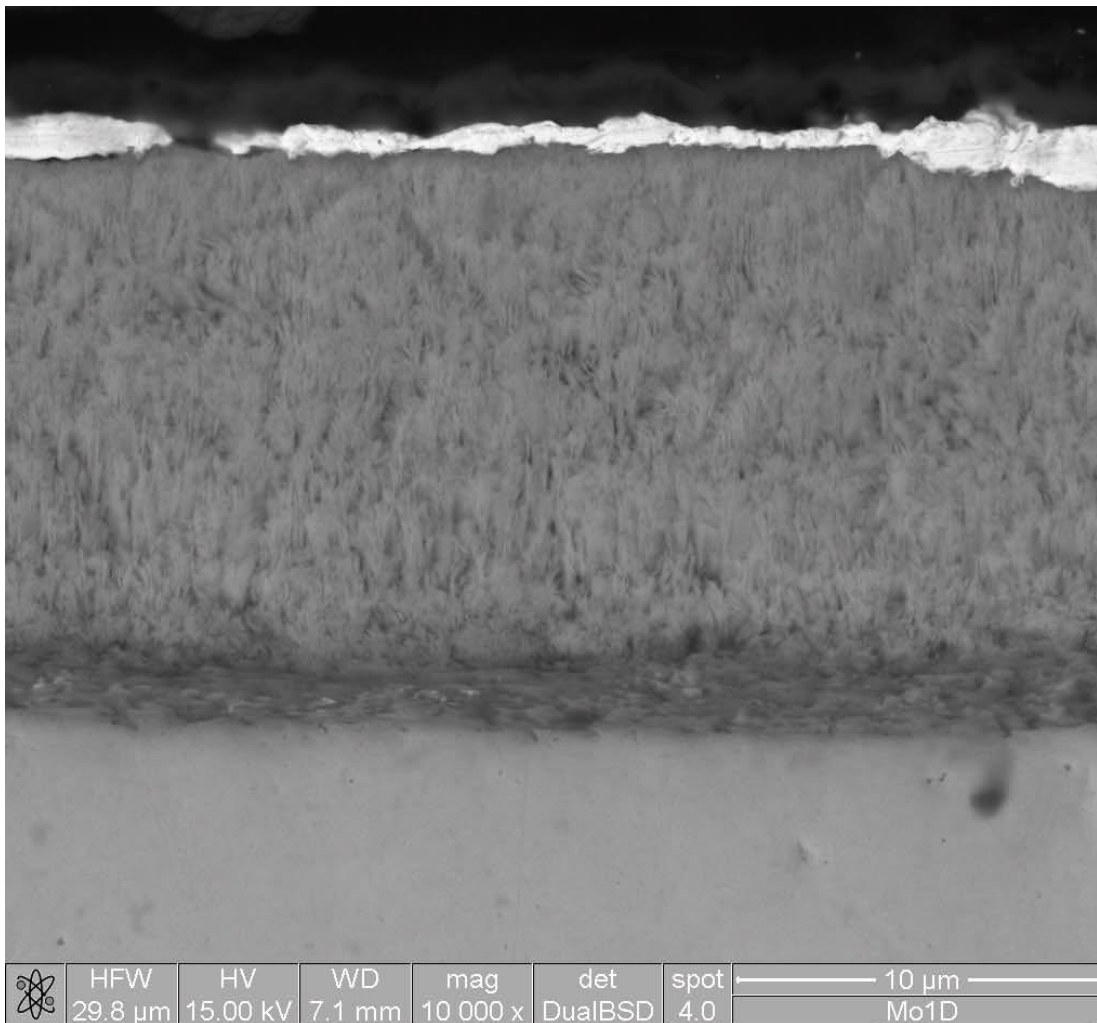


Cross-section of an MoS₂ scale formed on Mo with an indicated marker location



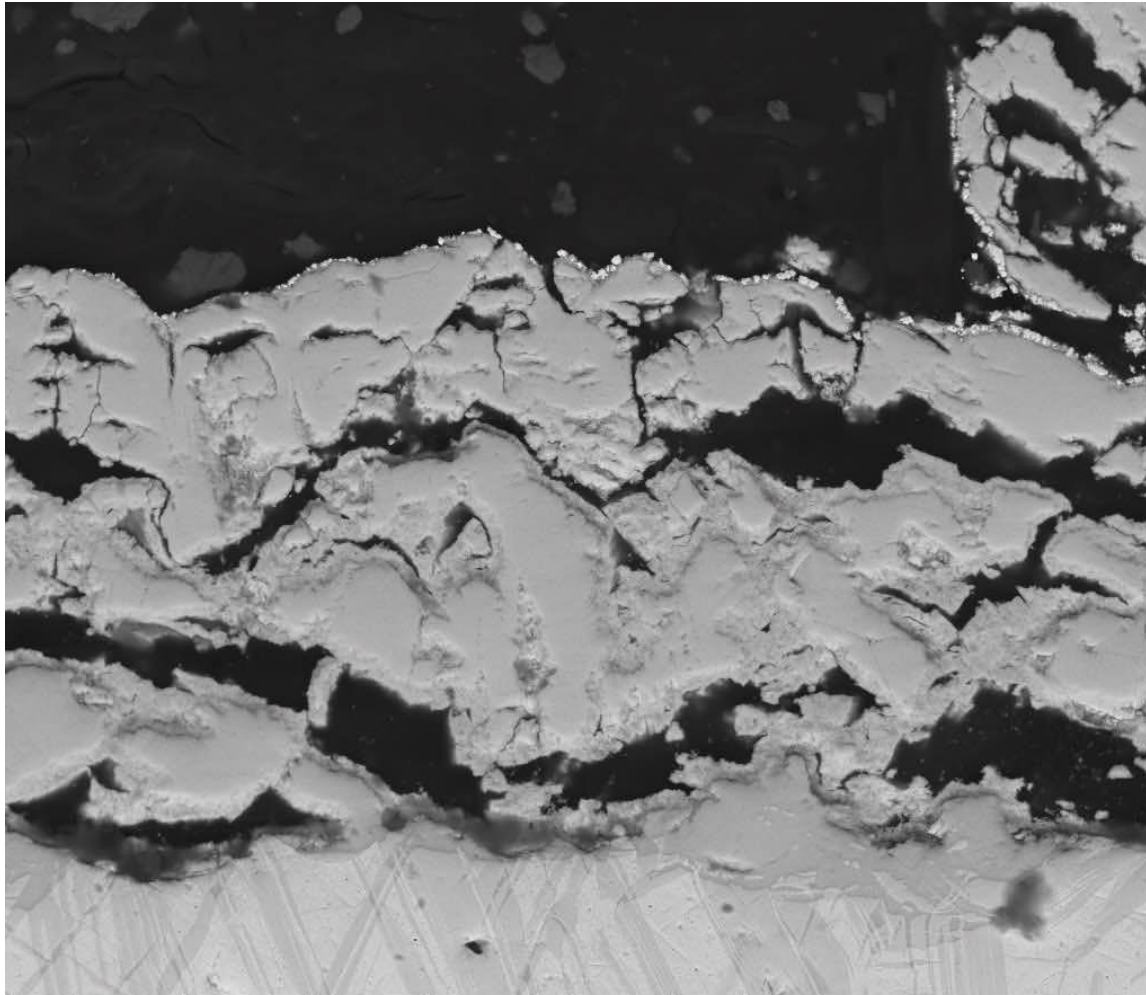
correctly
performed
experiment

Cross-section of an MoS₂ scale formed on Mo with an indicated marker location



incorrectly
performed
experiment

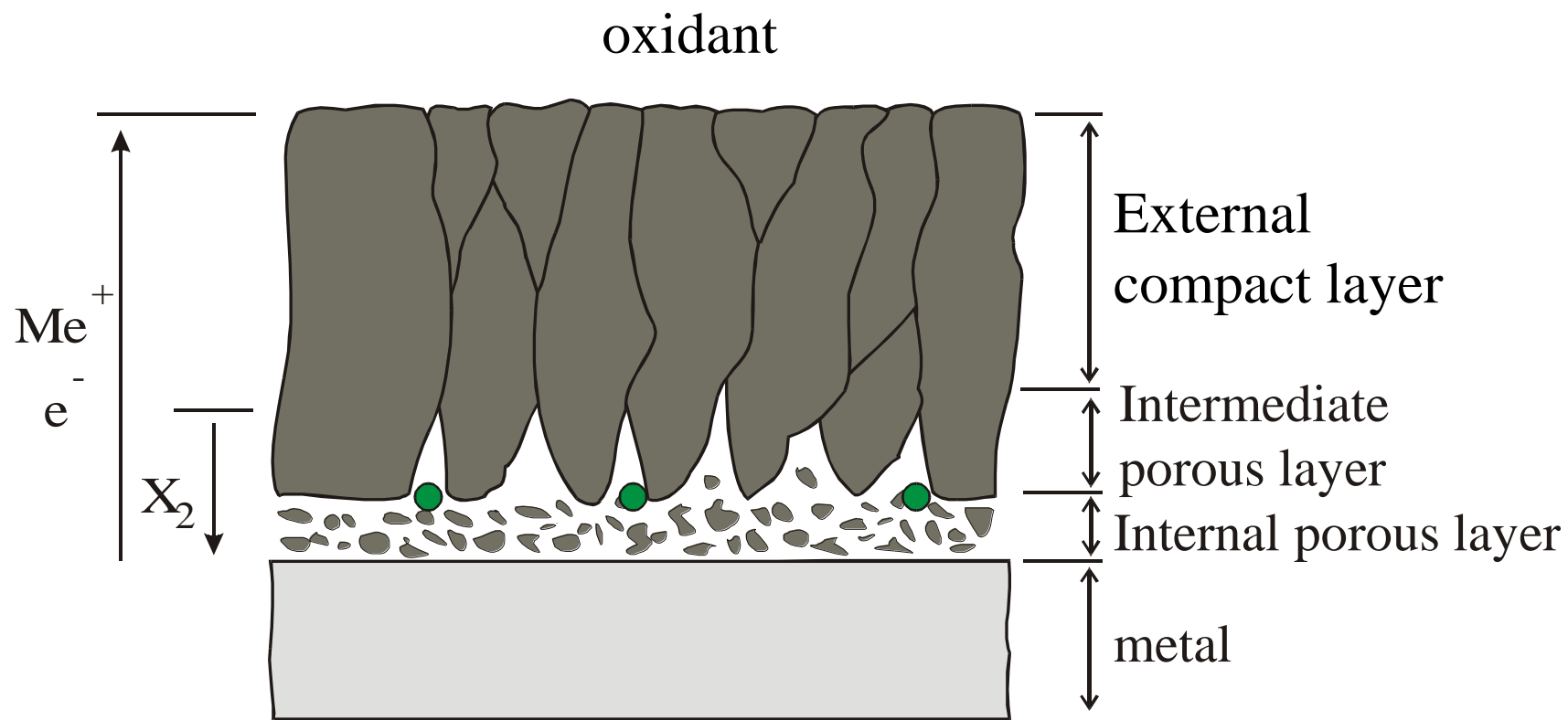
Cross-section of an TaS₂ scale formed on Ta with an indicated marker location



correctly
performed
experiment

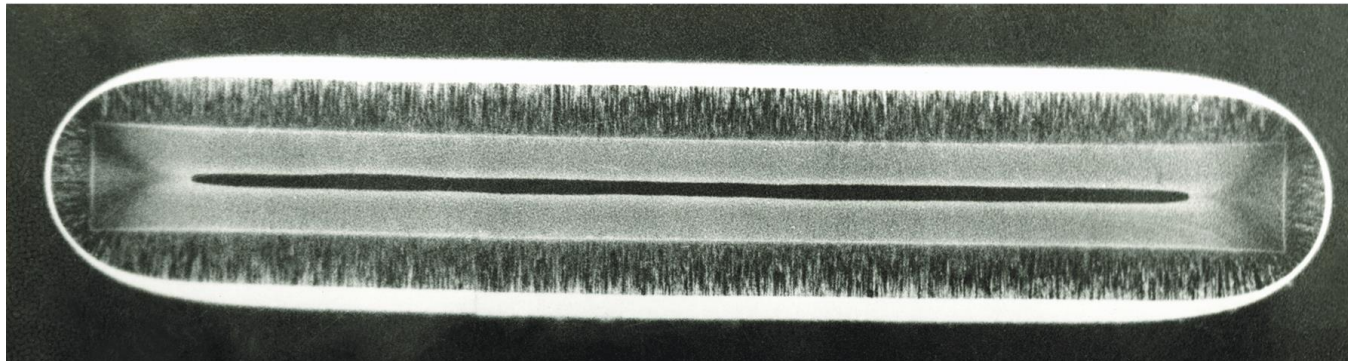
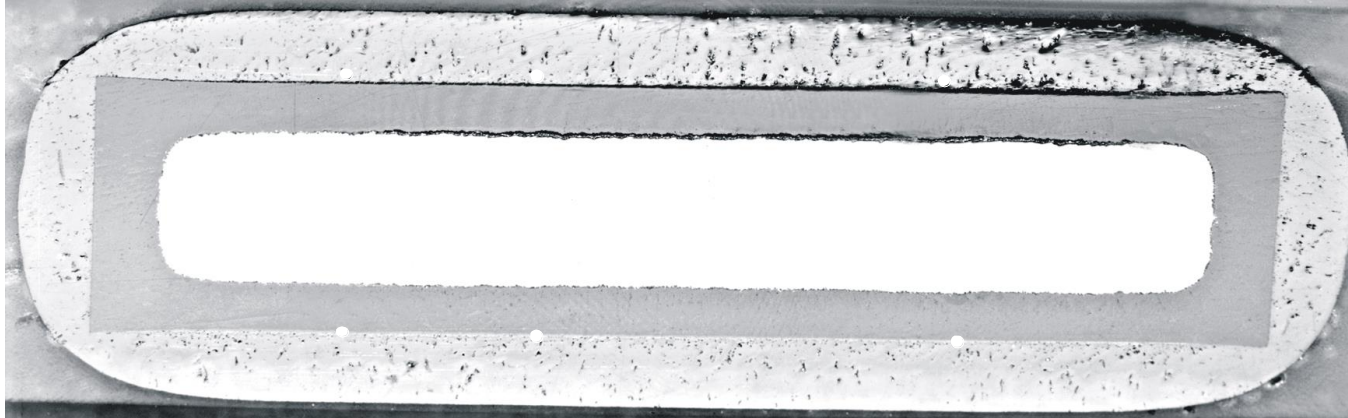
	HFW 99.5 μm	HV 15.00 kV	WD 6.4 mm	mag 3 000 x	det DualBSD	spot 4.0	30 μm pr3Pt
---	----------------	----------------	--------------	----------------	----------------	-------------	----------------

Cross-section of a triple-layer scale on a flat surface with an indicated marker location



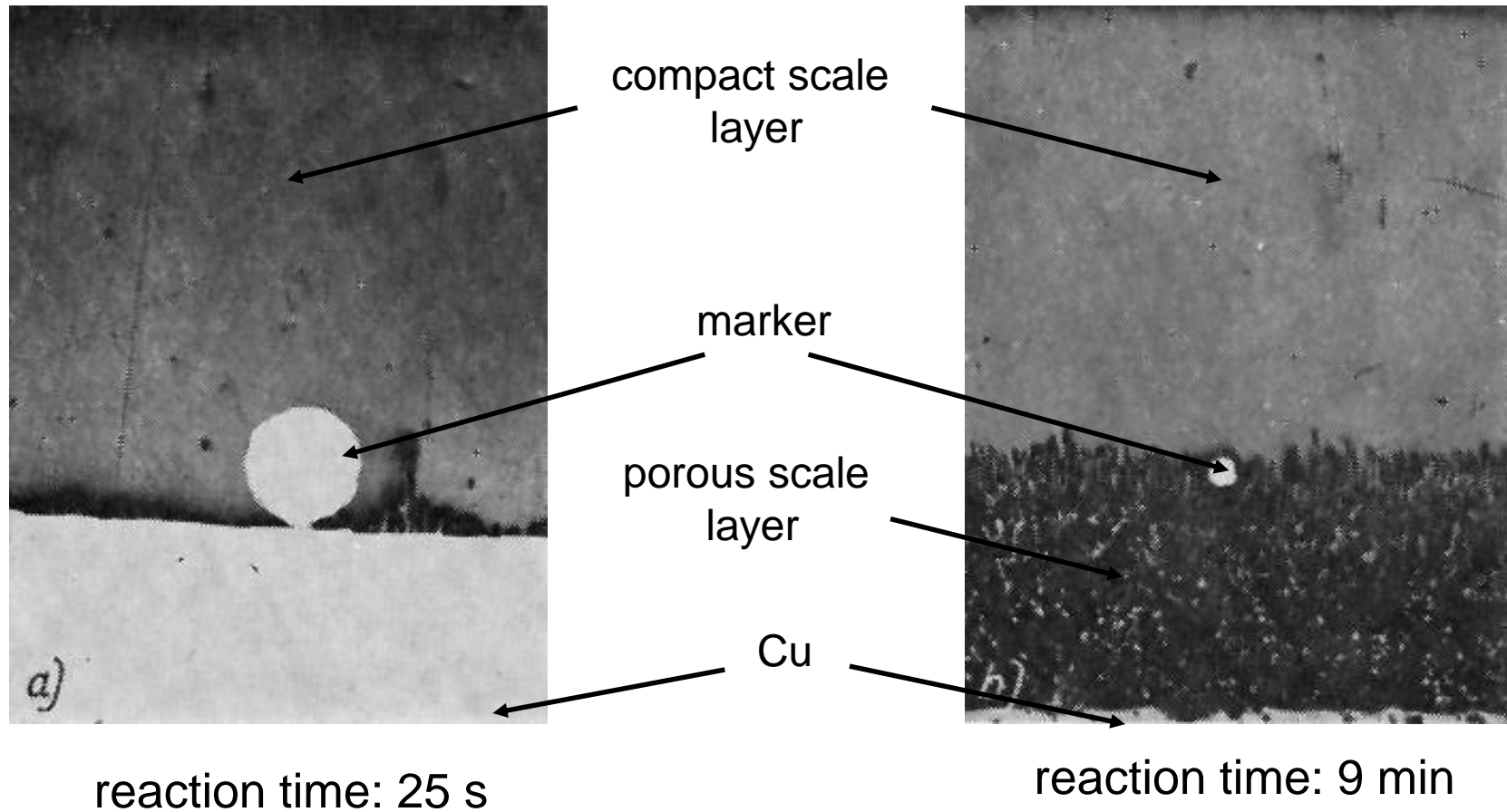
● Marker

Picture of dissociation crevices in a sulfide scale on Cu-9%Zn alloy, obtained in a two-stage sulphidation process



Autoradiogram

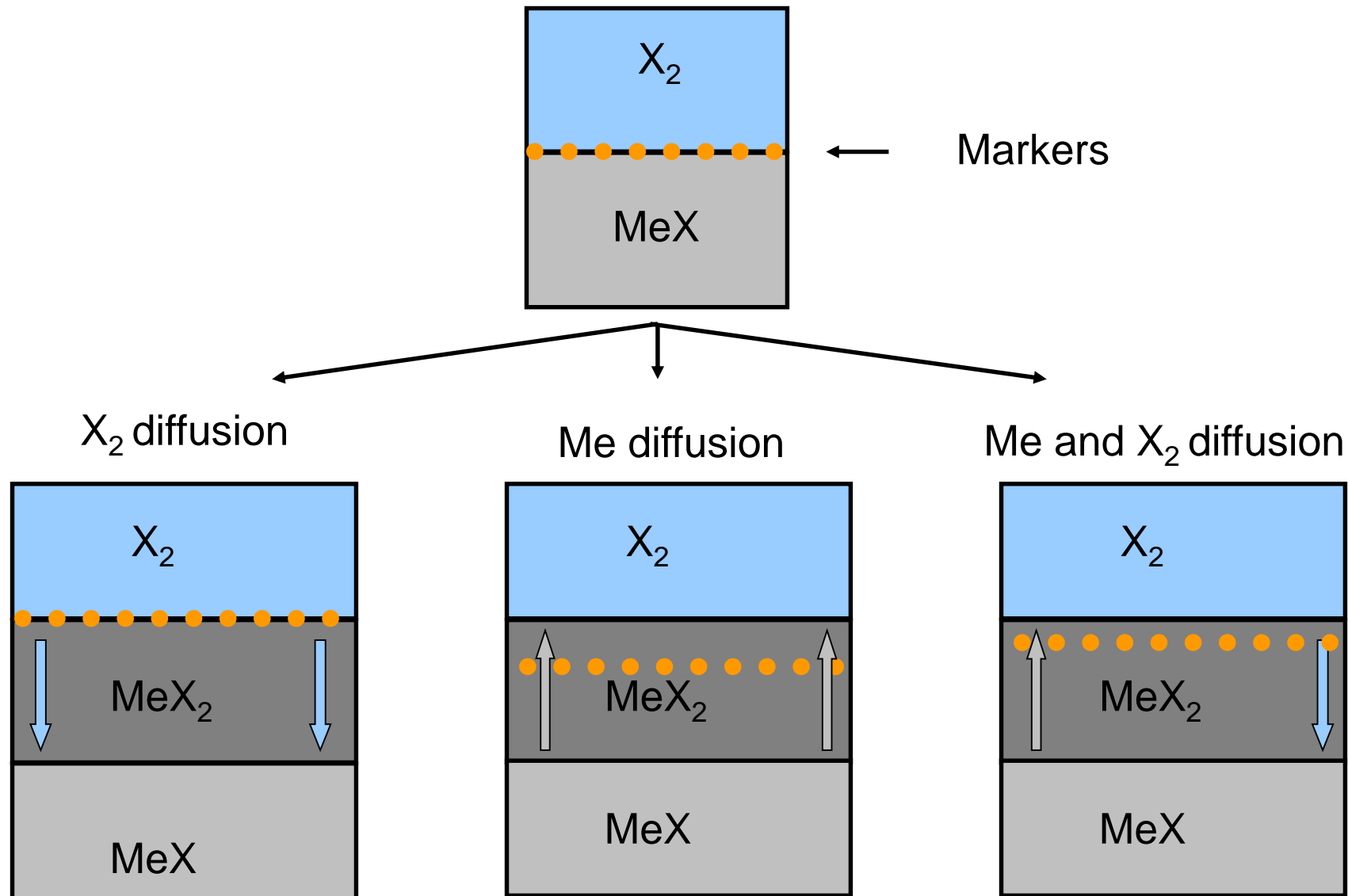
Cross-section of a sulfide scale on copper, obtained at 444 °C



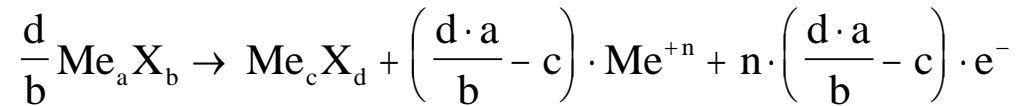
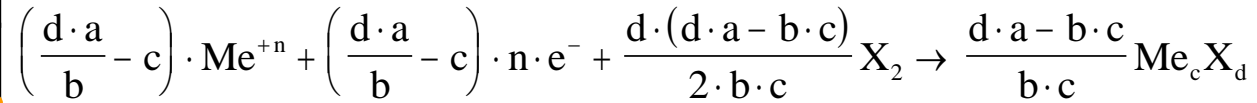
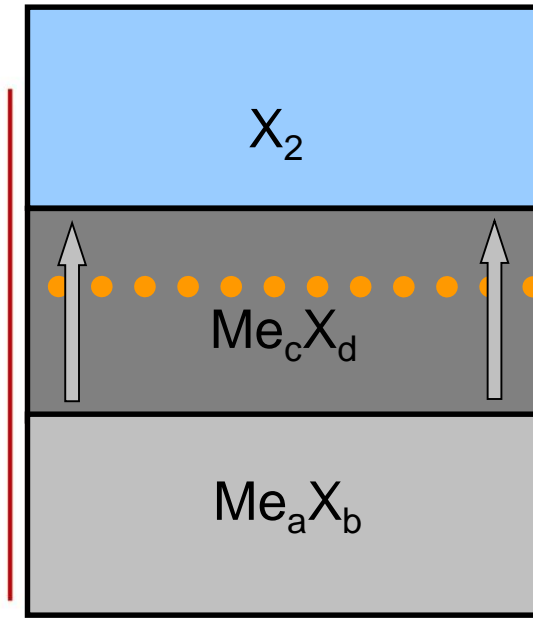
Marker method in a system with a ceramic substrate

- a) „classic” results interpretation
- b) point defect concentration in studied materials and the result of the marker experiment
- c) nuclei of the reaction product inside the substrate and the result of the marker experiment
- d) physical microdefects of the substrate and the result of the marker experiment

Schematic illustration of using the marker method in an oxide – oxidant system



Marker experiment interpretation in an oxide – oxidant system



Ratio of external thickness to the internal part of the $\text{Me}_c X_d$ oxide layer

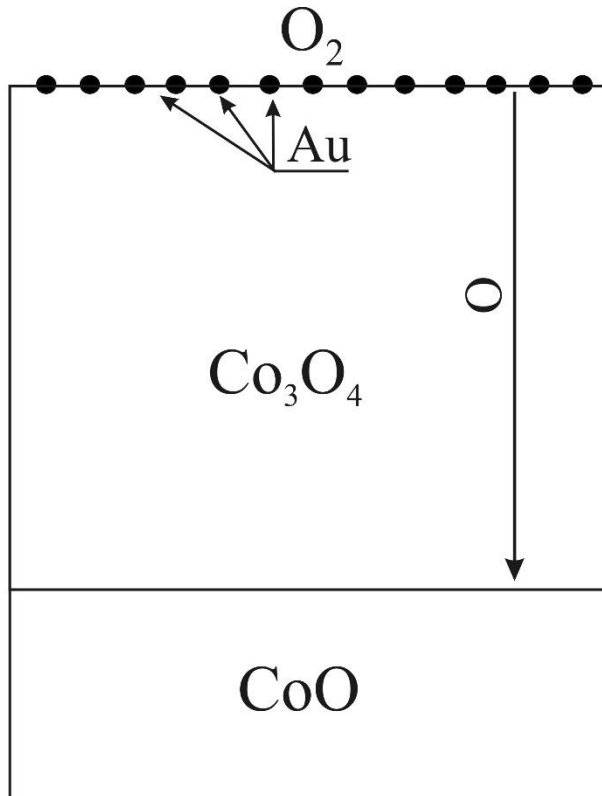
$$\frac{d \cdot a - b \cdot c}{b \cdot c}$$

