Self-passivating tungsten alloys for first wall applications

Christian Linsmeier

Freimut Koch, Christian Lenser, Stefan Lindig, Marcin Rasinski, Martin Balden, Annegret Brendel

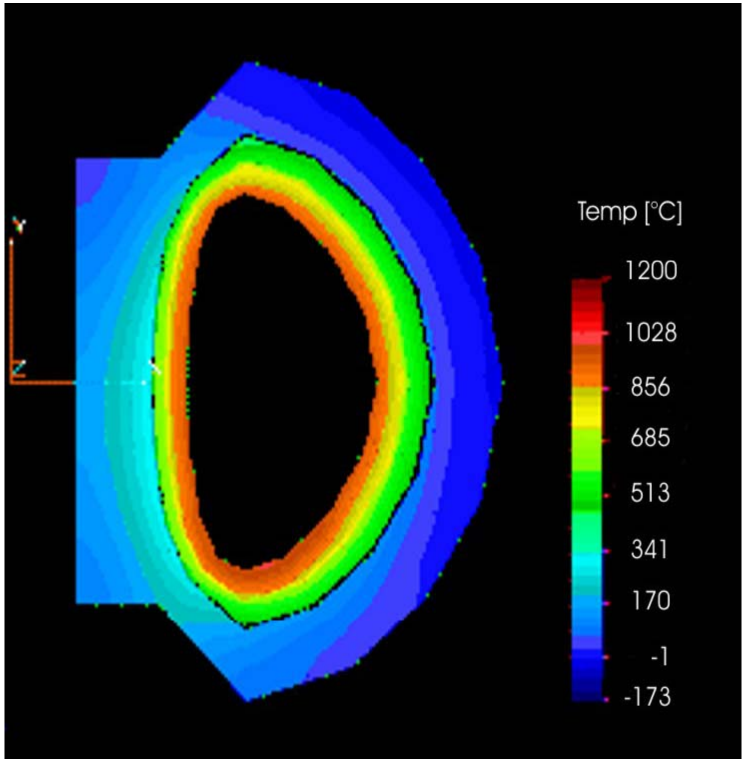
Max-Planck-Institut für Plasmaphysik
Garching b. München, Germany

Outline

- Applications: ITER and DEMO
- Self-passivation mechanism
- Quaternary alloys
- W-Si-Cr bulk materials

Accidential loss of coolant in reactor

Power plant conceptual study



Temperature profile in PPCS Model A, 10 days after accident with a total loss of all coolant.

[Final Report of the European Fusion Power Plant Conceptual Study, 2004]

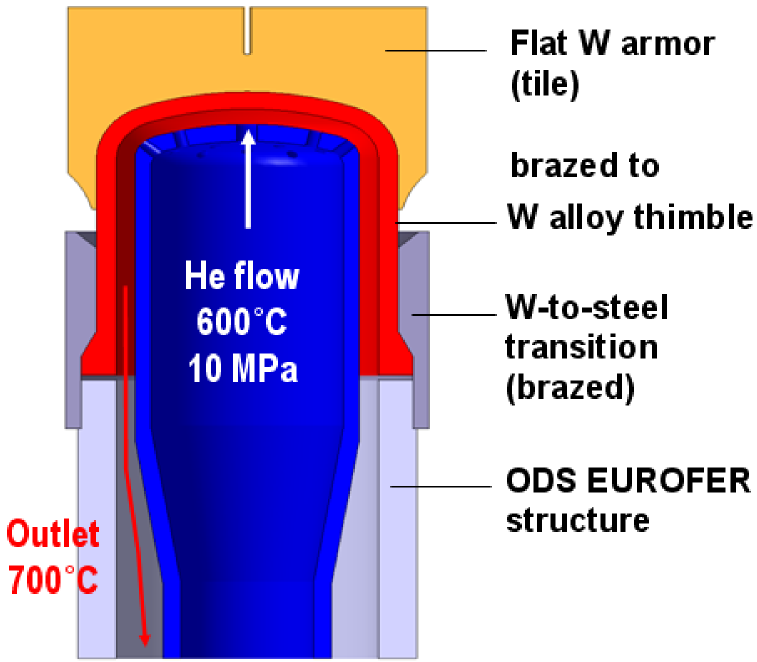
- Accidental loss of coolant: peak temperatures of first wall up to 1200 °C due to nuclear afterheat
- Additional air ingress: formation of highly volatile WO_3 (Re, Os)
- Evaporation rate: order of 10 -100 kg/h at >1000°C in a reactor (1000 m^2 surface)
  → large fraction of radioactive WO_3 may leave hot vessel

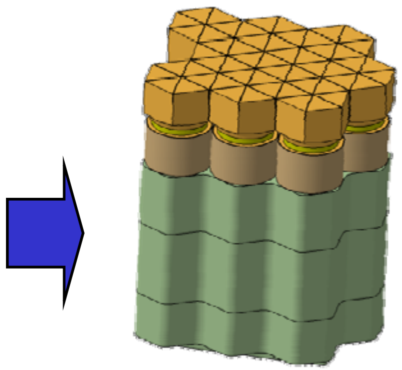
→ Development of self-passivating tungsten alloys

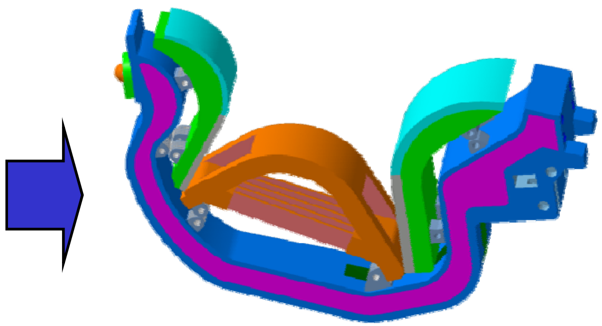
He-cooled divertor modular design for DEMO (KIT)

He-cooled multi-jet (HEMJ) concept

P. Norajitra, KIT







Test divertor module to be proposed for testing in ITER

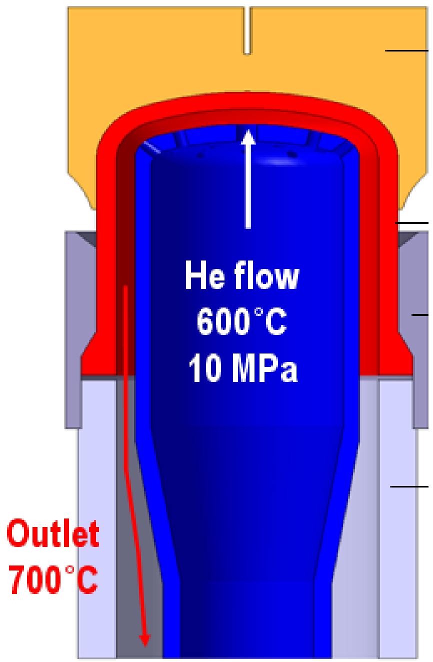
Goal: ≥ 10 MW/m^2,

100-1000 load cycles

He-cooled divertor modular design for DEMO (KIT)

He-cooled multi-jet (HEMJ) concept

P. Norajitra, KIT



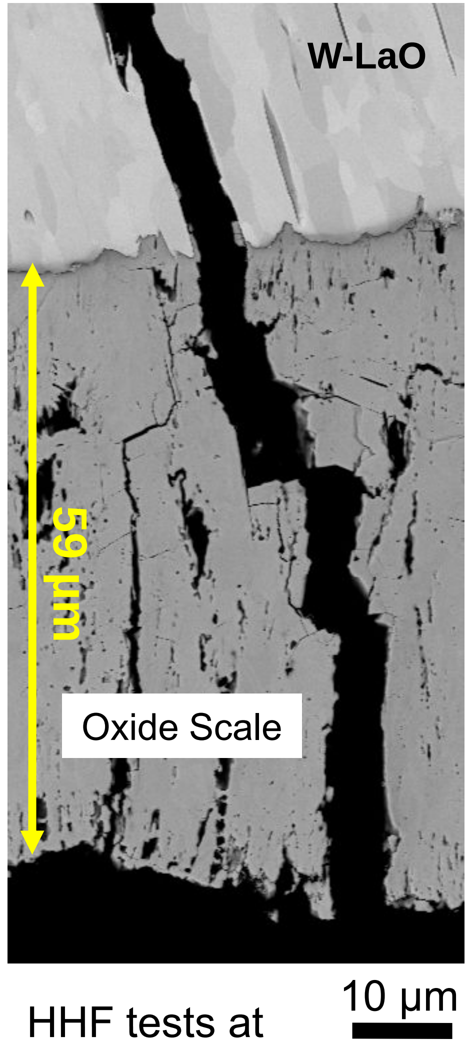
Post-examination after HHF tests at FZJ (90 load cycles at 9 MW/m²):

- Formation of thick oxide scale
- Crack propagation

Application for self-passivating tungsten alloys

Goal: ≥ 10 MW/m²,

100-1000 load cycles



HHF tests at Efremov (test range 5-13 MW/m²)

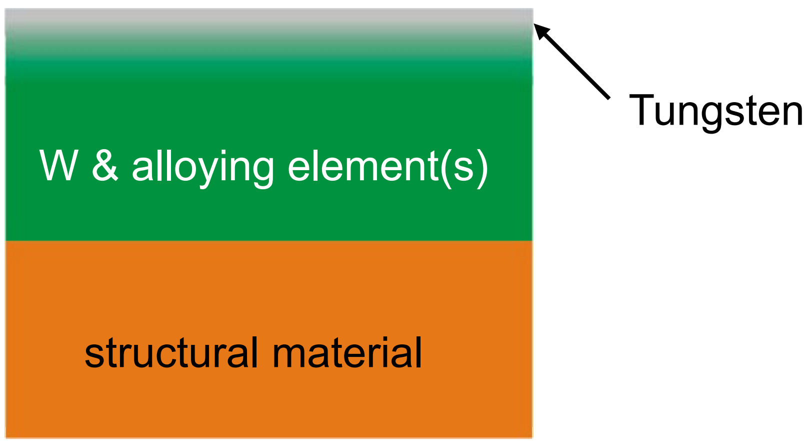
Idea: Tungsten alloys

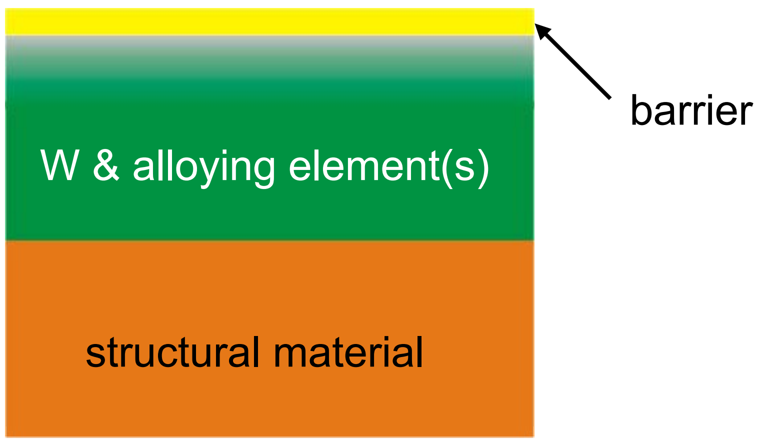
Self passivating tungsten-based alloys:

