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Oxidation behaviour of silicon-free tungsten alloys for use as first wall material

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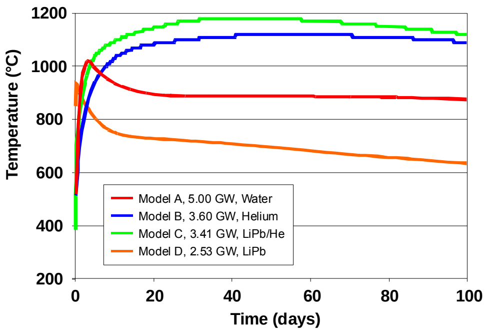
Motivation

A potential problem with the use of pure W in a fusion reactor is the formation of radioactive and highly volatile WO_3 compounds and their potential release in case of an accident with loss of all coolant.

The first wall temperature of a commercial power station with 3500 MW fusion power may rise up to 1200°C in such an accident due to the nuclear decay heat.

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



<u>Additional air ingress:</u>
formation of volatile WO_3 compounds

Evaporation rate:
order of 10 -100 kg/h at >1000°C in a reactor of 1000 m^2 surface

Therefore a large amount of radioactive WO_3 may leave hot vessel

Self-passivating tungsten-based alloys

Surface composition is self-adjusting to the required property.

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

Case of accident (air ingress, up to 1200°C):
Formation of protective barrier layer against tungsten oxidation

Was demonstrated for System

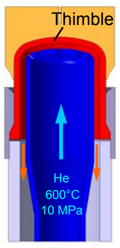
W-Cr-Si[2]

Advantage
- excellent self passivation

Drawback
- Formation of brittle intermetallic-phases WSi_2 and W_5Si_3

Investigations on alternative systems without Si

Oxidation of the inner surface of the thimble if helium contains traces of oxygen. The resulting damage of the system may be avoided using a coating of self-passivating tungsten alloy.



Finger mock-up of He-cooled modular divertor for DEMO[1]

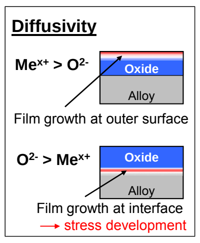
1) P. Norajitra et al.,Fusion Eng. Design 82 (2007) 2740–2744

2) F. Koch, S. Köppl, H. Bolt, Journal of Nuclear Materials 386–388 (2009) 572–574

Strategy

Criteria for alloying elements

	data available	
acceptable neutron activation behaviour	⊕	e.g.no Al
low volume increase by oxidation	⊕	see below
low vapour pressure of oxide	⊕	e.g. no V
high melting point (metal & oxide)	⊕	e.g. no Re
solubility in tungsten or intermetallic phase	⊕	e.g. W_5Si_3
formation of adhesive films	⊖	
low diffusivity of O^{2-} / Me^{x+} in metal oxide / alloy	⊖	



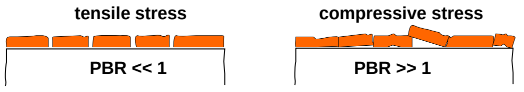
<u>Diffusivity</u>

$Me^{x+} > O^{2-}$ (Oxide / Alloy): Film growth at outer surface

$O^{2-} > Me^{x+}$ (Oxide / Alloy): Film growth at interface → stress development

Experimental investigations needed

Criterion volume increase:
Pilling-Bedworth ratio (PBR)



$$PBR = \frac{V_{Oxide}}{n_{Metal} V_{Metal}}$$

Oxide	MgO	Al_2O_3	ZrO_2	HfO_2	TiO_2	WO_2	Cr_2O_3	SiO_2	Ta_2O_5	WO_3
PBR	0.81	1.29	1.47	1.62	1.77	1.87	2.00	2.08	2.50	3.39

V: molar volume, n: number metal atoms

Experimental

Magnetron Sputter deposition

Advantages
- alloys of multiple elements
- any composition possible
- nanodispersive distribution
- ease of manufacturing

Drawback
- thickness only few microns

→ limited reservoir of alloying elements

<u>Investigations on Si-free systems:</u>
W-Cr-Ti, W-Ta-Ti, W-Ta-Zr, W-Ta-Hf, W-Hf-Ti, W-Cr-Zr, W-Zr-Ti

Oxidation tests

Films deposited on quartz substrates were used for evaluation of oxidation behaviour (mass increase).

- Setup for Thermal Gravimetric Analysis (TGA): STA 449 F1 (NETZSCH)
- synthetic air: 80% Ar + 20% O_2 through mass flow controllers
- temperatures: 600, 800, 1000°C
- one thermocouple next to the sample
- pumping system to evacuate setup before experiment ($p_0 = 10^{-5}$ mbar)
- resolution: < 0.1 µg

Acknowledgement
A part of this work has been performed within the project “SepaWolf” of the Bavarian Programme New Materials and has received funding from the Bayerisches Staatsministerium für Wirtschaft, Infrastruktur, Verkehr und Technologie.

