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LUND UNIVERSITY

EUROPEAN SPALLATION SOURCE

Formation of Oxide Layers in Mildly Oxidizing Gas

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Outline

- Background
  - ESS tungsten target
  - Tungsten oxides and oxidation kinetics
- Materials and Methods
  - Samples, atmospheres & temperatures
  - Experimental set-up
- Results
  - Mass changes
  - Oxide layer thickness
  - Surface analysis

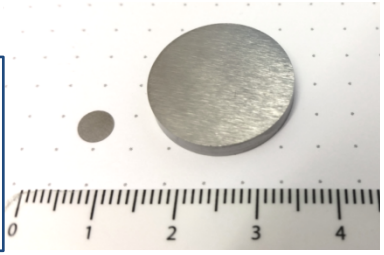
Target at ESS

- Tungsten heated during spallation
  - Max. temp ~450°C
  - Helium cooling system
- O_2 and H_2O impurities in He
  - Causing oxidation → Erosion of target?
  - Oxide vaporized >750°C → Release of radioactive particles
- Information on oxidation at different oxygen partial pressures useful under normal and off-normal operating conditions

Understanding the oxidation behaviour of pure W in mildly oxidizing gas mixtures

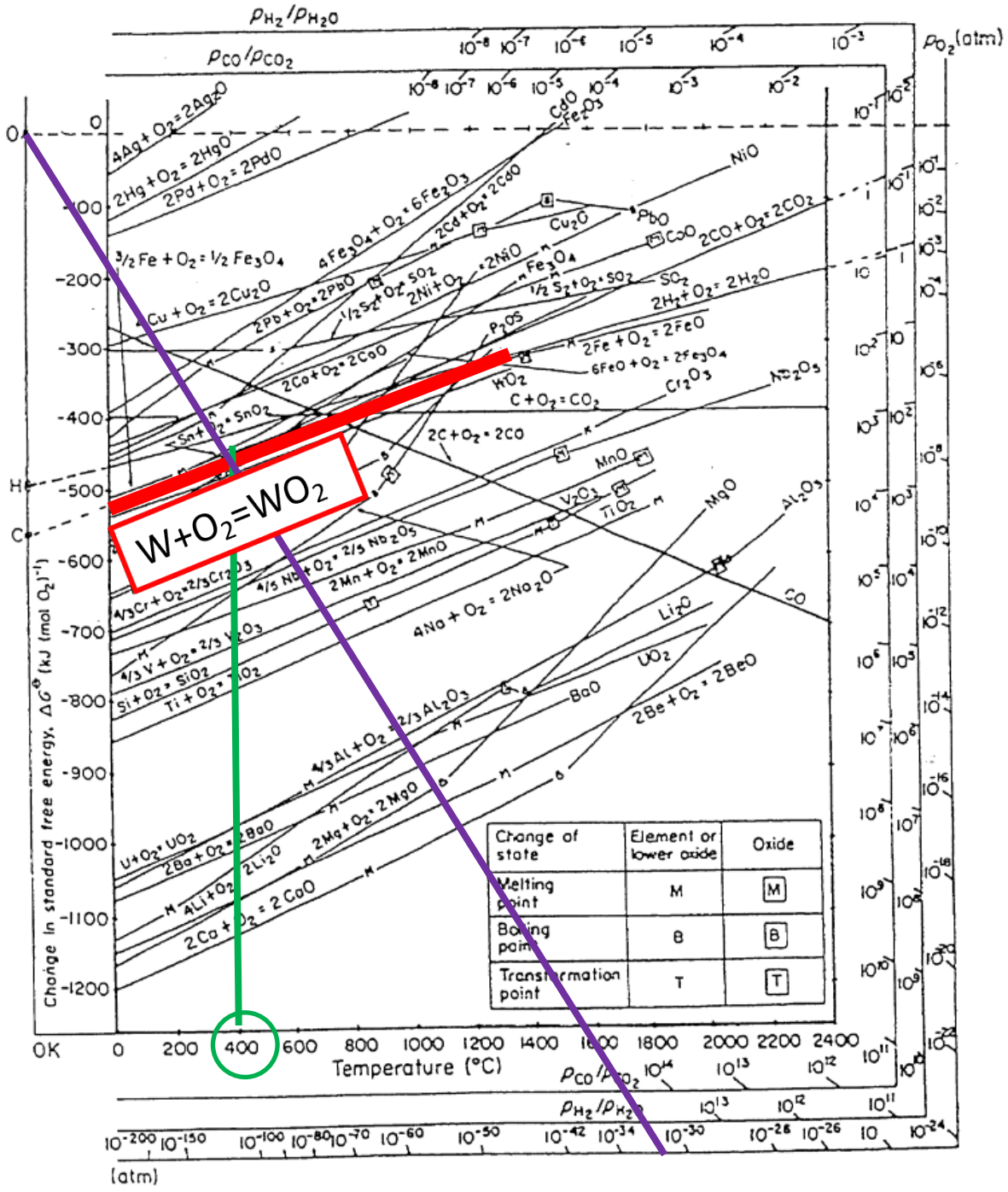
- Estimating the impact of impurities like O_2 and $H_2O(g)$ in He gas
- Study the formation of oxide layers on W in gas mixtures with different oxygen contents
  - 5%, 0.5% and 5ppm O_2
- Study the kinetics of oxidation and the nature of oxides formed
- Identify safe operation limits for target operation
  - Temperature, environment

E-polished, rolled W.
20mm dia, 3mm thick
5.5mm dia, 26 um thick



Protective gas atmosphere

- Prevent/minimize the oxidation of tungsten
- Requirement: $(p_{O2})_{He} < (p_{O2})_{W\text{-}WO_{3-X}\ equilibrium}$
- Monitoring the effective partial pressure of oxygen in the gas is crucial
- Purification of He gas to reduce O_2 and moisture levels



Ellingham diagram

$W+O_2=WO_2$ at 400°C

→ $\underline{pO_2 < 10^{-32}\ \text{atm.}}$

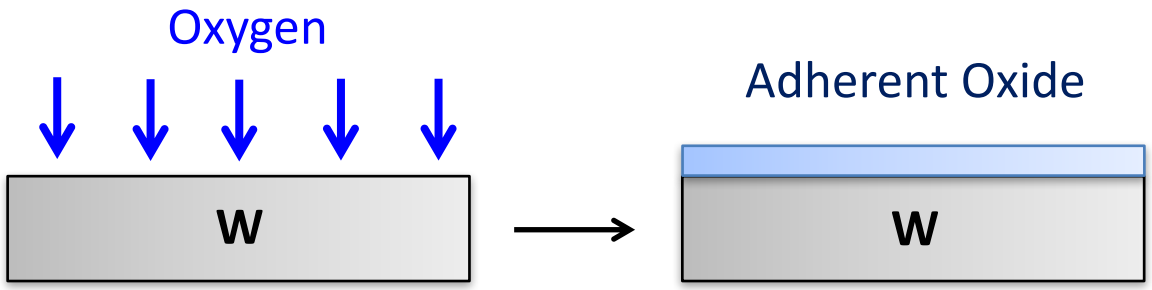
In order to keep W free from oxide

Tungsten oxidation process

The overall tungsten oxidation process can be divided into three different stages:

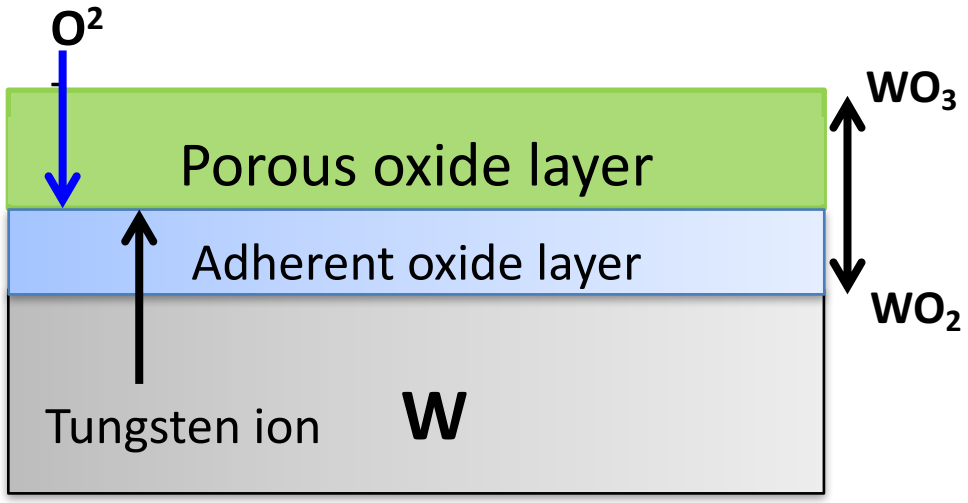
1. Phase boundary controlled
   - Formation of first oxide layer
2. Diffusion controlled
   - Growth of dark and protective layer
   - Growth of porous WO_3
3. Sublimation of WO_3

Formation of oxide layer > 600°C



- Initial oxidation is phase boundary controlled.
- This oxide layer is thin, adherent and protective.
- Rate is limited according to the rate of diffusion of O^{2-} ions through the oxide scale → parabolic oxidation rate

Formation of tungsten oxides between 600°-750°C



- WO_3 forms on top of the first layer
- Porous, not very adhesive, volume ratio of 3.35 → WO_3 creates high stresses, oxide layer cracks, exposes fresh metal surface.
- The non-protective nature of WO_3 results in a linear oxidation rate
- W/O ratio varies, lowest oxide closest to metal surface
- Sublimation takes place <750°C
  - Conflicting data on threshold temp for sublimation in literature. Dependent on P_{O2} and P_{H2O}

