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Processing and Characterisation of (Ta,Hf)C Ultra-High Temperature Ceramics.

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Ultra-high Temperature Ceramics: Materials for Extreme Environment Applications III, Gold Coast Australia, April 13th 2015.

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TaC-HfC system

- TaC-HfC compounds extremely high melting (~4000°C).
- Some disagreement about T_m in literature.
- Information on properties is scarce.
- Difficult to process due to high temperatures needed.

Conceptual Hypersonic Vehicle [1]

Phase	Crystal System	Structure Type	Space Group	Lattice parameter a (Å)
TaC	B1 Cubic	NaCl	*Fm3m*	4.456
HfC	B1 Cubic	NaCl	*Fm3m*	4.641

[1] P. DiMare, Smithsonian Air & Space Magazine, September 2007.

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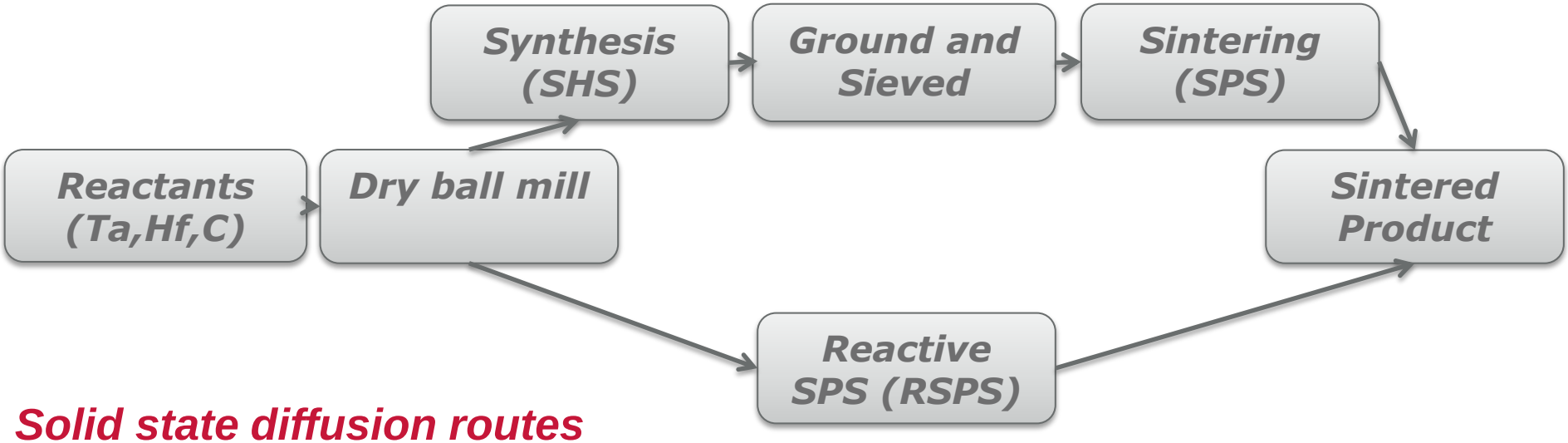
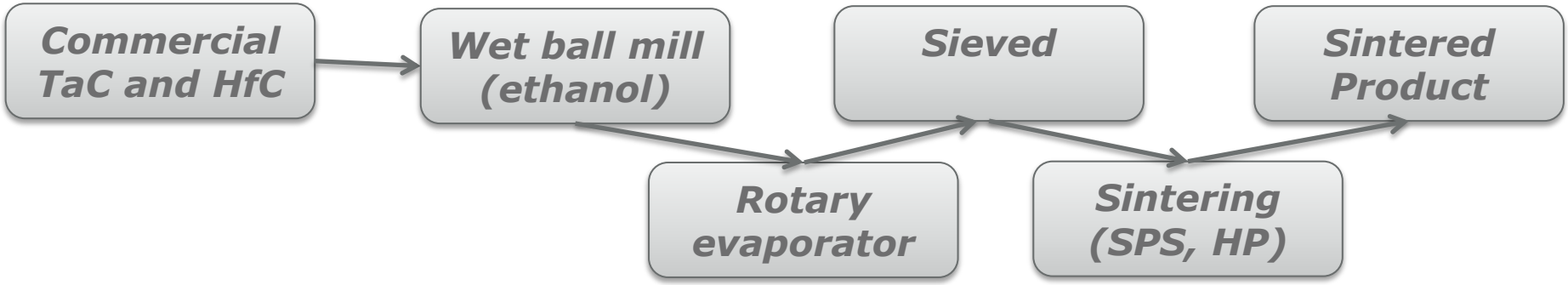
Processing Routes