Methods of depositing markers on the surfaces of ceramic substrates

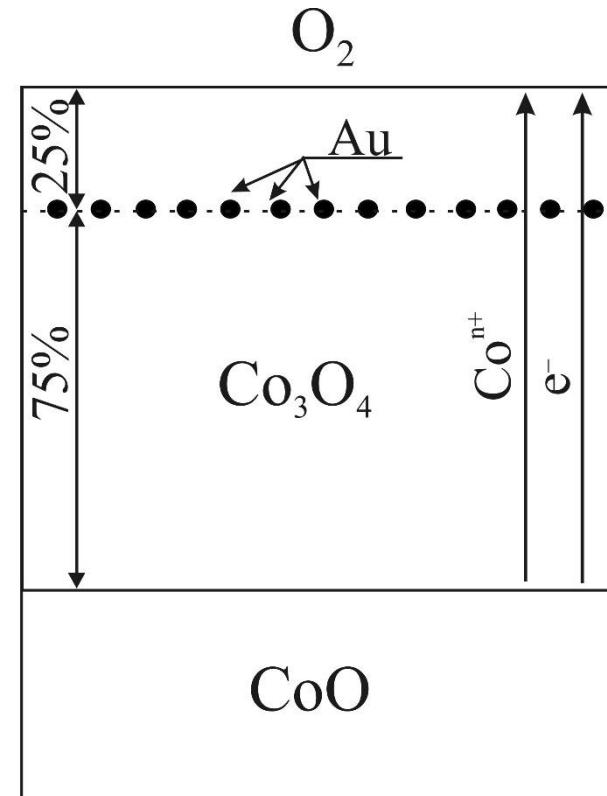
- depositing a marker (Pt, Au) through an appropriate mesh (Cu – SEM; Al)
- photolytic method
- covering the sample surface with a diluted platinum paste

Schematic illustration of the marker location in Co_3O_4 resulting from CoO oxidation

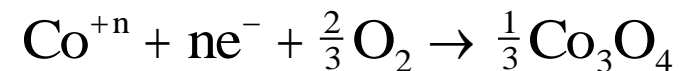
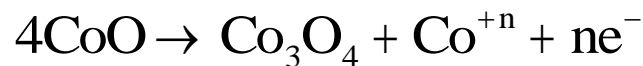
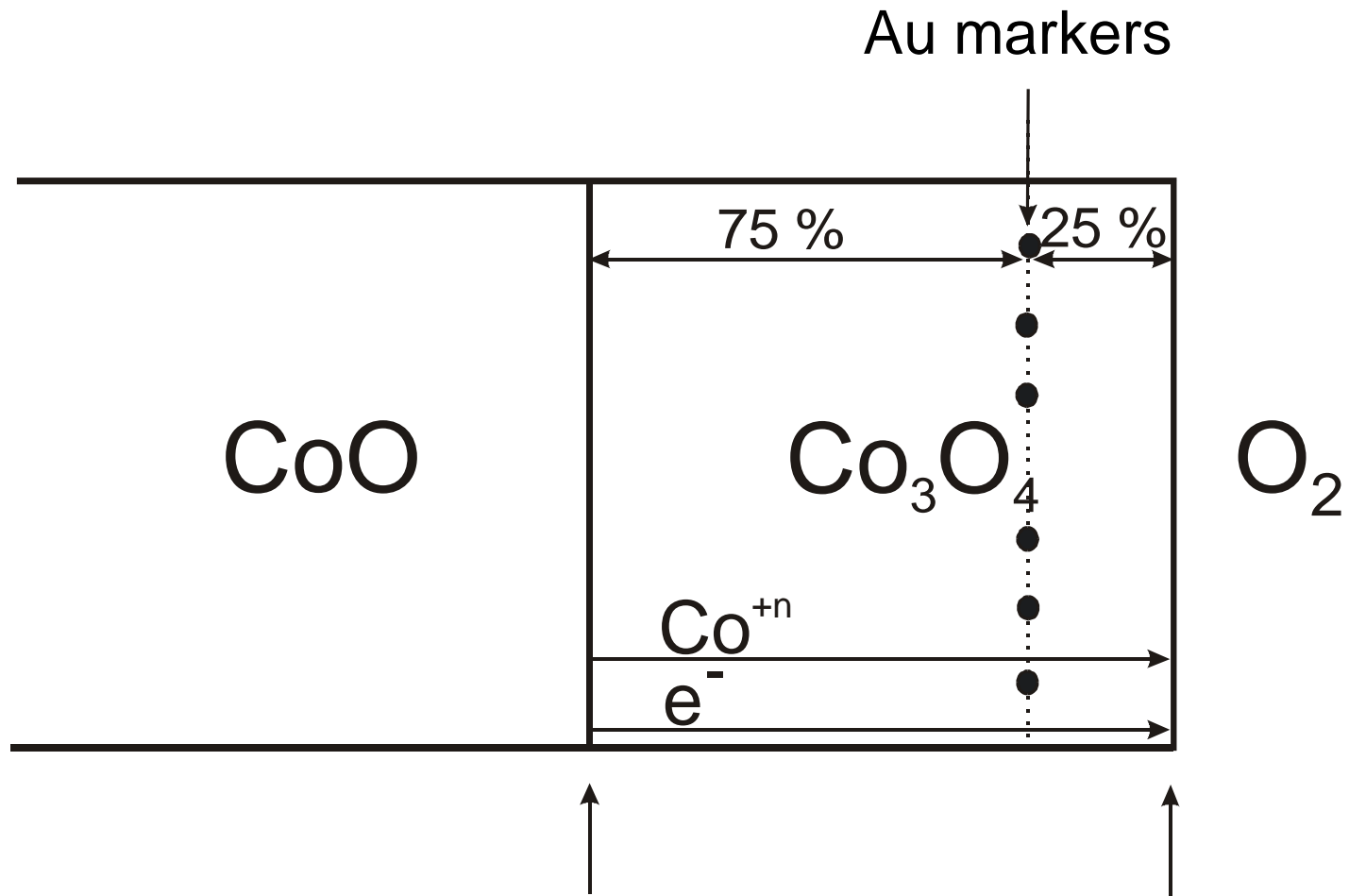
Anion sublattice of Co_3O_4 is defected



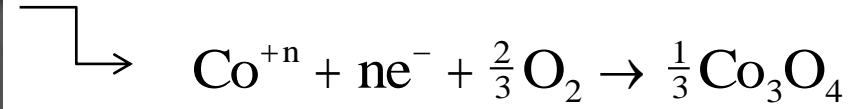
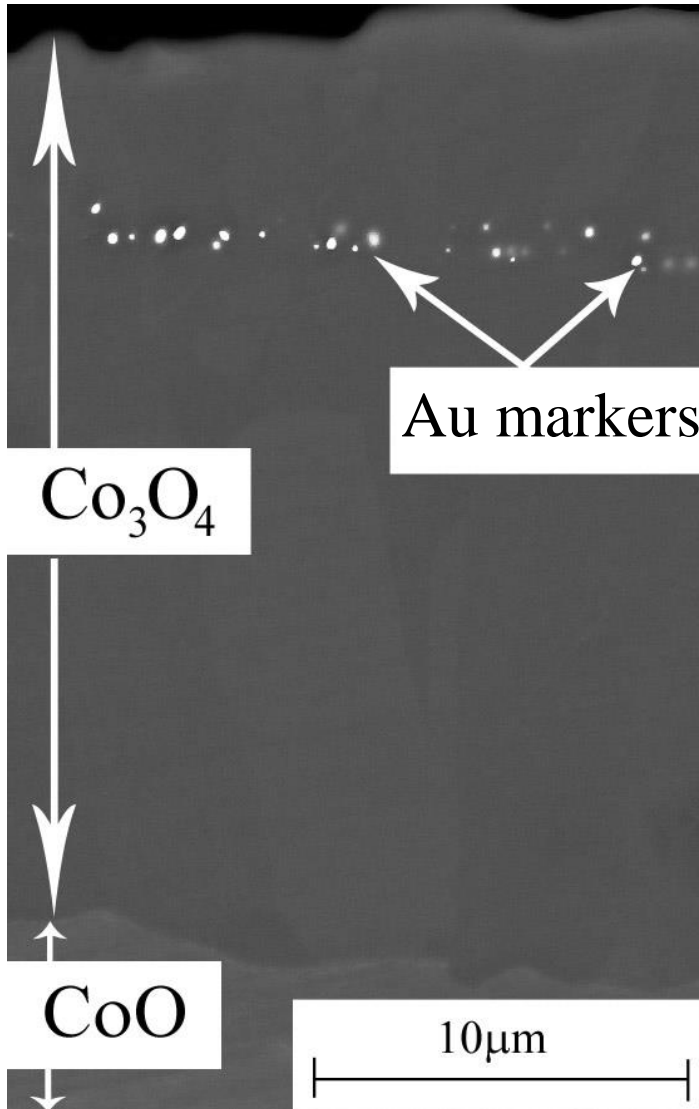
Cation sublattice of Co_3O_4 is defected

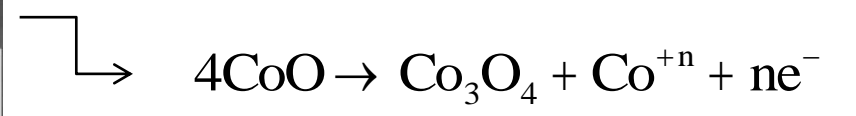


Schematic illustration of marker location in Co_3O_4 grown during CoO oxidation, in the case where the cation sublattice of Co_3O_4 exhibits predominant disorder

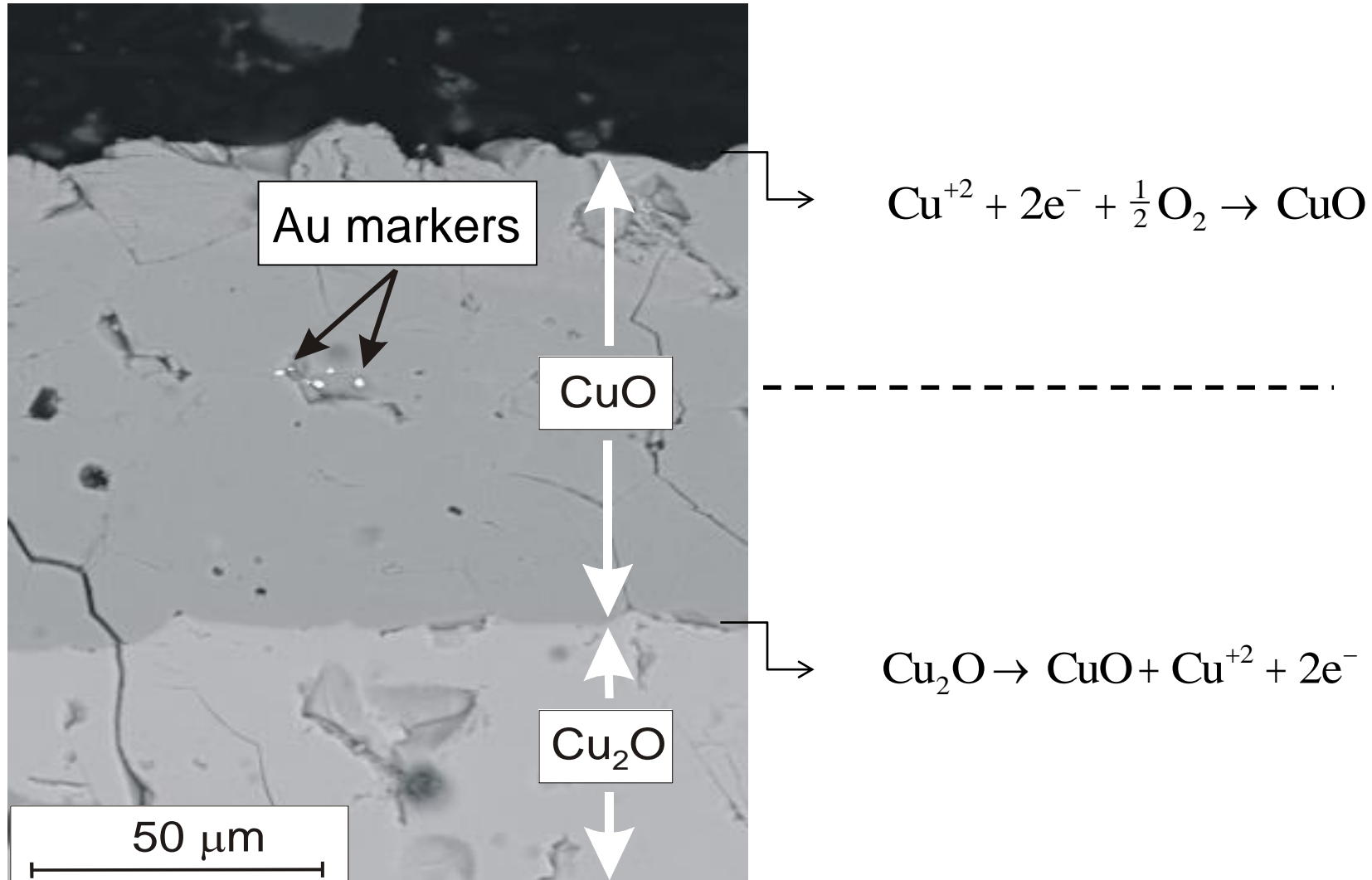


Co₃O₄ scale cross-section grown CoO with an indicated marker location

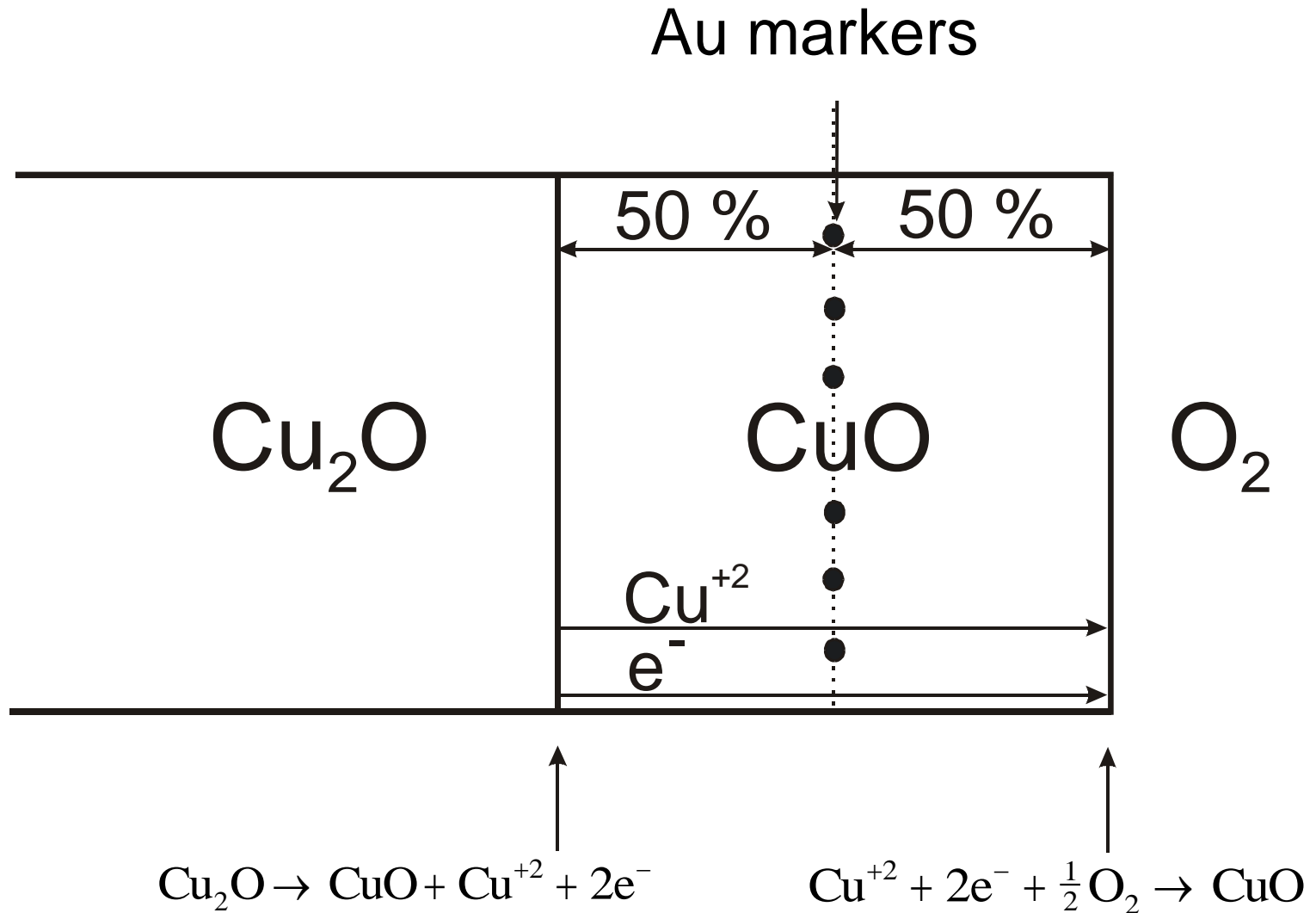




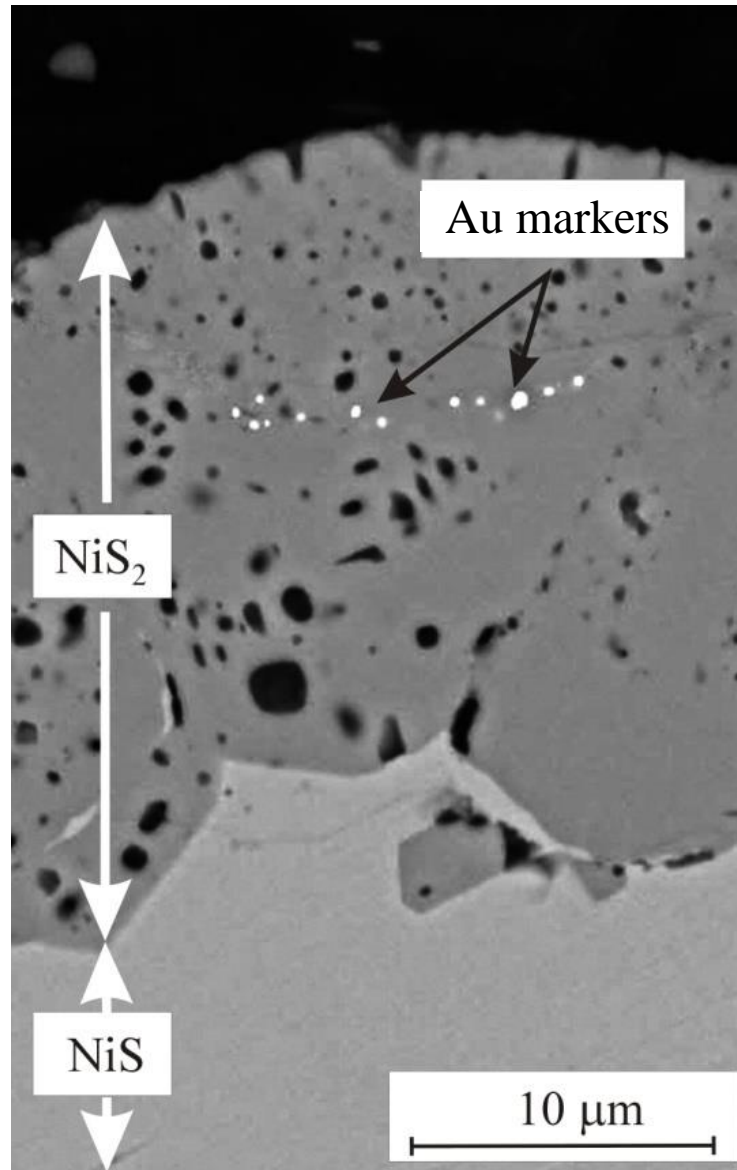
Cross-section of CuO scale grown on Cu₂O with an indicated marker location



Schematic illustration of marker location in CuO grown during oxidation of Cu₂O, in the case where the cation sublattice of CuO exhibits predominant disorder

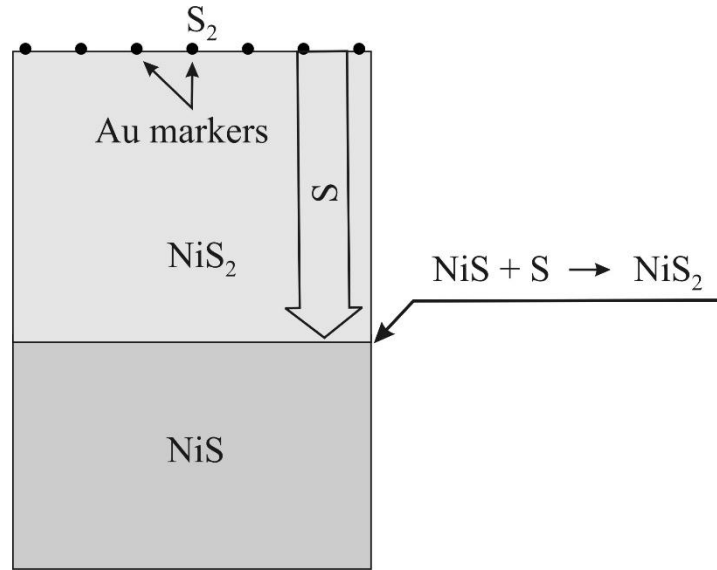


NiS₂ scale cross-section grown during NiS sulphidation with an indicated marker location