Tungsten in contact with H_2O

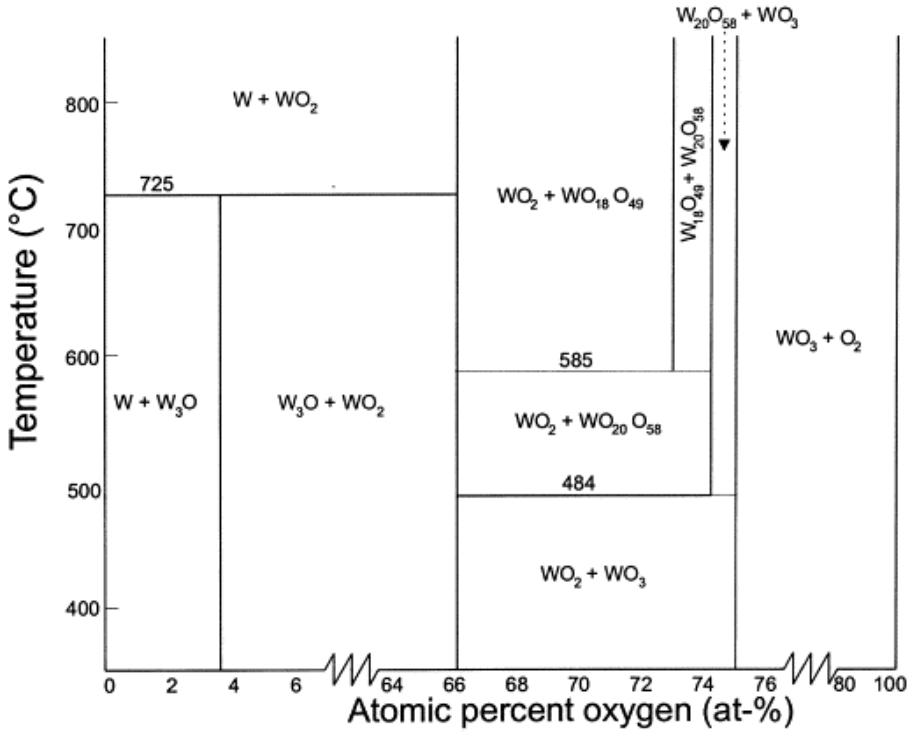
Reaction: $WO_3(s)+H_2O(g)=WO_3H_2O(g)$

- Formation of some gaseous species contribute to the sublimation of tungsten oxides (above 750°C)
- The above reaction is pushed to the right as the product (tungstic acid) is formed and removed quickly.

- Green et. al, *Vaporization of tungsten in flowing steam at high temperatures* (2001):
  - 100% steam superheated to 140°C
  - Formation of $WO_3H_2O(g)$ at as low as 800°C

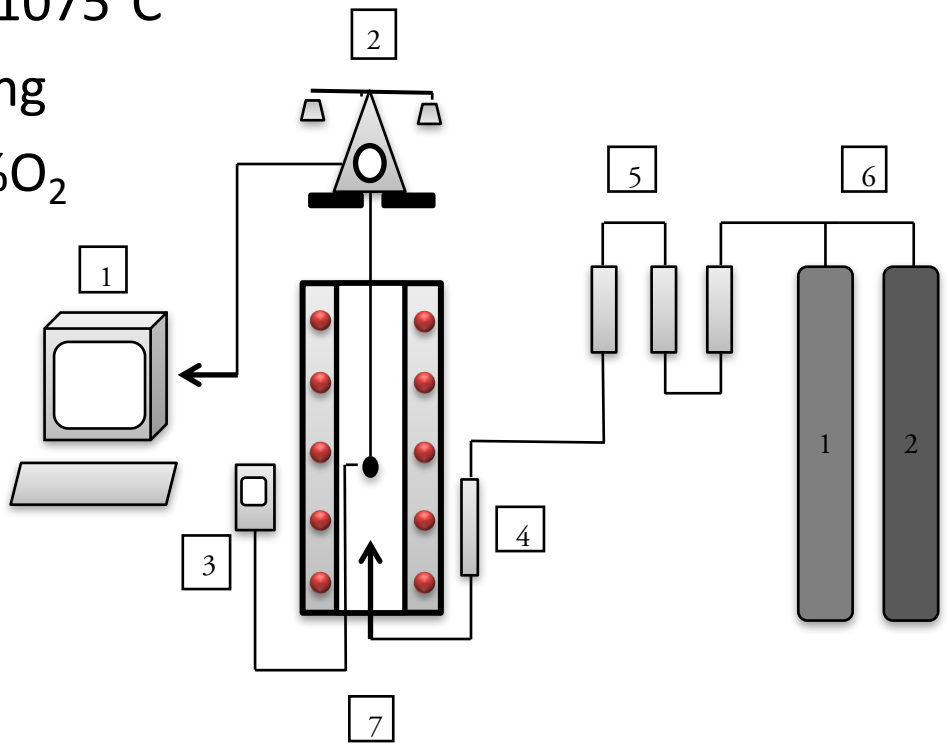
Various W oxides, W-O system

- Oxides with higher oxygen content are near the oxide-oxygen phase boundary
- The oxides most frequently mentioned are:
  - WO_2, $WO_{2,72}$ ($W_{18}O_{49}$), $WO_{2,9}$ ($W_{20}O_{58}$) and WO_3
- Other oxides mentioned in the literature
  - ex. $WO_{2,75}$, $WO_{2,92}$ and $WO_{2,96}$



Experimental setup (TGA)

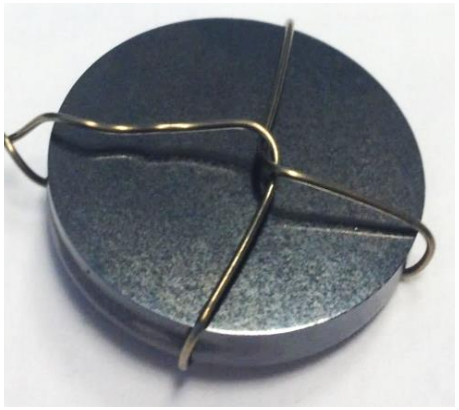
- Thermogravimetric analysis
  - Isothermal studies from 400°-1075°C
  - N_2 protective gas during heating
  - Reactant gas mixture of He-x%O_2 where x = 5ppm to 5%
  - 2h holding time



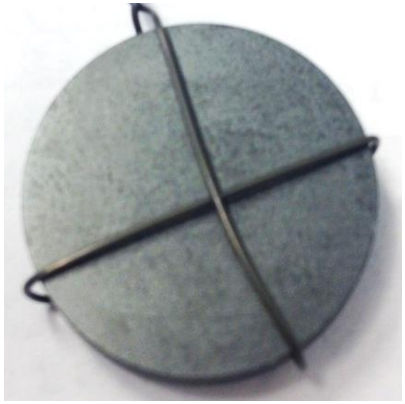
(1) Data aquisition, (2) Balance with suspended sample, (3) Thermocouple (4), Flow meter, (5) Drierite & calciumcloride, (6) Gas cylinders (7) Furnace

W-samples after oxidation in He+Ar+H_2O gas mixture *(2h, p_{H2O} ~0.0078 atm.)*

400°C



500°C



600°C

700°C

750°C

800°C

900°C

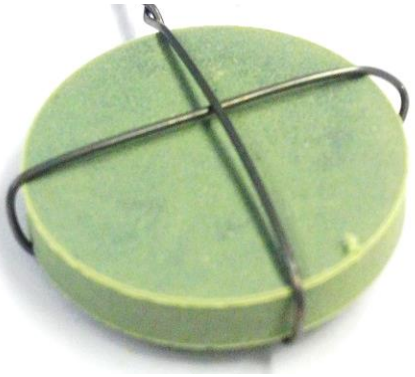
W-samples after oxidation in He+0.5%O_2 gas mixture *(2h, p_{O2} ~0.005 atm.)*