Surface composition automatically adjusts to the requested property

Normal operation (600°C)**:**
Formation of tungsten surface by depletion of alloying element(s) due to preferential sputtering

Accidental conditions:
(air ingress, up to 1200 °C)
Formation of protective barrier layer





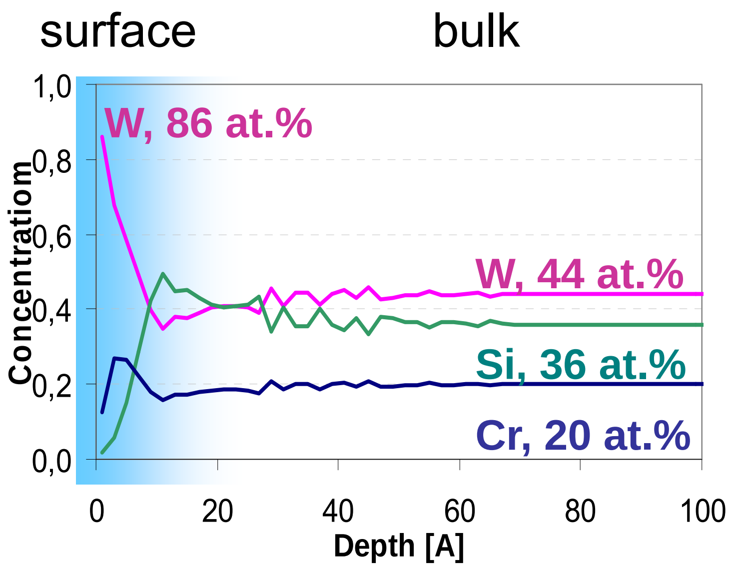
Idea: Tungsten alloys

Self passivating tungsten-based alloys:

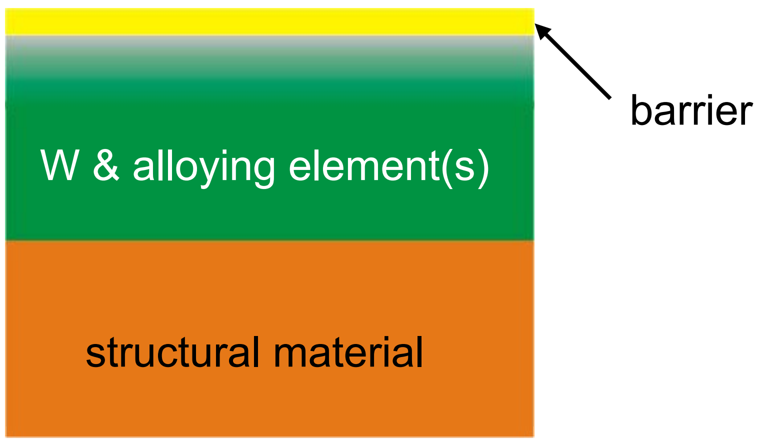
Surface composition automatically adjusts to the requested property

Normal operation (600°C):

TRIDYN numerical simulation of sputter erosion of W-Si-Cr alloy (D ions, 30 eV, fluence $10^{18}/cm^2$)



Accidental conditions:
(air ingress, up to 1200 °C)
Formation of protective barrier layer



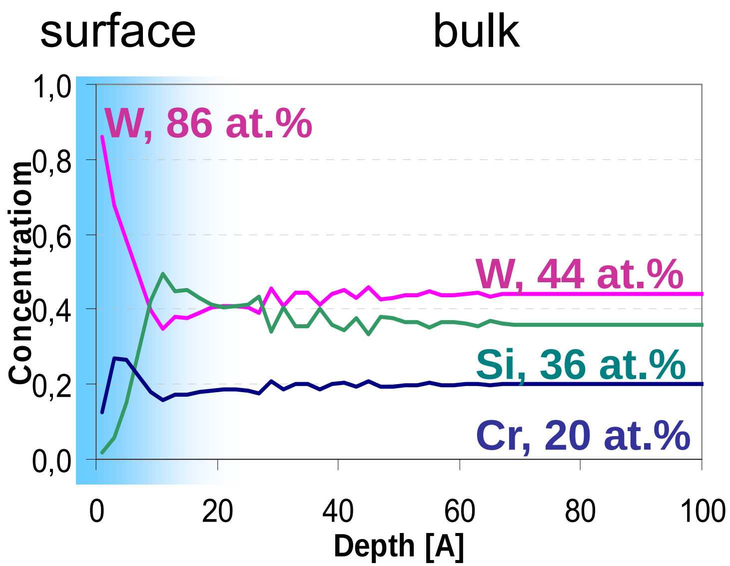
Idea: Tungsten alloys

Self passivating tungsten-based alloys:

Surface composition automatically adjusts to the requested property

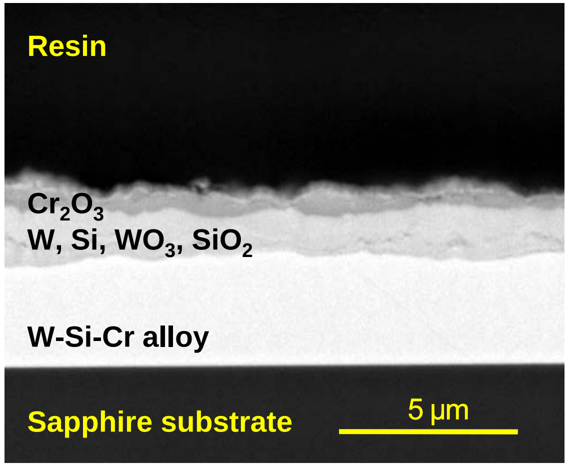
Normal operation (600°C)**:**

TRIDYN numerical simulation of sputter erosion of W-Si-Cr alloy (D ions, 30 eV, fluence $10^{18}/cm^2$)



Accidental conditions:

Cross section of sputter deposited W-Si-Cr film after oxidation at 1000°C for 1h



Quaternary tungsten based alloys

Addition of reactive elements to W-Si-Cr to improve oxide film formation and adherence

Co-deposition by Magnetron sputtering

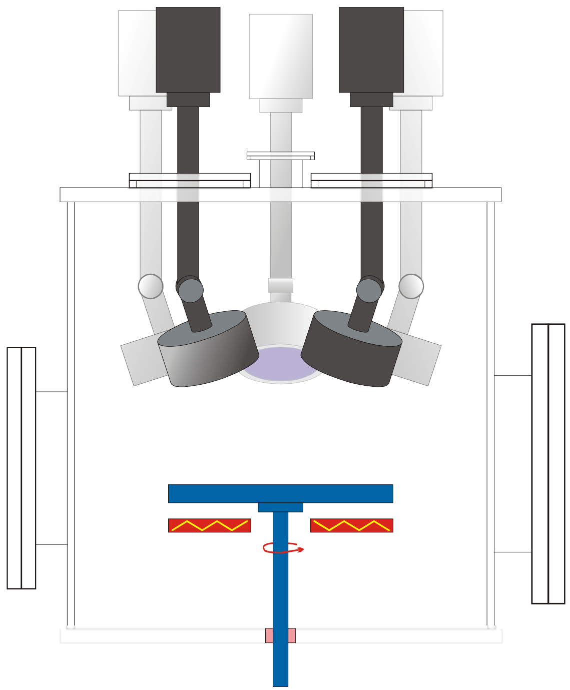
– Film thickness ~ 4µm

– SiO_2 and Al_2O_3 substrates used for oxidation

Investigated systems

- W-Si-Cr-Zr
- W-Si-Cr-Y

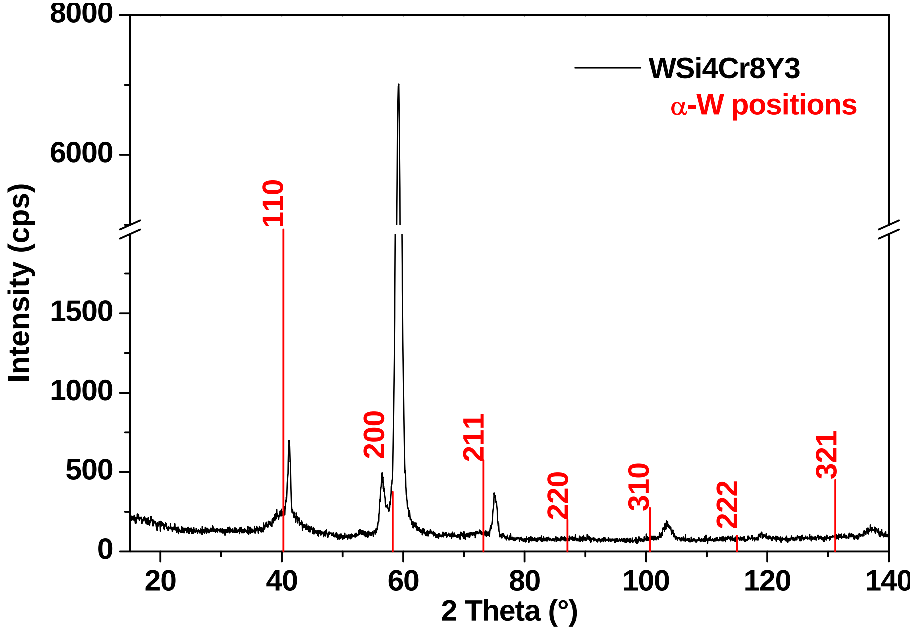
(different concentrations)