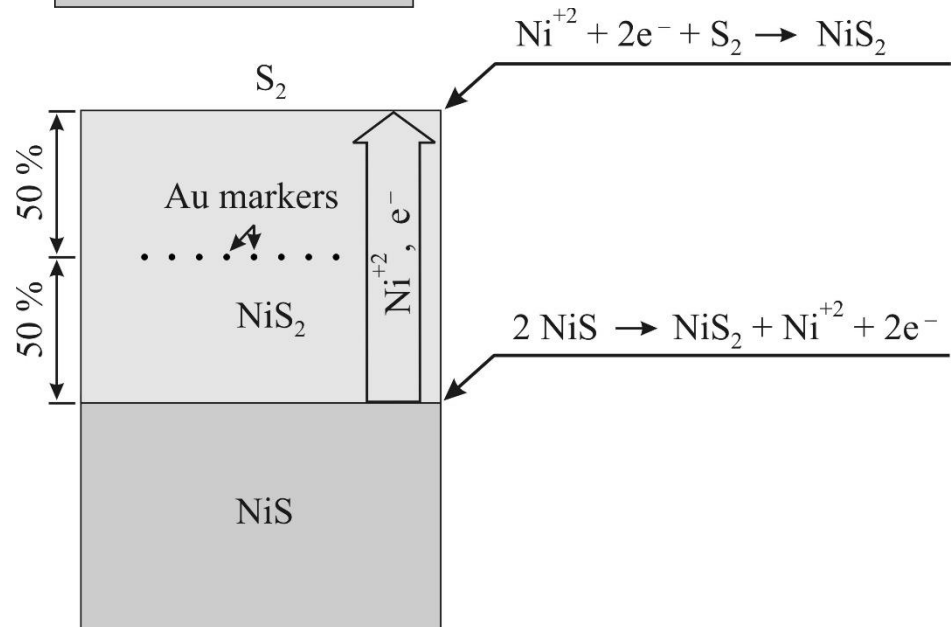


Schematic illustration of marker location in NiS₂ grown during NiS sulphidation

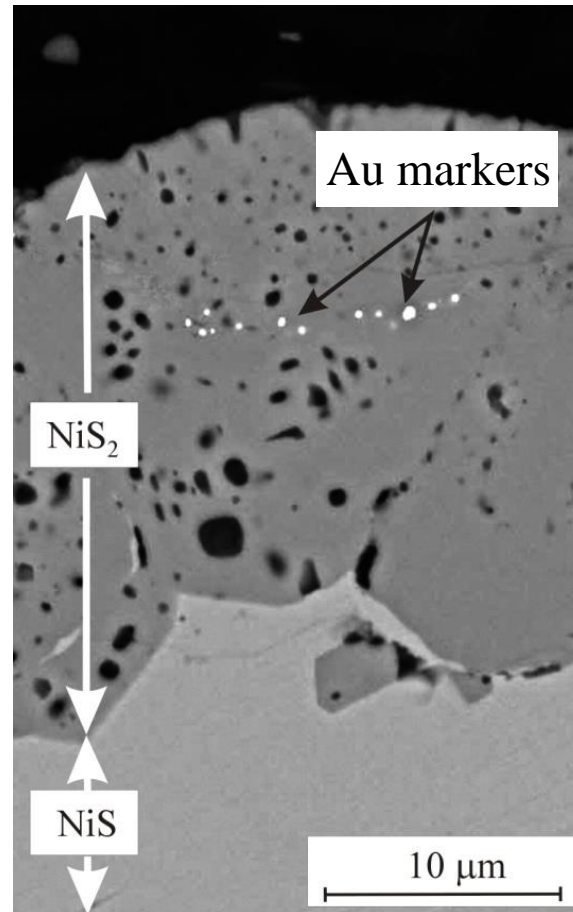
disordered NiS₂
anion sublattice



disordered NiS₂
cation sublattice

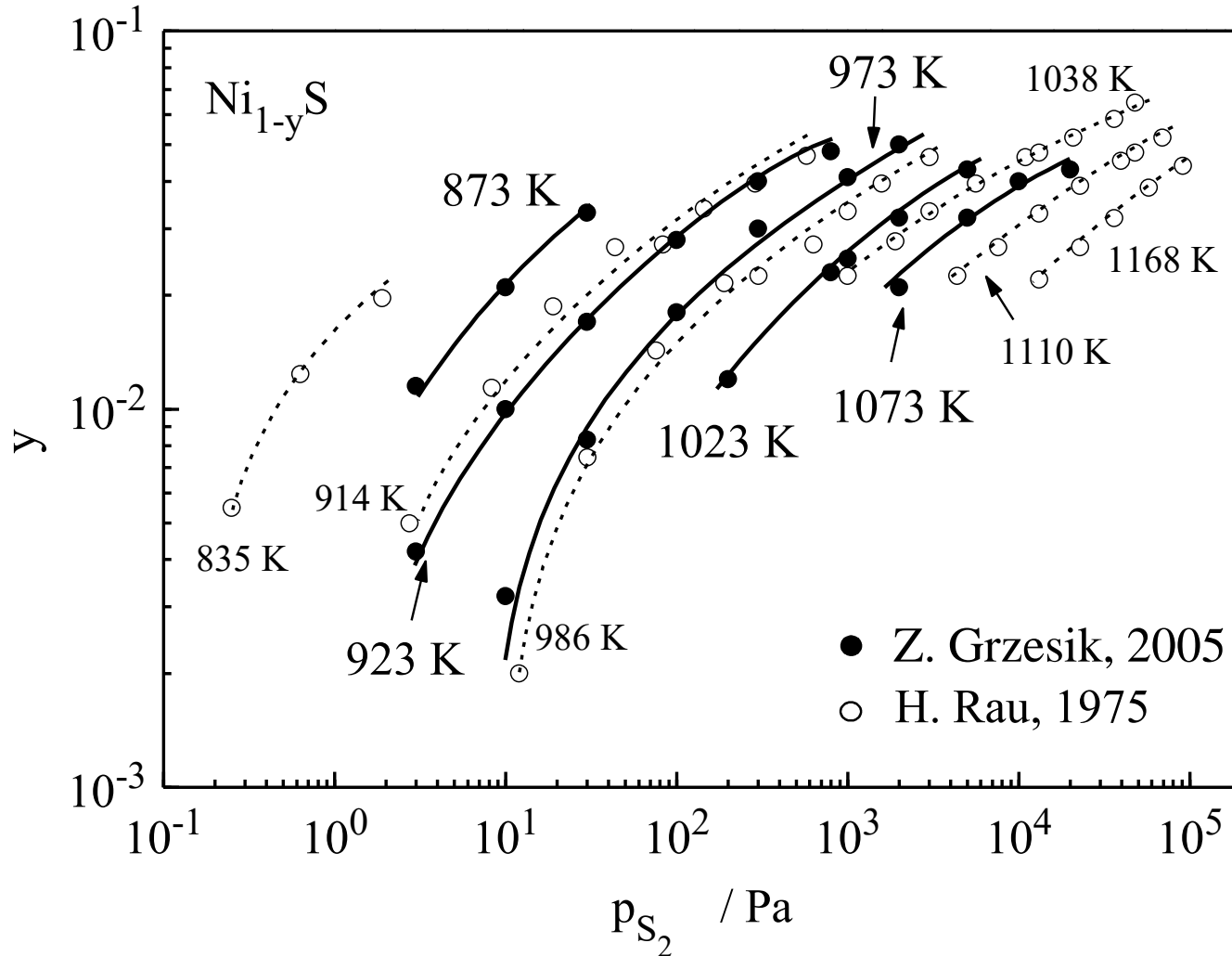


NiS₂ scale cross-section grown during NiS sulphidation with an indicated marker location



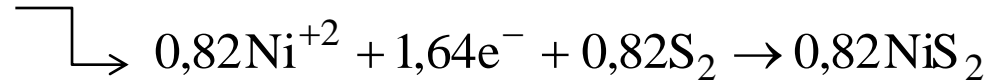
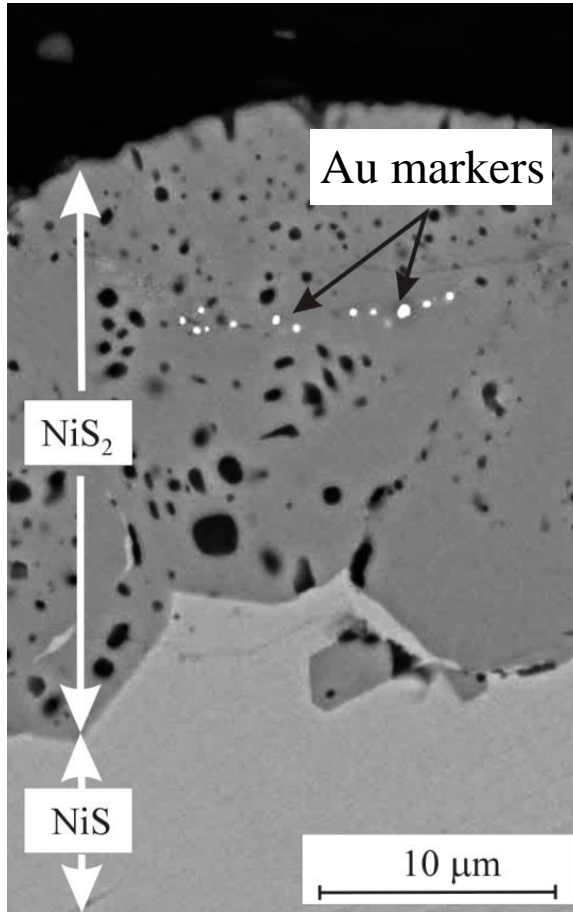
Ratio of external thickness to the internal part of NiS₂ equals around 0,82

Correlation between deviation from stoichiometry in Ni_{1-y}S and sulfur vapor pressure



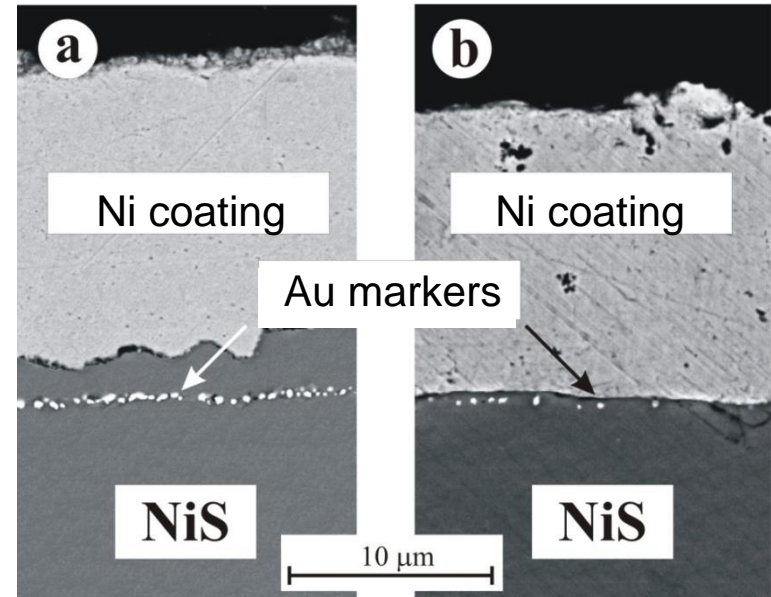
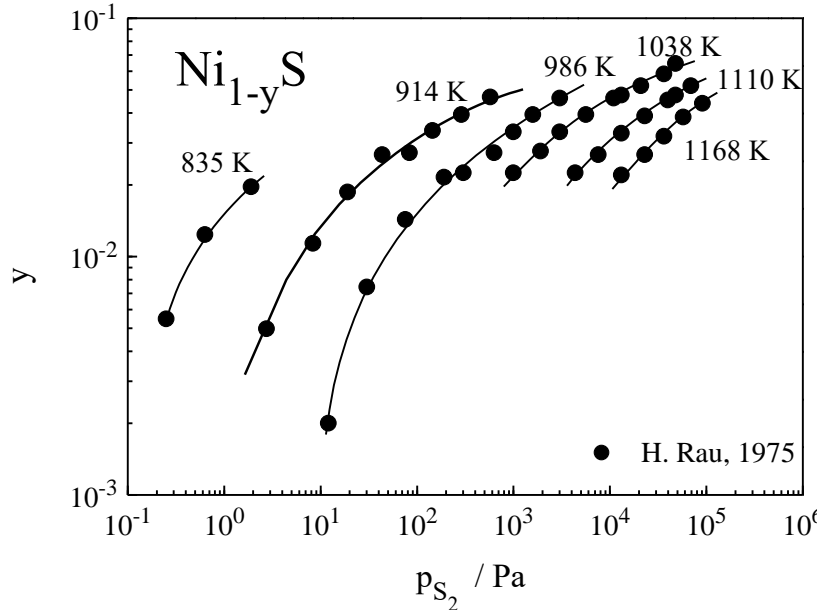
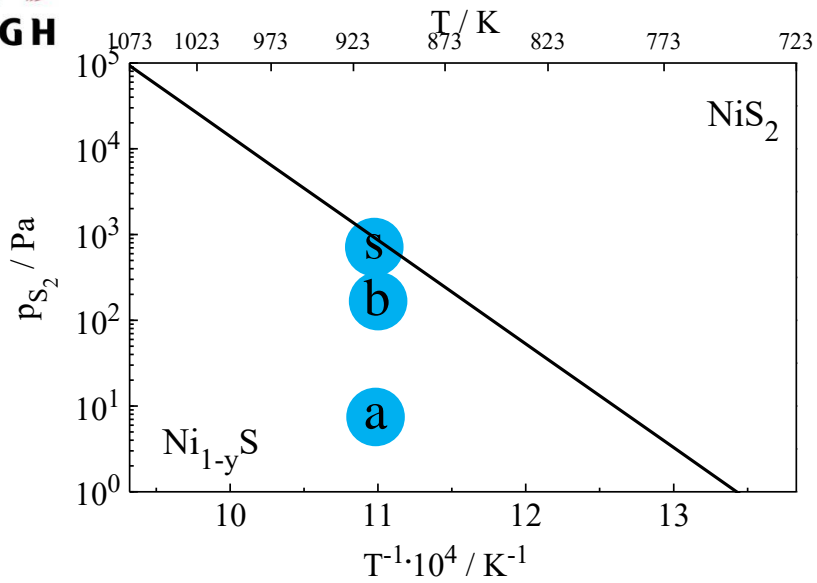
y_{max} in $\text{Ni}_{1-y}\text{S} \approx 0,09$

NiS₂ scale cross-section grown during NiS sulphidation with an indicated marker location



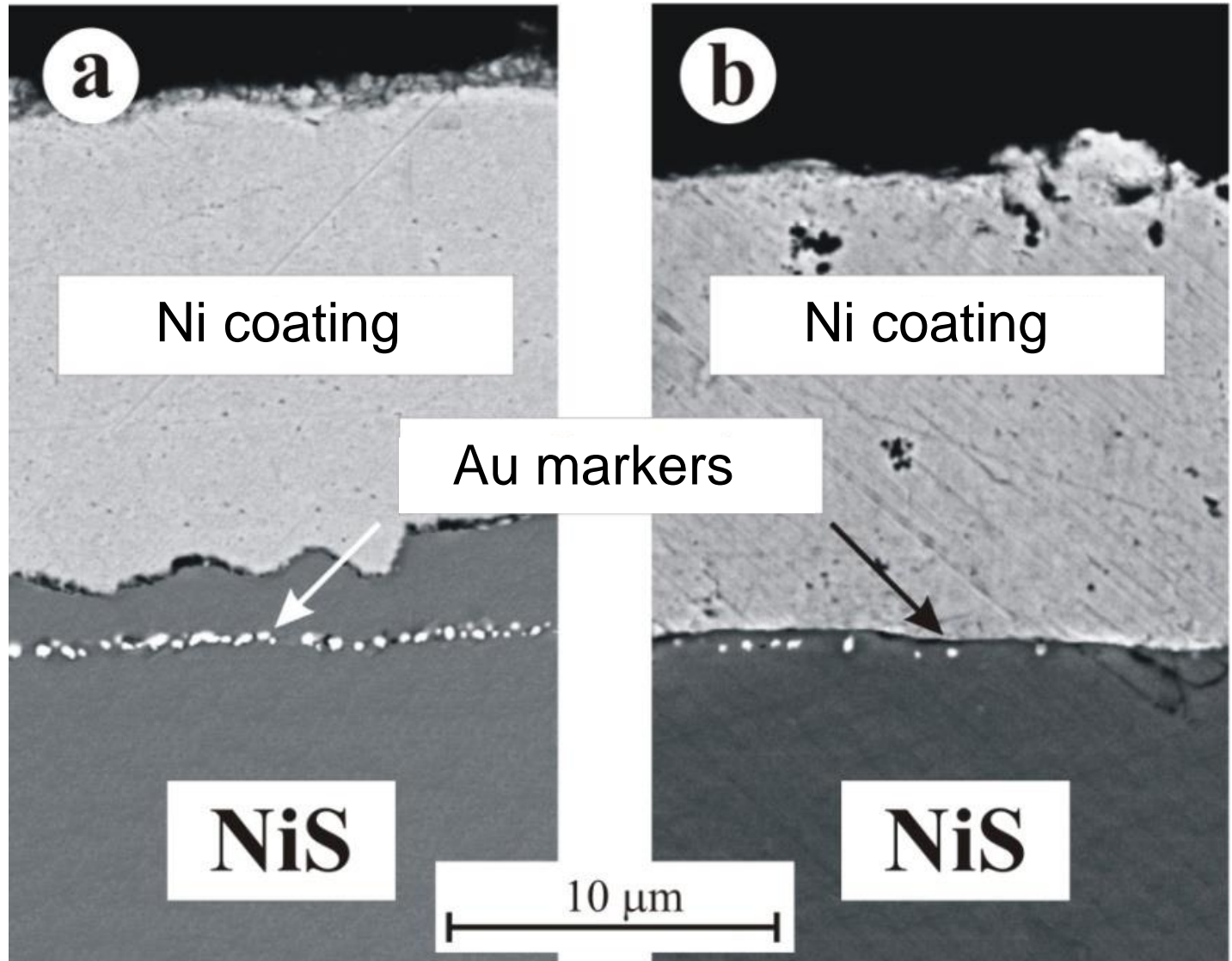
The experimentally determined ratio between external thickness and the internal part of the NiS₂ sulfide equal to 0,82 remains in accordance with the theoretical value obtained under the assumption that deviation from stoichiometry is present in Ni_{1-y}S on the level of 0,91

Influence of NiS homogenization parameters on marker location at the initial stage of NiS₂ formation

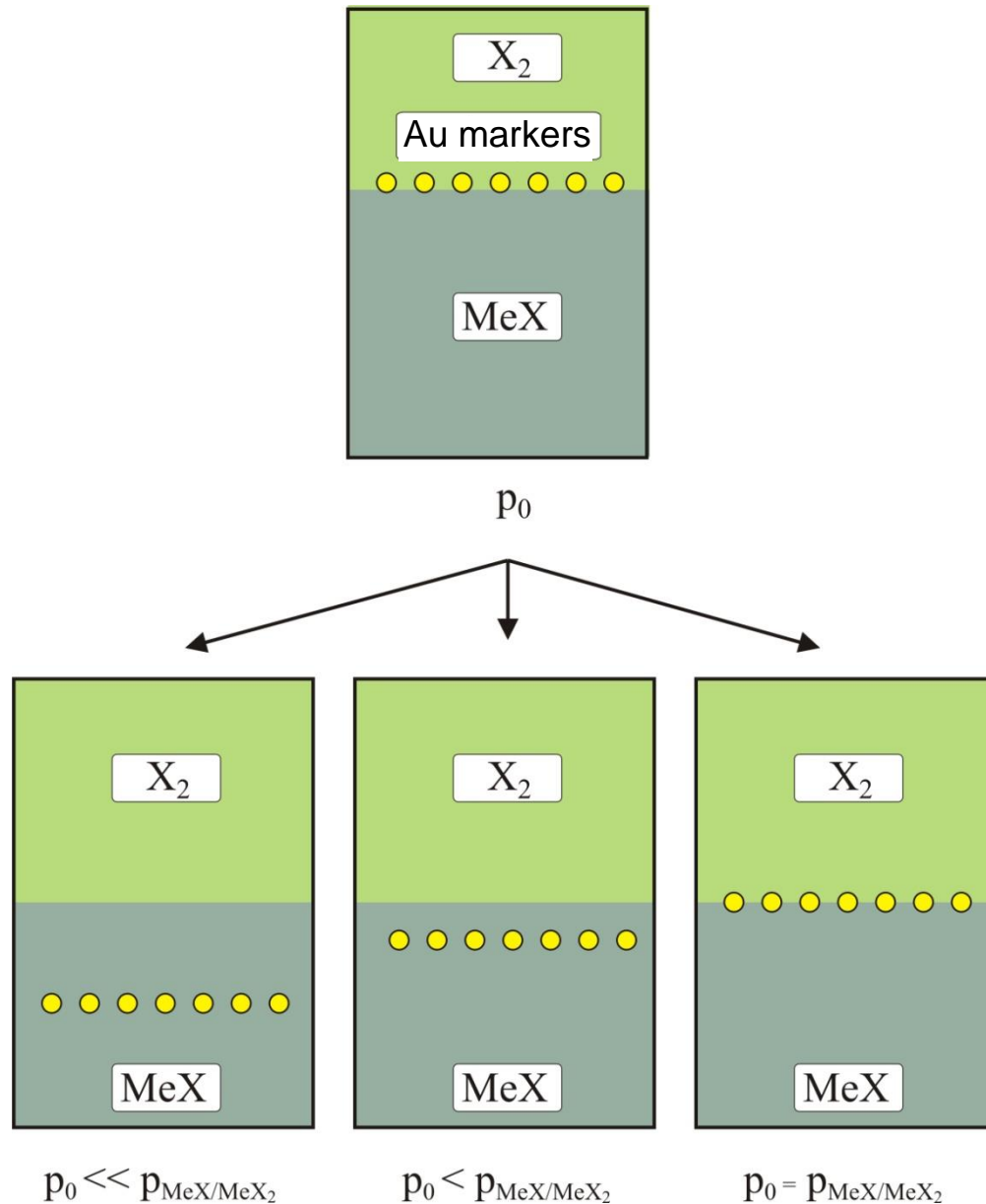


- a homogenization: 873 K, 10 Pa, 24 h
- b homogenization: 873 K, 200 Pa, 24 h
- s sulphidation: 873 K, 1000 Pa, 5 min

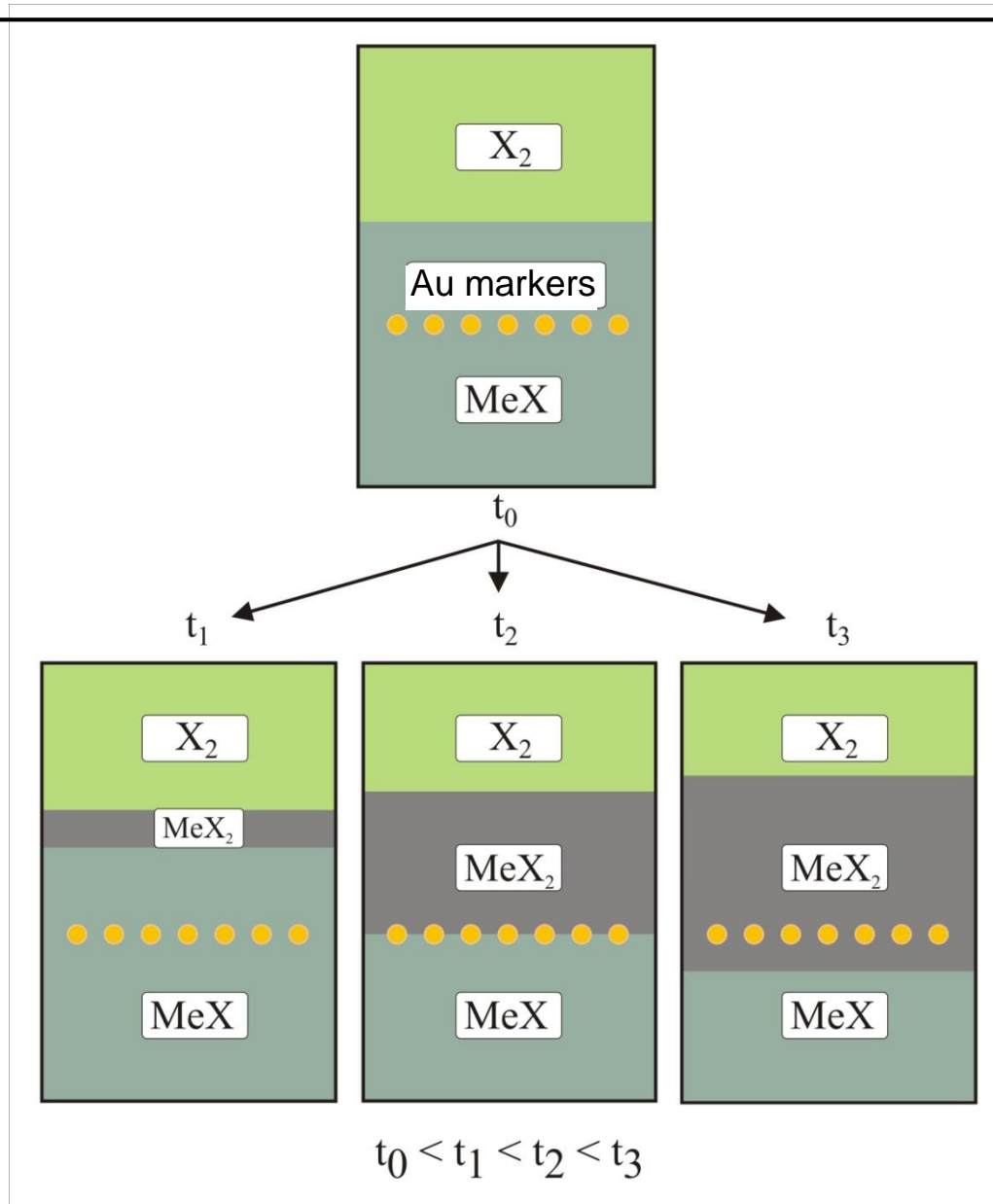
Marker location after NiS homogenization



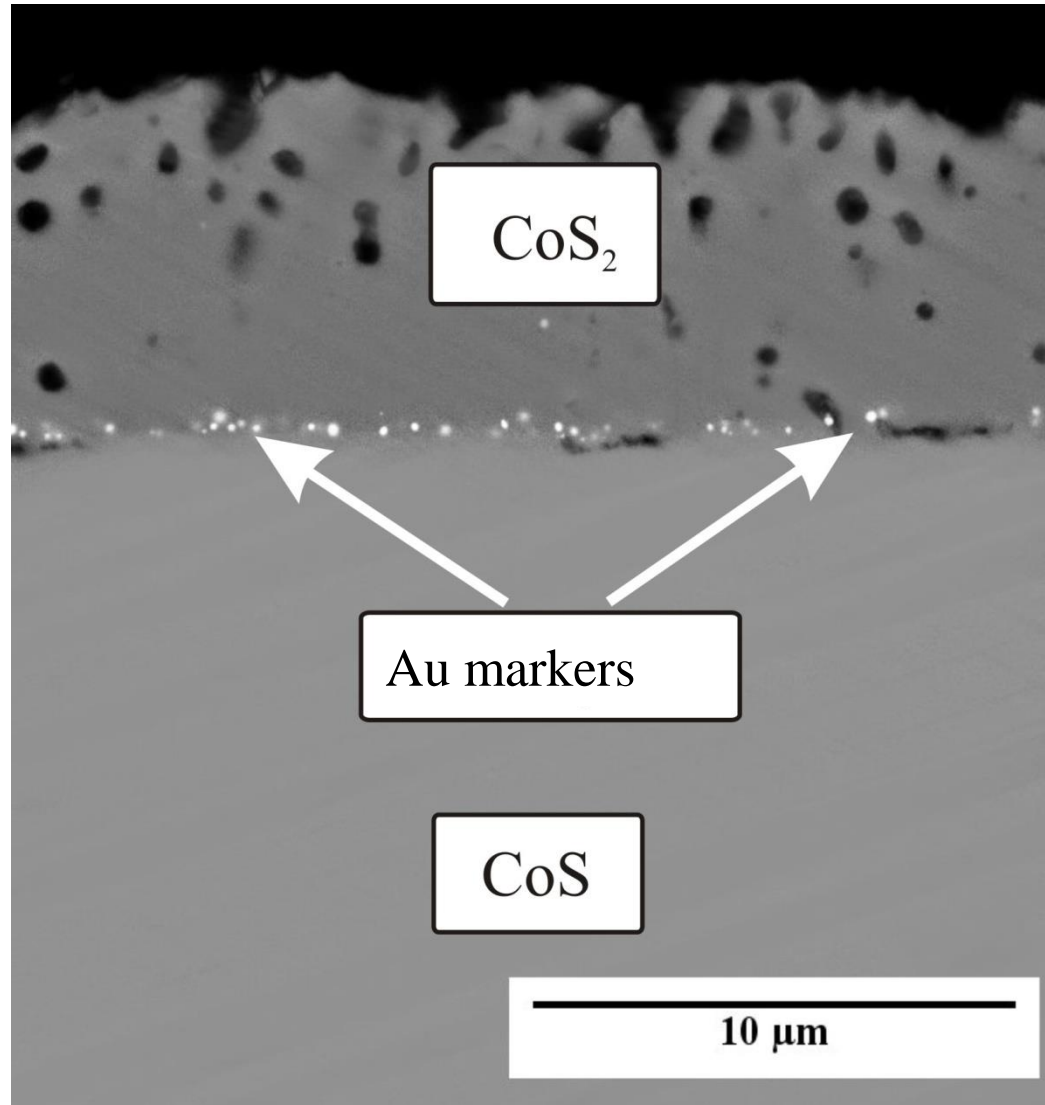
Influence of MeX homogenization parameters on marker location at the initial stage of MeX₂ formation