400°C

500°C

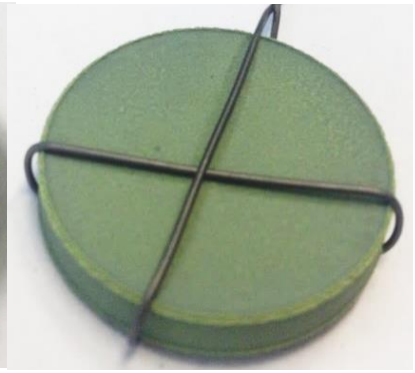
600°C

700°C



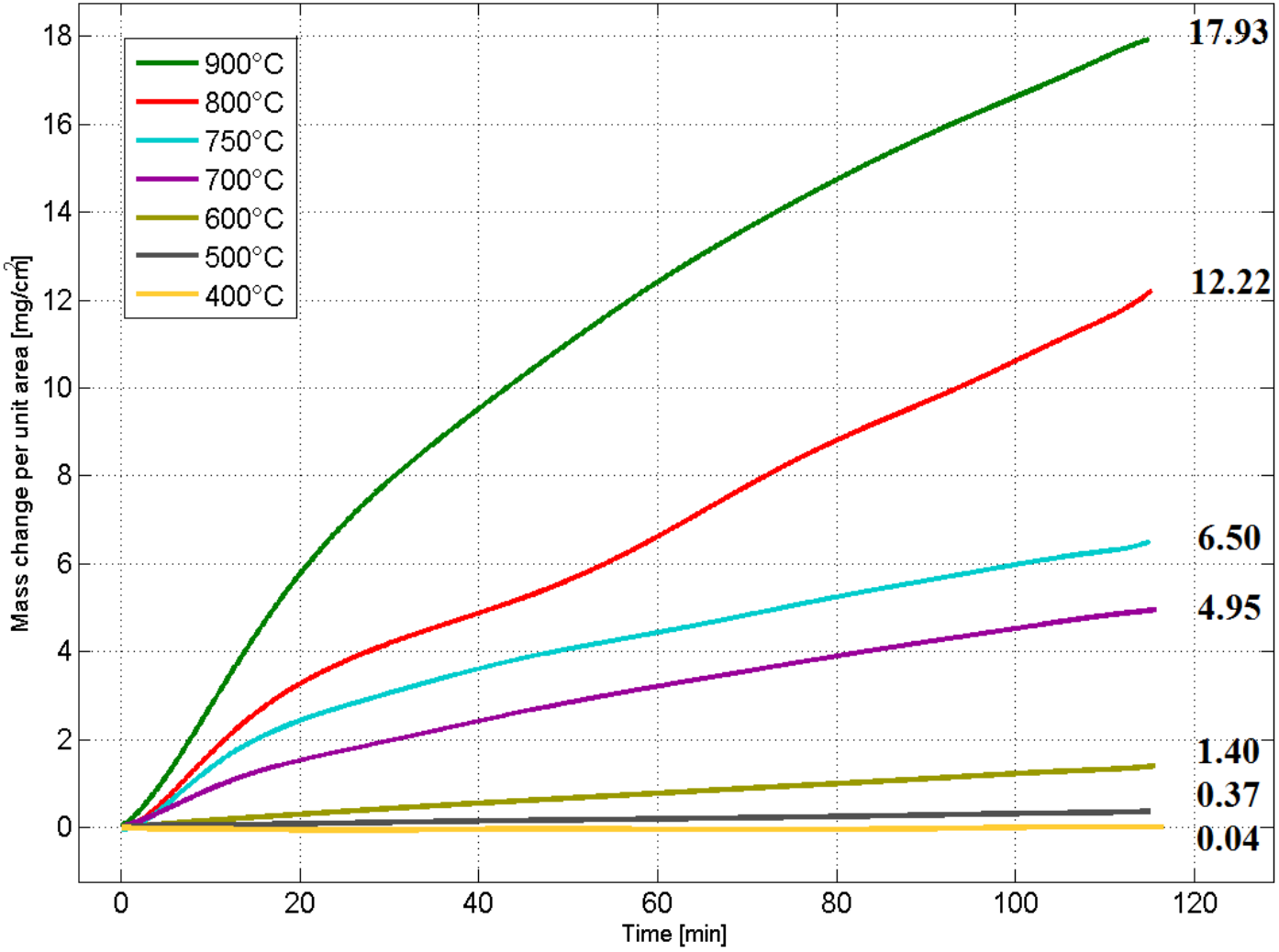
750°C

800°C

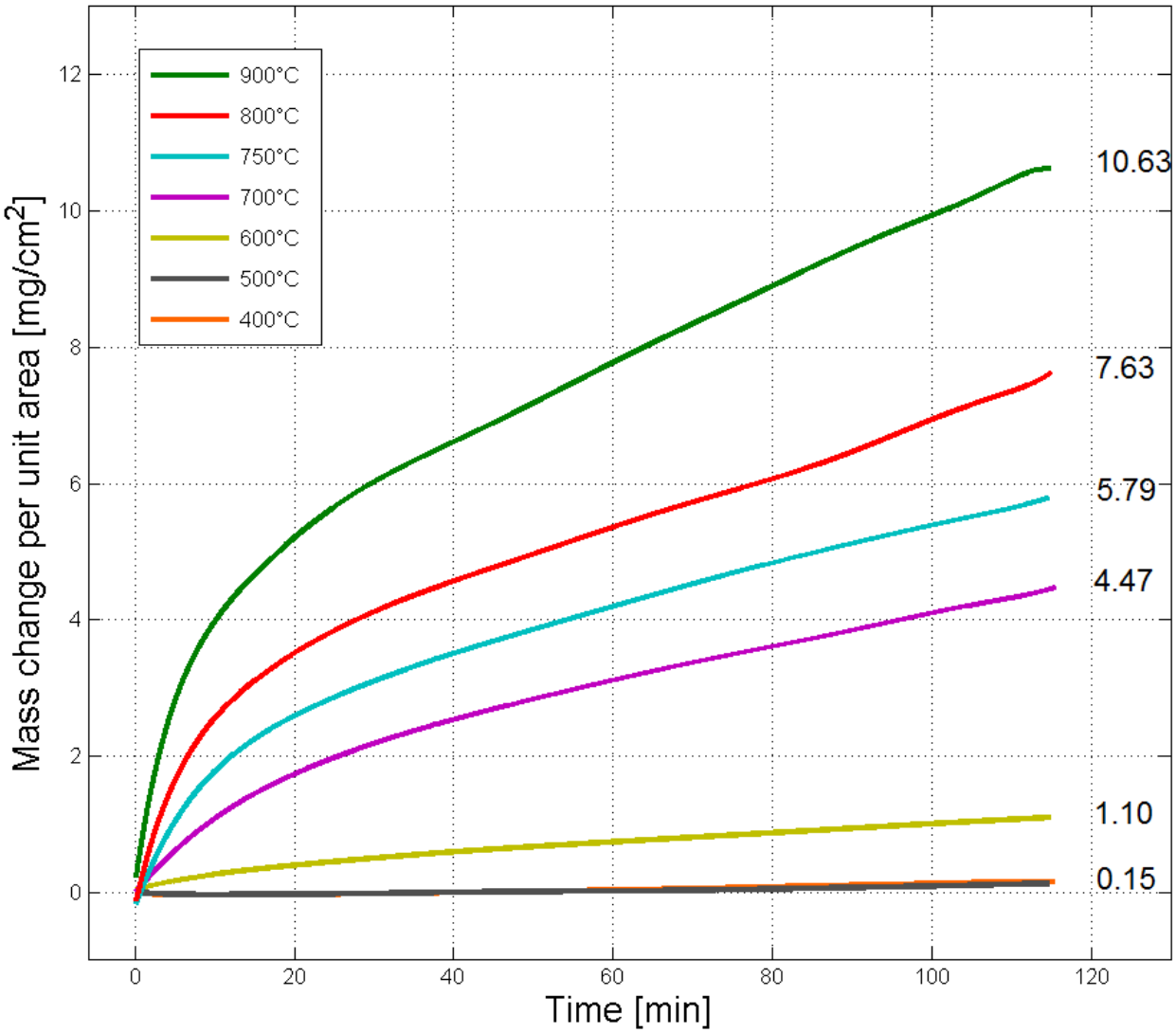


900°C

Tungsten in He+0.5%O_2 gas mixture *(2h, p_{O2} ~0.005 atm.)*



Tungsten in He+Ar+H_2O gas mixture (pH_2O= 7.8×10^{-3}atm)



Results from STA (p_{O2}~$5 \cdot 10^{-6}$)

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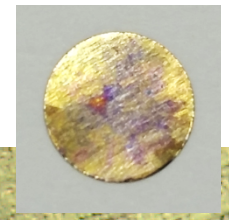
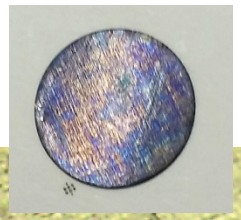


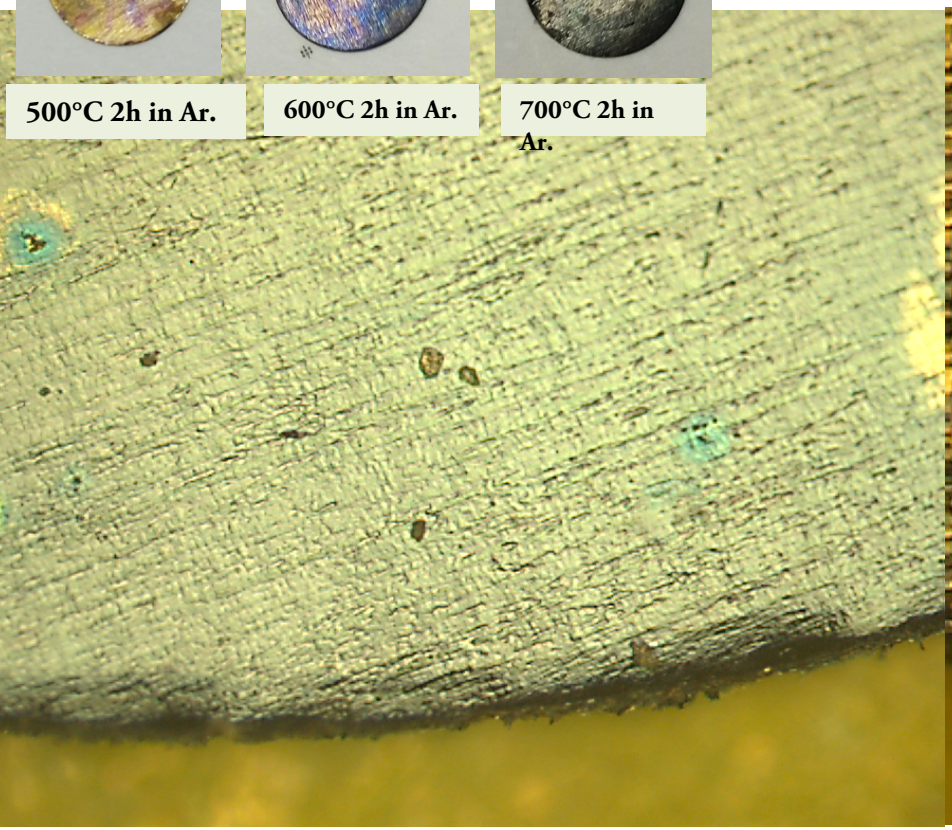
500°C 2h in Ar.

