Self-passivating bulk tungsten-based alloys manufactured by powder metallurgy

P. López-Ruiz[a], N. Ordás[a], S. Lindig[b], F. Koch[b], C. García-Rosales[a]

[a]CEIT and Tecnun (University of Navarra), E-20018 San Sebastian, Spain

[b]Max-Planck-Institut für Plasmaphysik, EURATOM Association, D-85748 Garching, Germany

Introduction

Tungsten and tungsten alloys → candidate materials for the **first wall** (FW) armour of future fusion reactors (**DEMO**).

Important safety concern: loss-of-coolant accident with simultaneous air ingress into reactor vessel → ↑ temperature up to 1000 °C in the in-vessel components due to decay heat → **evaporation of radioactive $(WO_3)_x$-clusters**.

➡ **Addition of stable oxide-forming** alloying elements to W → **self-passivating oxide layer** prevents further W oxidation.

Thin films W-alloys:

- Different binary and ternary W-alloys produced by **magnetron sputtering** exhibit self-passivating behaviour. **WCr10Si10** (wt.%) → **oxidation rate (k_p) three orders of magnitude lower than pure W** up to 1000 °C.
- Si-free alloys (**WCr12Ti2.5**) even lower k_p than WCr10Si10 , while brittle silicides avoided ⇒ See poster: P23B
- But magnetron sputtering not applicable to DEMO: thickness of several mm required → **Powder metallurgical route**

Previous work on bulk W-alloys:

- First **WCr10Si10** samples produced by mechanical alloying (MA) in **SPEX mill** + hot isostatic pressing (HIP). Main phase **$(W,Cr)_5Si_3$** + large W grains
- First **oxidation tests**: ↓ parabolic oxidation rate at 600 °C but ↑ at 1000 °C compared to thin films. ≠ oxide scale in thin films (**Cr_2WO_6**) and bulk W-alloys (**Cr_2O_3**) → ≠ oxidation mechanism ➡ Large pure W grains must be avoided.

Aim of this work: Manufacturing of self-passivating **bulk W-Cr-Si** (optimization) and **W-Cr-Ti** (first trials) alloys by **PM: MA (Planetary ball mill)+ HIP**.

Experimental

Manufacturing:

Elemental powders (WCr10**Si10**, WCr10**Ti2.5**) ➡ **Mechanical alloying** (Planetary ball mill, Argon, BPR: 5:1 / 2:1, 300 / 250 rpm) ➡ **Uniaxial pressing** (75/50 MPa) ⬇ **Glass encapsulation** ⬅ **HIP** (1 h, 200 MPa, 1300 or 1350 °C)

Ø16 mm, h~4 mm

Materials characterization:

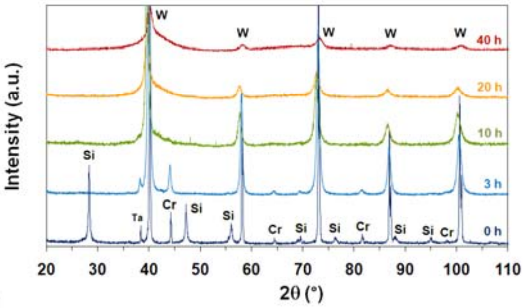
- FEG-SEM, EDX mapping, FIB and XRD.
- Open porosity by He pycnometry.
- Vickers microhardness (9.8 N for 15 s).
- Impurities content (O and C by LECO).
- Thermal conductivity Netzsch LFA 427.

Mechanical alloying

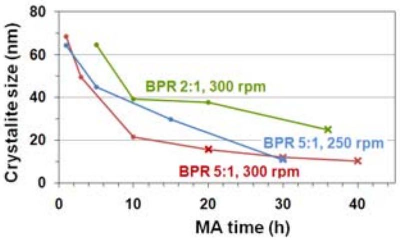
XRD of WCr10Si10 (BPR 5:1, 300 rpm)

- **10 h:** incipient alloying; **shoulder of new phase** on high angle side of 40,2° W peak .
- **20-40 h: progress in alloying (not completed)**, broad peaks at 40-50° and 65-70° → silicides + pure W.

*BPR: Ball-to-powder weight ratio



Crystallite size *vs.* milling time

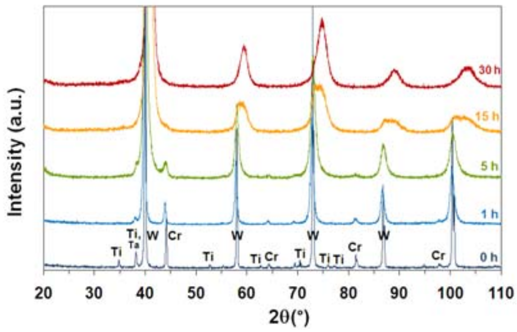


- ↓ BPR → less effective milling
- ↓ Milling speed (300 → 250 rpm) no effect on crystallite size after 30 h.