Schematic view of deposition facility

XRD analysis: alloys as deposited

Peak shift due to Lattice Distortion

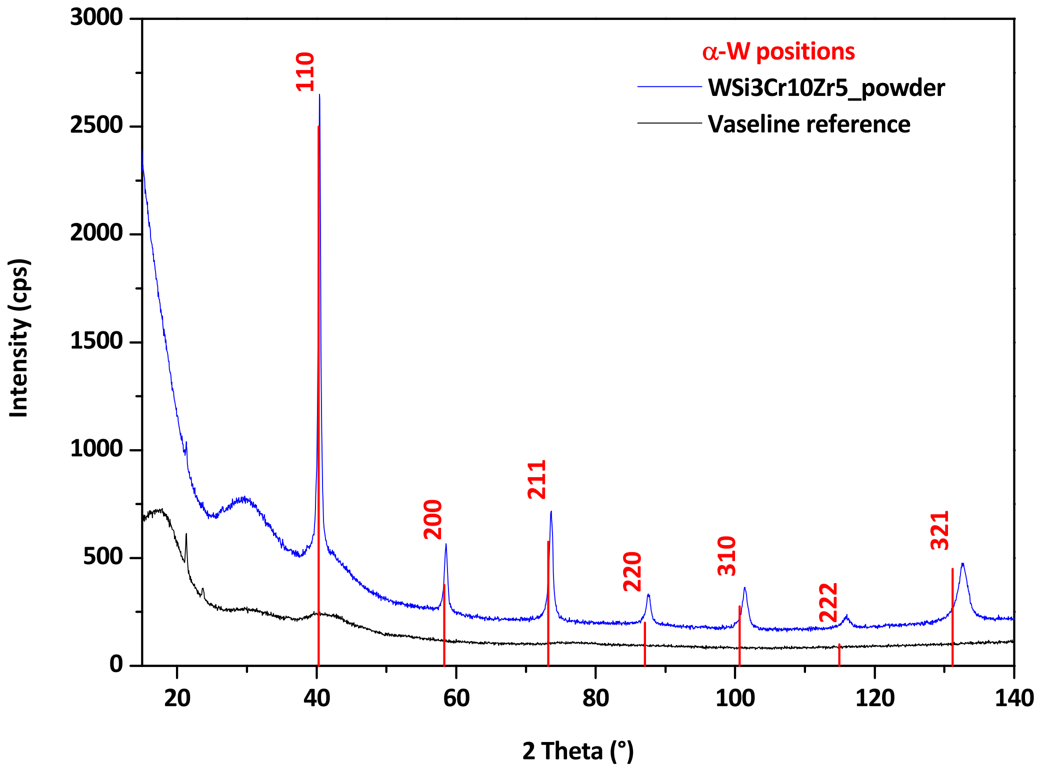


d	2*θ*	*h*	*k*	*l*
Angström	°			
2,2976	39.177	1	1	0
2,1922	41.1438	1	1	0
1,5567	59.3162	2	0	0
1,3043	72.3989	2	1	1
1,2668	74.8987	2	1	1
0,9823	103.2851	3	1	0
0,8283	136.8753	3	2	1

- Fifth order polynomial by Gust et al. used to calculate W concentration in assumed binary W-Cr lattice
- *c*(Cr) = 27.5 at-% from peak shift; *c*(Cr) = 29.2 at-% from RBS

Gust, W.; Predel, B.; Roll, U.: Journal of the Less-Common Metals, 69, pp. 331-353, 1980

XRD analysis: annealed alloys



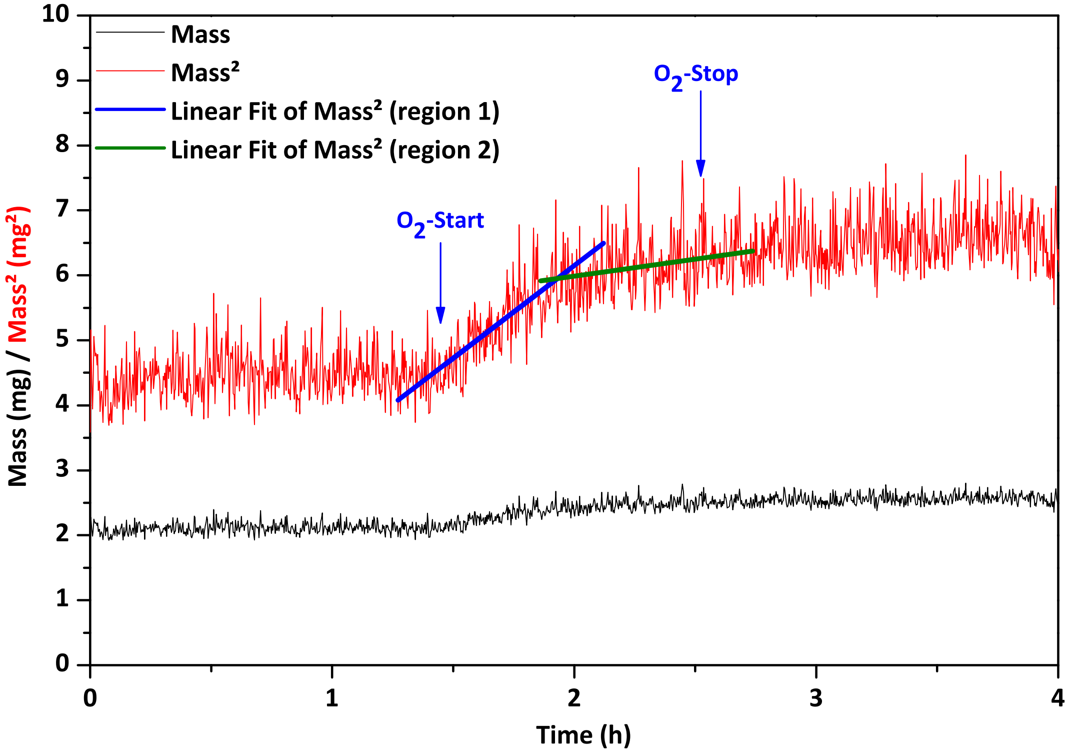
WSi3Cr10Zr5 powder

(annealed at 1000 °C under Ar)

- c(Cr) = 24 at-% after deposition (RBS); c(Cr) = 6.75 at-% after annealing
- Thermodynamic equilibrium: *c*(Cr) = 7 at-% (Gust et al.)
- Cr precipitates from the binary lattice

Oxidation experiments

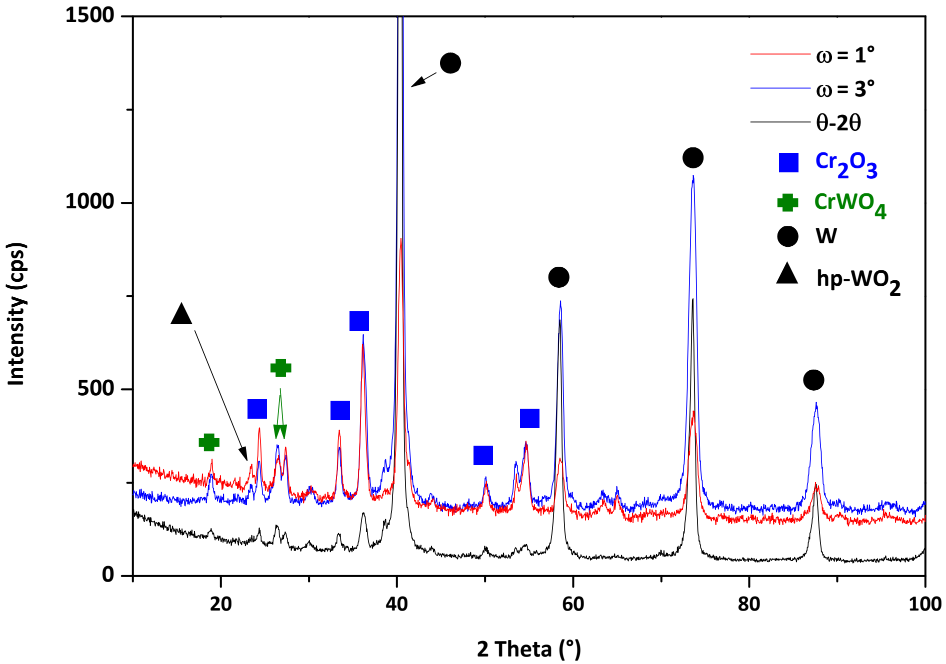
Oxidation of W-Si4-Cr8-Y3 at 1000°C for 1 hours



- Heating under inert gas flow
- Start of oxygen at stable temperature

- Parabolic oxidation rates: $(\Delta m)^2 = k\ t$: → Diffusion-governed process
- Two oxidation rates discernible

XRD analysis: oxidized alloys



WSi3Cr10Zr5 (oxidized 1h at 1000 °C)

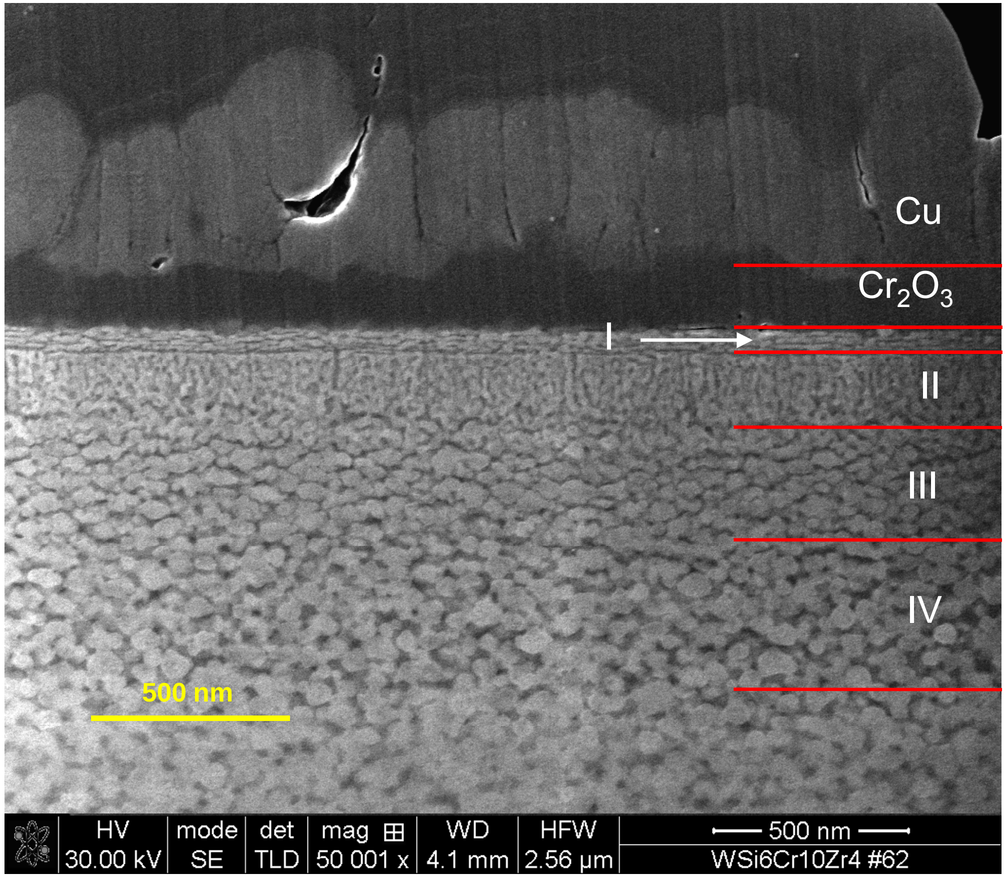
Phases identified by XRD

Ox. temp.	600°C	800°C	1000°C
Ox. time	48 h	4 h	1 h
	Cr_2O_3	**Cr_2O_3**	**Cr_2O_3**
	$CrWO_4$	**$CrWO_4$**	**$CrWO_4$**
	W	**W**	**W**
	WO_2	**WO_2**	
	hp-WO_2	**hp-WO_2**	**hp-WO_2**
	$ZrSiO_4$		

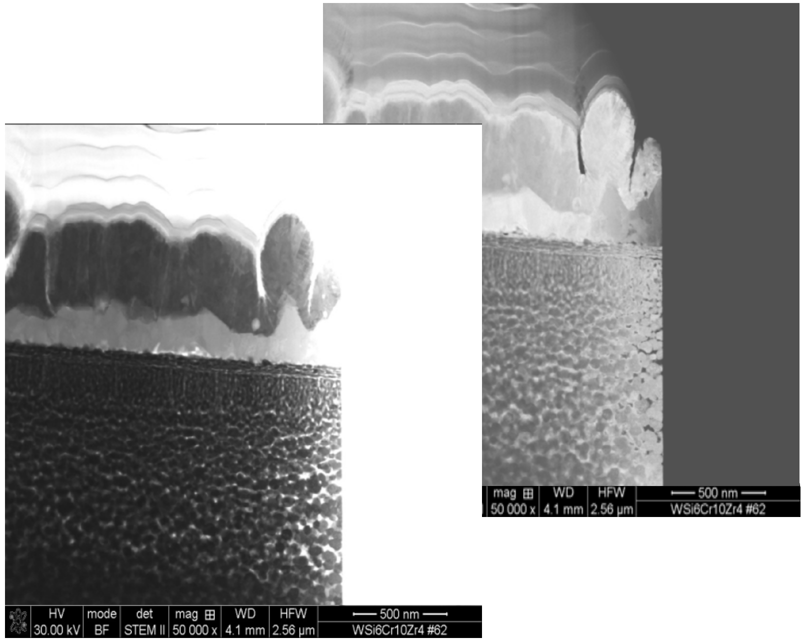
→ no volatile WO_3 formed!