Reactive routes



Solid state diffusion routes



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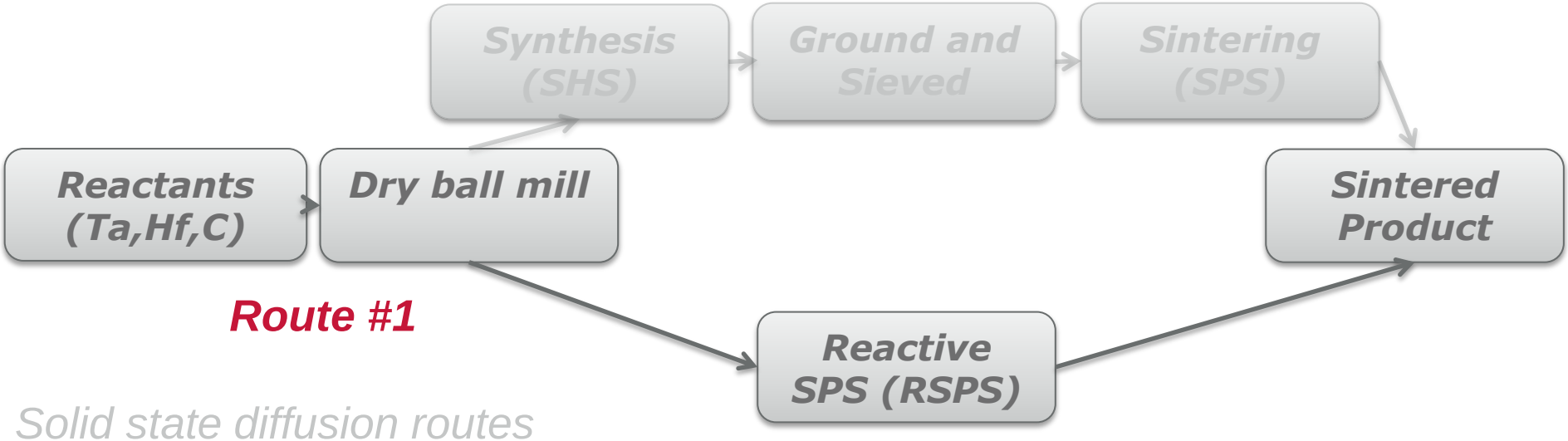
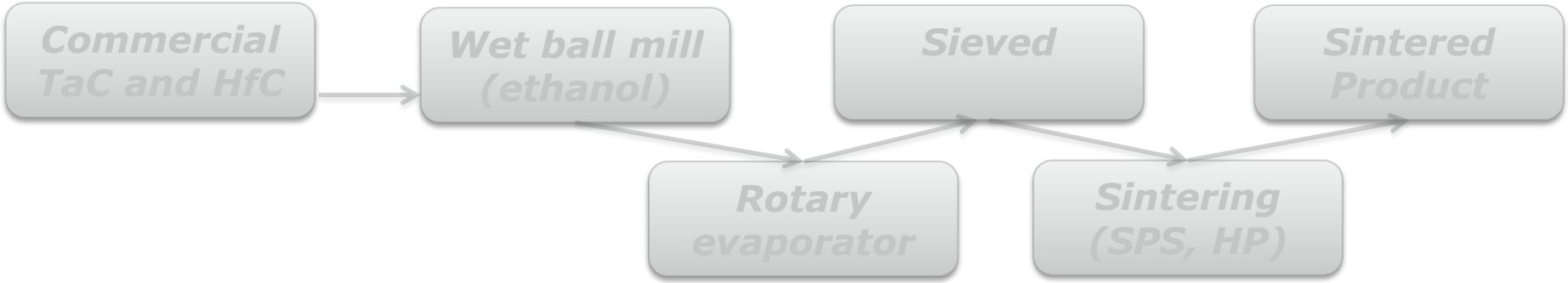
Processing Routes