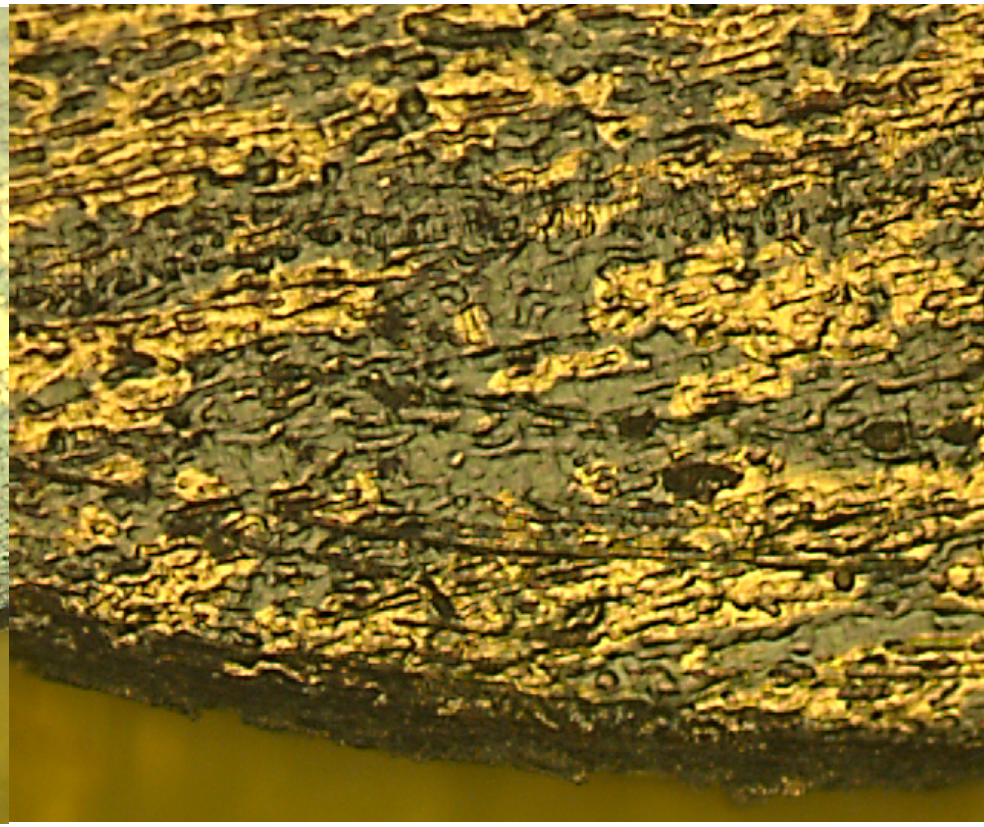


600°C 2h in Ar.

700°C 2h in Ar.

Foil in STA for 48h in pure Argon

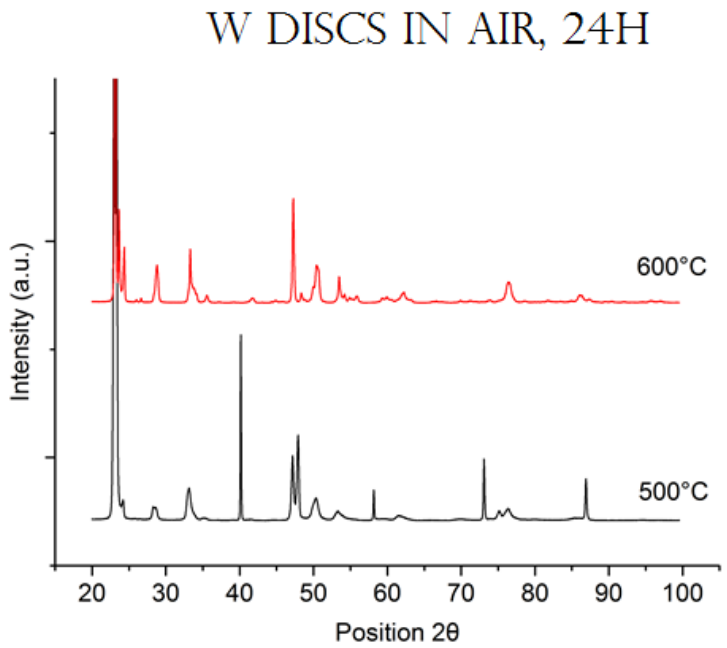


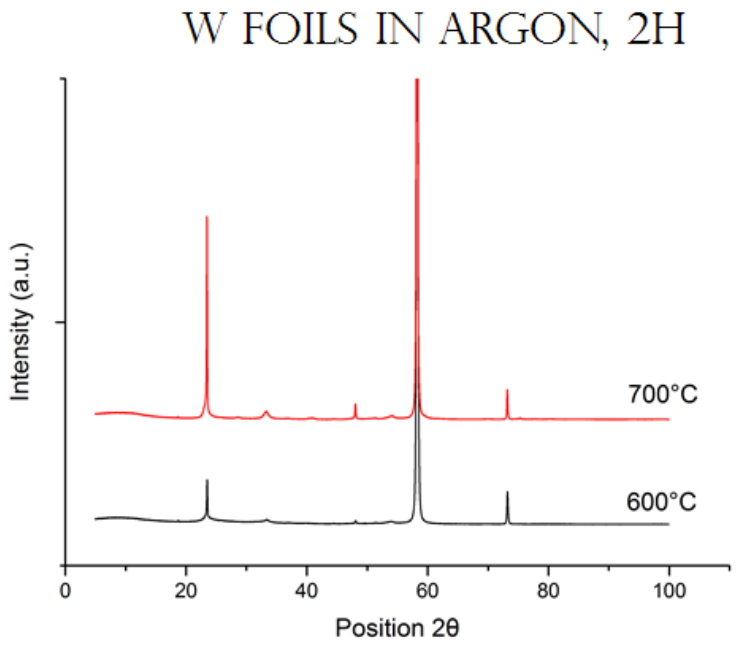


500°C

550°C

XRD measurements





Results from the XRD measurements indicate the following oxides :

AIR		ARGON	
600°C	WO_3	700°C	$W_{10}O_{29}$
500°C	$W_{18}O_{49}$	600°C	$W_{18}O_{49}$ / $W_{10}O_{29}$

Oxidized tungsten samples (He-5%O2, 2h)

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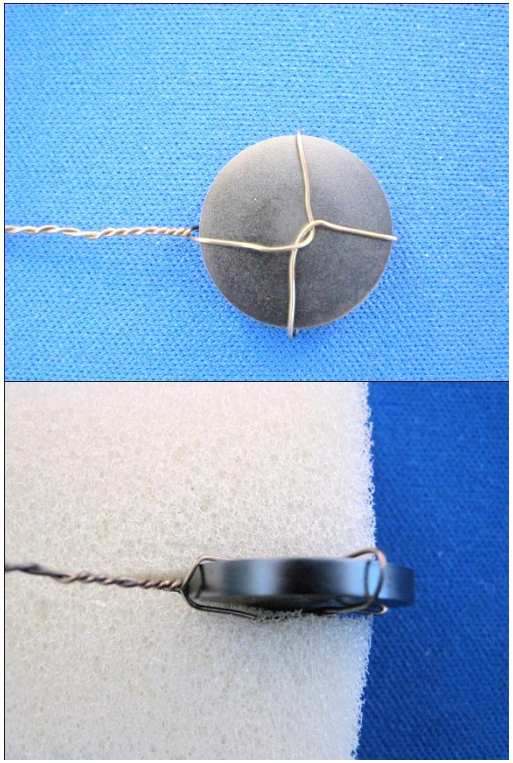
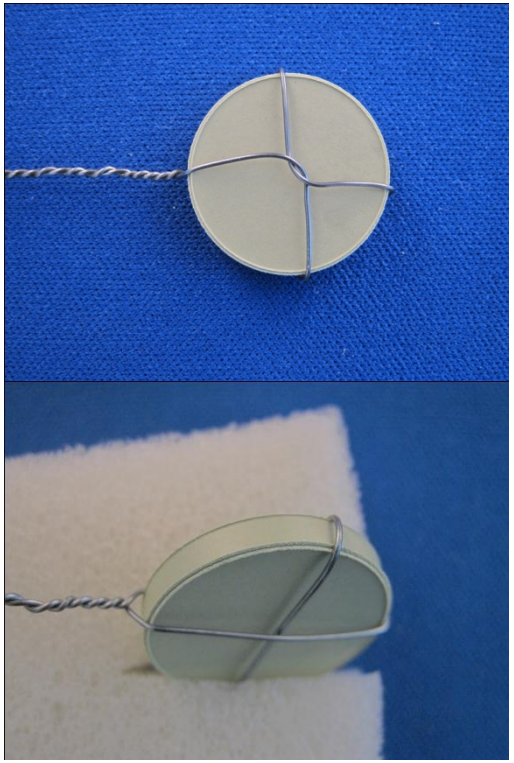
600°C