Microstructure of oxidized alloys

WSi3Cr10Zr5:



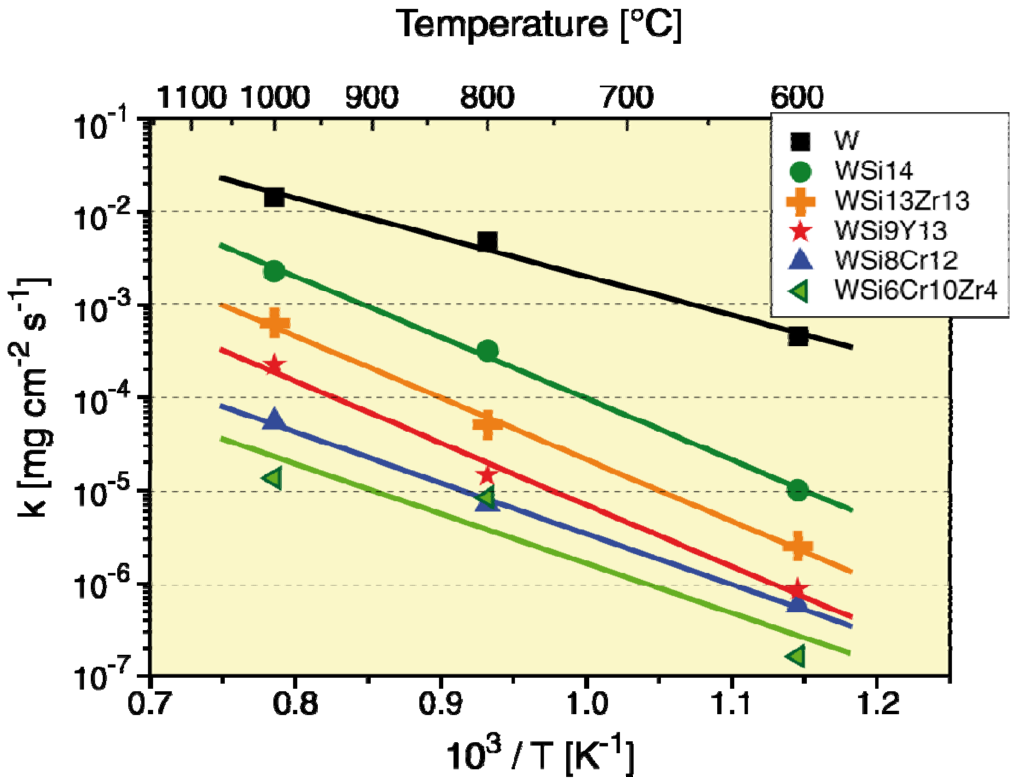
SEM of cross section (FIB), 1000°C, 1h



- Dense Cr_2O_3 barrier scale
- Cr is main diffusing species
- Mixed oxide zone(s)
- Cr depletion zone with voids
- No formation of WO_3

Comparison of oxidation results

Arrhenius plot of oxidation rates of tungsten and tungsten alloys



Oxidation rate (k) has been calculated from weight increase versus time, linear fit.

Alloy	**W**	**Si**	**Cr**	**Zr**
WSi8Cr12	46	30	24	-
WSi3Cr10Zr5	56	13	24	7

Composition in at.%

Linear oxidation rates of W-Si-Cr & quaternary alloys comparable.

Quaternary alloys show distinct parabolic oxidation behavior at reduced level of alloying elements.

Summary: Quaternary alloys

- Quaternary alloys show better passivation behavior than ternary while containing more W
- Active elements (Y/Zr) do not form oxide layers, but improve oxide scale adhesion
- Surface oxide consists of Cr_2O_3
- Oxide phases formed are Cr_2O_3, $WCrO_4$, WO_2 (2 modifications), $ZrSiO_4$ (600°C), but no WO_3 → passivation successful
- Two step-oxidation: switch in oxidation mechanism during oxidation
- Different oxidation mechanisms at different temperatures
- Restructuring induced by the precipitation of Cr from the W lattice

Ternary alloys: bulk samples

Samples:

8W-Cr-Si2 and 8W-Cr-Si4

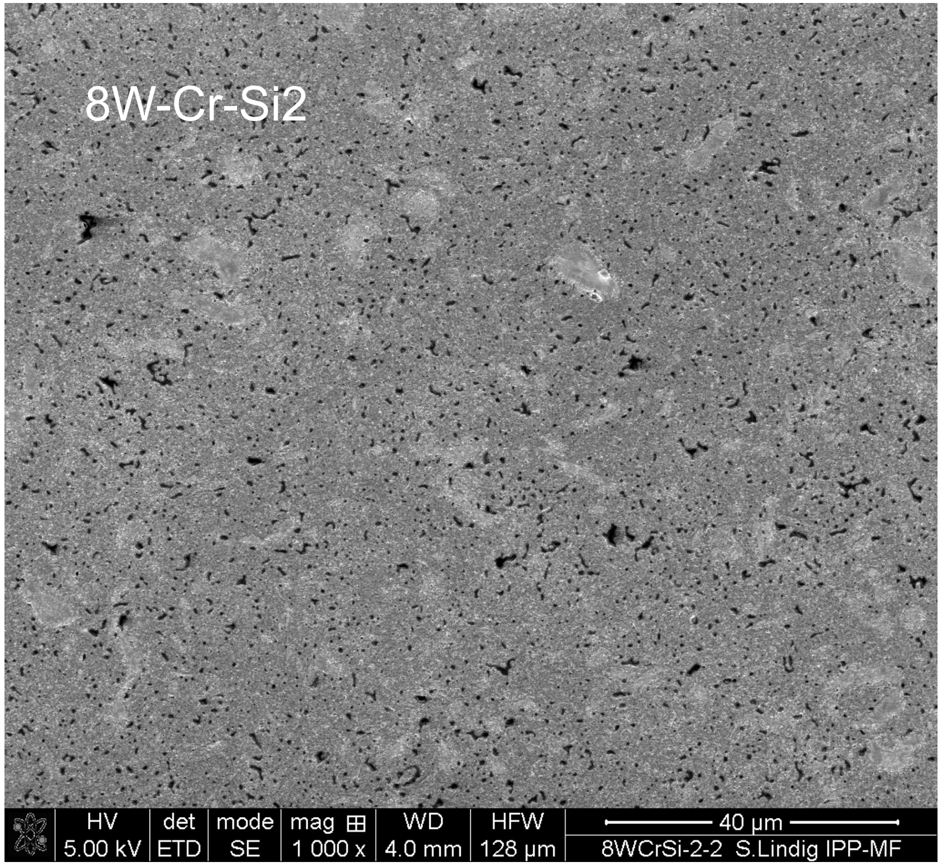
nominal composition: **W Si10 Cr10**

Investigated properties:

- morphology
- element distribution
- thermal diffusivity
- hardness / Young‘s modulus
- oxidation behavior

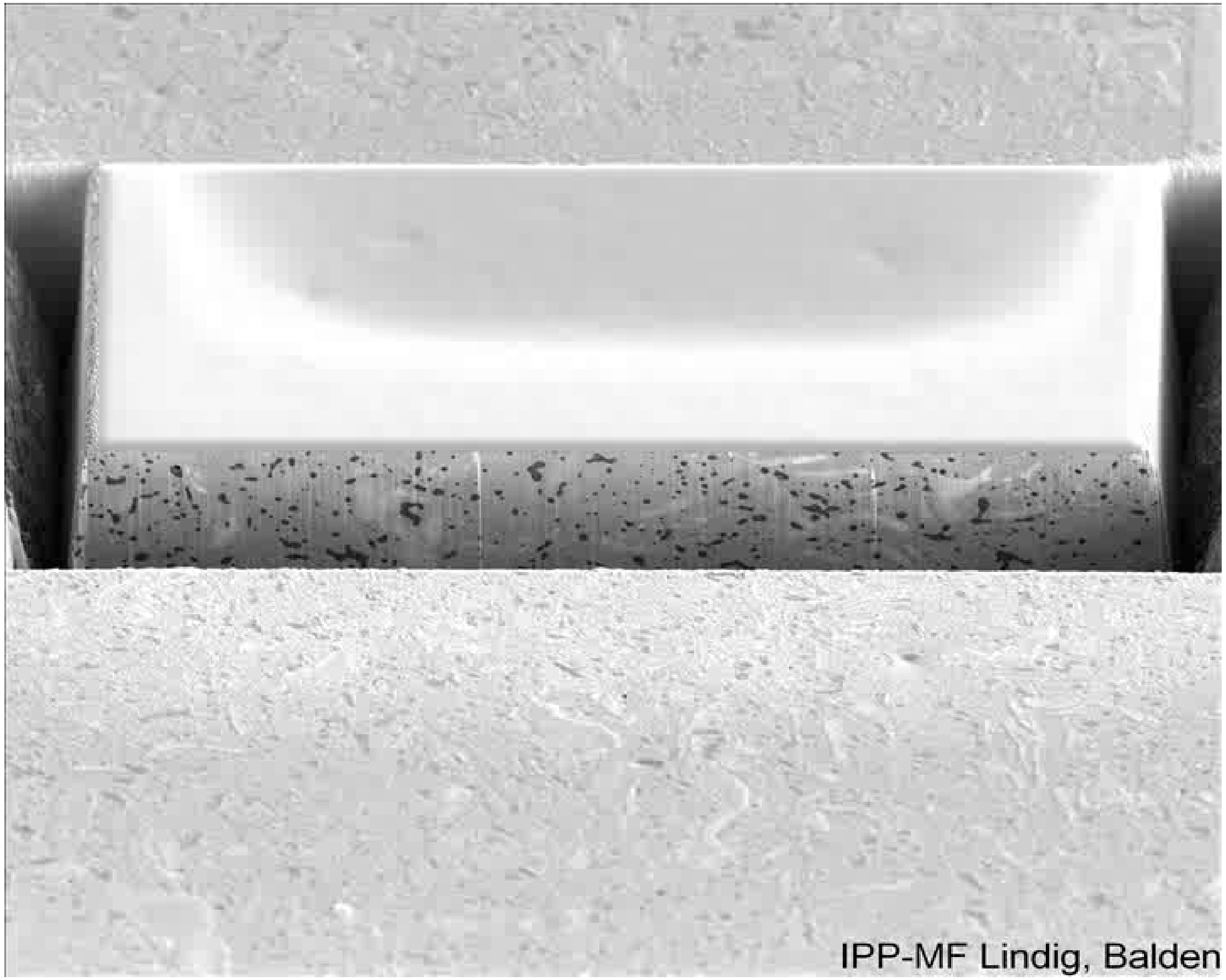
Collaboration with CEIT / San Sebastián

Morphology: SEM



- W phases dominate: gray areas
- pure W (bright) to W alloys
- small oxidic precipitates (no W!)