Reactive routes



Solid state diffusion routes



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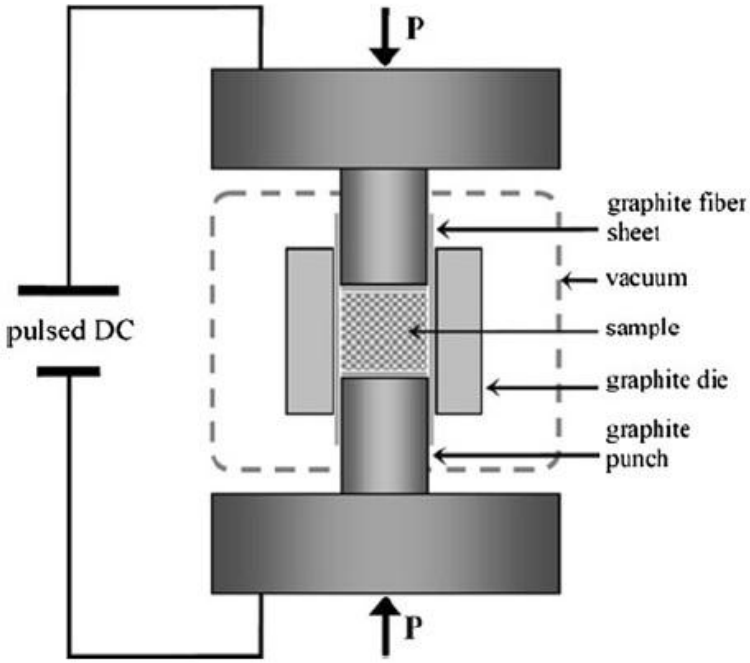
Synthesis and Sintering of 4TaC-1HfC by RSPS

- **Strongly exothermic, self-propagating high-temperature synthesis (SHS) using Ta, Hf powders and carbon black.**
- **SHS rapidly densifies UHTCs at high T in short t.**
- **Combination of methods used to synthesize and sinter TaC-HfC ceramics in one step.**
- **A minimum of 20 MPa applied. Higher loads (60 MPa) applied after SHS reaction (1400°C). Heating rate of 210°C/min used for all samples.**



Schematic of an SPS furnace [2]

[2] M. Stuer, Z. Zhao, U. Aschauer, and P. Bowen: J. Eur. Ceram. Soc., 2010, vol. 30, pp. 1335–43.