700°C

800°C



Oxidized tungsten samples (He-5%O2, 2h)

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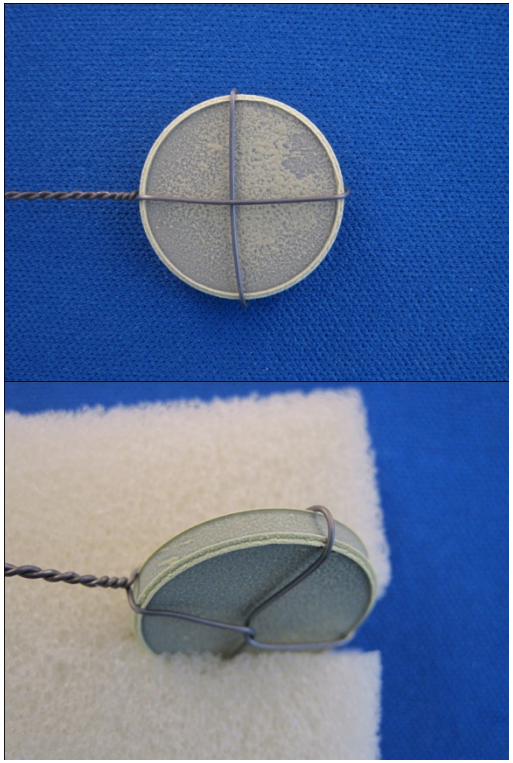
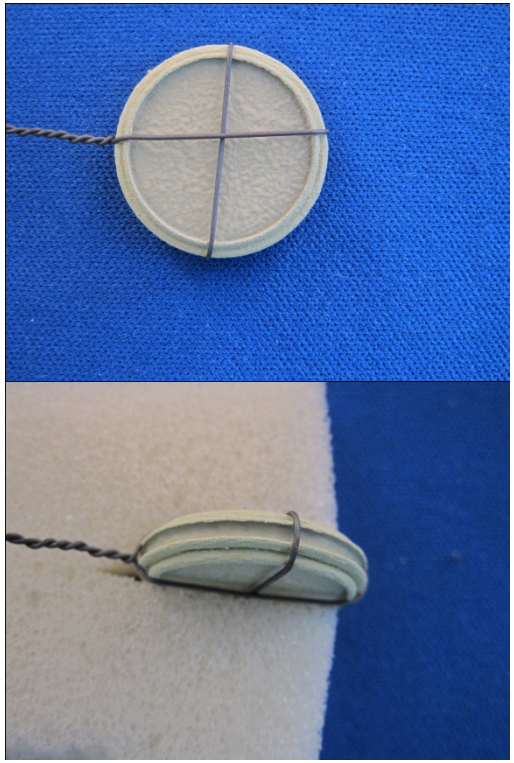
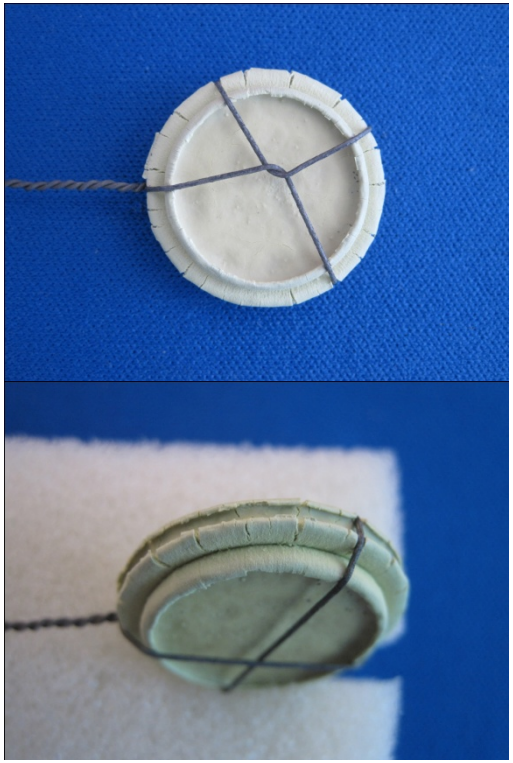
900°C