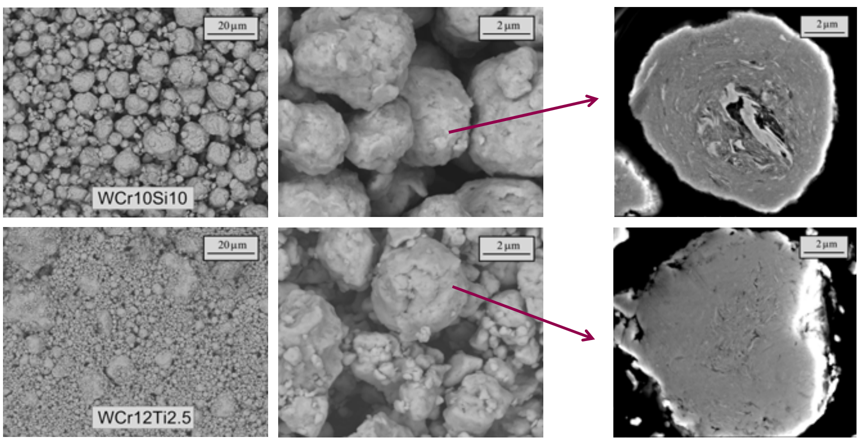
➡ **Selected MA conditions: BPR 5:1 , 250 rpm, 30 h**

XRD of WCr12Ti2.5 (BPR 5:1, 250 rpm)

- **5 h:** alloying not started (Cr peaks still visible).
- **15 h:** alloying starts → new metastable bcc phase appears, pure W present.
- **30 h: alloying almost complete** → majority ternary bcc phase (solid solution of W, Cr and Ti) + residual pure W.



Powder (BPR 5:1, 250rpm, 30h)

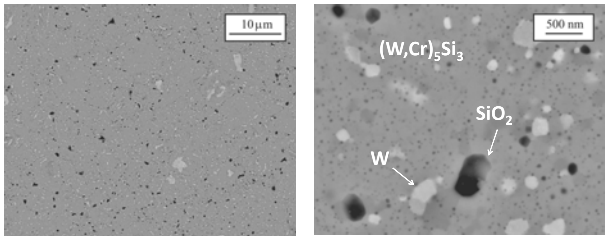


- **WCr10Si10:** Bimodal particle size distribution → ~ steady-state. **Core**: flattened pure W coarsely mixed with Cr and Si; cold welding with progressively finer layered powder → **shell**: very fine microstructure, spec. at surface: true alloying.
- **WCr12Ti2.5:** Broad particle size distribution → no equilibrium of cold welding and fracture, large fraction of very small particles. **Core**: pure W flakes hardly distinguishable, fine microstructure. **Shell**: ternary phase + scarce small W flakes; much finer microstructure.

Composition	Stops	O (wt.%)	C (wt.%)
WCr10Si10	Yes	0.40	0.022
	No	0.123	0.026
WCr12Ti2.5	Yes	0.40	0.034
	No	0.114	0.014

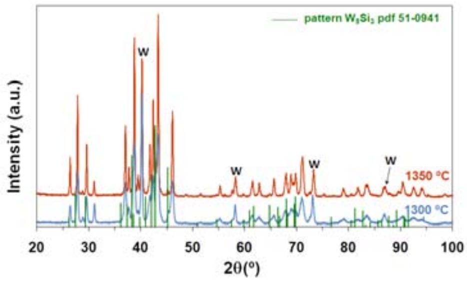
- Starting powders (0.065 % O, 0.006 % C).
- Low impurities content after MA.
- Stops for sampling → ↑ O content, C not influenced.

HIP



WCr10Si10 (BPR 5:1, 300rpm, 20 h) HIPed at 1300 °C

- Fine and homogeneous microstructure; larger W grains from milled particles remain almost unchanged after HIP.
- Ultrafine-ODS intergranular phase inhibit grain growth.
- Similar microstructure at 1300 and 1350 °C (no grain growth).

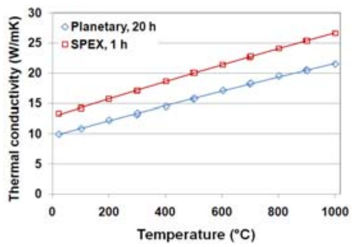


- Narrower peaks at 1350 °C → ↑ phase homogenization.
- Ternary silicide, probably $(W,Cr)_5Si_3$ + pure W.

- Densification > 95%.
- Hardness typical for silicides (much higher than pure W).

HIP temp. (°C)	Density (%)	HV 1.0
1300	95.2	1414
	100	---
1350	96.6	1374

Thermal conductivity



- Sample from planetary slightly lower conductivity → much finer microstructure ⇒ largely enhanced density of grain boundaries.
- Low thermal conductivity but enough for application at blanket FW.

Conclusions

- Bulk **WCr10Si10** alloys produced by MA (Planetary) + HIP → densities > 95%.
  - MA at **BPR 5:1, 250 rpm, 30 h** → effective milling, low contamination.
  - Core of large powder particles shows heterogeneous phase distribution → after HIP large pure W flake-like grains remaining. Alloying not completed: silicides + W → more work required to further improve microstructure.
  - Nevertheless, **microstructure significantly refined** compared to previous work → **enhanced oxidation resistance expected**.
- First results on MA of **WCr12Ti2.5**:
  - **Very homogeneous structure** inside powder particles.
  - **Ternary metastable bcc phase** + traces of W.
  - A very fine and homogeneous microstructure besides better thermal and mechanical properties than WCr10Si10 can be expected after HIPing.

Acknowledgments This work has been funded by the European Community within the framework of EFDA WP08-09 under the contract of EURATOM/CIEMAT, and by the Spanish Ministry for Science and Innovation (ENE2009-09511, subprogram FTN).

13th PFMC Workshop and 1st FEMaS Conference, 9 – 13 May 2011, Rosenheim (Germany)