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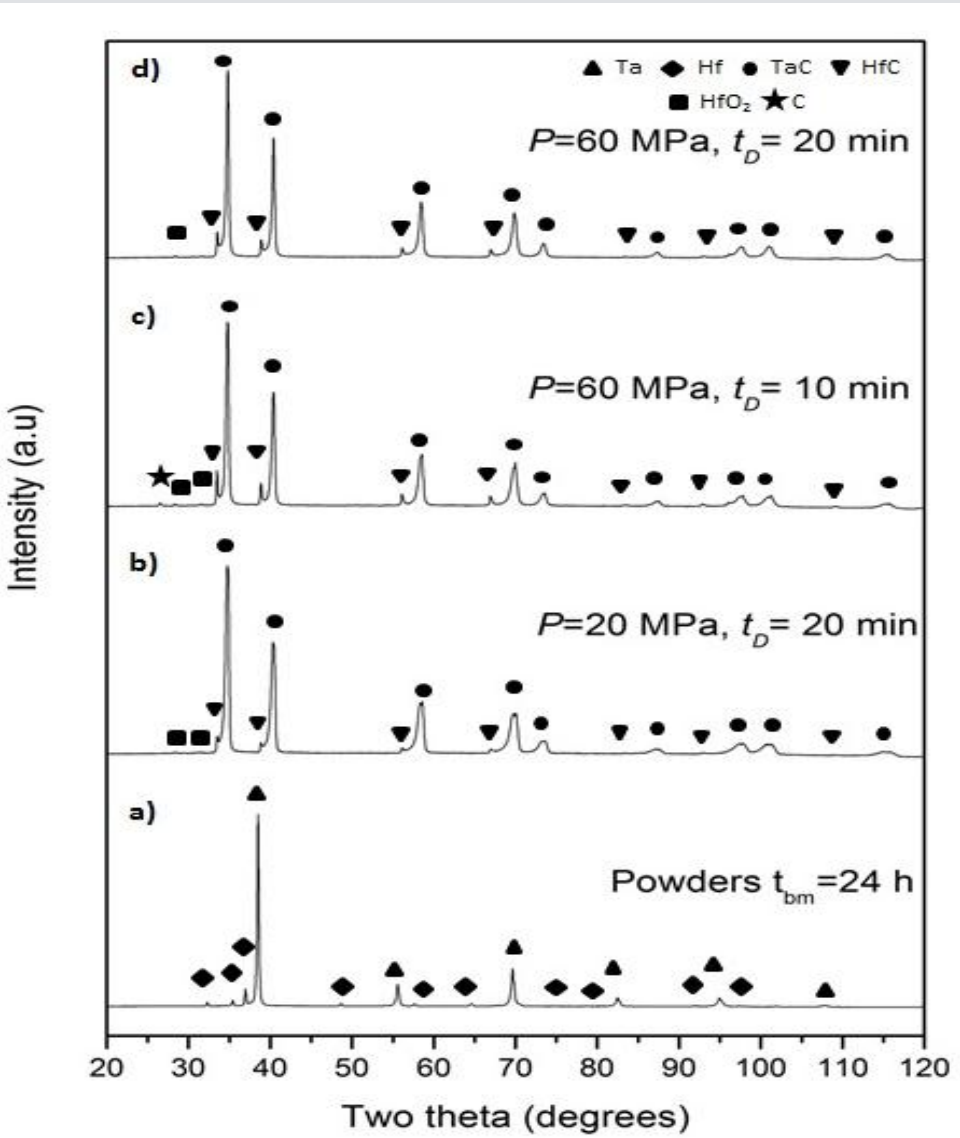
Sintering conditions, density and XRD analysis

Sintering conditions (t_D, P)	Density ρ (g/cm$^{3)}$	Relative density %
20 min, 20 MPa	8.7 ± 0.39	62.6 ± 0.30
10 min, 60 MPa	11.7 ± 0.18	83.3 ± 0.13
20 min, 60 MPa	12.5 ± 0.38	89.6 ± 0.36