1000°C



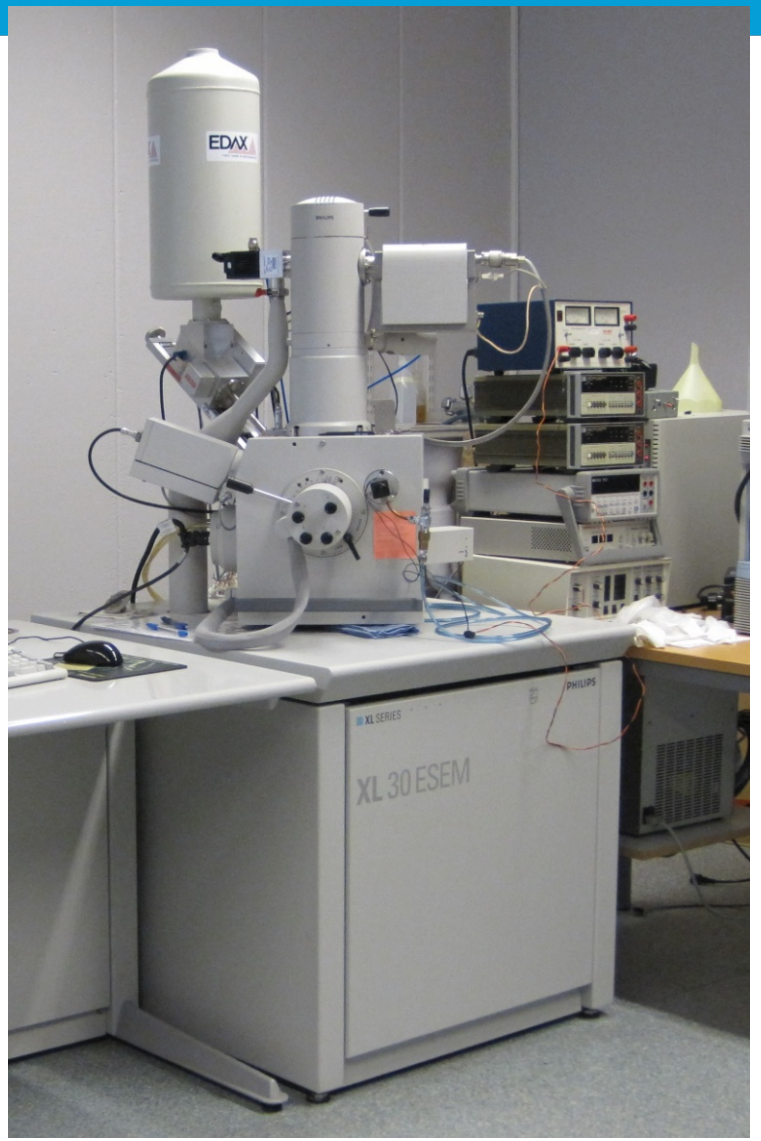
1075°C



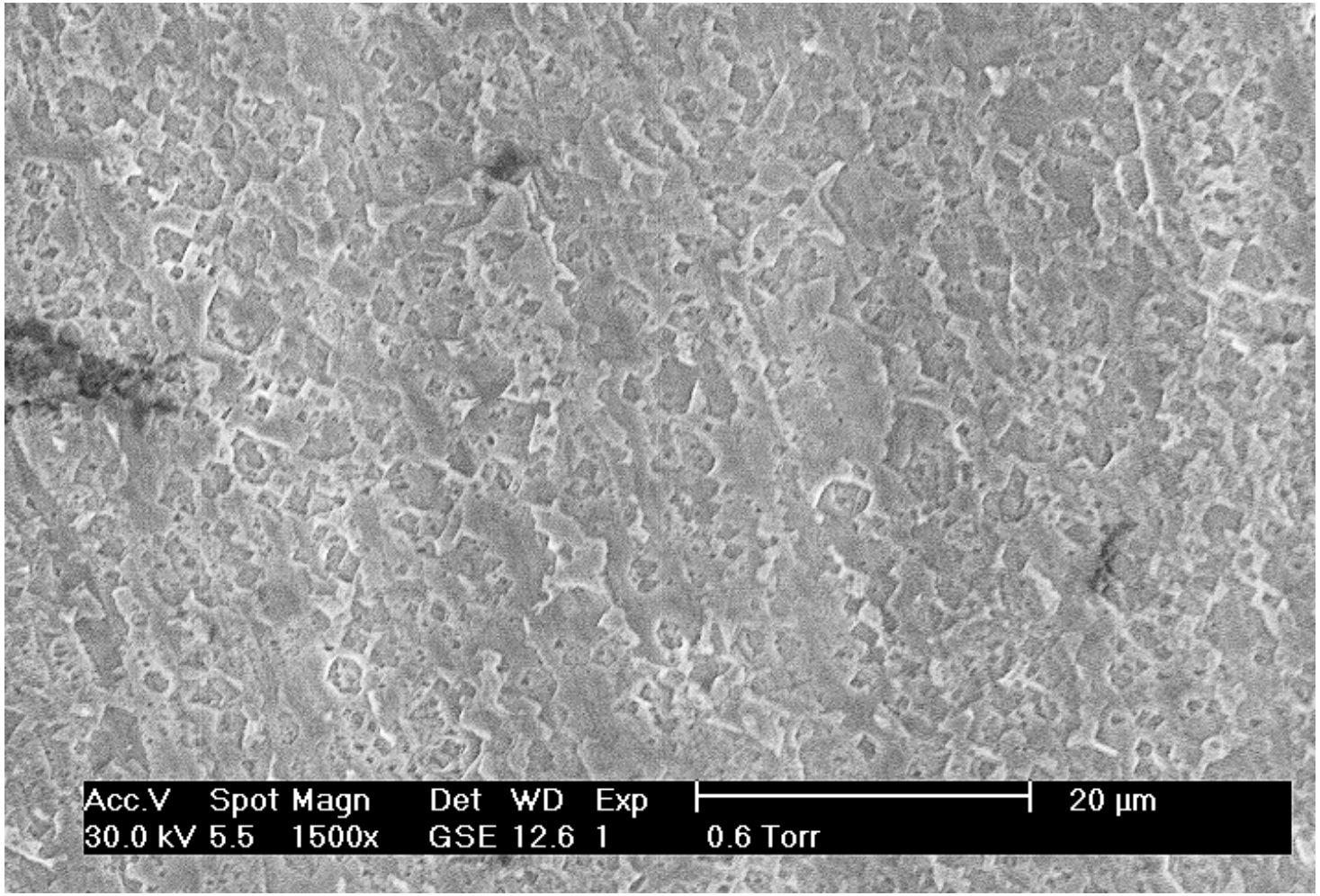
Dynamic studies on oxidation

- W-foil
- *In situ* studies in an ESEM* using a hot stage
- Heated from 25° to 1000°C
- Atmosphere of water vapour at low pressure (~100Pa)

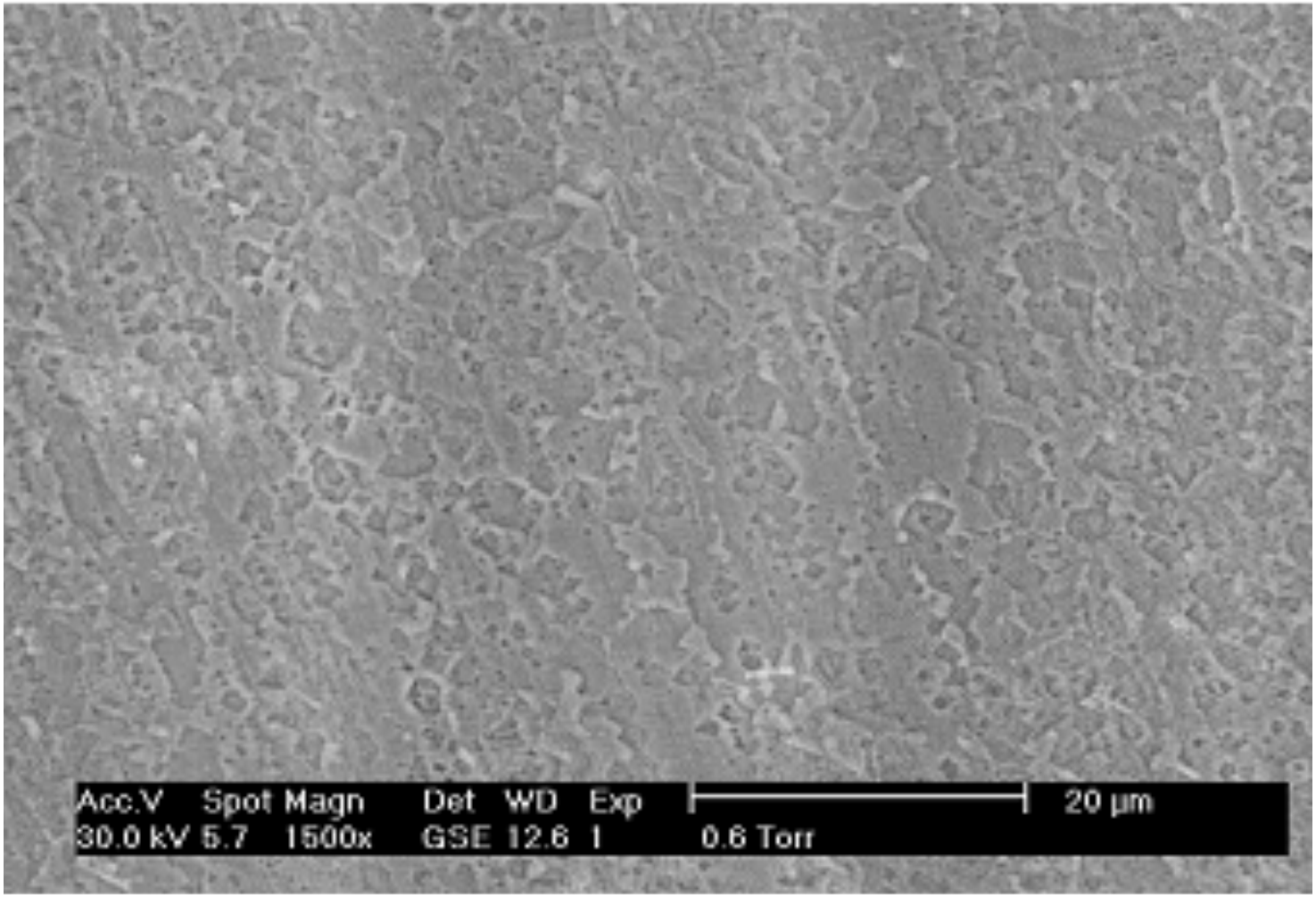
**Enviromental Scanning Electron Microscope*