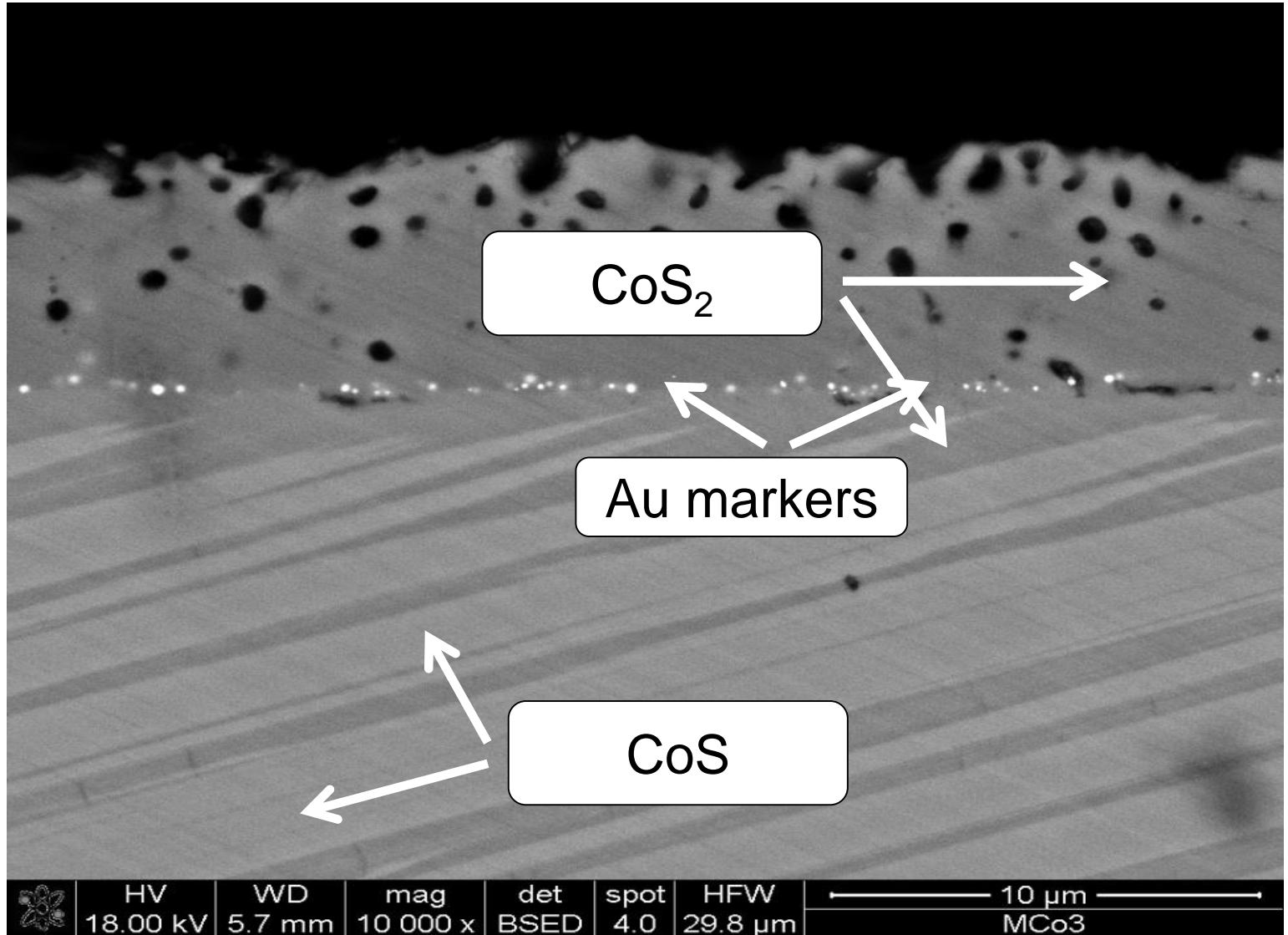
Marker location after MeX homogenization in the case where oxidant pressure is lower than MeX₂ dissociation pressure



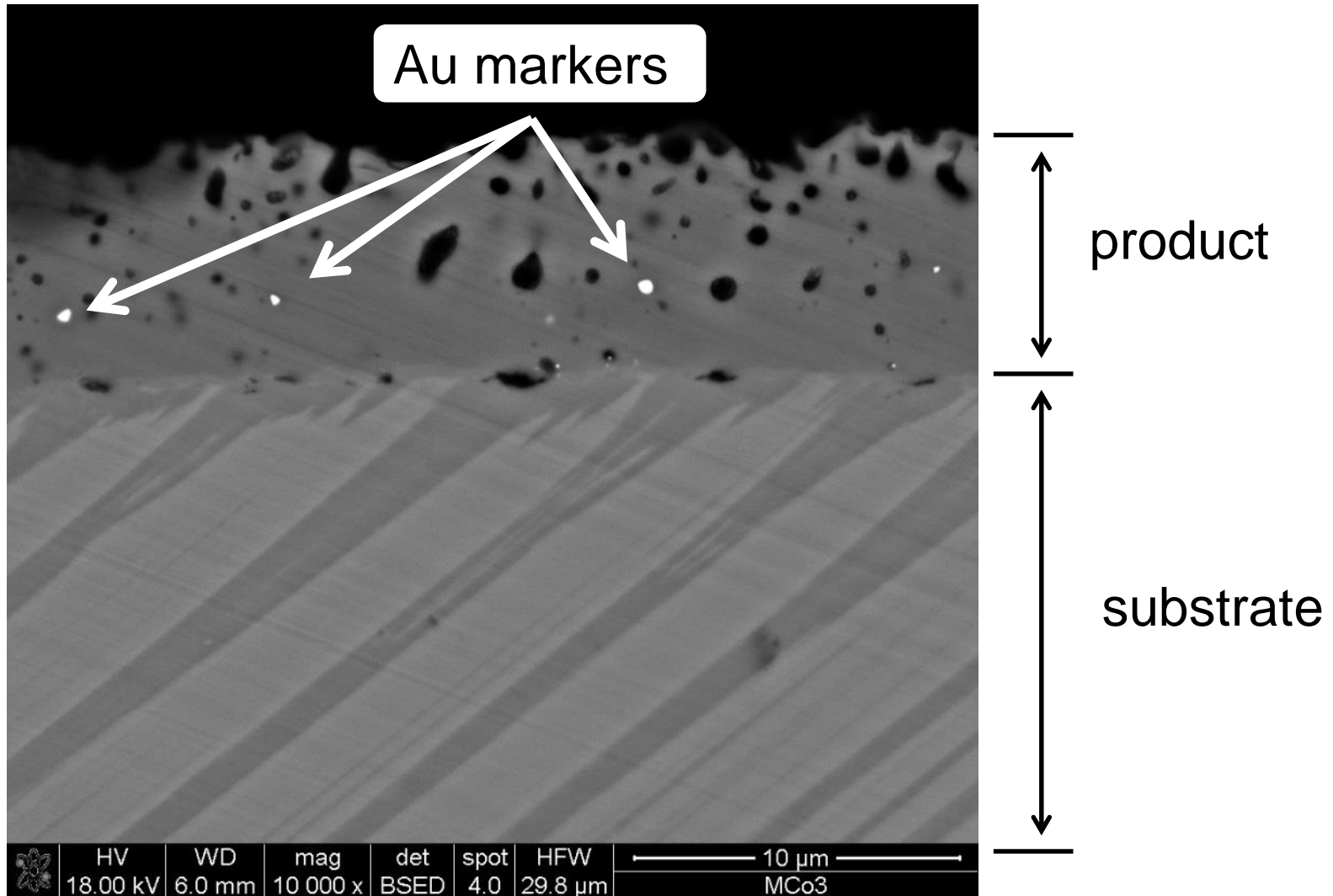
Marker location after sulphidation of CoS to CoS₂ (SEI)



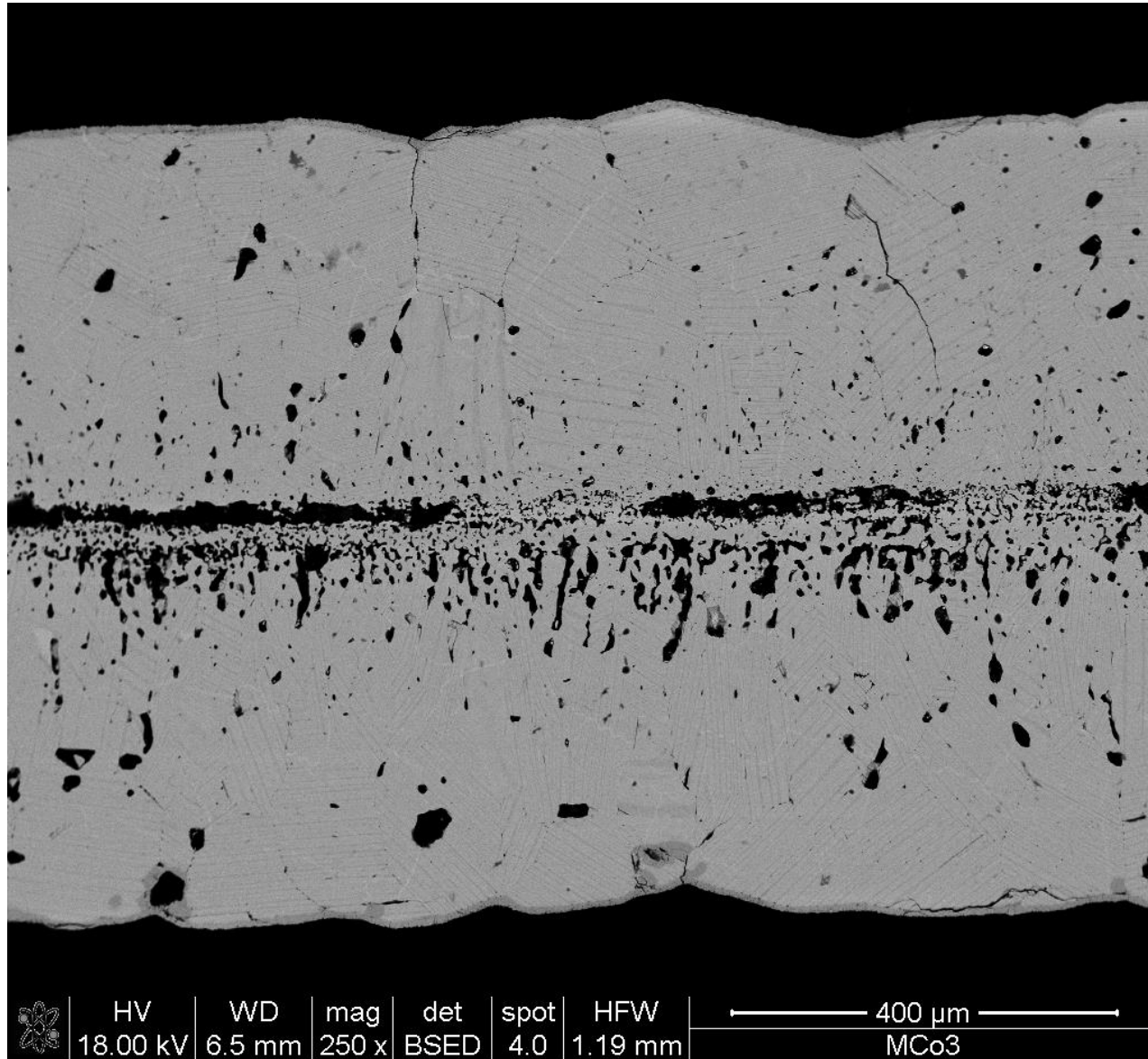
Marker location after sulphidation of CoS to CoS₂ (BSE)



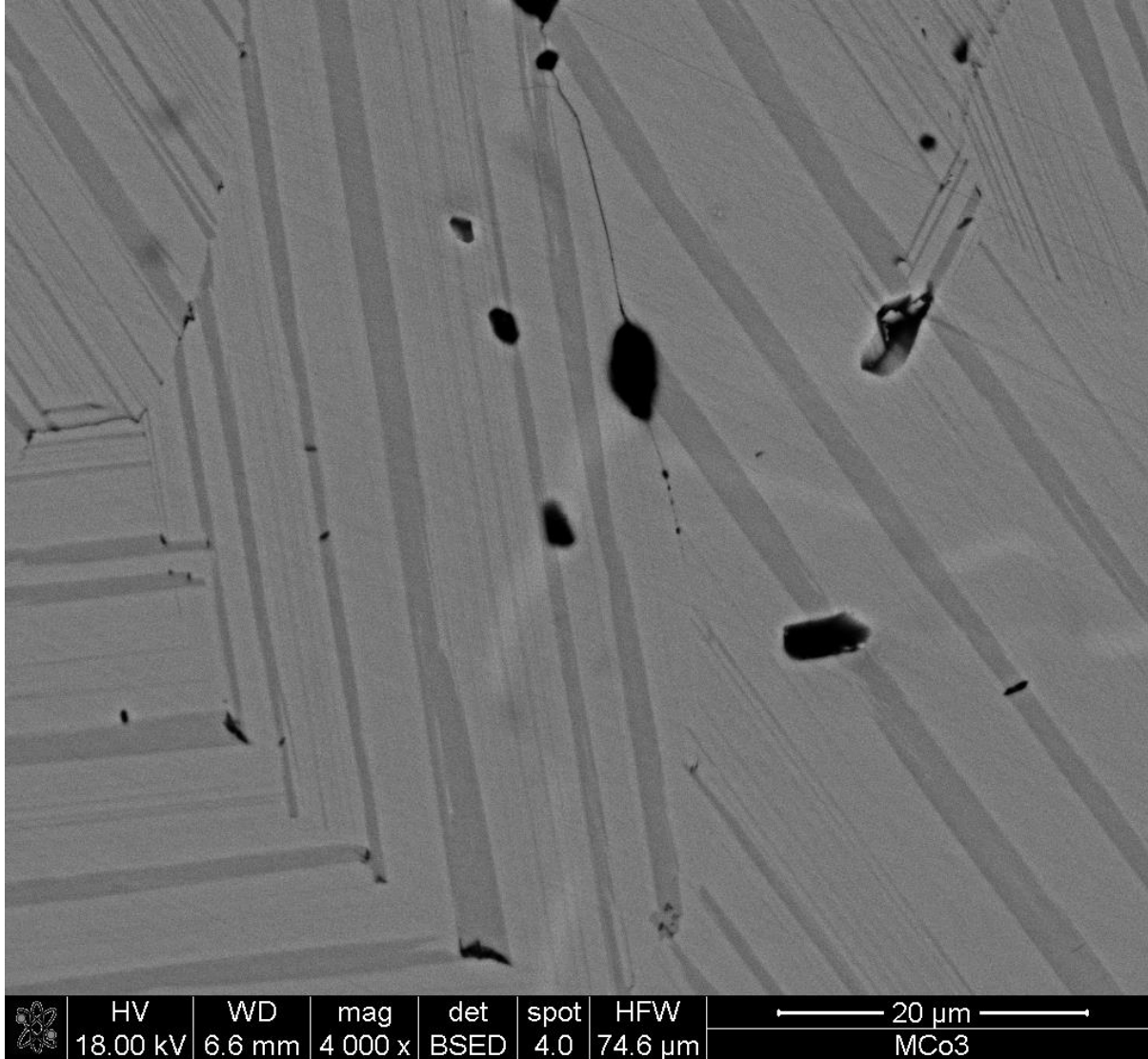
Marker location at the initial stage of CoS_2 formation on the surface of CoS homogenized at the CoS_2 dissociation pressure



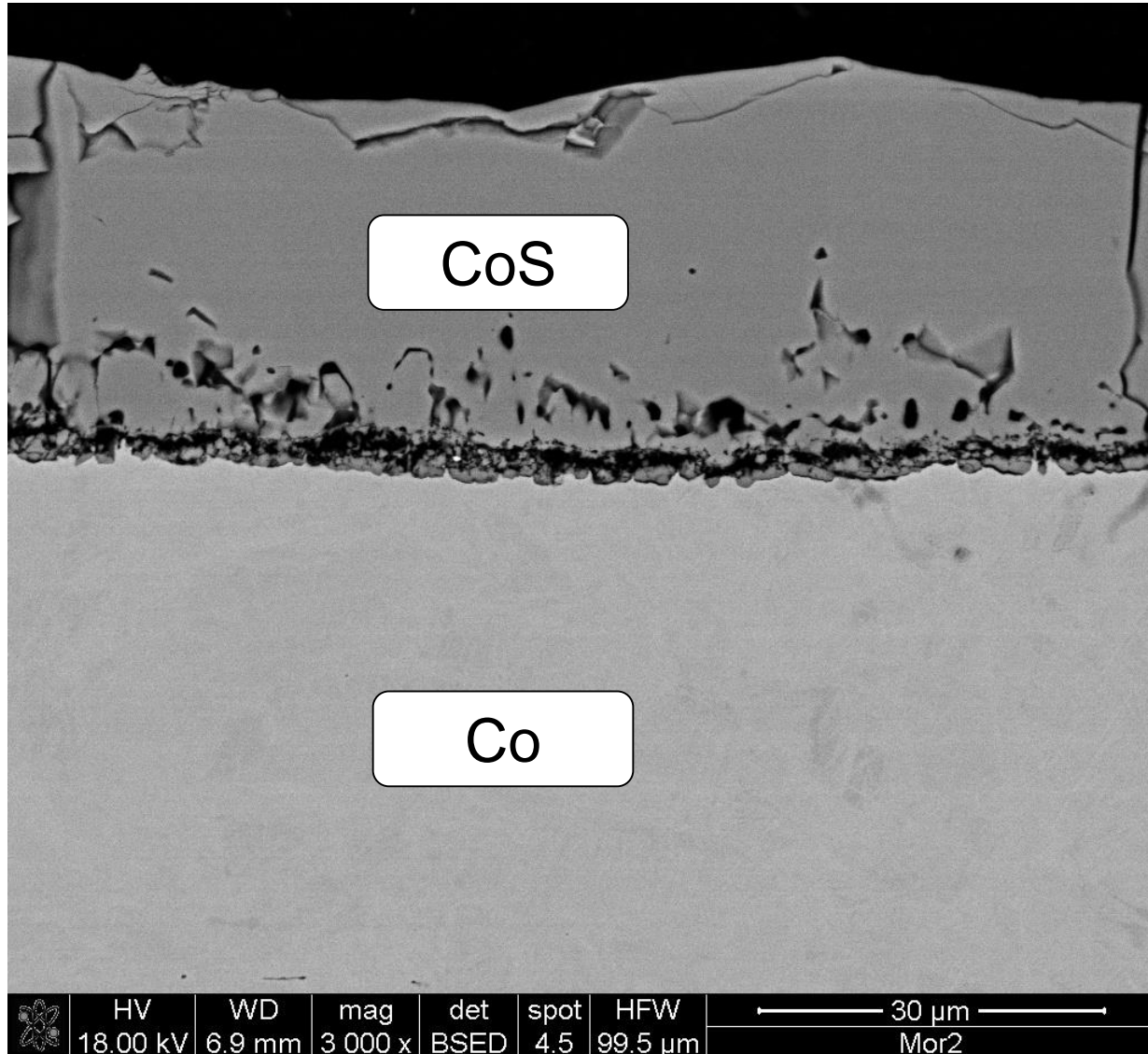
CoS cross-section sulphidized at a sulfur vapor pressure that enables CoS_2 formation



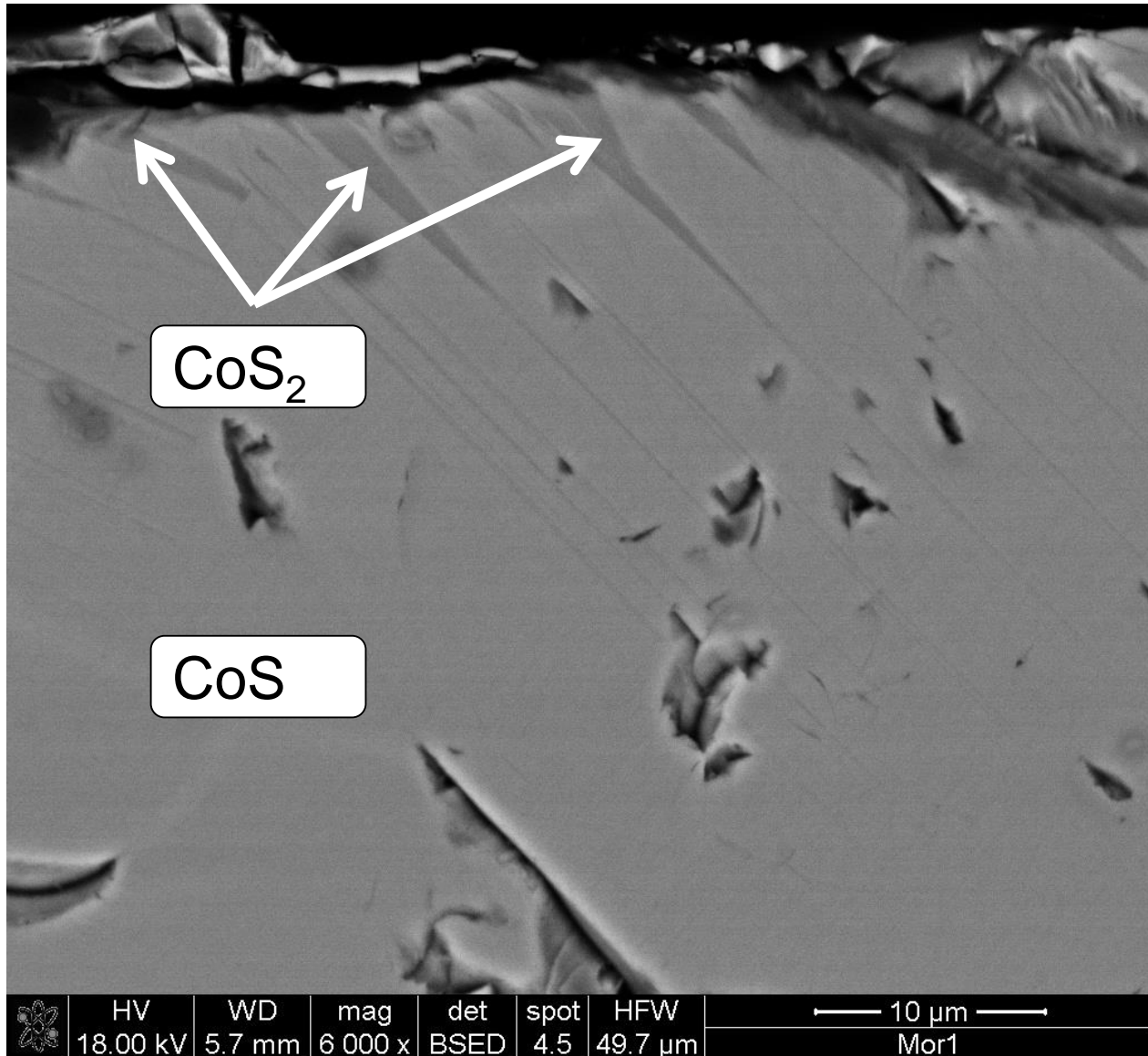
Interior of CoS sulphidized at a sulfur vapor pressure that enables CoS_2 formation