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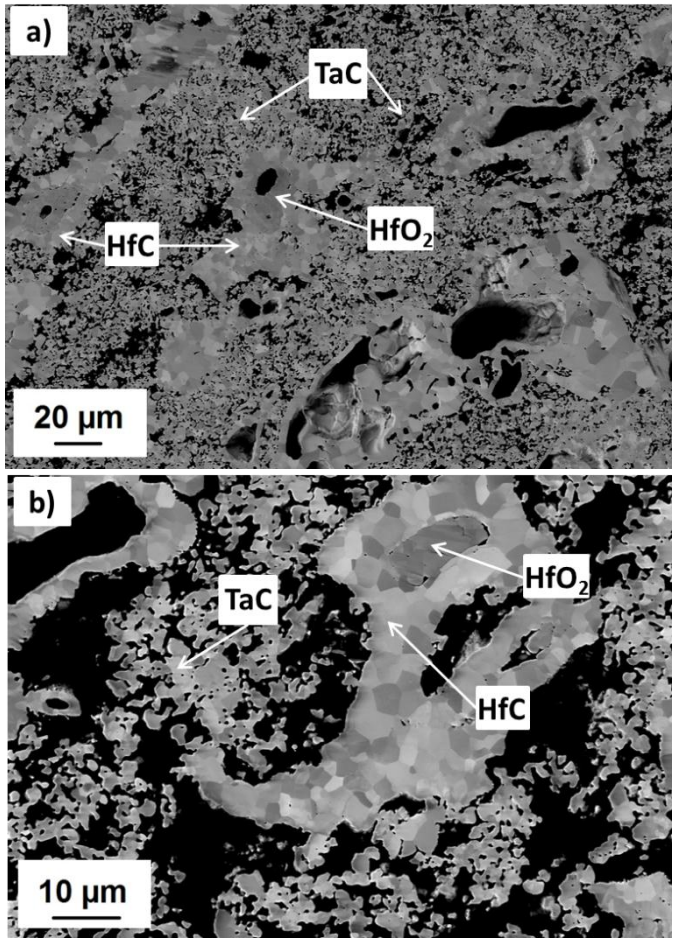
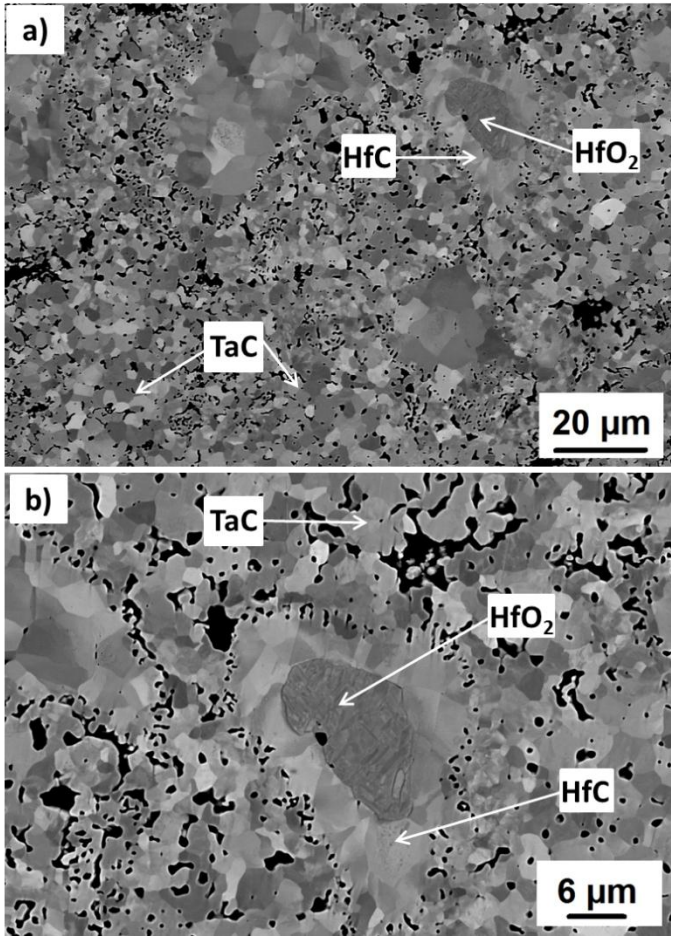
SEM analysis of RSPS'd 4TaC-1HfC (BSEI)



20 min, 20 MPa



20 min, 60 MPa

- **TaC and HfC but little solid solution plus HfO_2 contamination.**
- **Core/rim structure of HfO_2/HfC, separate from TaC.**