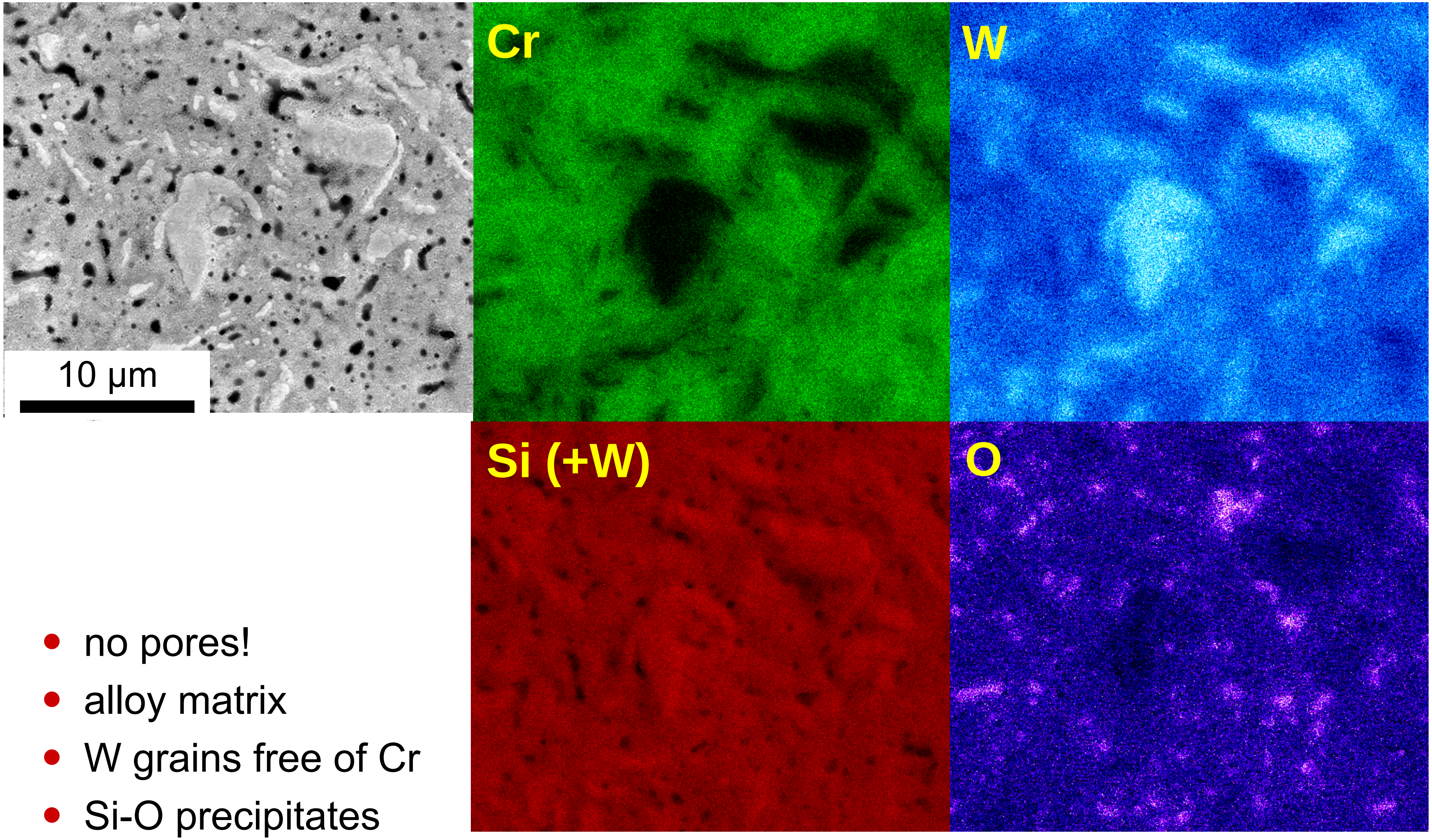
3D analysis: Focused ion beam



width of cut: ~75 µm

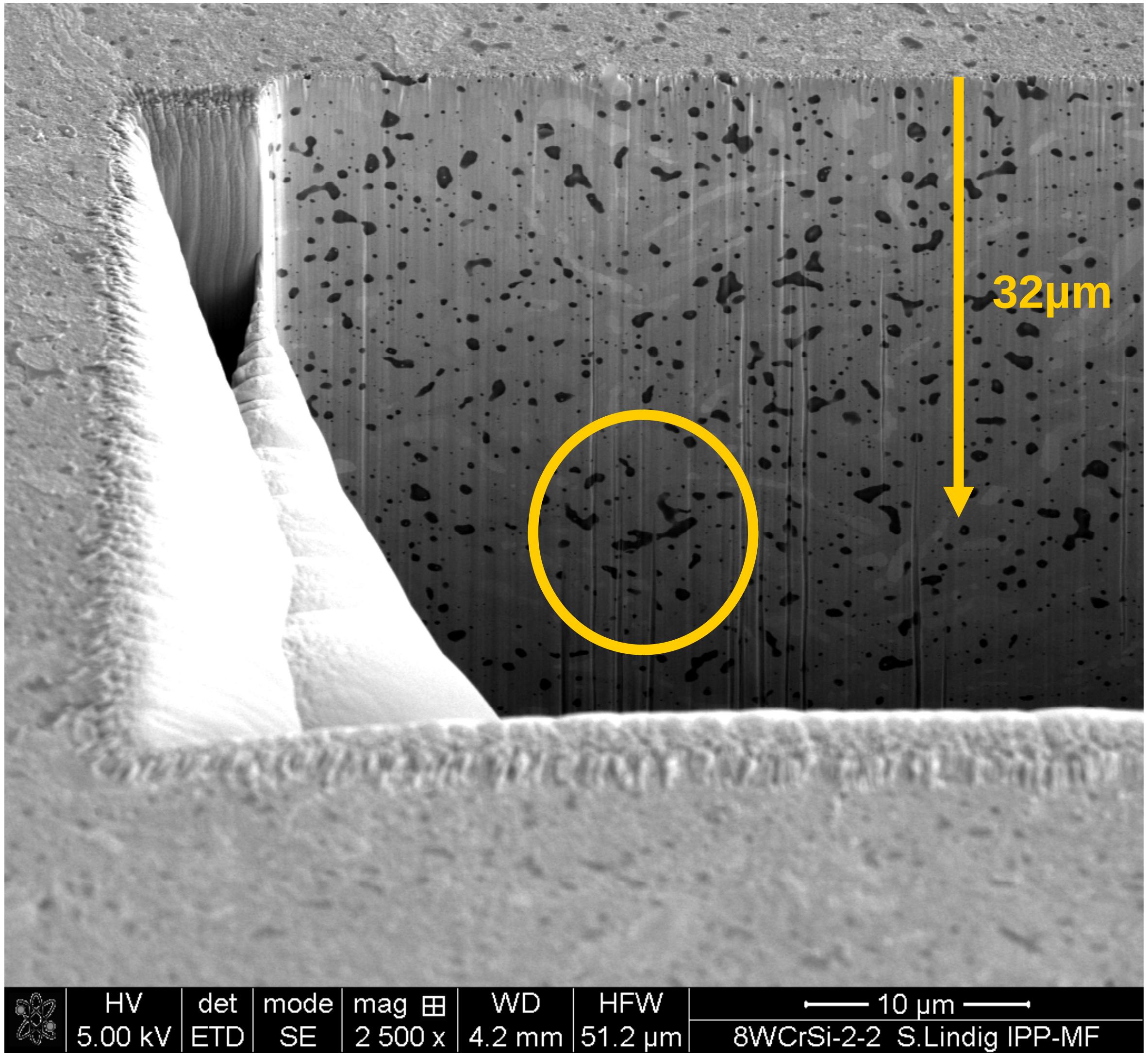
- 3D morphology identical to surface

2D element distribution

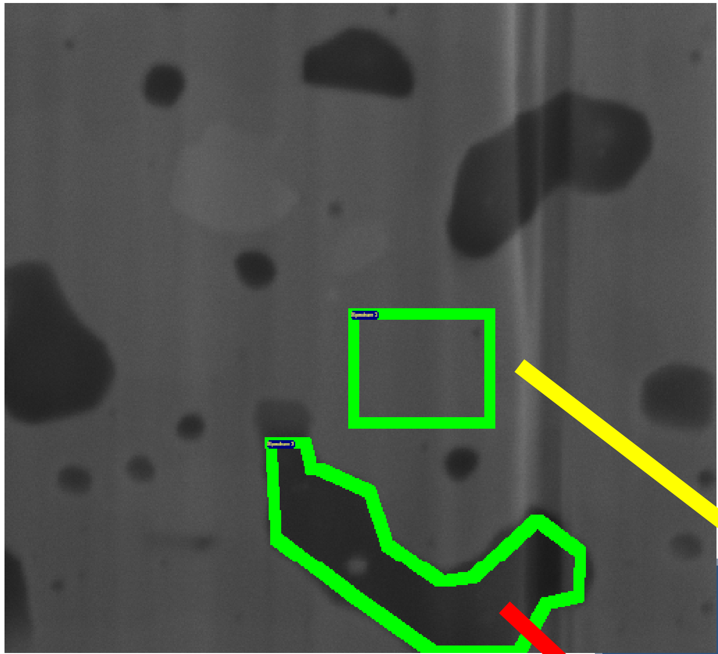


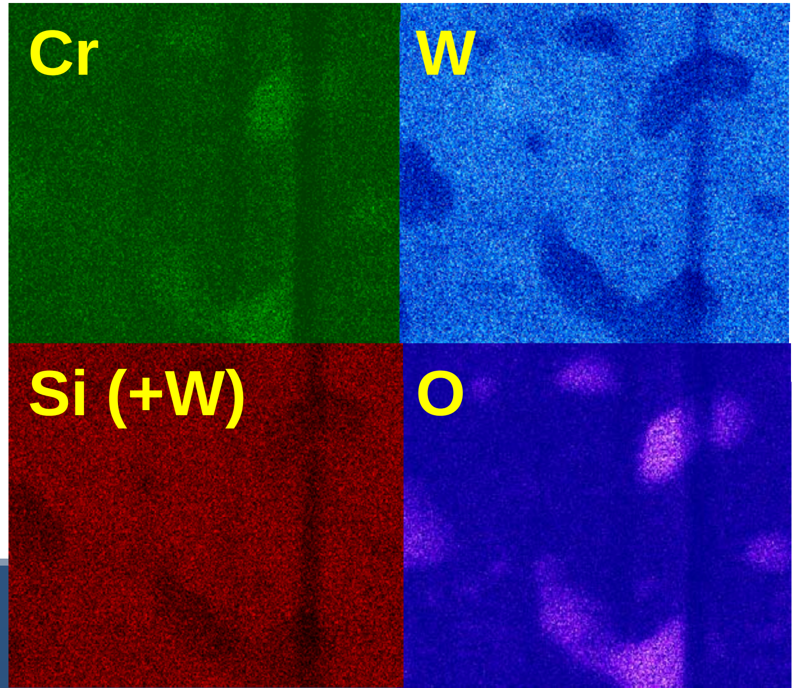
- no pores!
- alloy matrix
- W grains free of Cr
- Si-O precipitates