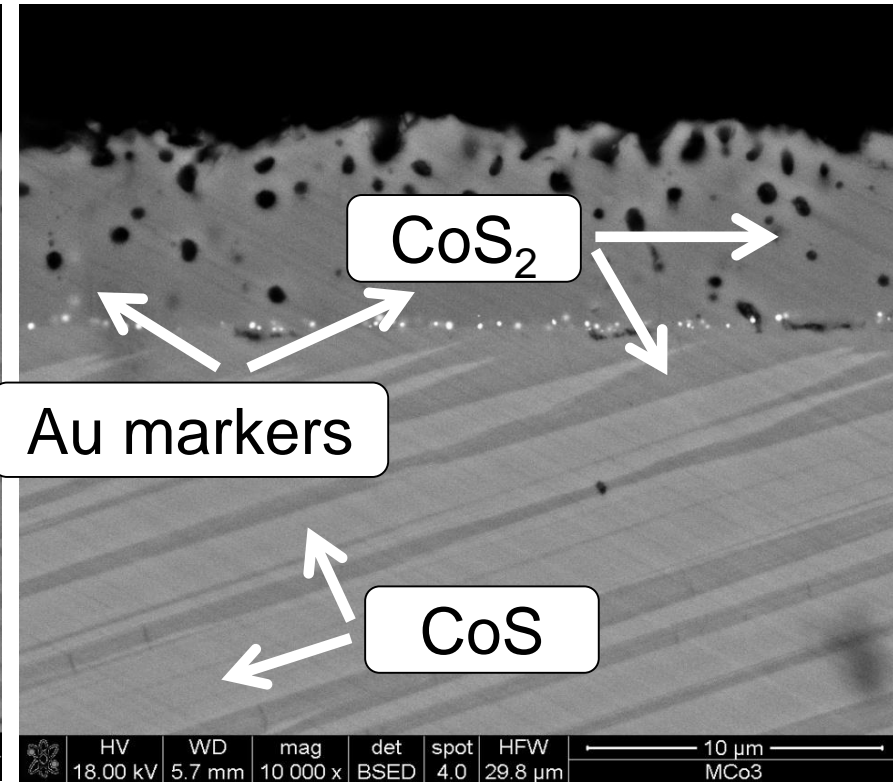
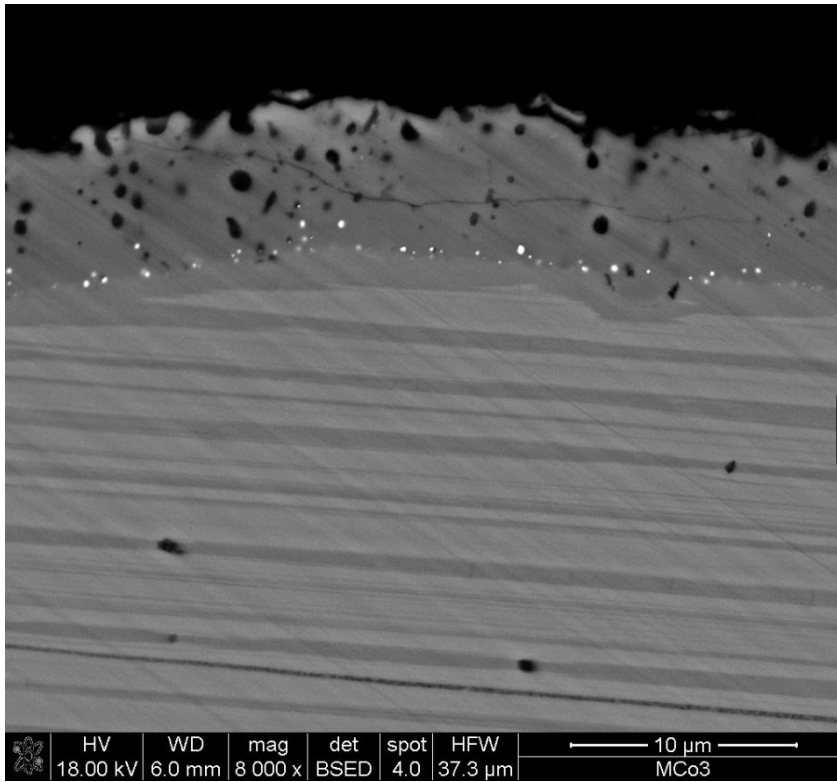
Cross-section of a Co sample covered with CoS



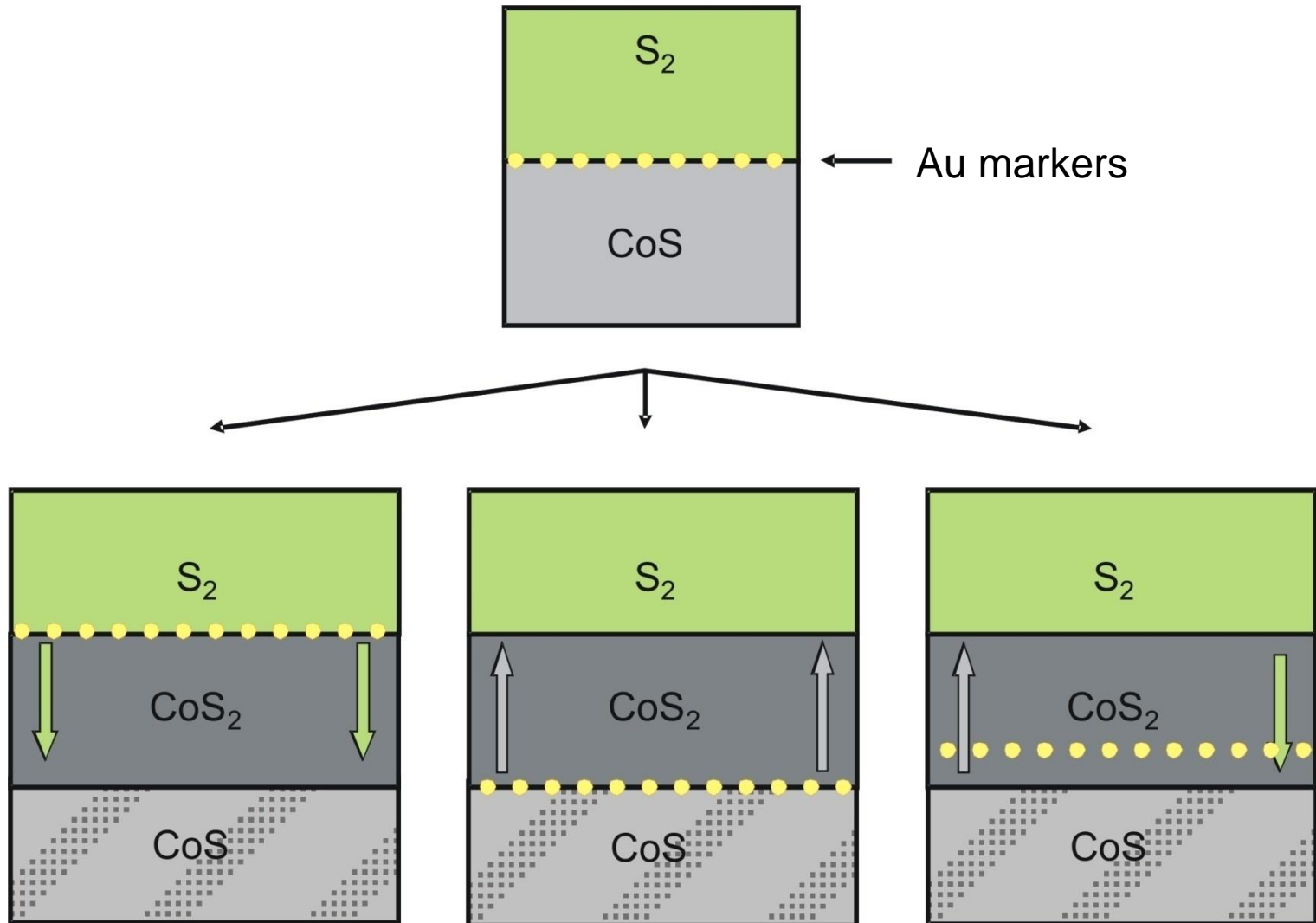
Initial stage of CoS_2 formation inside CoS



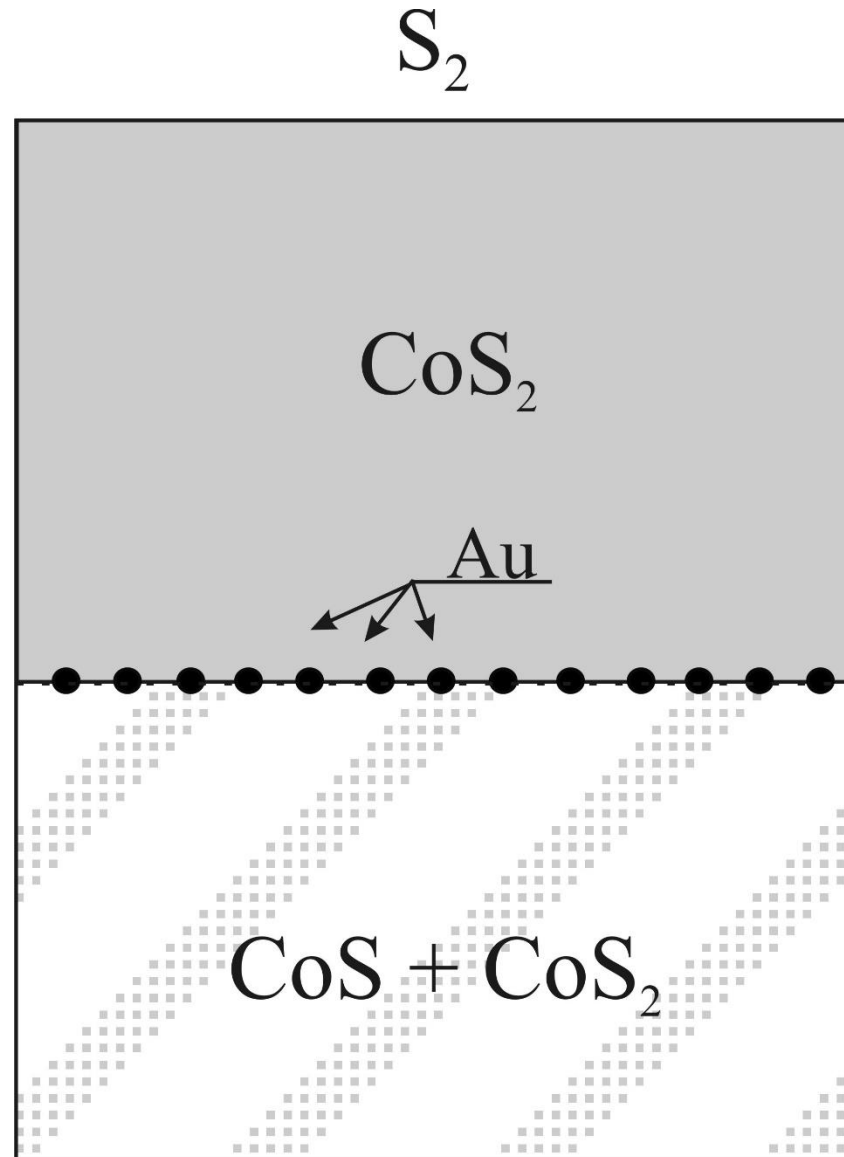
Marker location in CoS sulphidized to CoS_2



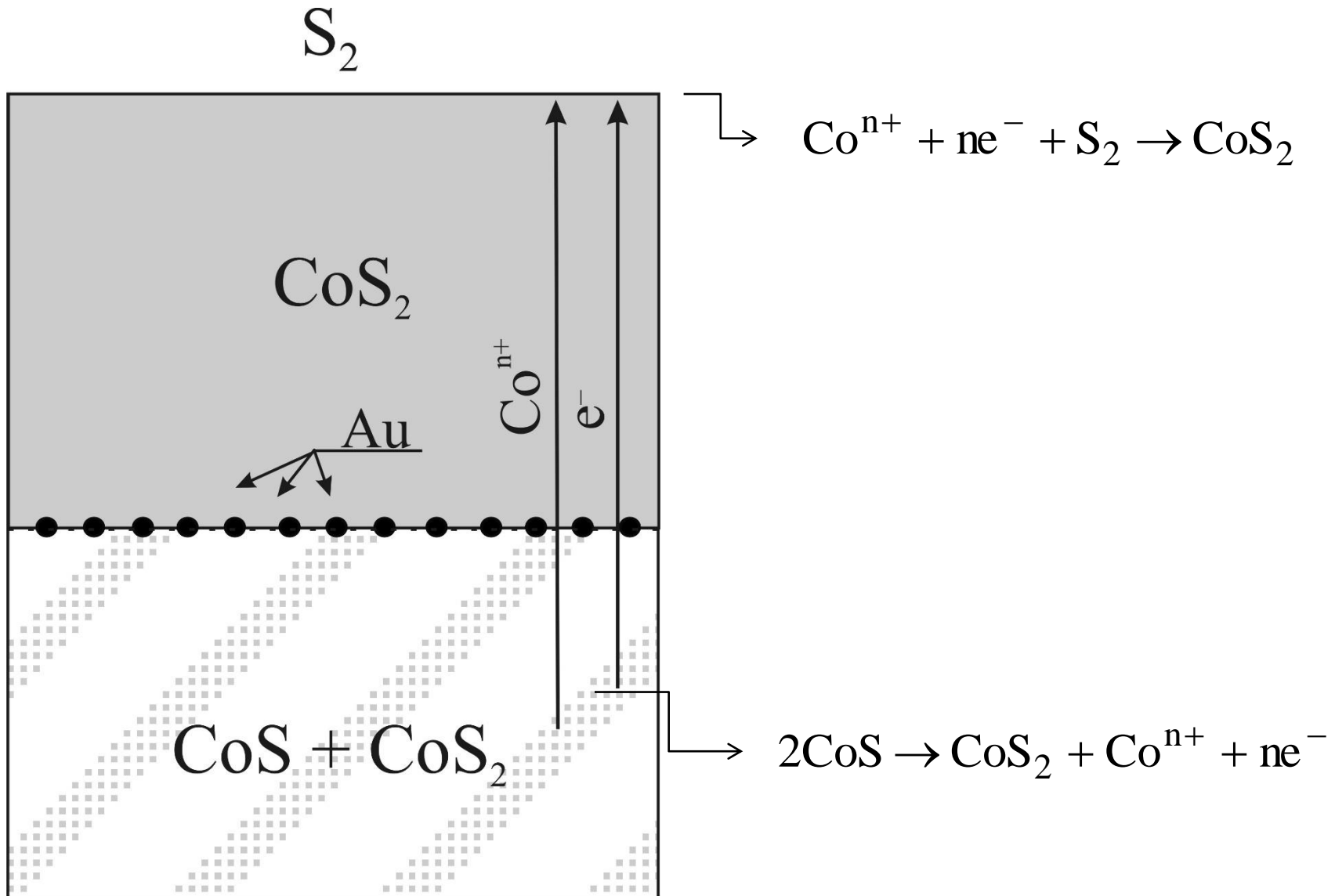
Possible marker locations in a CoS-CoS₂ system depending on the predominant direction of reagent diffusion



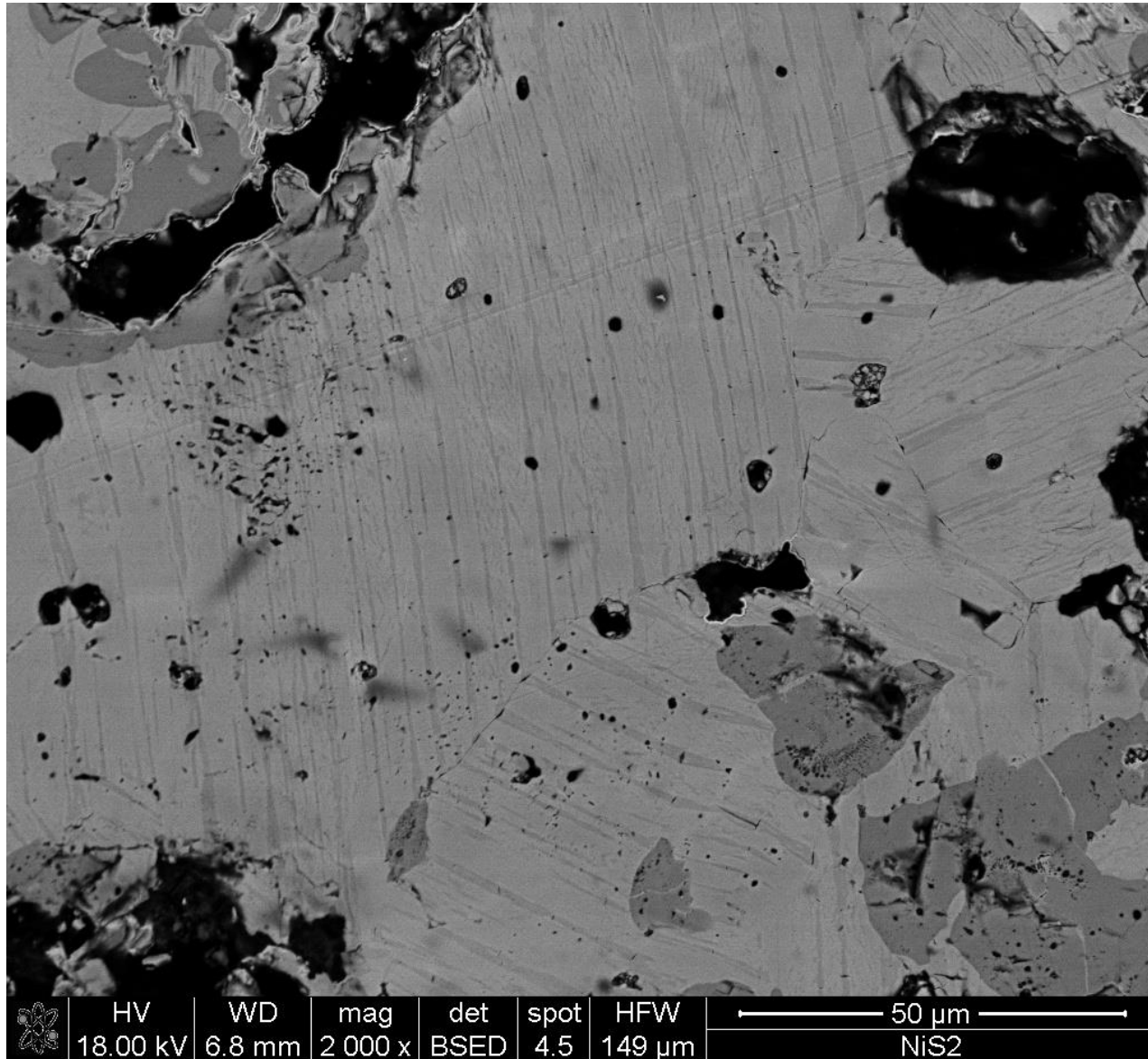
Schematic illustration of marker location in CoS sulphidized to CoS_2



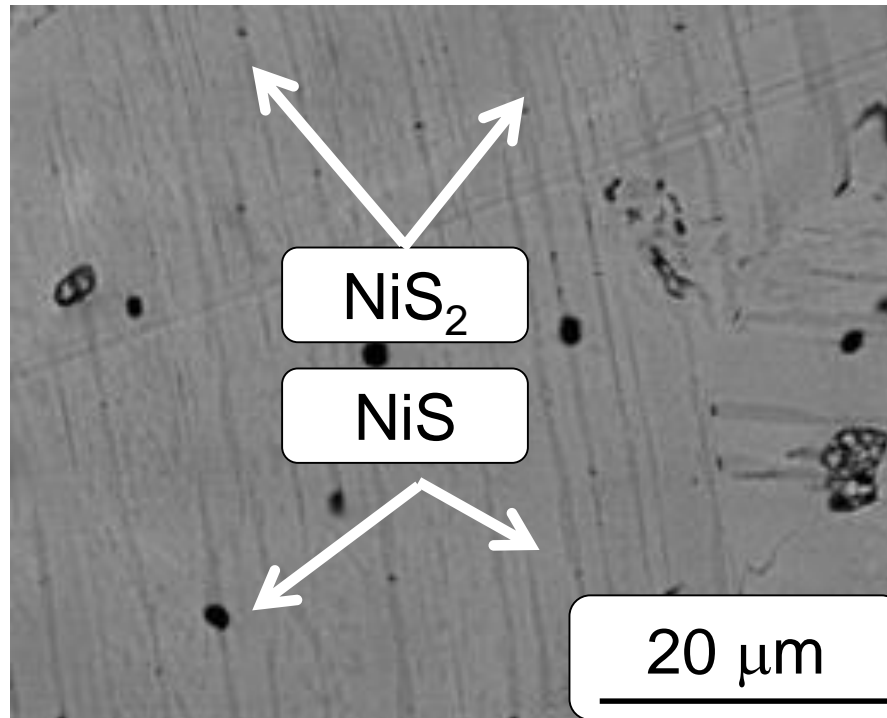
Schematic illustration of marker location in CoS sulphidized to CoS₂



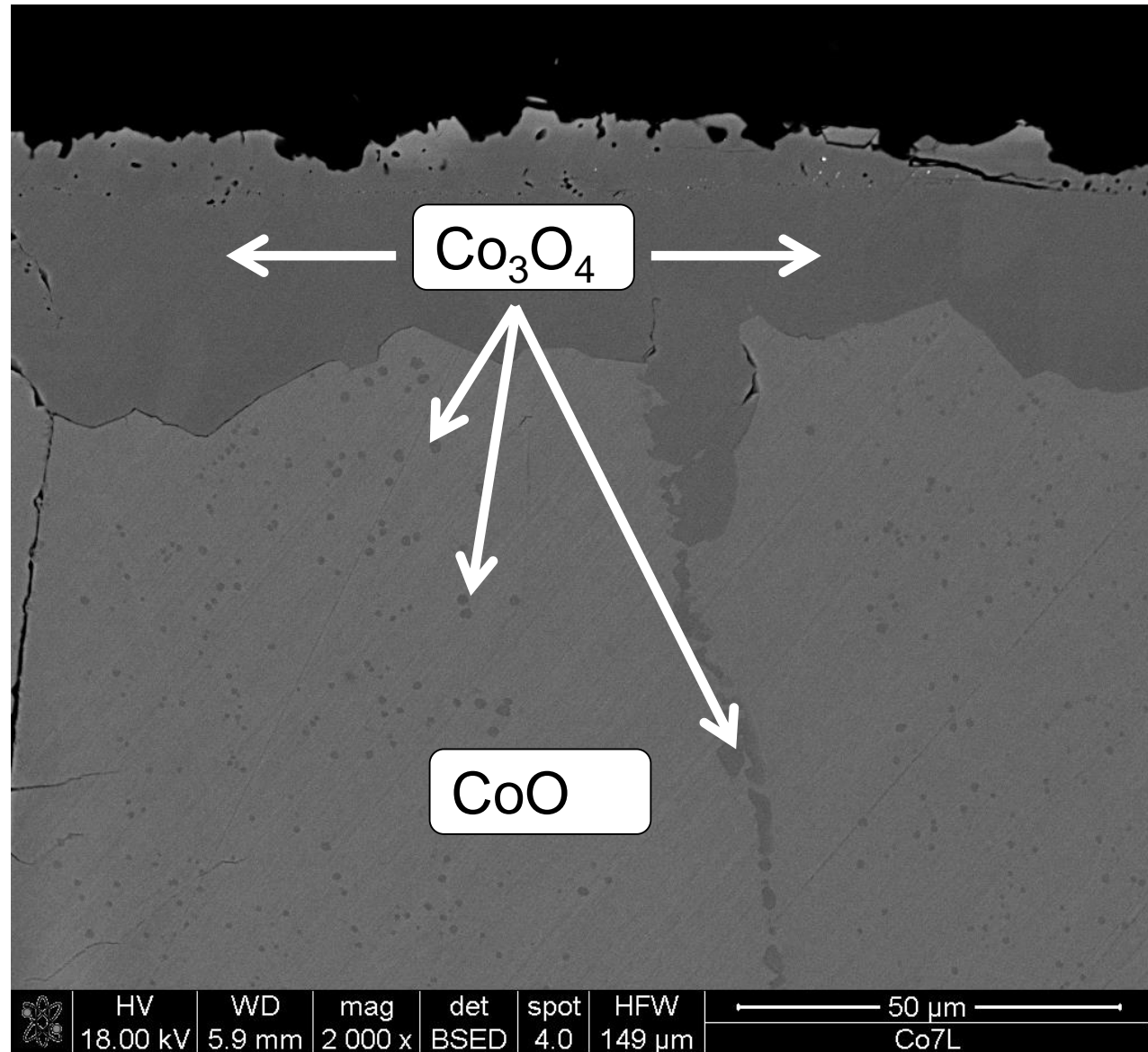
Interior of NiS sulphidized at a sulfur vapor pressure that enables NiS₂ formation



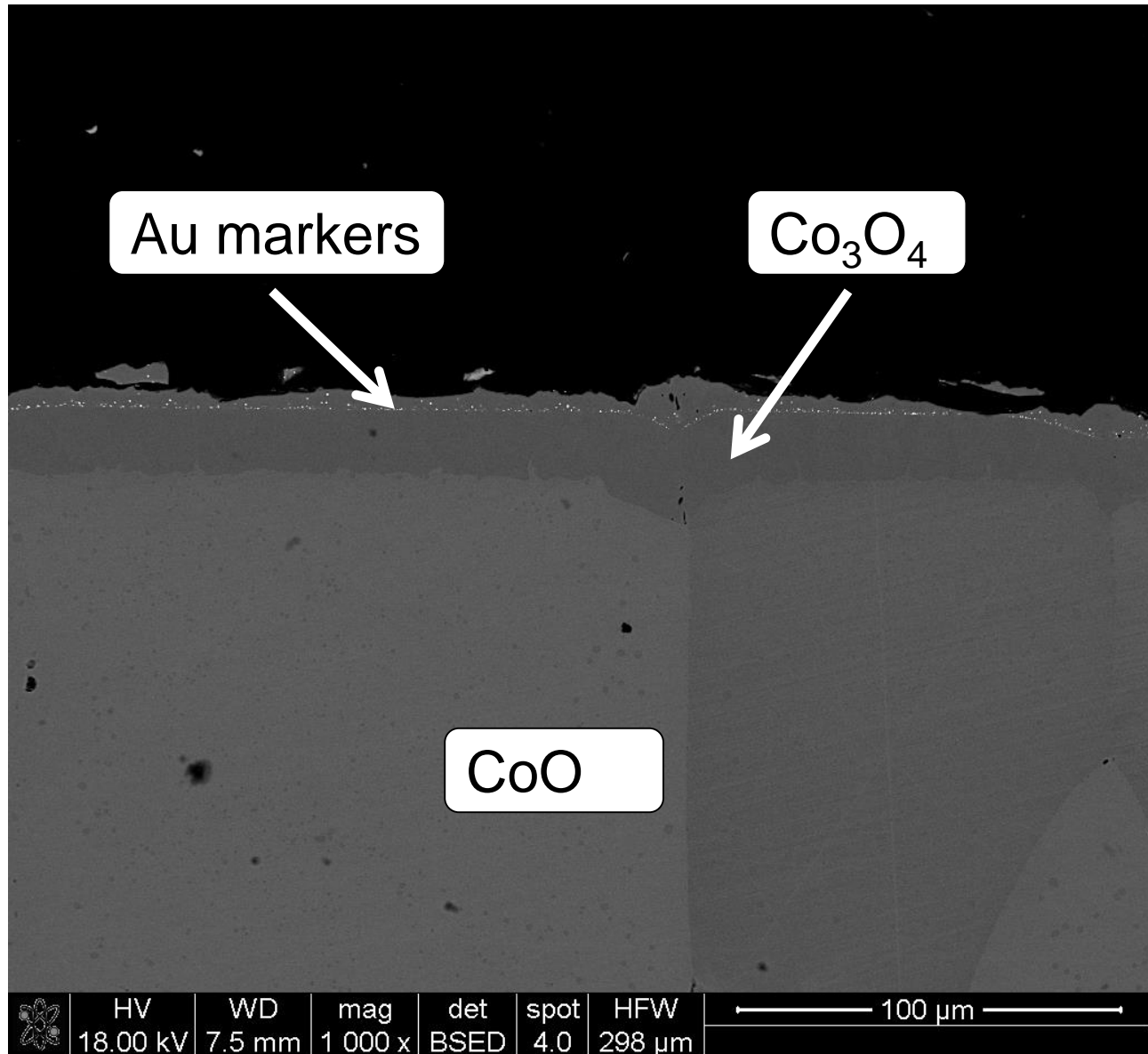
Interior of NiS sulphidized at a sulfur vapor pressure that enables NiS₂ formation