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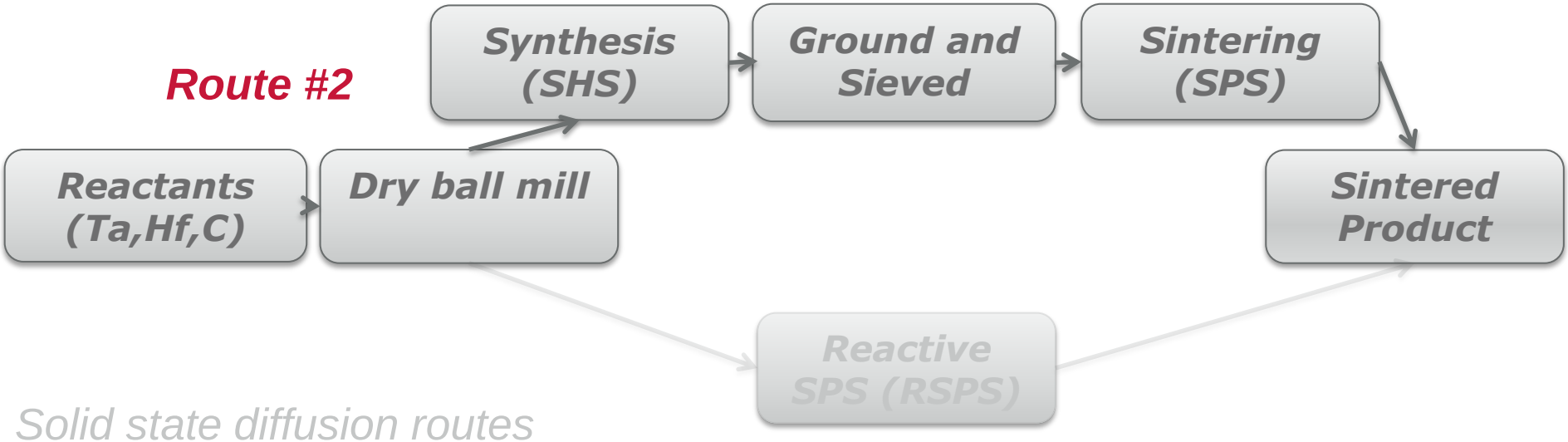
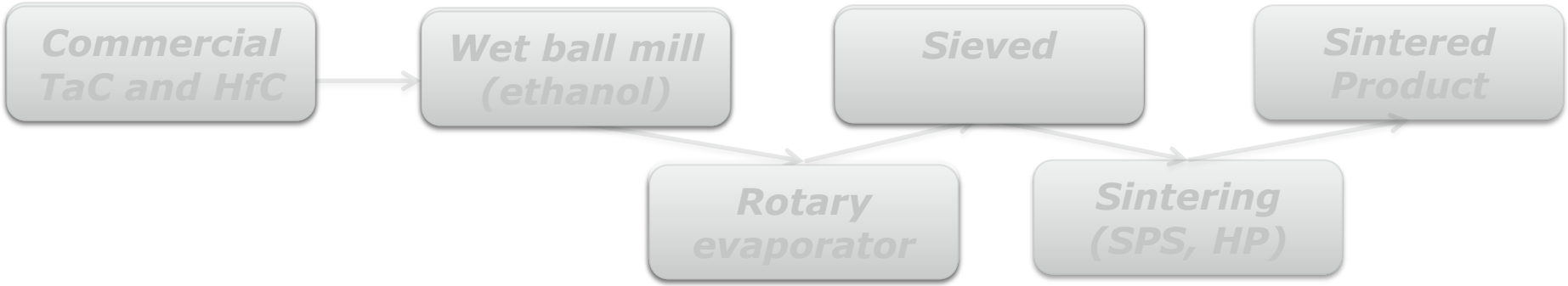
Processing Routes