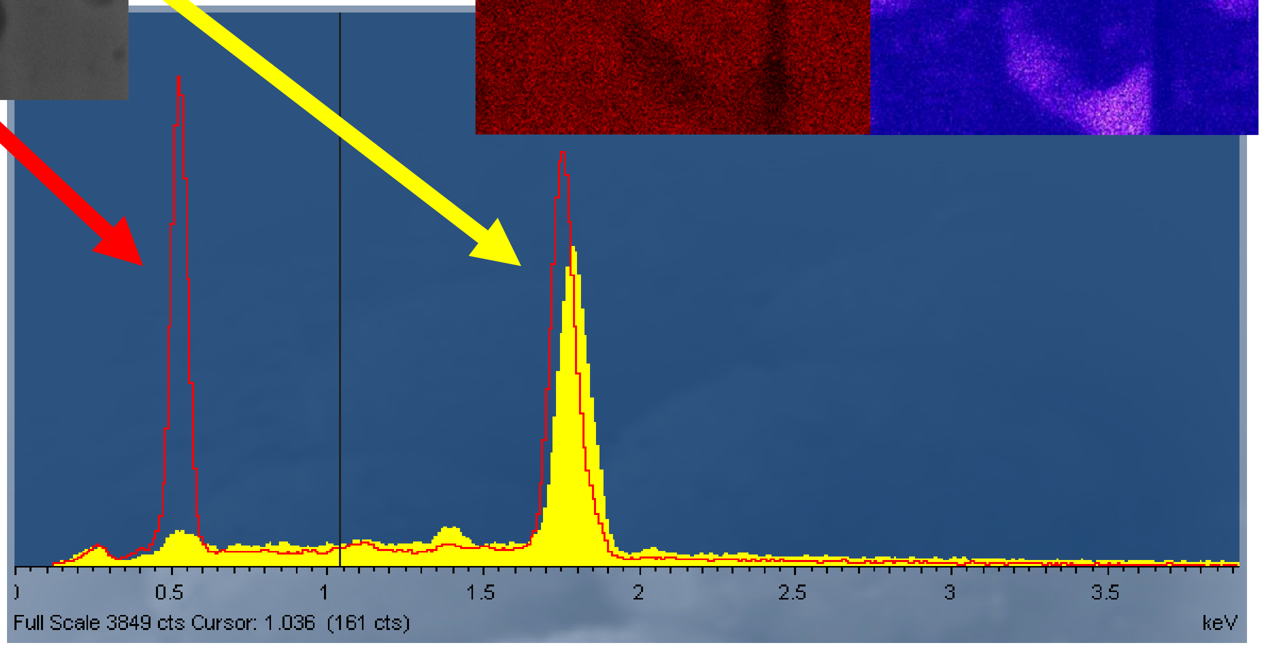
Cross-section 8W-Cr-Si2



3D element distribution

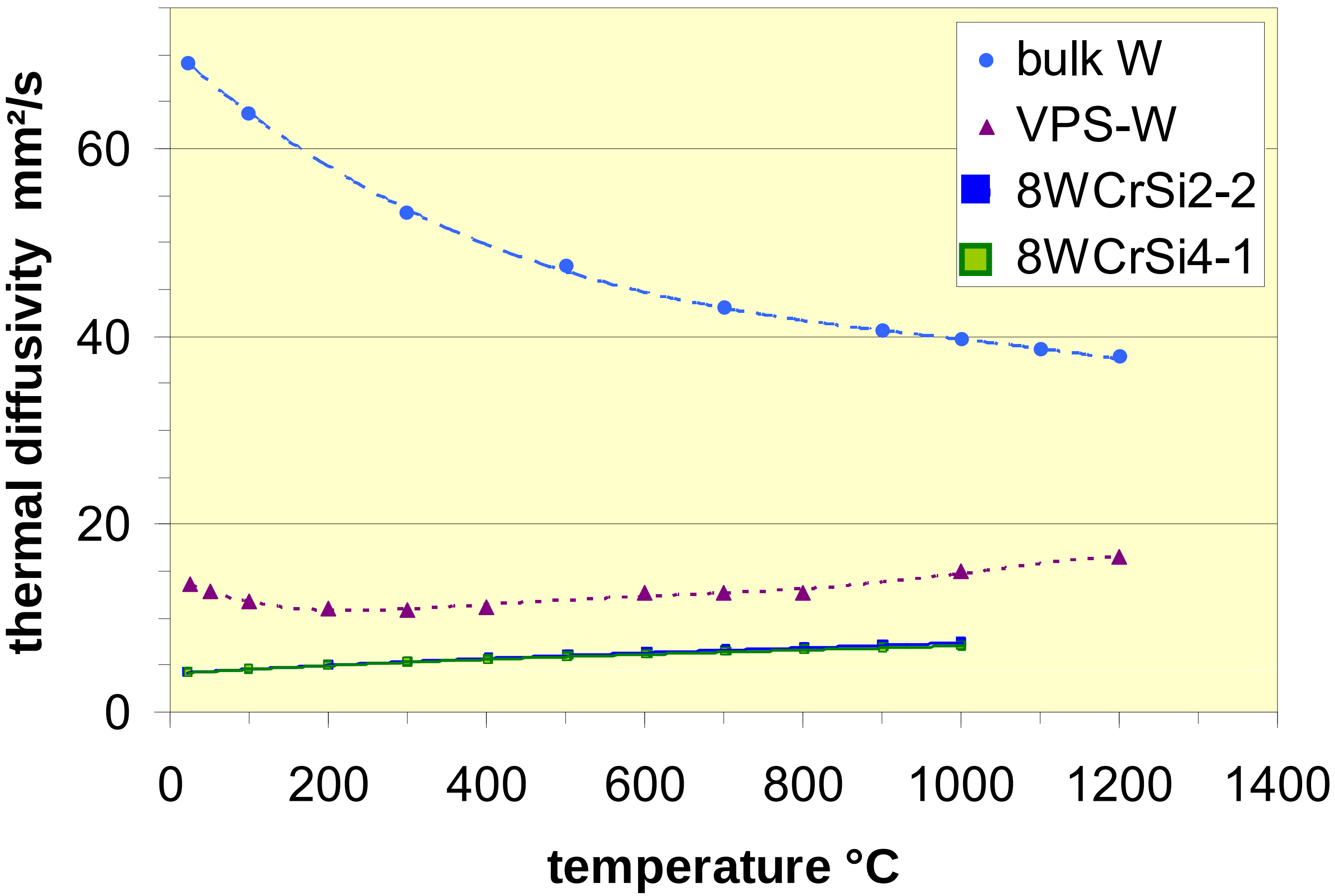






- no pores!
- alloy matrix
- W grains free of Cr
- Si-O precipitates

Thermal diffusivity



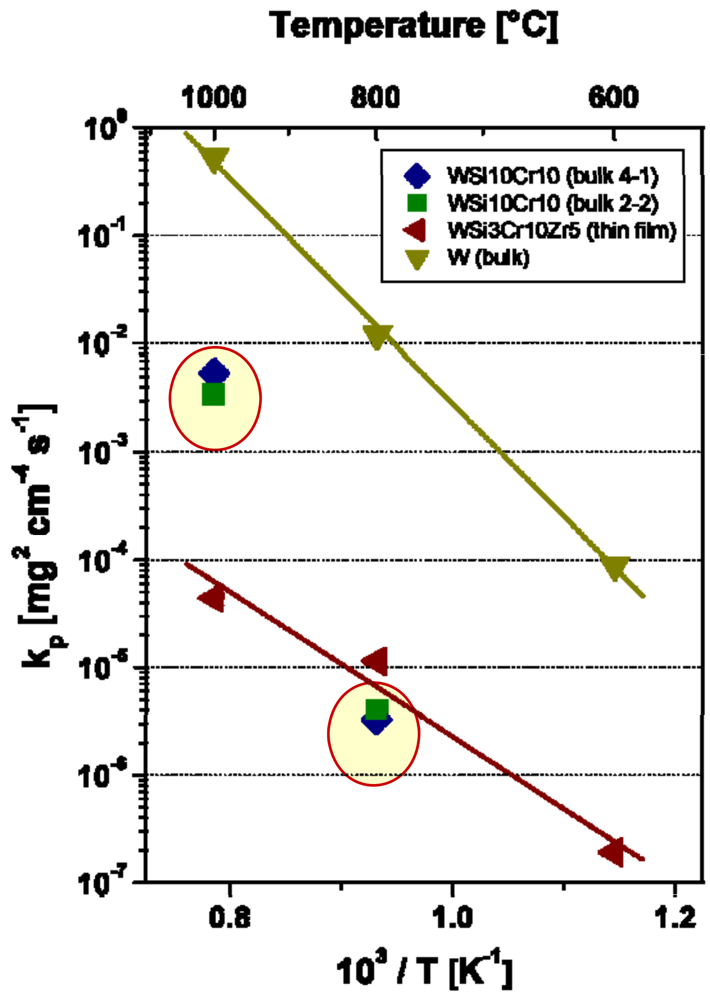
- constant thermal diffusivity
- 50% value of VPS-W

Hardness / Young’s modulus

Nanoindenter: micro-hardness, Young’s modulus

	Micro-hardness [GPa]	Young’s modulus [GPa]
alloys:		
8W-Cr-Si2	15.6	320
8W-Cr-Si4	15.5	321
comparison:		
W_f/W (fiber)	9.1—9.8	480—535
W_f/W (CVD-W)	7.5—8.1	455—530
(dense bulk W		410**)**