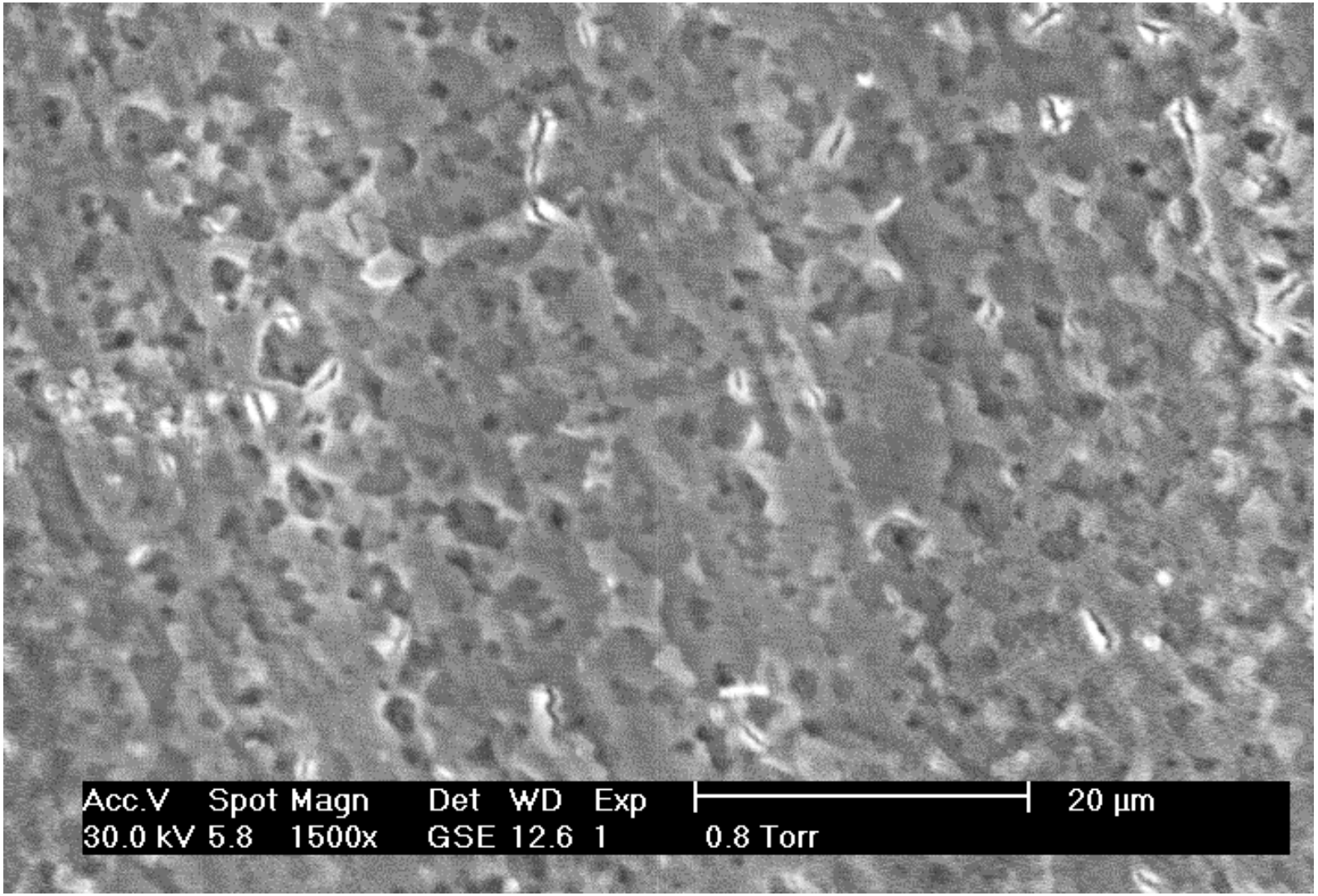
W-foil surface at 25°C



W-foil Surface at 605°C

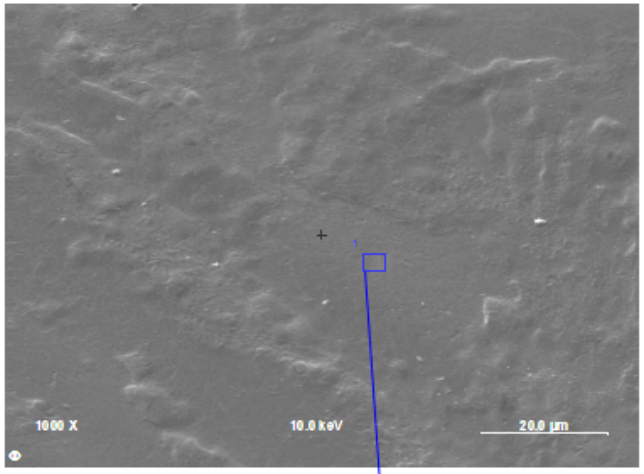


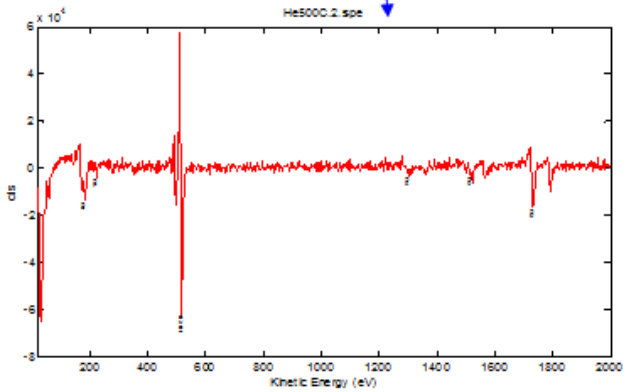
W-foil surface at 700°C



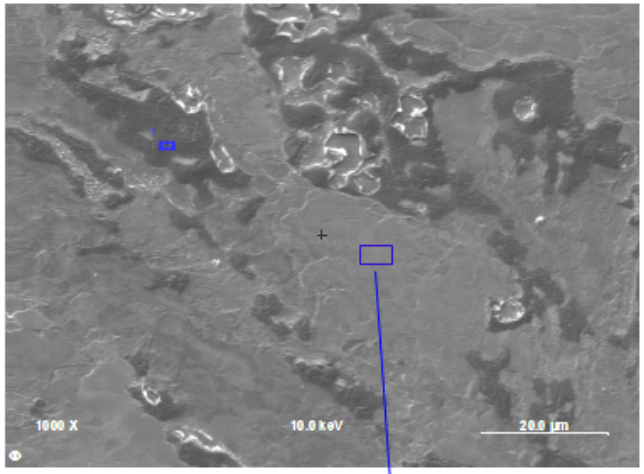
AES of (500°C, He, 2h)-sample

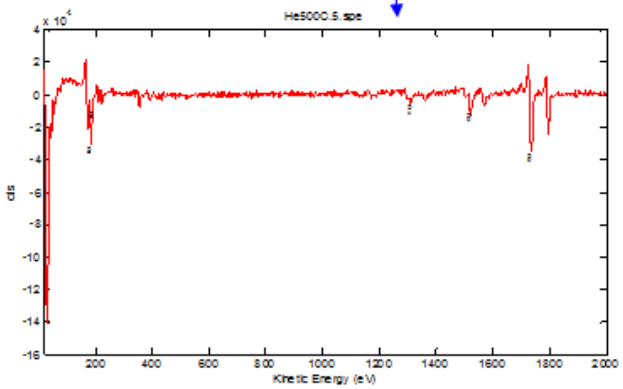
Before sputtering



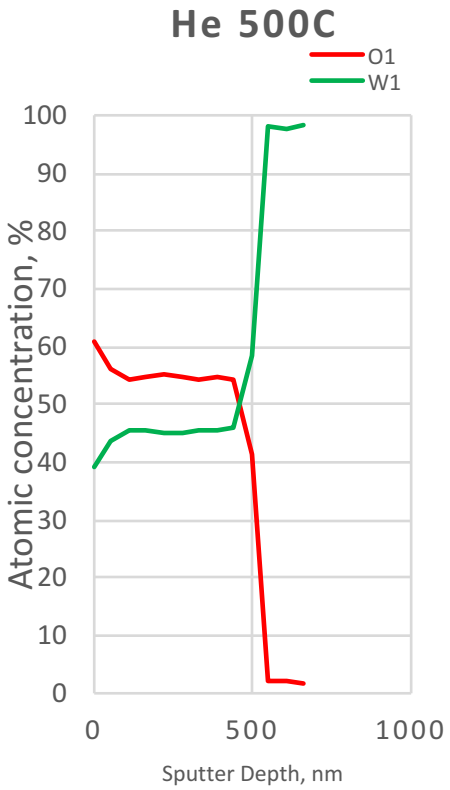


After 12 min sputtering





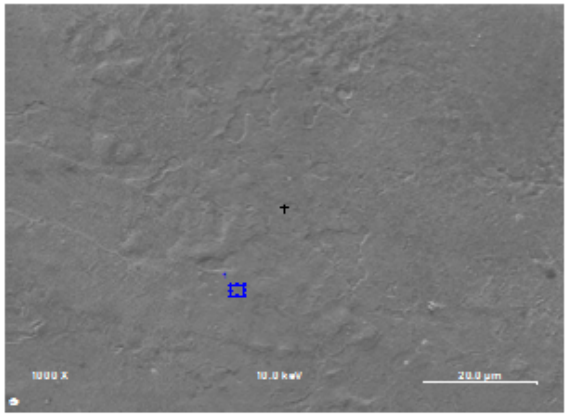
The survey spectrums before and after sputtering