Reactive routes

Route #2



Solid state diffusion routes



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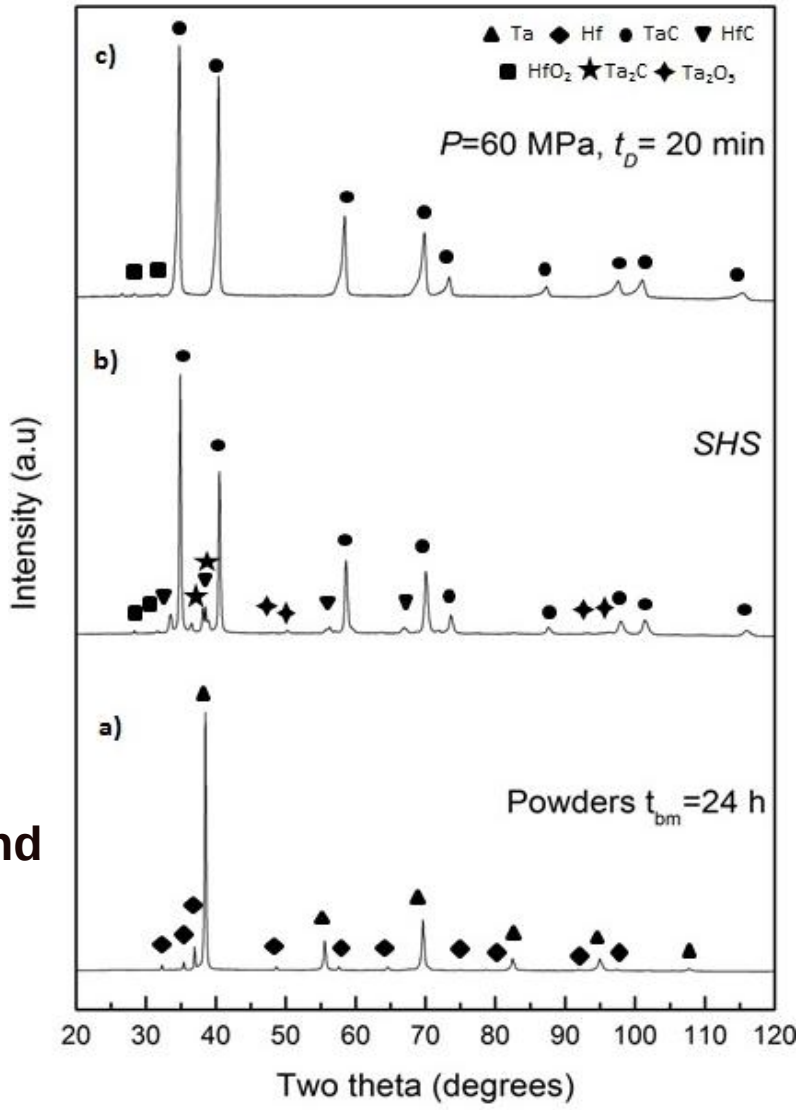
Sintering conditions, density, MGS and XRD analysis

4TaC-HfC after SHS+SPS

Sintering conditions (T_D, t_D, P)	Density (g/cm^3)	Relative density (%)	Mean Grain Size (μm)	Grain size range (μm)
2100°C, 20 min, 60 MPa	13.8 ± 0.19	98.22 ± 0.13	6.4	1.4-20.5

- After SHS have TaC, HfC plus Ta_2C, HfO_2 and Ta_2O_5 contamination present.
- After high temp. SPS all Ta_2C disappears.