Oxidation rates for bulk W Si10 Cr10

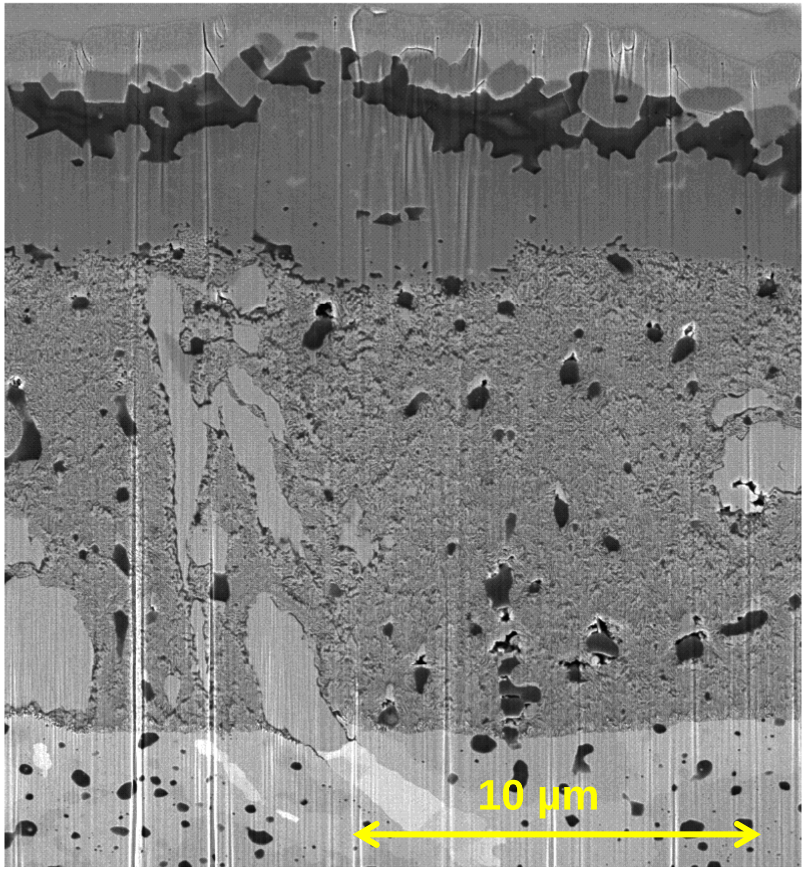


Comparison of parabolic rate constants

- strong passivation at 800°C, comparable to quaternary alloy layers

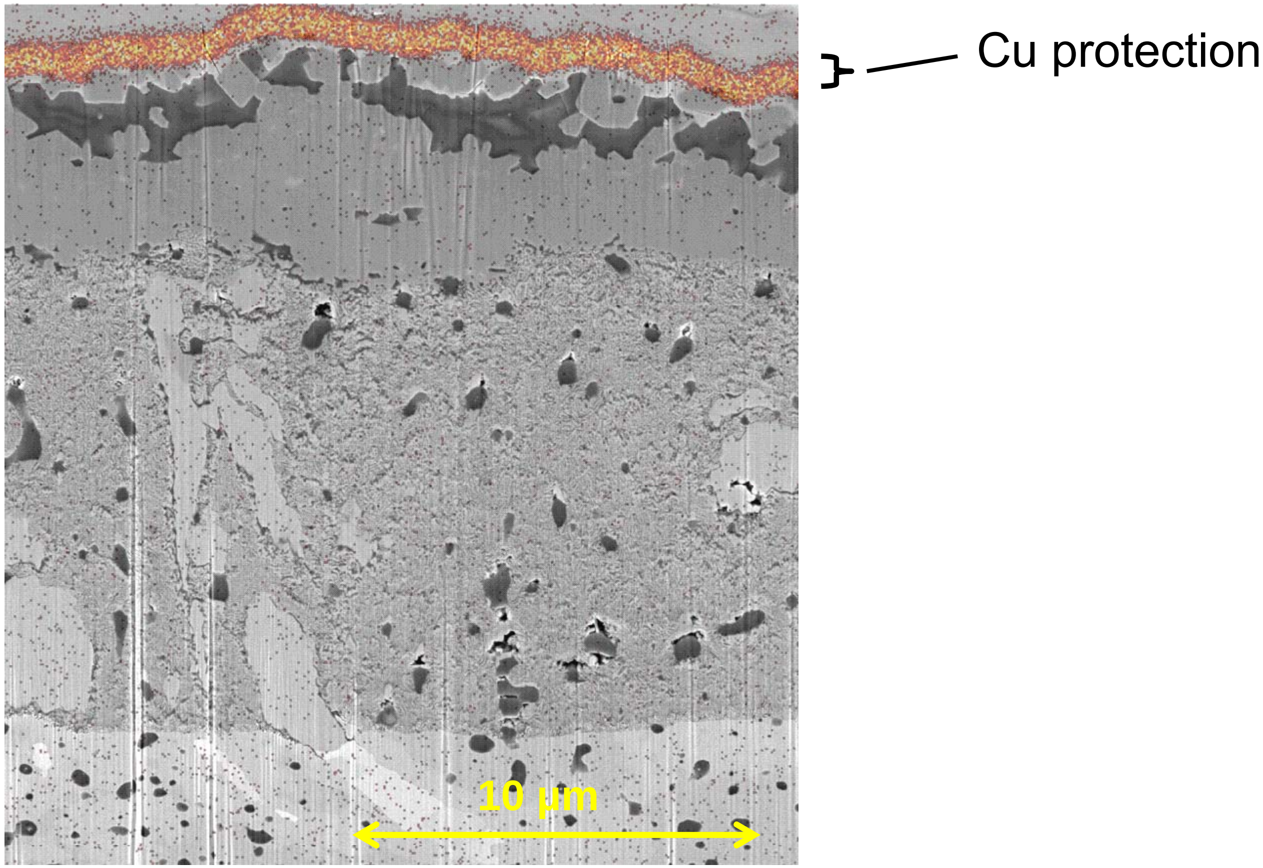
Oxidation tests: W Si10 Cr10 at 1000 °C, 3h

Cross section



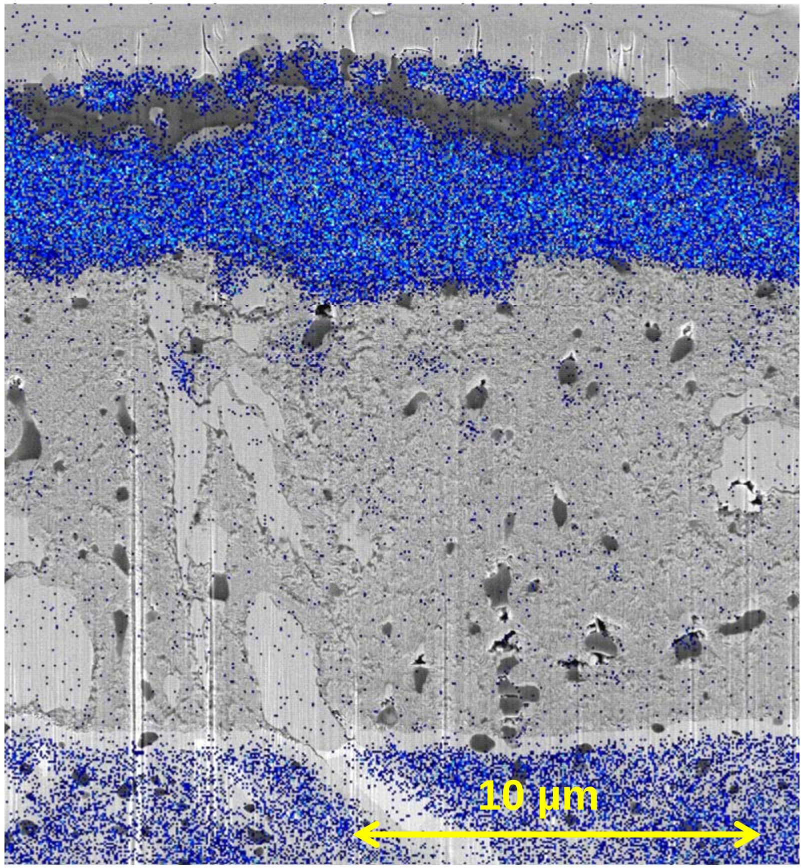
Oxidation tests: W Si10 Cr10 at 1000 °C, 3h