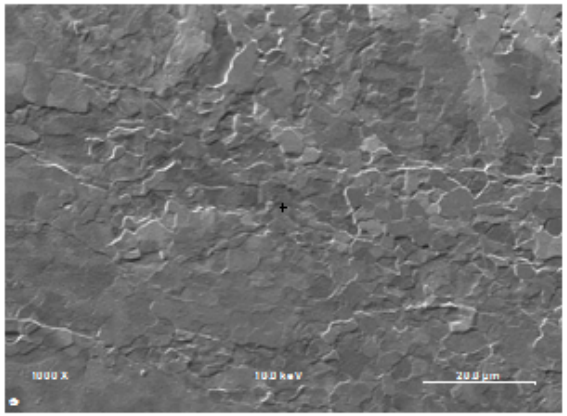


Oxide layer thickness ~550 nm

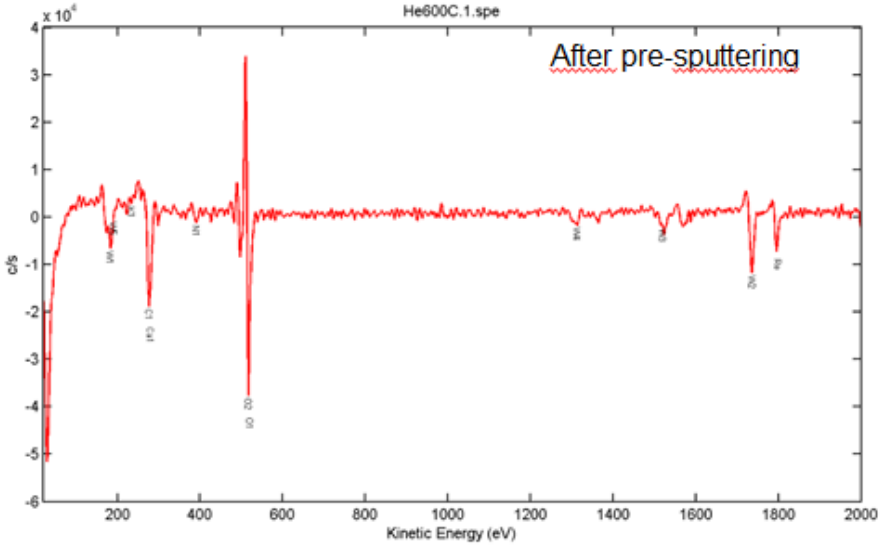
AES of (600°C, He, 2h)-sample

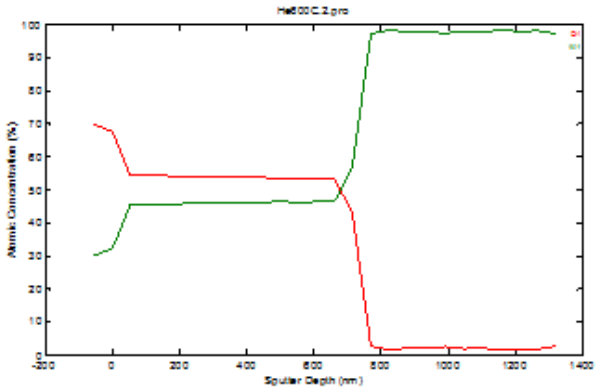
AES: survey & depth profile





After 24 min sputtering





Oxide layer thickness: ~770 nm

AES: He+Ar+H_2O, 500C, 2h

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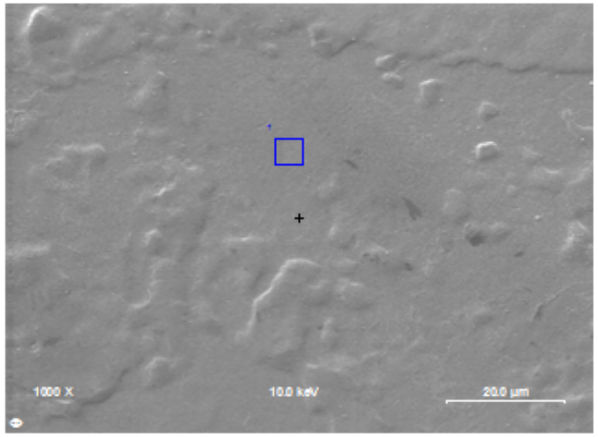
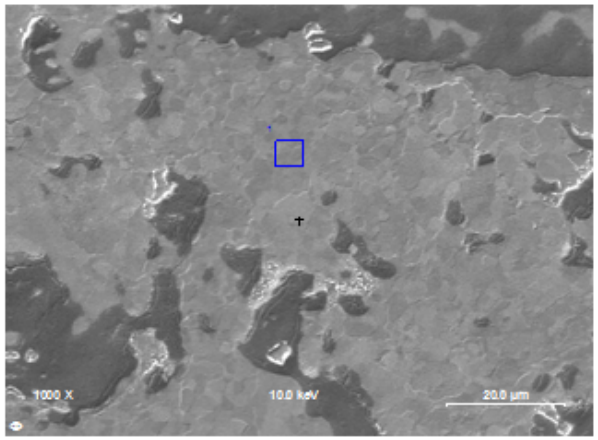
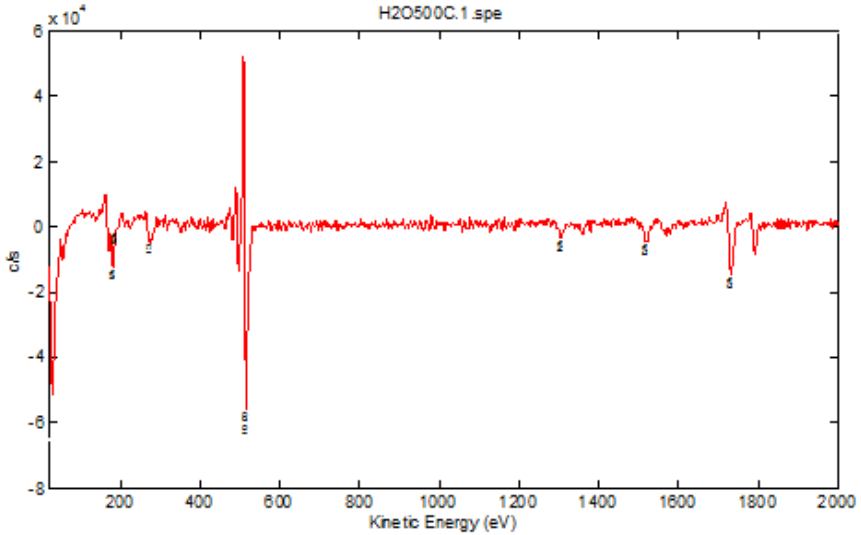
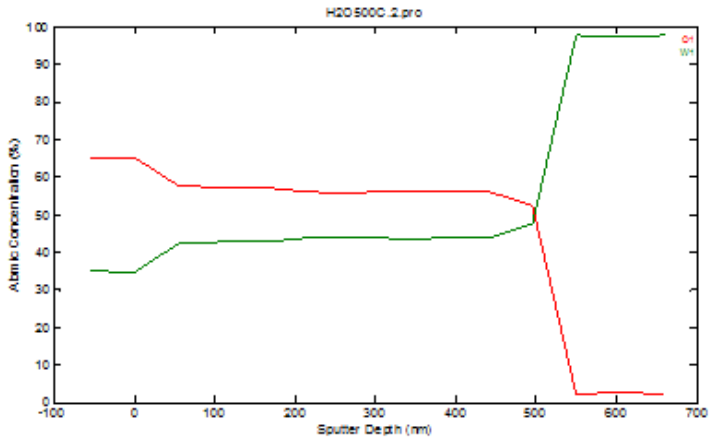
AES: survey & depth profile





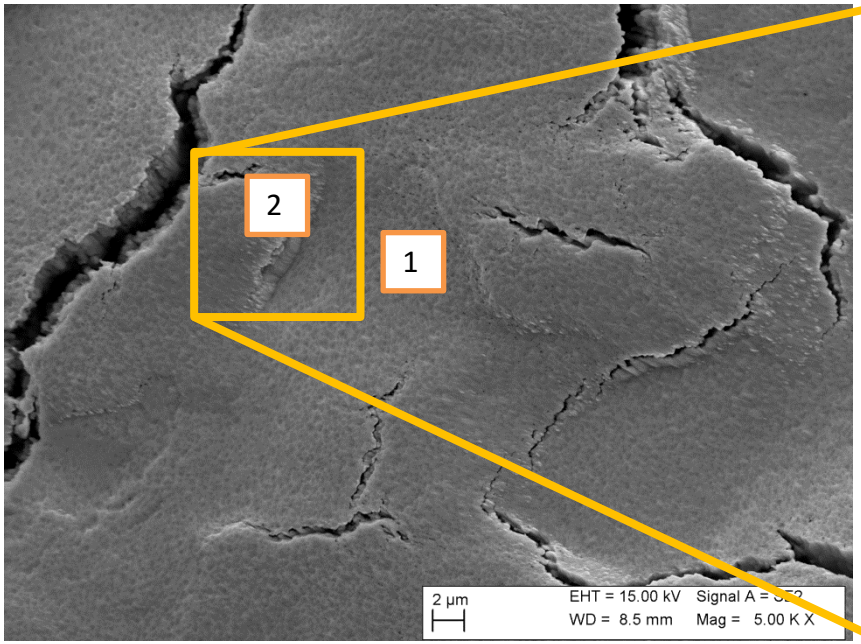
After 12 min sputtering

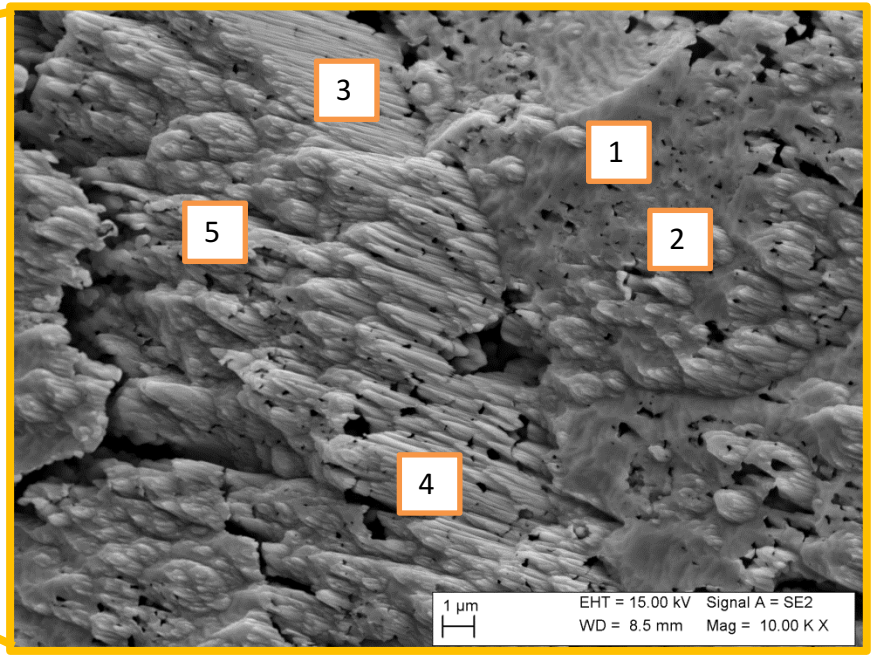




Oxide layer thickness: ~550 nm

EDS+SEM on (700°C, He+Ar+H_2O, 2h)-sample





Position	at. % O	at. % W	O/W
1	71.96	28.04	2.57
2	66.58	33.42	1.99

Position	at. % O	at. % W	O/W
1	73.06	26.94	2.71
2	67.23	32.77	2.05
3	75.36	24.64	3.06
4	70.24	29.76	2.36
5	71.75	28.25	2.54

Summary

- Oxidation behaviour of pure W has been studied
  - Methods: Thermogravimetry, TG/STA/DSC, In situ Microscopy. Isothermal & non-isothermal studies. XRD, EDS, AES. Temp: 400-1075°C
- Oxidation environment
  - He+5%O_2, He+0.5%O_2, He+5ppmO_2, H_2O(g), Ar/He, Ar+He+H_2O, Air
- Lower oxides of W are formed during the initial stages of oxidation and are stable at relatively low temperatures and partial pressures of oxygen
- Oxides formed below 600°C are dark, adhesive and protective. Oxide layers formed at higher temperatures are porous and non-protective.
- Water vapor oxidizes tungsten less than oxygen, but contributes to the sublimation of WO_3.

Summary cont.

- Oxidation is parabolic initially, tending to be linear at higher T and for longer oxidation (48h). At low T, W shows oxidation tendencies even at low oxygen levels.
- Activation energy for He+0.5%O_2 (95 kJ/mol) is lower than for He+Ar+H_2O (183kj/mol)
- Activation energy for He-5%O_2 above 700°C (127 kJ/mol) agrees well with the diffusion of oxygen ions in WO_3.
- Sublimation is not significant below 1075°C

- <u>The results indicate that oxidation occurs in inert gases containing oxygen impurity (max. 5ppm O_2)</u>