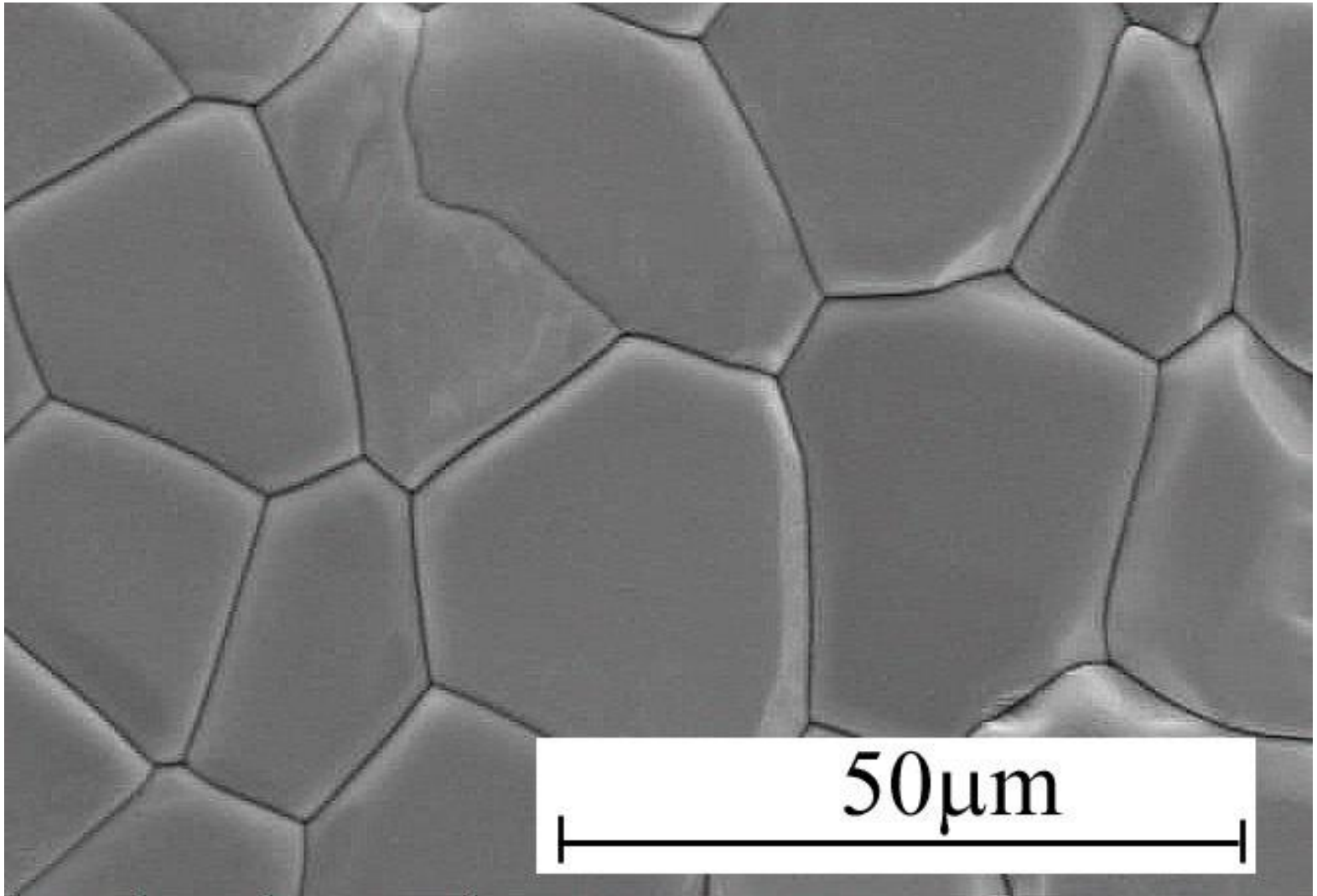
Cross-section of a CoO sample covered with Co_3O_4



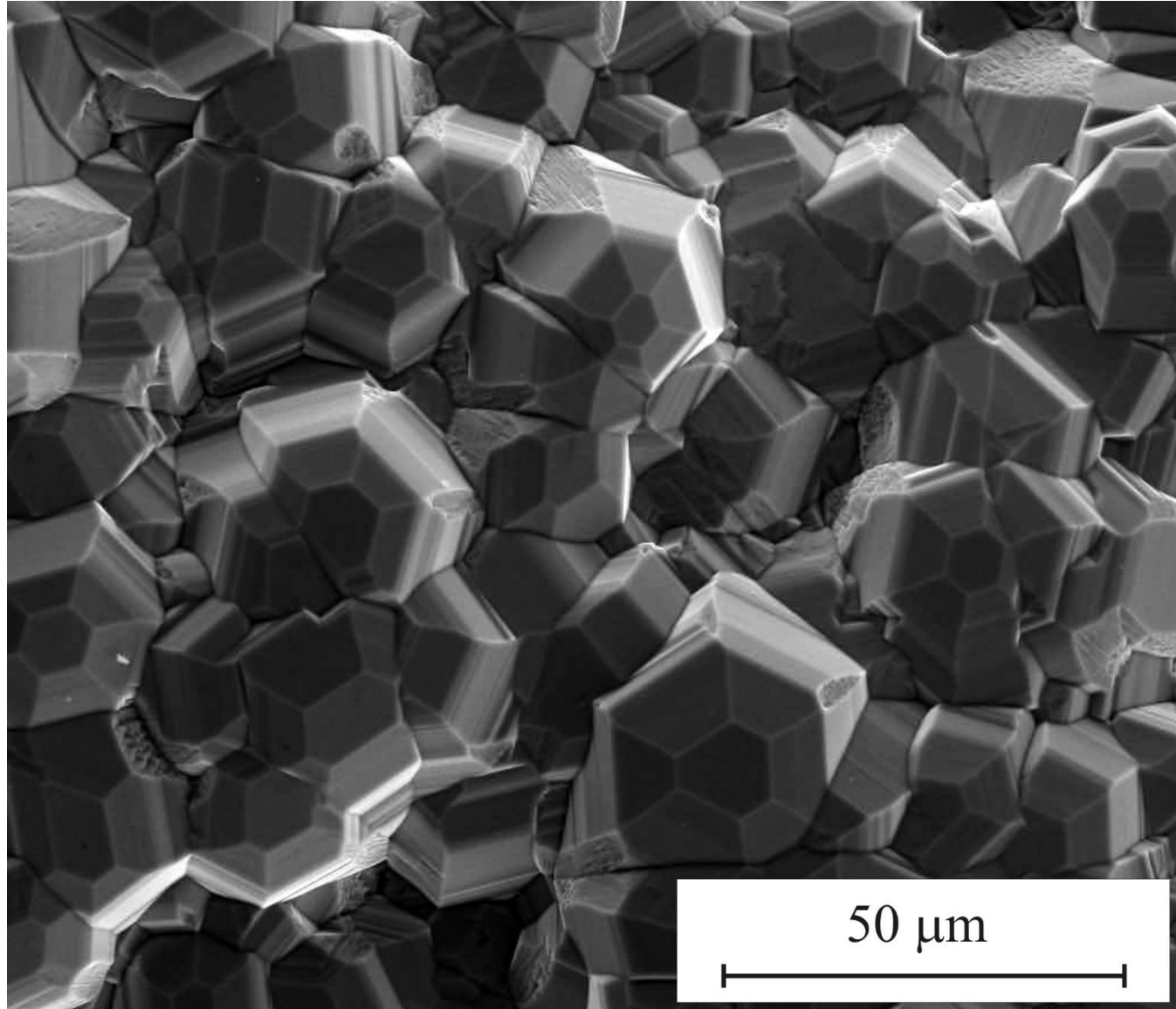
Marker location in Co_3O_4 growing on CoO



Surface of CoO formed as a result of Co oxidation
at 900°C and at 1000 Pa oxygen pressure

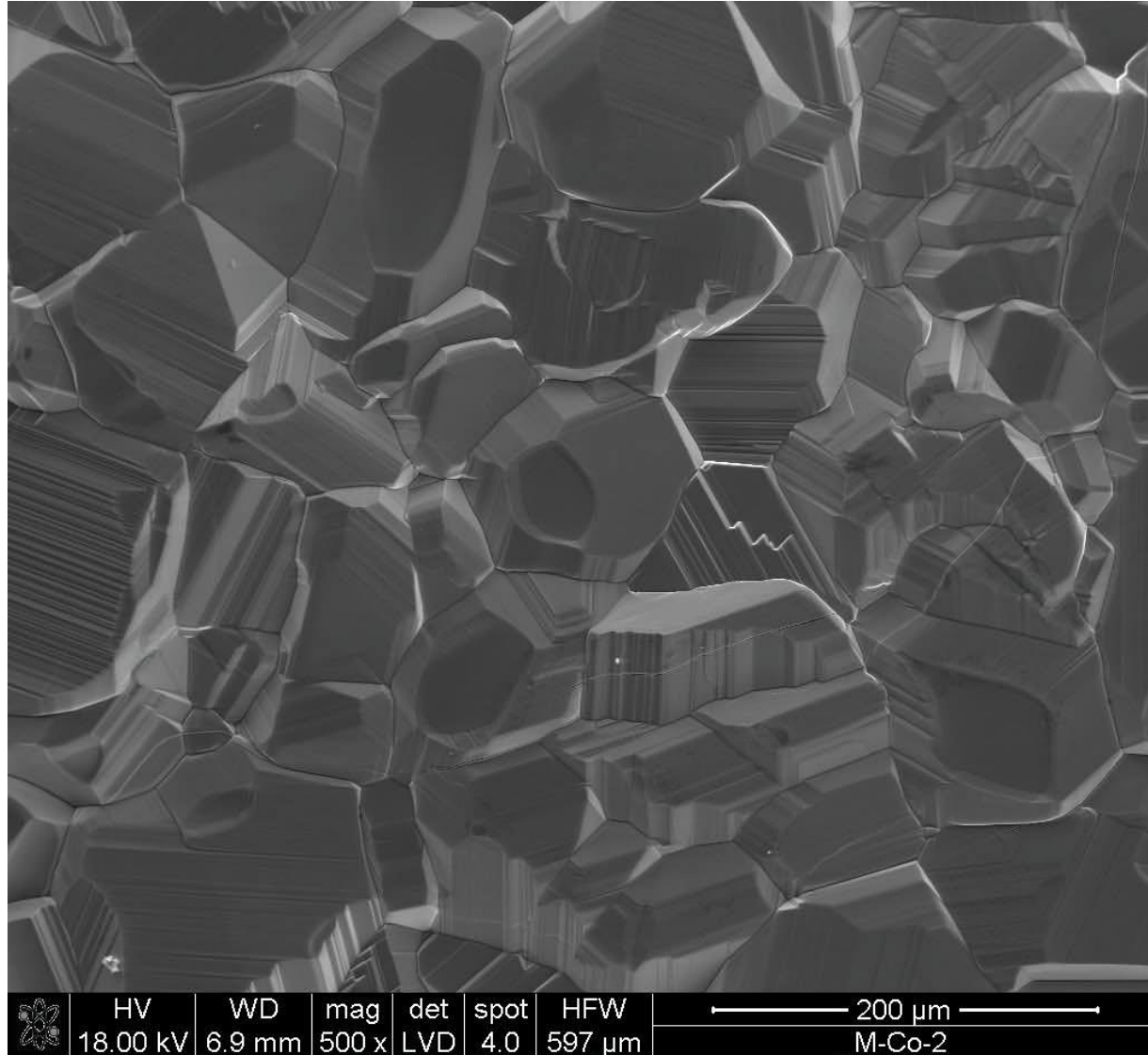


Surface of NiS formed as a result of Ni sulphidation at 700°C and at 1000 Pa sulfur vapor pressure

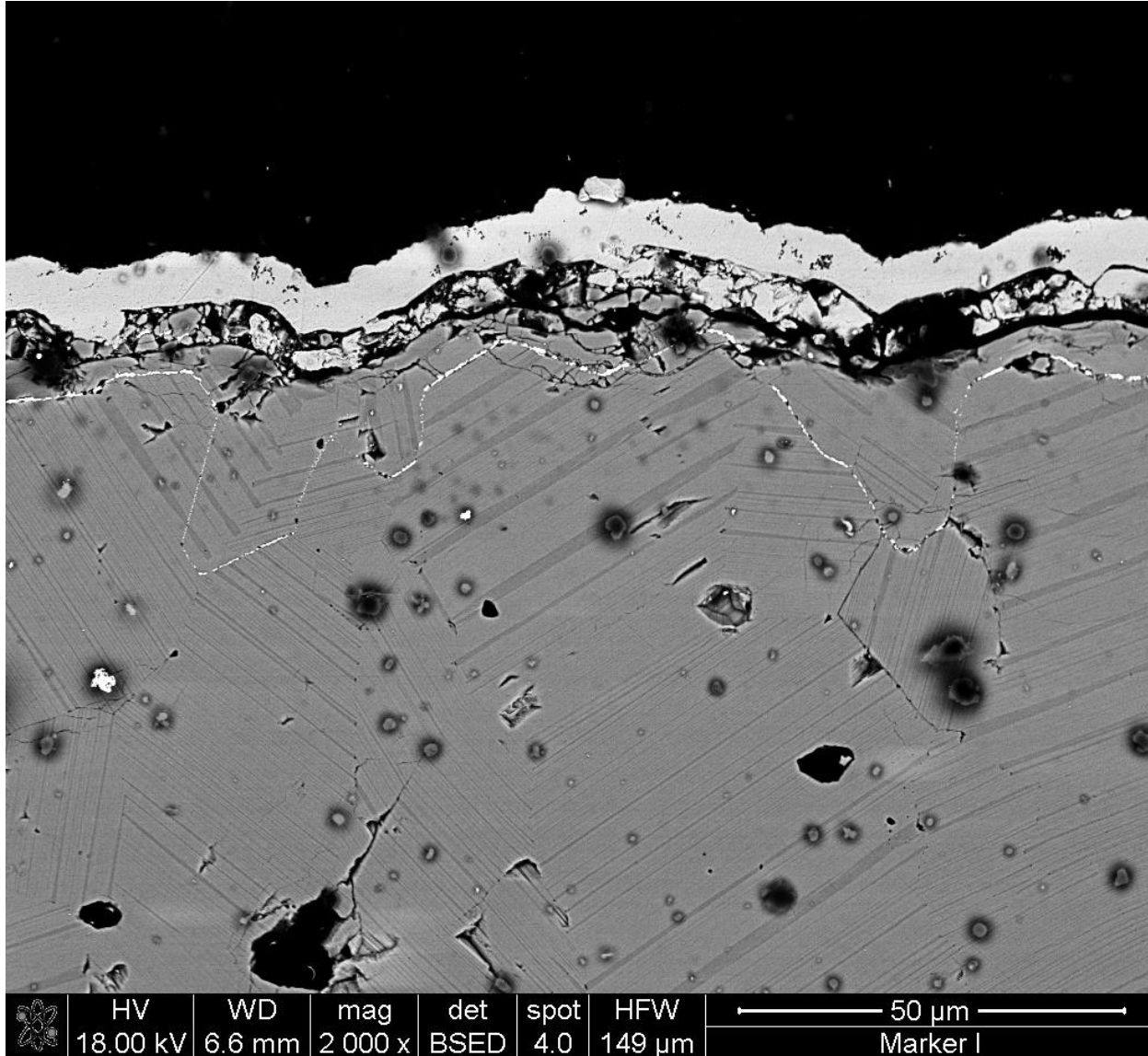


50 μm

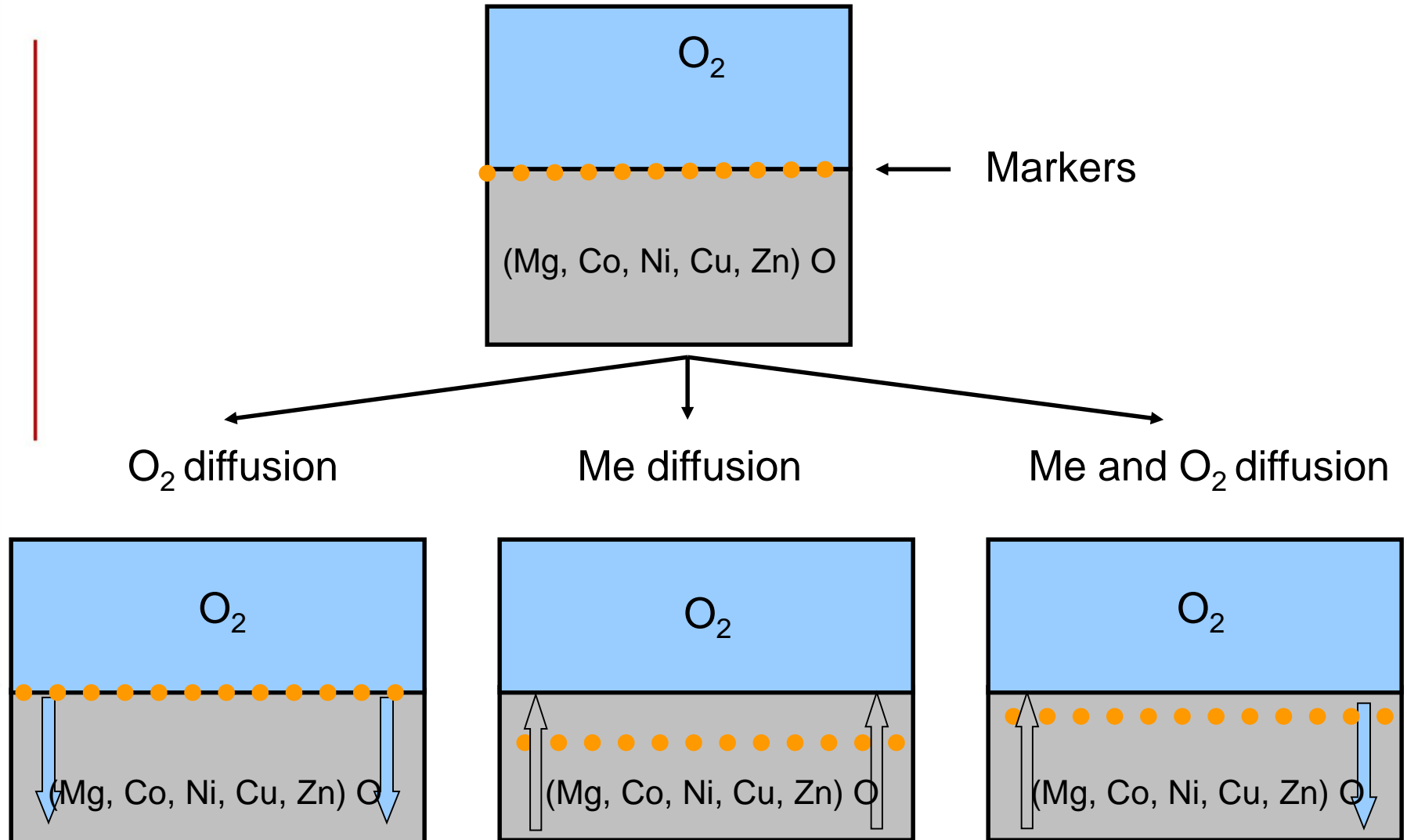
Surface of CoS formed as a result of Co sulphidation at 700°C and at 1000 Pa sulfur vapor pressure



Marker location on a developed CoS surface

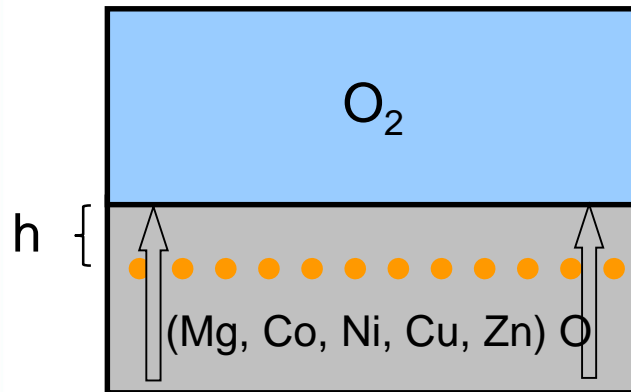


Marker method – oxidation of a high entropy oxide (Mg, Co, Ni, Cu, Zn) O

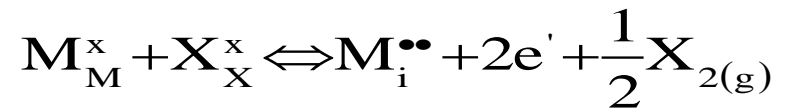


Marker method – oxidation of a high entropy oxide (Mg, Co, Ni, Cu, Zn) O

Presence of predominant disorder inside the cation sublattice



reaction location:



$$h = A \cdot d \cdot \Delta m$$

where:

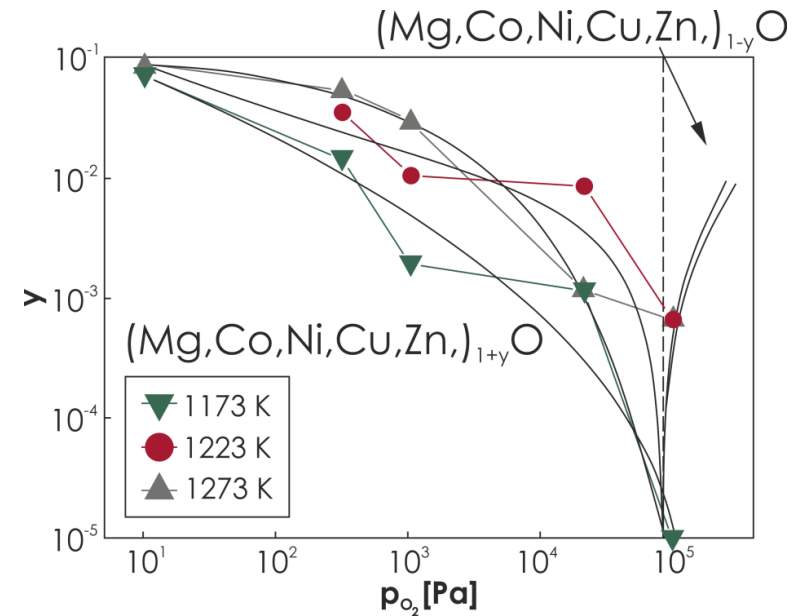
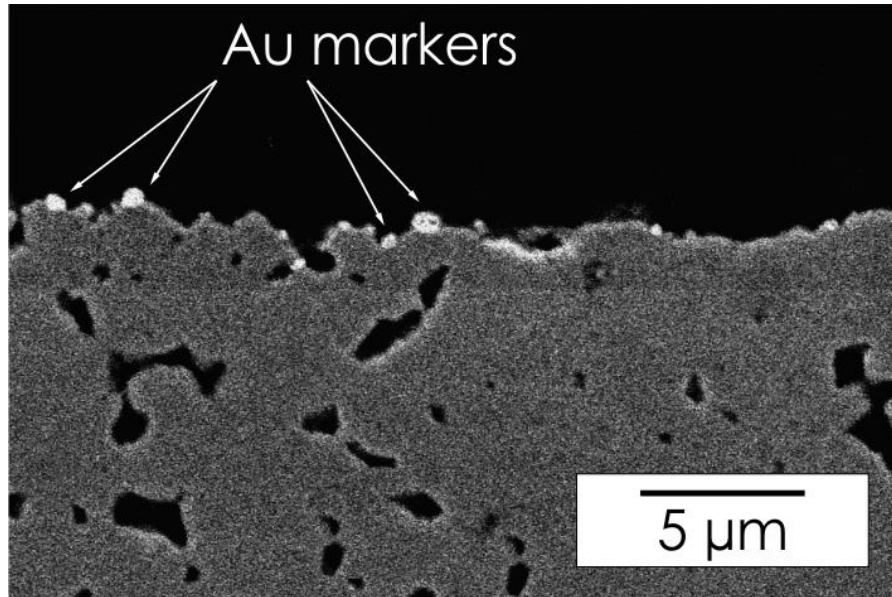
h – thickness of the oxide formed on the marker layer

A – proportionality coefficient

d – oxide density

Δm – oxide mass change during oxidant pressure change

Marker method – oxidation of a high entropy oxide (Mg, Co, Ni, Cu, Zn) O



$$h = 12 \mu\text{m}$$

Conclusion:

In the case where predominant disorder exists in the cation sublattice, markers should be located 12 micrometers below the oxide surface.

Necessary conditions for obtaining reliable results using the modified marker method

- Before marker deposition the oxide sample must be heated at oxygen pressure lower than that used during oxidation of the sample covered with markers.
- The change in deviation from stoichiometry of the studied oxide must be large (order of a few percent) during the marker experiment.
- Sample thickness should exceed 1 mm.
- Reequilibration time of defect concentration during oxygen pressure change should be many times greater than around 1 minute (which means a small chemical diffusion coefficient for defects and/or a large sample thickness).