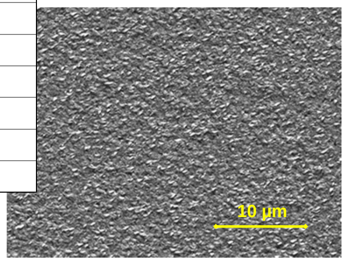
Results

Screening oxidation tests at 800° C

Alloy [wt.%]	Composition [at.%]			Oxidation tests
W-Cr14-Ti2	62	31	7	slow oxidation
W-Cr18-Ti2	53	42	5	slow oxidation
W-Cr16-Zr9	49	38	12	film delamination
W-Hf17-Ta15	67	16	18	film delamination
W-Hf44-Ti2	49	42	8	film delamination
W-Ta12-Ti2	82	12	7	film delamination
W-Ta66-Zr2	30	66	5	fast oxidation
W-Ti5-Zr1	85	10	5	film delamination

Film delamination: development of stress during oxidation lead to catastrophic failure of coating system.

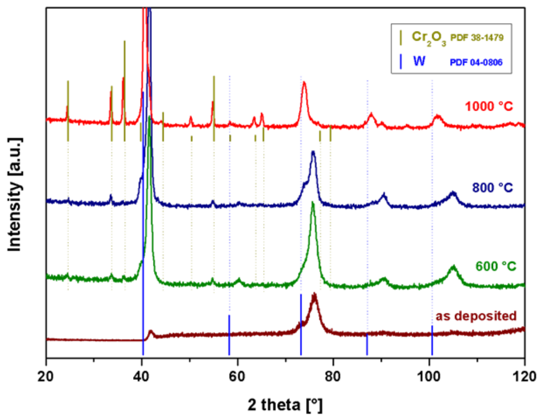
Promising system: **W-Cr-Ti**



SEM:
Surface of WCr18Ti2 as-deposited

WCr18Ti2: results as-deposited and after oxidation

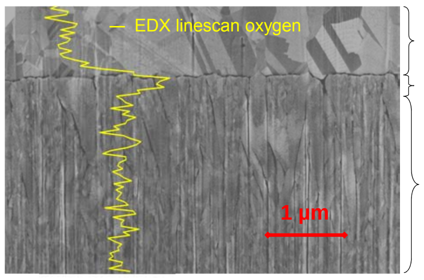
Comparison of XRD spectra



- As deposited: α-W,Cr supersaturated mixed crystal (38 at.% Cr)* and α-W, highly textured
- Formation of Cr_2O_3 during oxidation
- Oxidised at 1000°C: α-W,Cr mixed crystal with thermodynamic Cr content (9 at.% Cr)*
- No hints to volatile WO_x phase

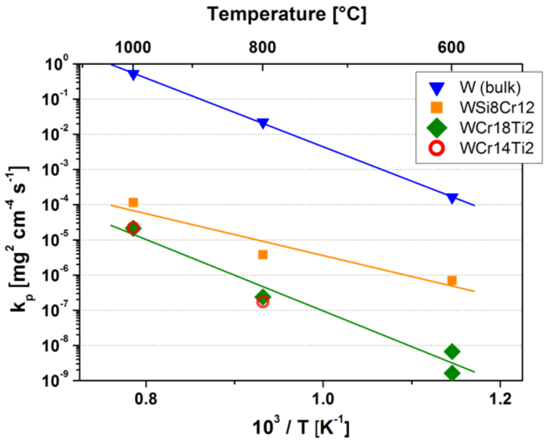
**Calculated from shift of tungsten peak according to Vegard’s law.*

Oxidised 45 min at 1000°C, SEM cross section



<u>EDX analysis:</u>
Thin oxide film at surface, thickness: ~200 nm. Corresponds quantitatively to measured weight gain assuming Cr conversion to Cr_2O_3.

Arrhenius plot of oxidation rates of W and W alloys



- Excellent self-passivation, compared to pure tungsten oxidation rates are 4 orders of magnitude lower
- Oxidation protection is also promising in comparison to previously developed W-Cr-Si alloys

Parabolic oxidation rate (k_p) has been calculated from quadratic weight increase versus time, linear fit.

Conclusion

- **Criteria for alloying elements: not possible to make unambiguous predictions. Screening tests needed.**
- **Common failure: total delamination of the film during oxidation due to development of stress (large oxide volume).**
- **W-Cr-Ti alloys form stable protective oxide scale of Cr_2O_3 and show excellent self-passivation properties**

Outlook

- **Bulk material production (collaboration with CEIT, Spain and Renner Company, Germany)**
- **Mechanical characterisation using bulk material**
- **Investigations on mechanism of self-passivation**
- **Investigations on hydrogen inventory and hydrogen erosion**

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