Cross section, EDX mapping: Cu



Oxidation tests: W Si10 Cr10 at 1000 °C, 3h

Cross section, EDX mapping: Cr



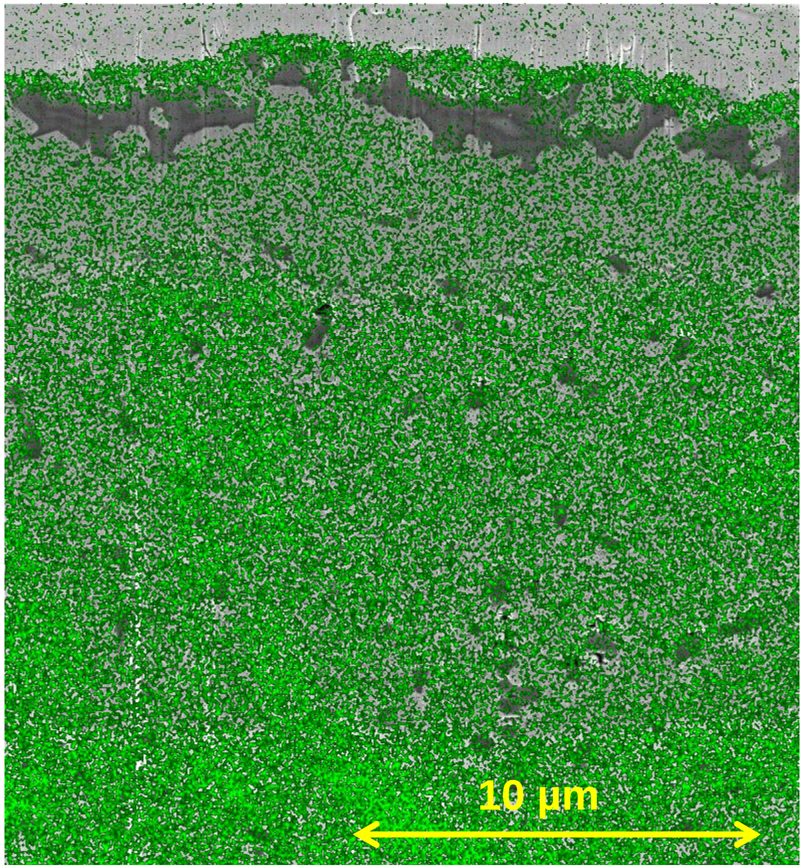
Cr_2WO_6

CrO_x, CrW_xO_y

Alloy

Oxidation tests: W Si10 Cr10 at 1000 °C, 3h

Cross section, EDX mapping: W



Cr_2WO_6

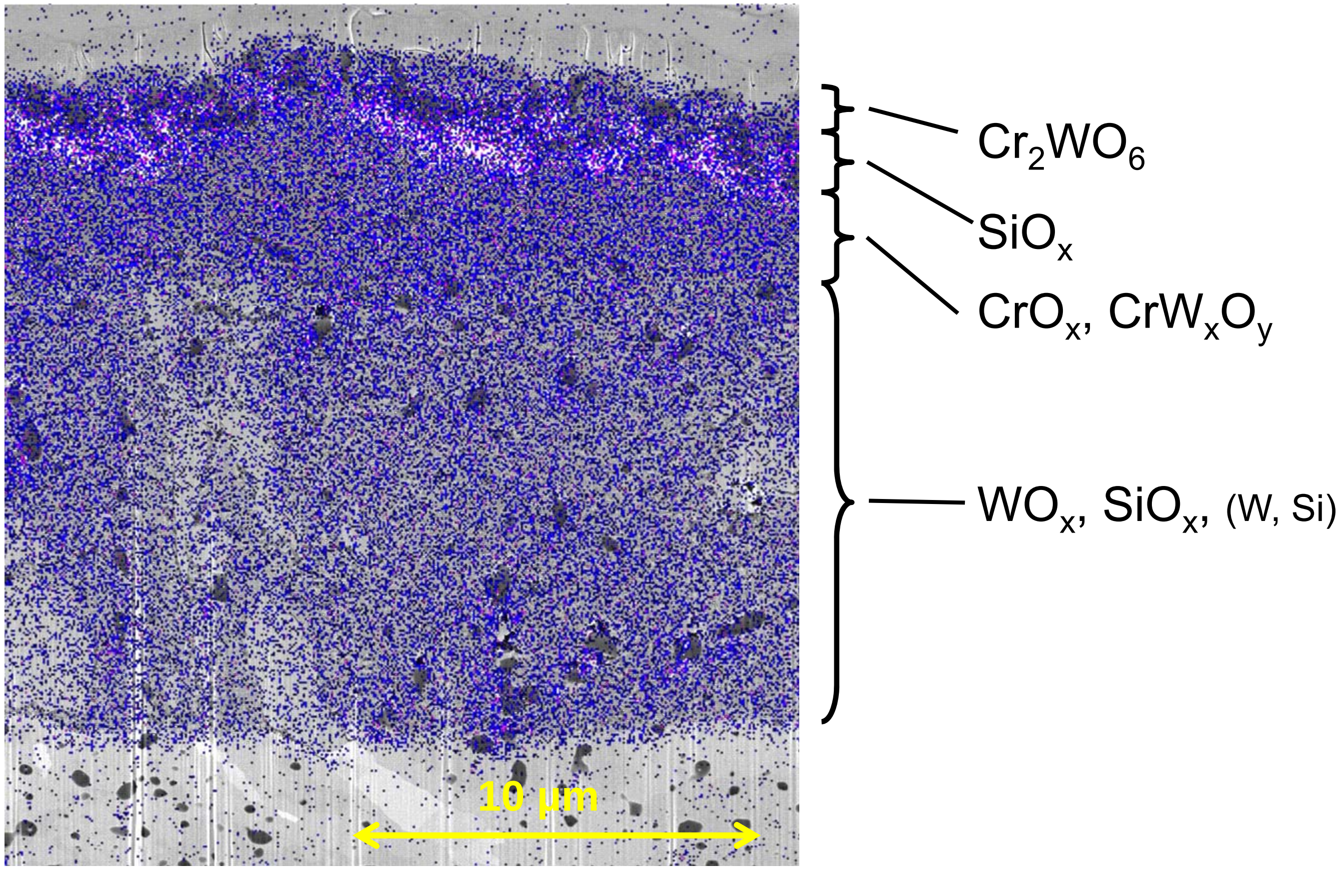
CrO_x, CrW_xO_y

WO_x, SiO_x, (W, Si)

Alloy

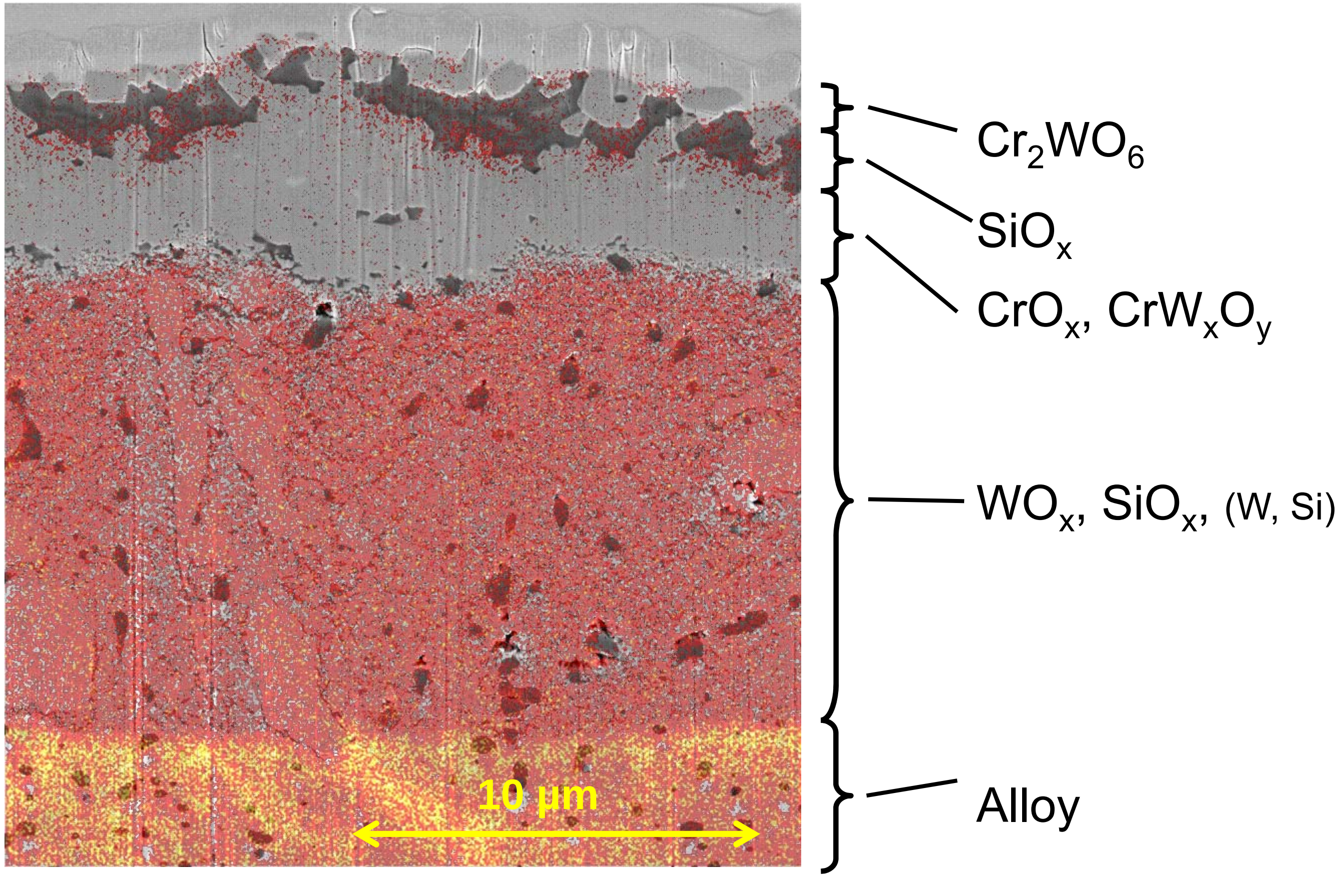
Oxidation tests: W Si10 Cr10 at 1000 °C, 3h

Cross section, EDX mapping: O



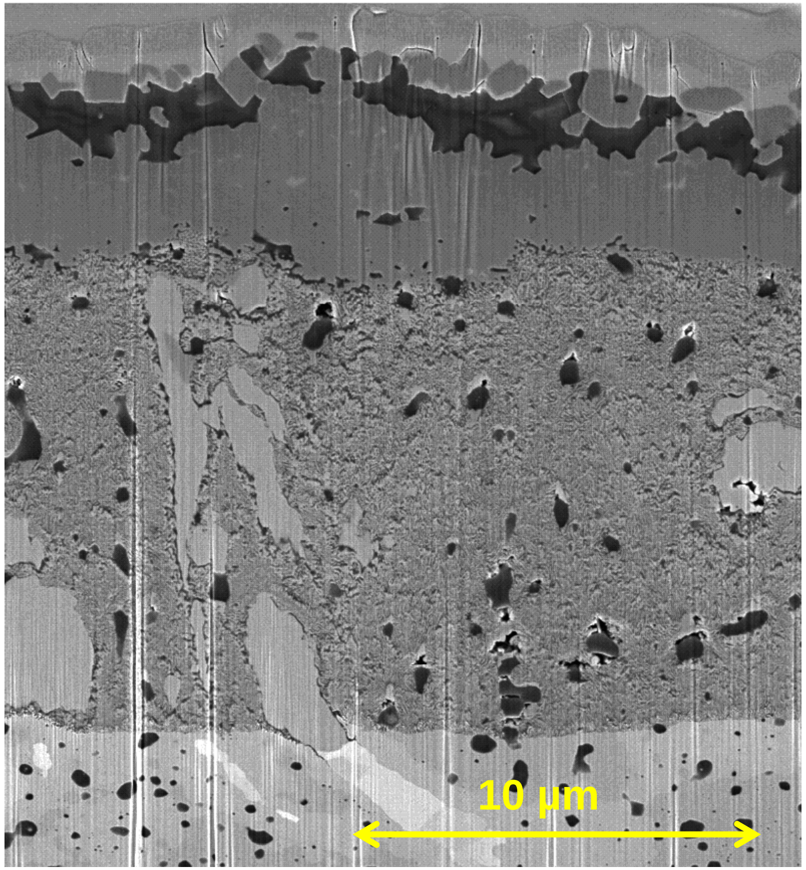
Oxidation tests: W Si10 Cr10 at 1000 °C, 3h

Cross section, EDX mapping: Si (+ W)



Oxidation tests: W Si10 Cr10 at 1000 °C, 3h

Results of EDX and XRD analysis



- Cu protection
- Cr_2WO_6
- SiO_x
- CrO_x, CrW_xO_y
- WO_x, SiO_x, (W, Si)
- Alloy

Bulk alloys: summary

- W-Cr alloys
- W-Si: hints from XRD
- pure W phase still present in precipitates
- Si-O precipitates
- no visible pores
- oxidation rates promising at 800°C,
  CrO_x and Cr_2WO_6 at 1000 °C

Outlook: W alloys

Further investigations, ideas:

- optimization (Si-free alloys, increase W fraction in quaternary alloys …)
- production and characterization of bulk alloys (IPP in co-operation with CEIT)
- preferential sputtering with H / D / He …
- true surface composition at different annealing states
- retention and release of hydrogen isotopes
- comparison of surface layers with bulk alloys (same composition)
- surface chemical reactions as a plasma-facing material ("material mixing")

➔ Promising self-passivating material for a reactor application