Conclusion:

Complete interpretation of a modified marker experiment is possible after finishing both marker studies, as well as point defect concentration and mobility studies in a given oxide.

Marker experiment – summary

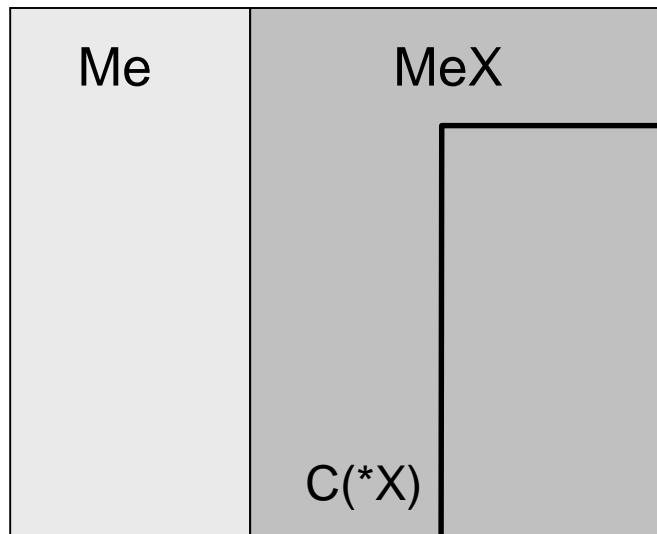
Obtaining reliable results during predominant disorder studies using the marker method in ceramic systems, especially porous systems, is a much more difficult task compared to metal-oxidant systems. In order to interpret results, precise analysis of the reaction product growth location in the substrate is necessary. In the case of ceramic substrates with high point defect concentration, the materials should be homogenized before the “marking” process at a highest oxidant pressure, at which the chemical compound constituting the substrate remains stable. In the case of compounds exhibiting large deviation from stoichiometry, this should be taken into account when writing the appropriate chemical reactions, on the basis of which marker locations inside the reaction product can be foreseen.

Two-stage oxidation method

OUTWARD LATTICE METAL DIFFUSION

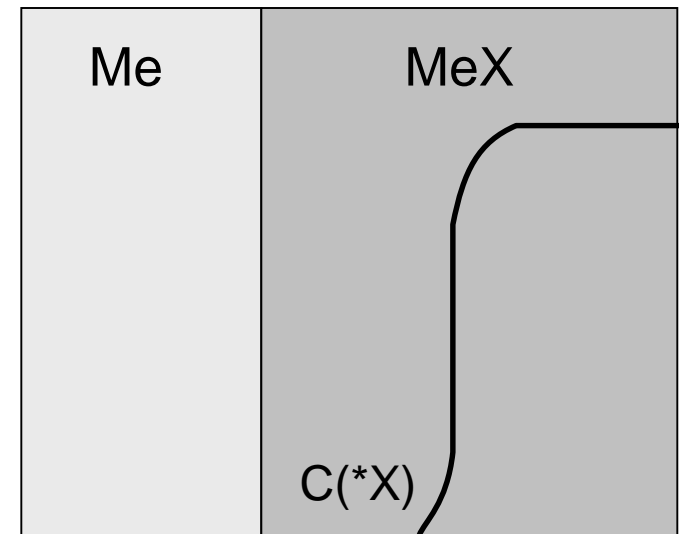
Ideal case

(X and *X atoms do not mix together)



Real case

(X and *X atoms mix together)



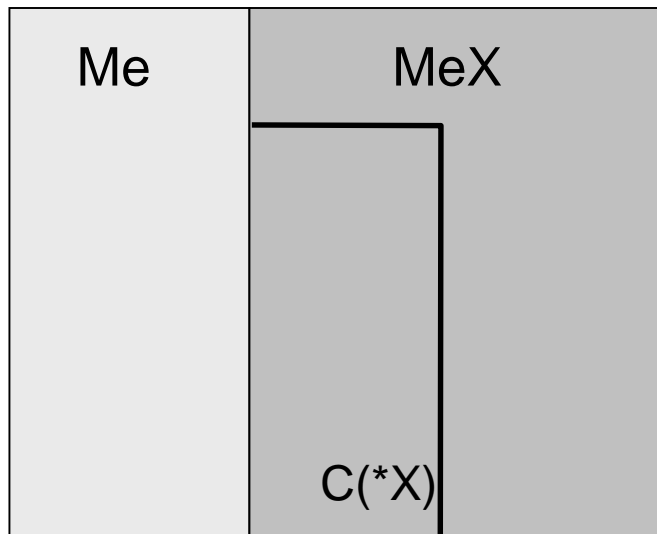
$C(*X)$ – concentration of the oxidant isotope (tracer)

Two-stage oxidation method

INWARD OXIDANT DIFFUSION ALONG GRAIN BOUNDARIES

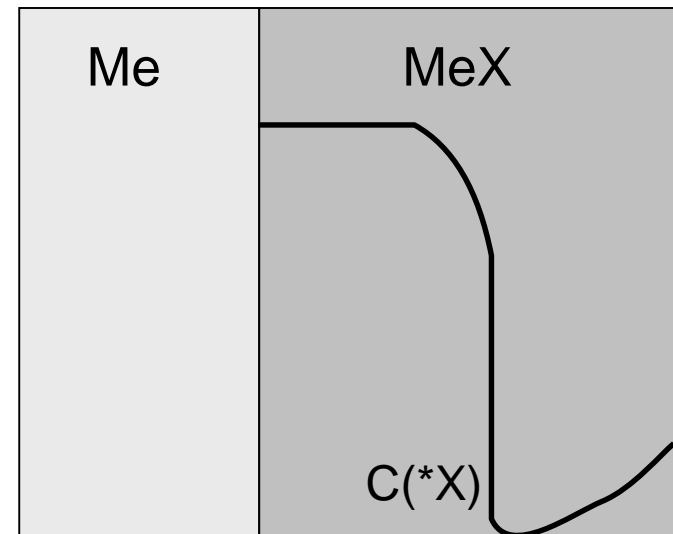
Ideal case

(X and *X atoms do not mix together)



Real case

(X and *X atoms mix together)

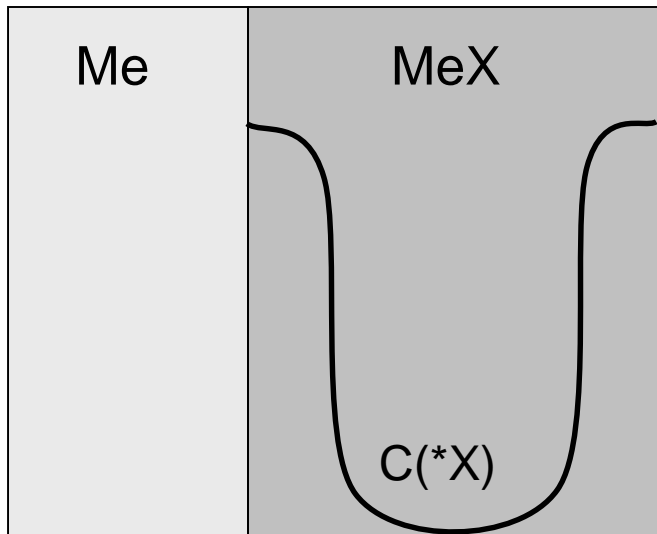


$C(*X)$ – concentration of the oxidant isotope (tracer)

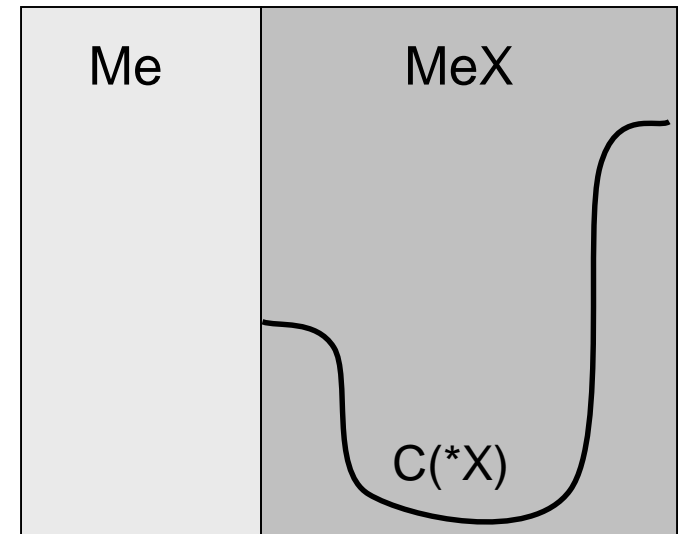
Two-stage oxidation method

SIMULTANEOUS DIFFUSION OF BOTH REAGENTS

Slow mixing together of X and *X atoms

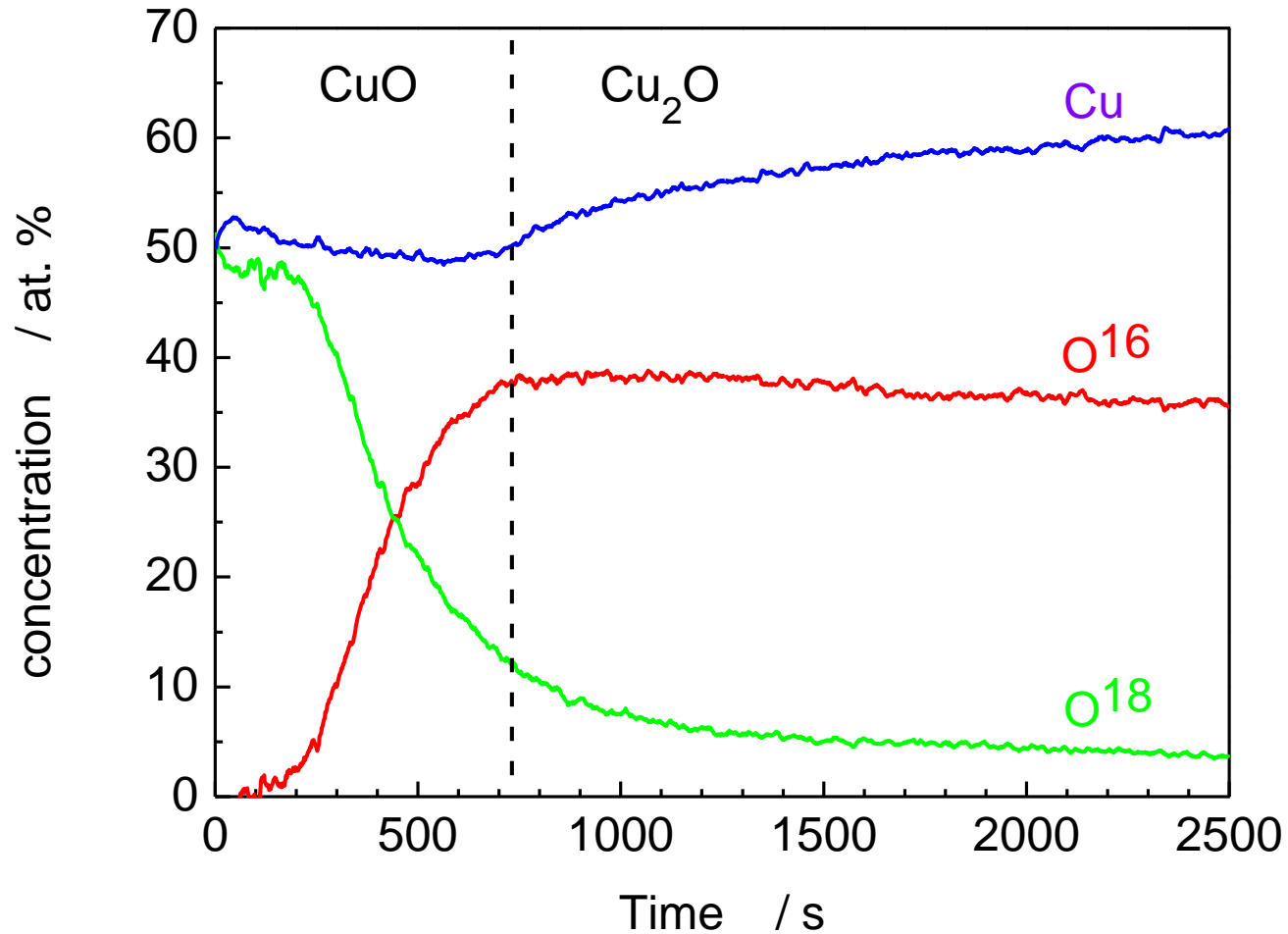


Fast mixing together of X and *X atoms



$C(*X)$ – concentration of the oxidant isotope (tracer)

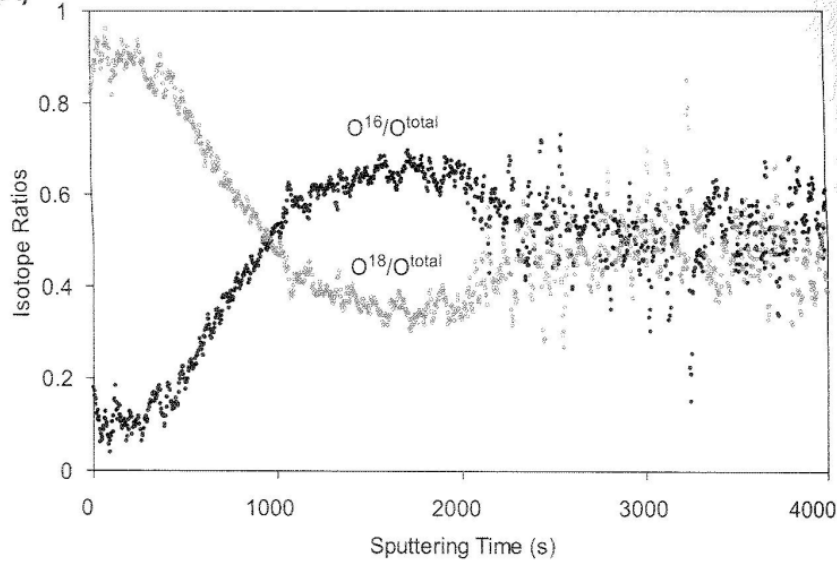
Cu, O¹⁶ and O¹⁸ concentration profiles inside a sample obtained during Cu₂O oxidation at 1273 K and 10⁵ Pa oxygen pressure



O^{16} and O^{18} concentration profiles in an Ni-Cr sample after two-stage oxidation at 1323 K

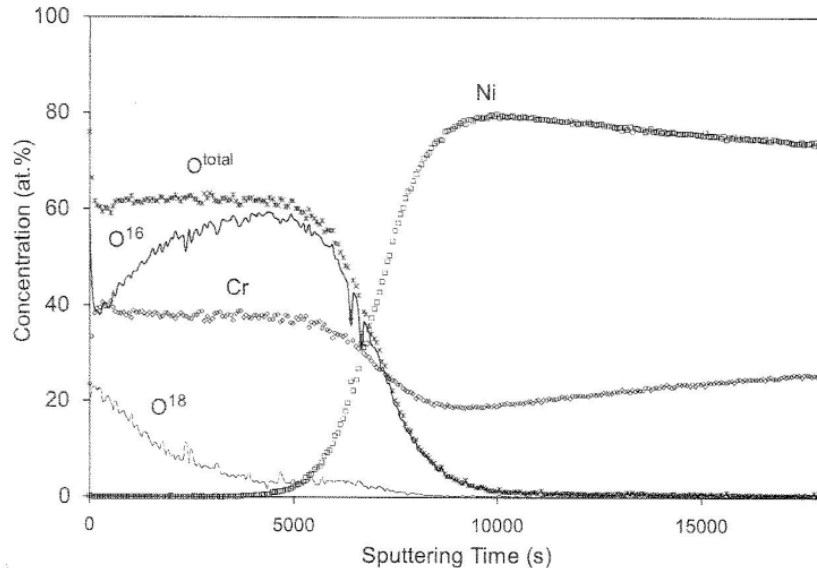


AGH (A)



I stage: Ar-20% $^{16}O_2$; 0,5 h
II stage: Ar-20% $^{18}O_2$; 2 h

(B)



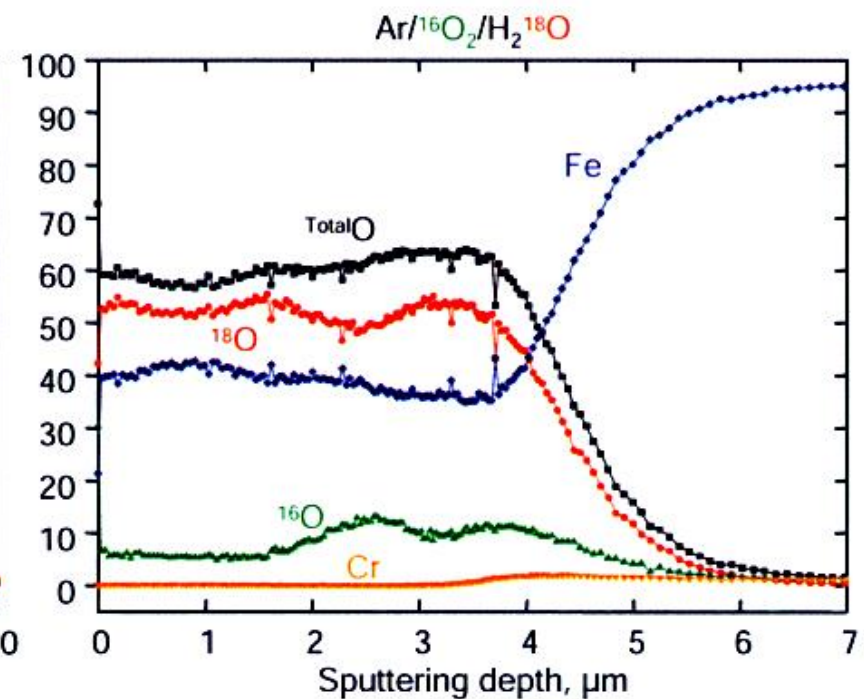
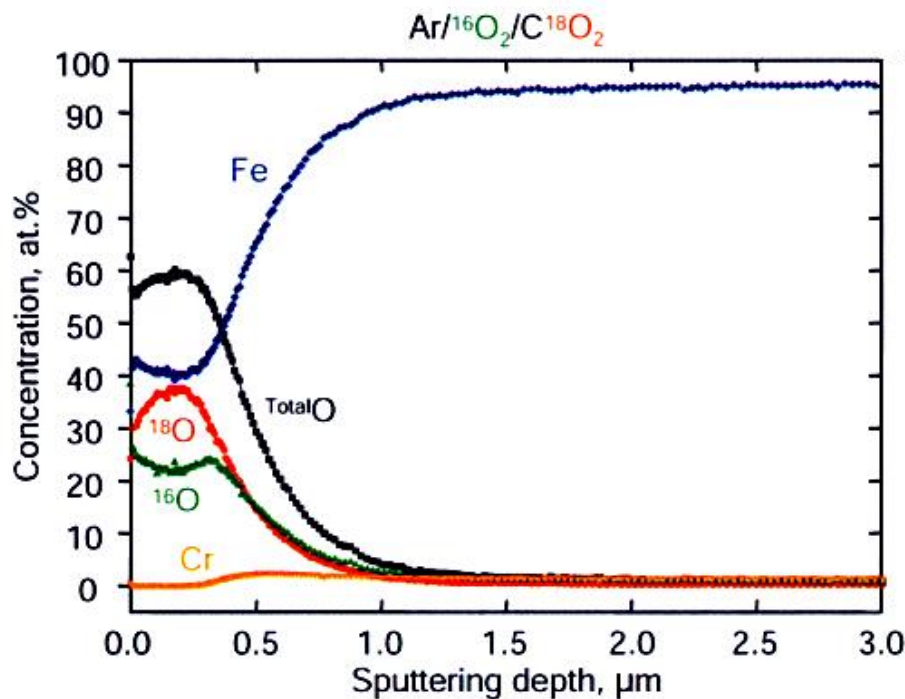
I stage: Ar-4% H_2 -2% $H_2^{16}O_2$; 0,5 h
II stage: Ar-4% H_2 -2% $H_2^{18}O_2$; 2 h

David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2016

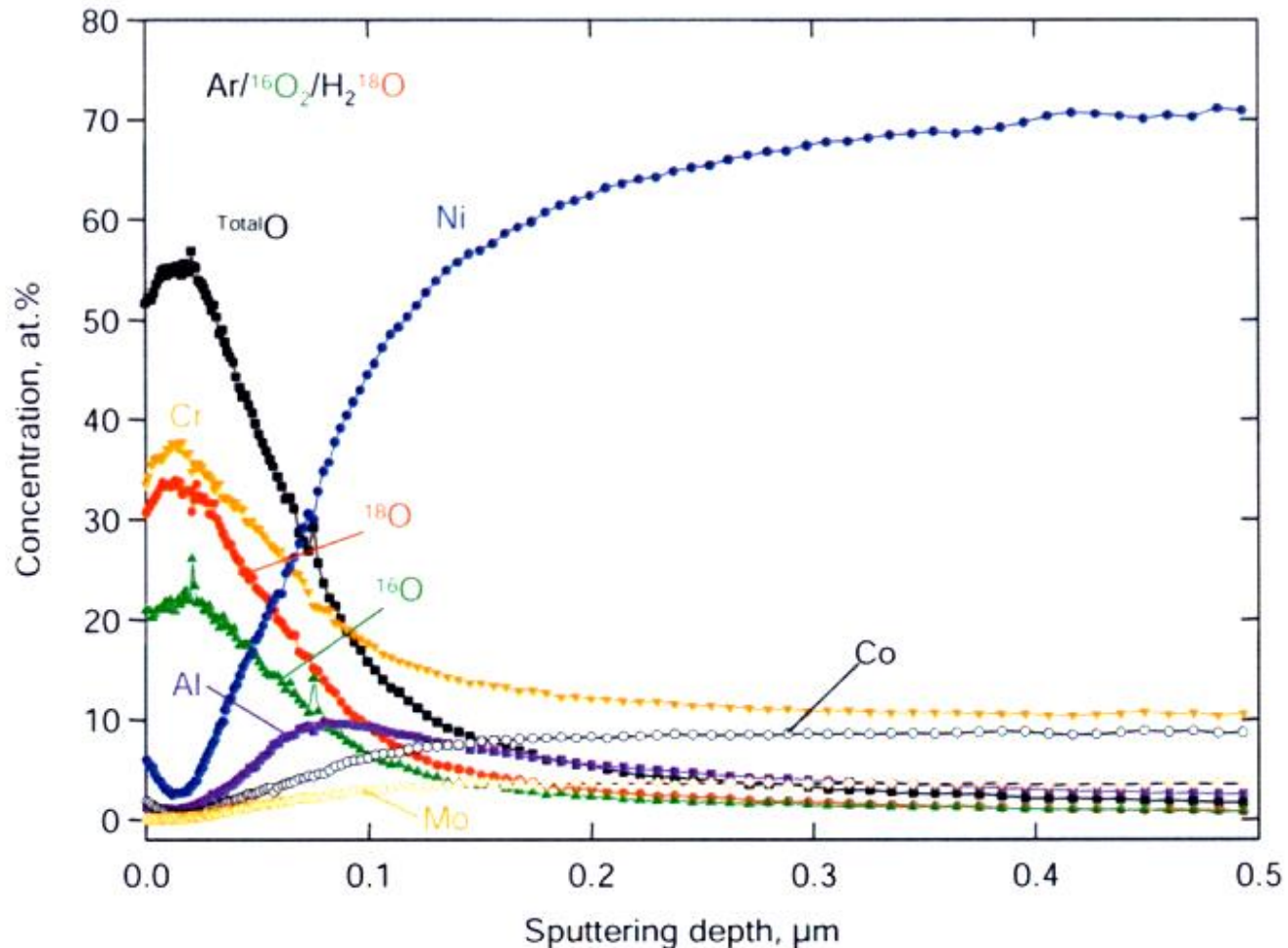
Cr, Fe, O¹⁶ and O¹⁸ concentration profiles in 13CrMo4-4 steel after oxidation at 823 K

Ar / 1% ¹⁶O₂ / 1% C¹⁸O₂; 2 h

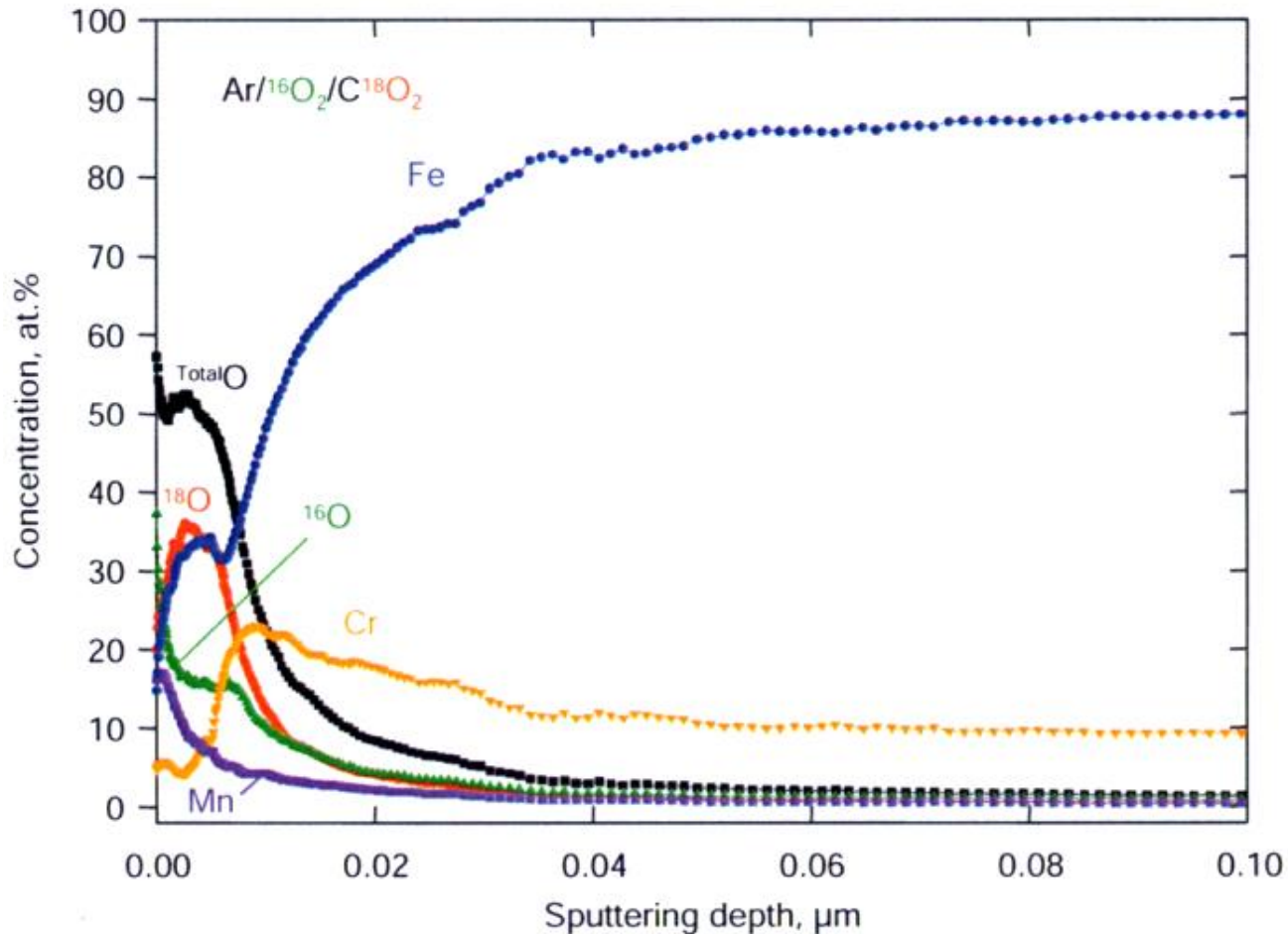
Ar / 1% ¹⁶O₂ / 2% H₂¹⁸O; 2 h



Concentration profile of elements in a P92 steel sample after oxidation in Ar / 1% $^{16}\text{O}_2$ / 1% C^{18}O_2 atmosphere at 923 K

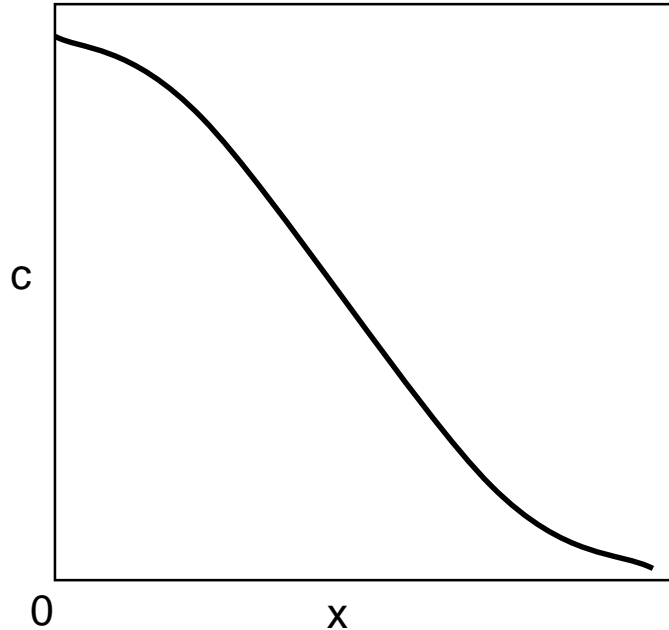


Concentration profile of elements in an INCONEL 617 sample after oxidation in Ar / 1% $^{16}\text{O}_2$ / 2% H_2^{18}O atmosphere at 1173 K

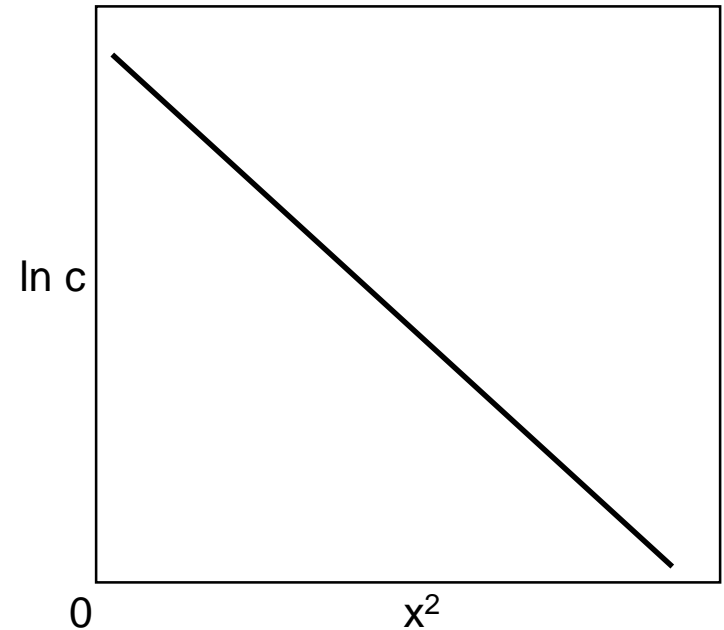


Self-diffusion coefficient studies

Distribution of the concentration of a tracer inserted into the near-surface layer of a MeX crystal (lattice diffusion)



$$c = \frac{c_0}{2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

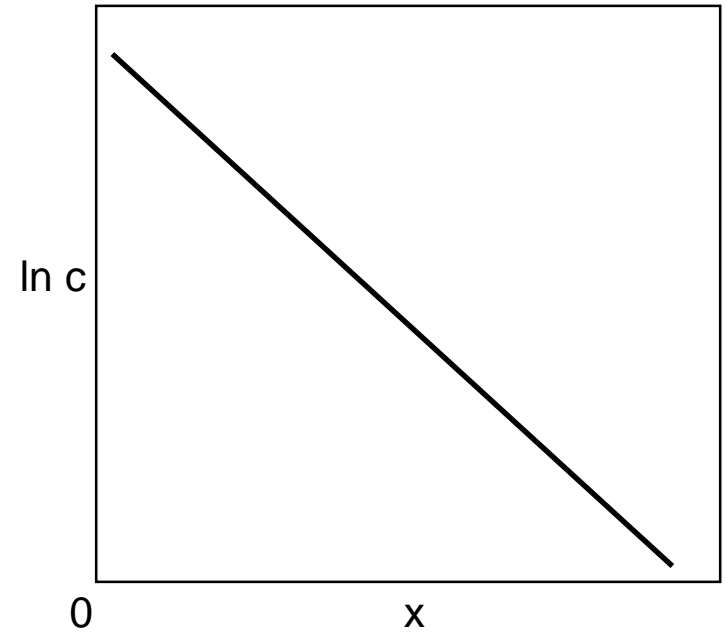
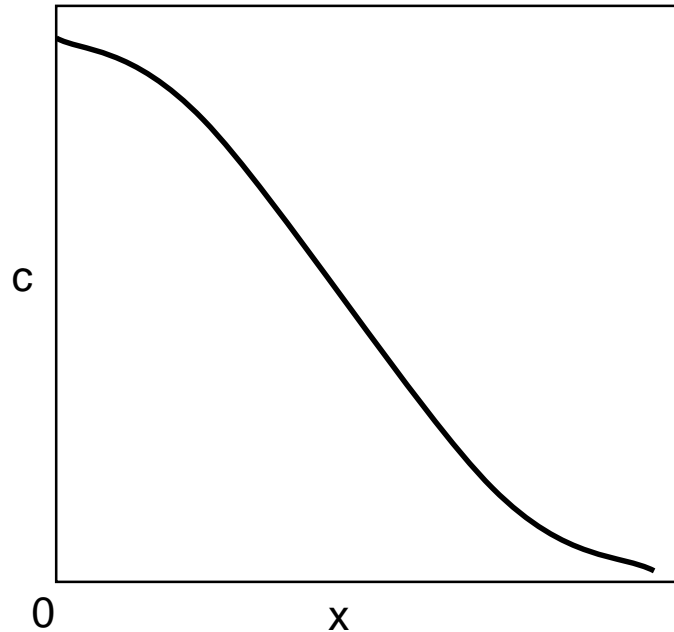


$$\ln c = \ln\left(\frac{c_0}{2\sqrt{\pi Dt}}\right) - \frac{x^2}{4Dt}$$

- c – tracer concentration at distance x from the crystal surface,
- c_0 – tracer concentration on the surface before beginning the heating process,
- t – heating time
- D – self-diffusion coefficient (tracer)

Self-diffusion coefficient studies

Distribution of the concentration of a tracer inserted into the near-surface layer of a MeX crystal (intergranular diffusion)



$$\ln c = - \left(\frac{2 \left(D_V / D_g \right) \sqrt{d}}{\sqrt[4]{\pi D_V t}} \right) \cdot x + \text{const}$$

c – tracer concentration at distance x from the crystal surface,

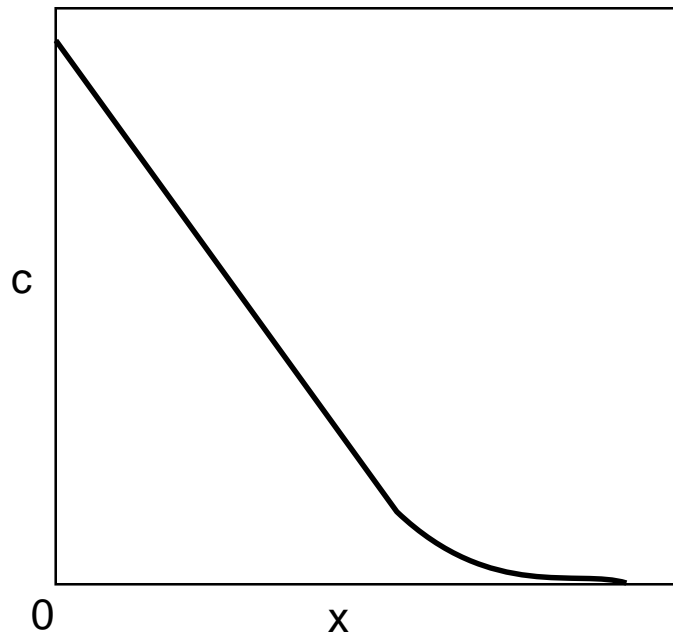
t – heating time

D_V – lattice diffusion coefficient

D_g – intergranular diffusion coefficient

Self-diffusion coefficient studies

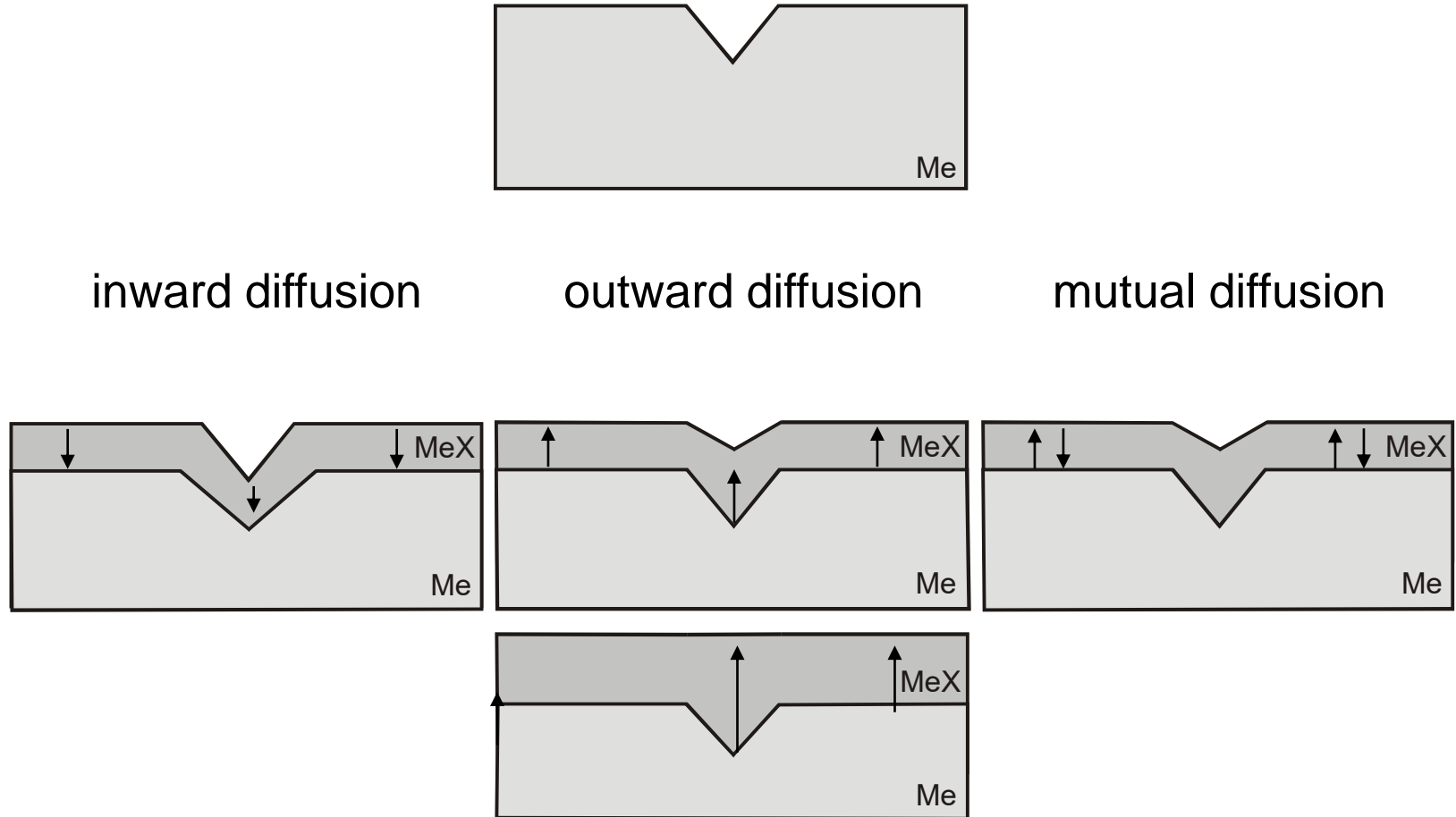
Distribution of tracer concentration in a MeX crystal, when tracer concentration on the crystal surface is constant (lattice diffusion)



$$c = c_0 \left(1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}} \right)$$

- c – tracer concentration at distance x from the crystal surface,
- c_0 – tracer concentration on the surface before beginning the heating process,
- t – heating time
- D – self-diffusion coefficient (tracer)

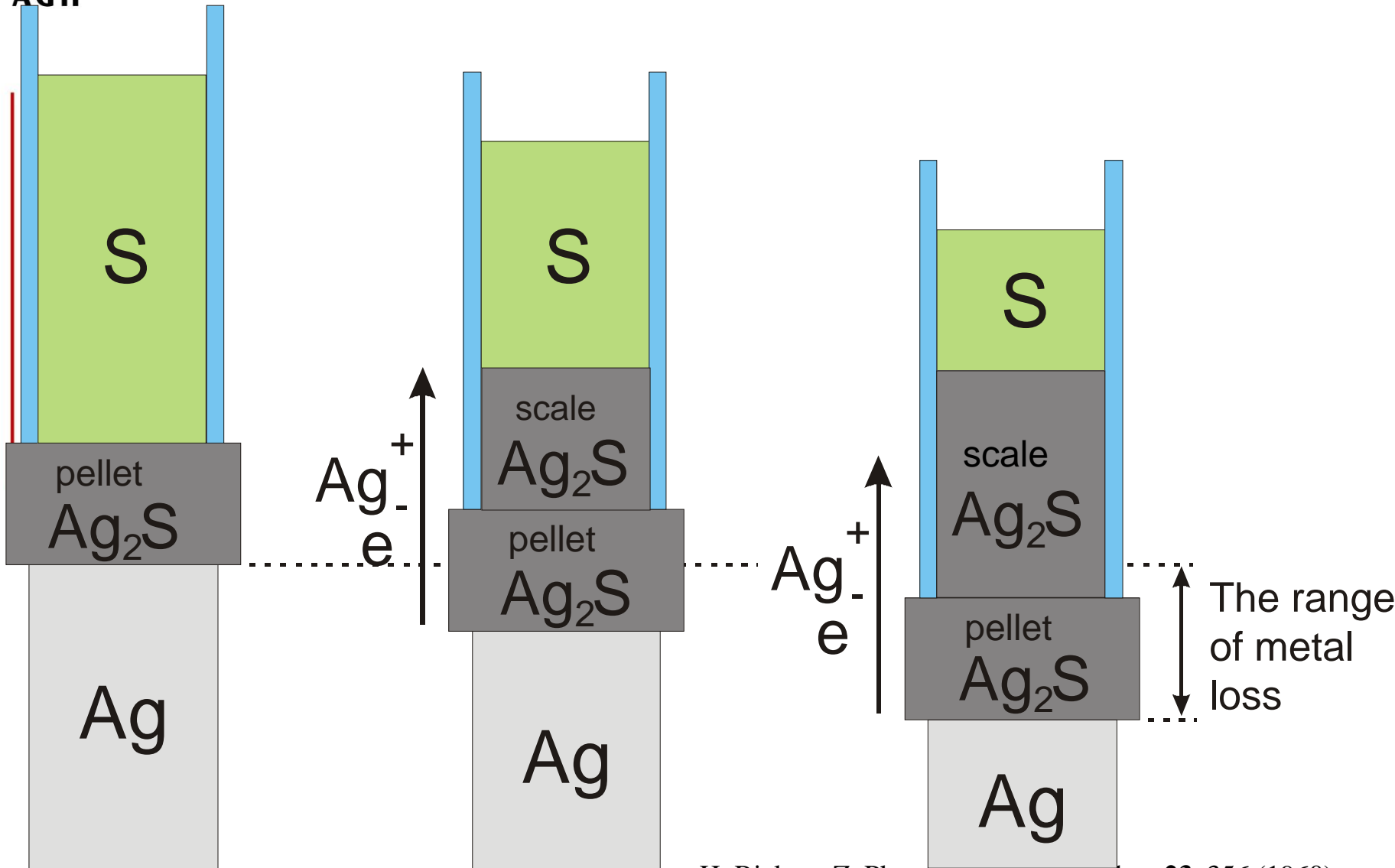
Scratch method



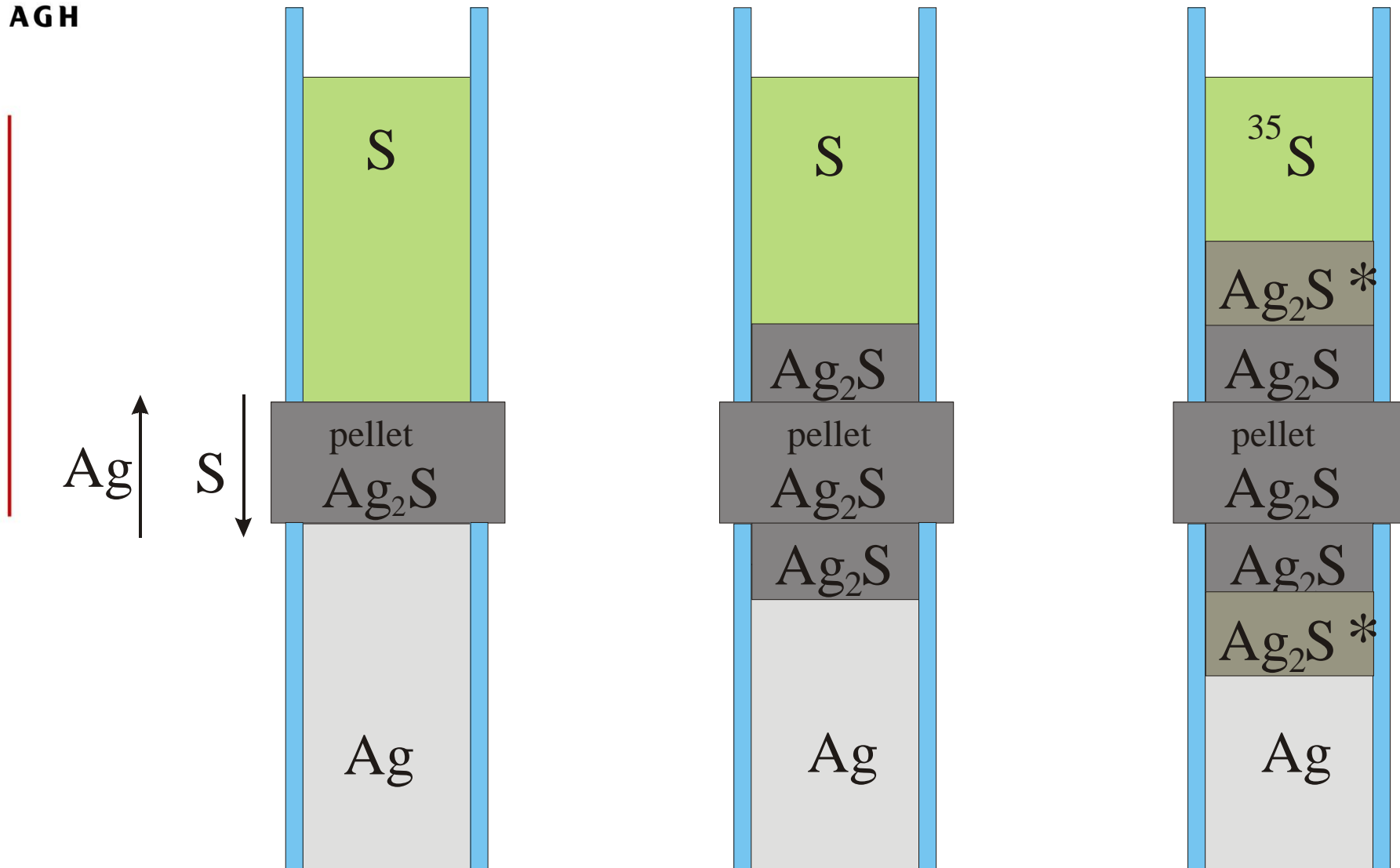
Wagner's pellet method



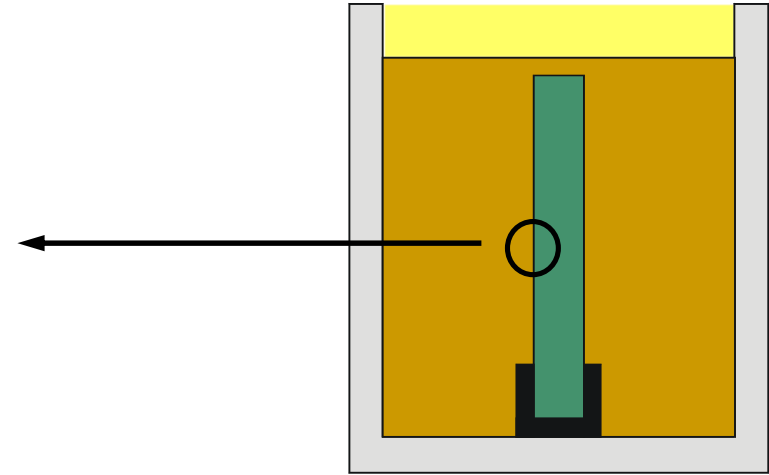
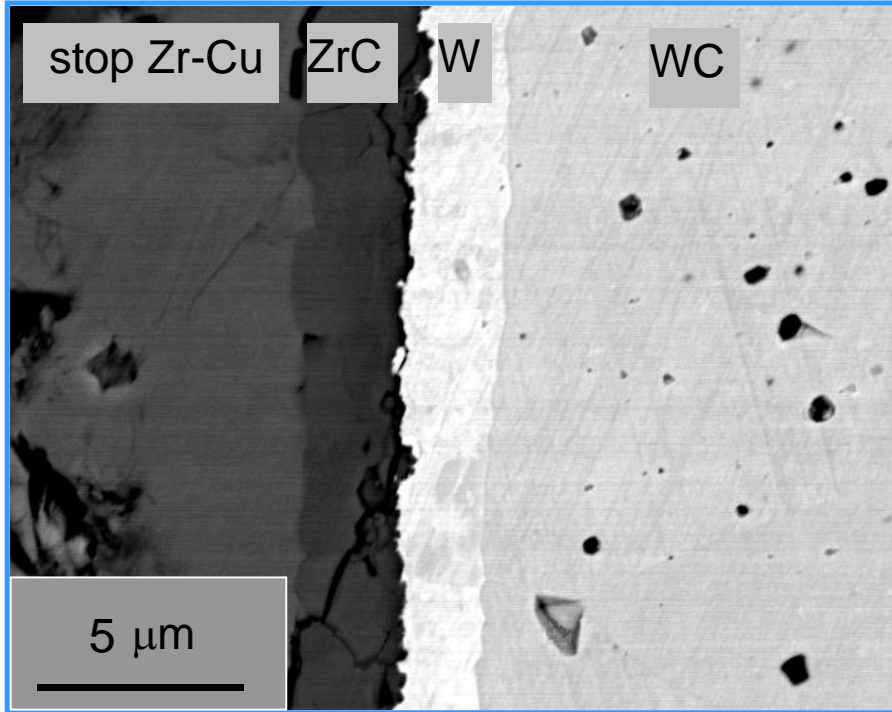
AGH



Modified Wagner's pellet method



Cross-section of a WC sample that reacted with Zr



temperature: 1400 °C

time: 1,5 h



THE END