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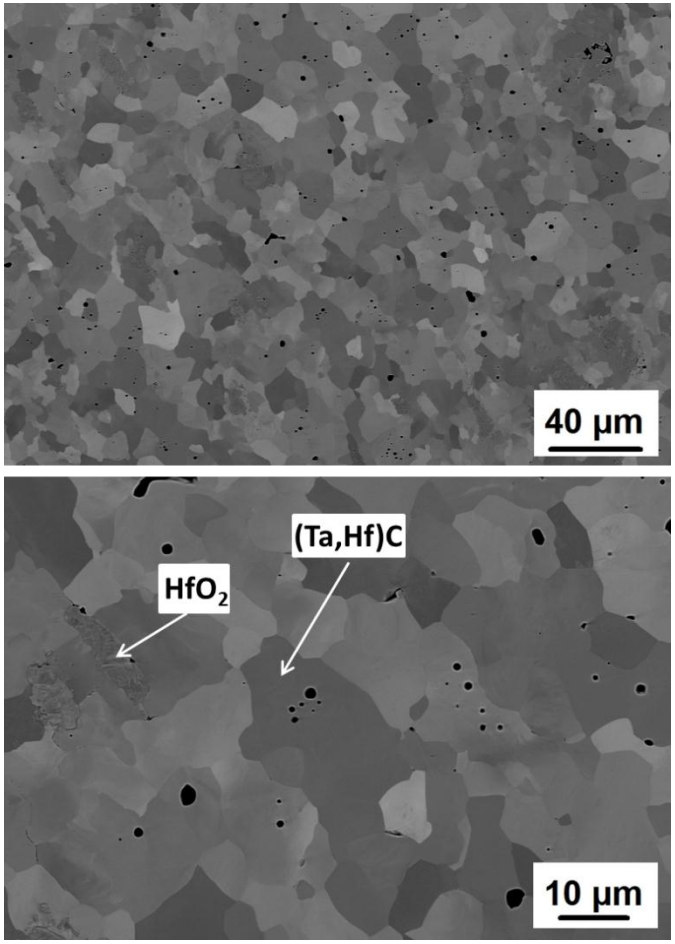
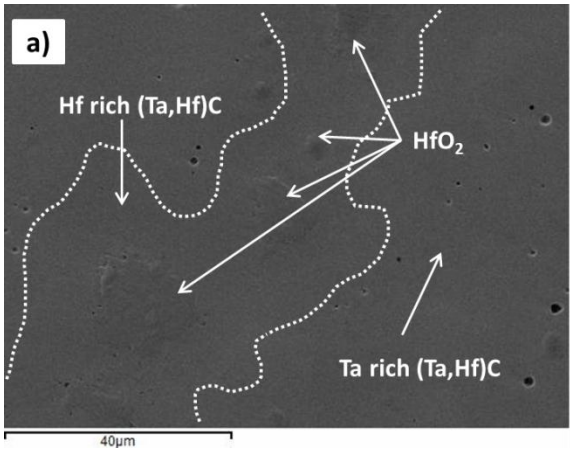
SEM and EDS of 4TaC-1HfC after SHS+SPS

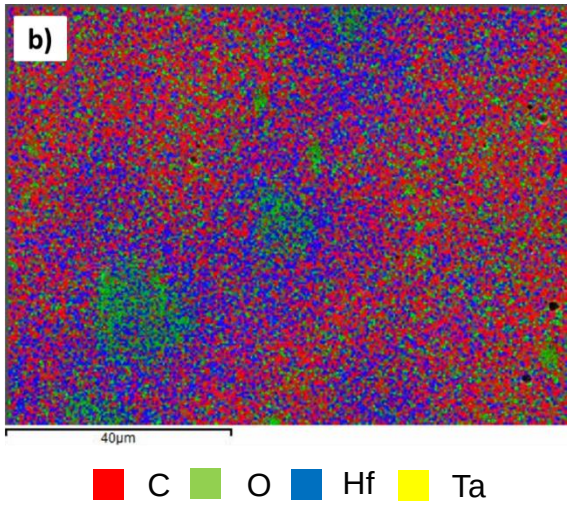
BSE images



SE image



EDS map



Note region of Hf-rich solid solution close to HfO_2 and more remote region of Ta-rich solid solution.

Proximity to HfO_2 leads to Hf-rich solid solution.

2100°C, 20 min, 60 MPa

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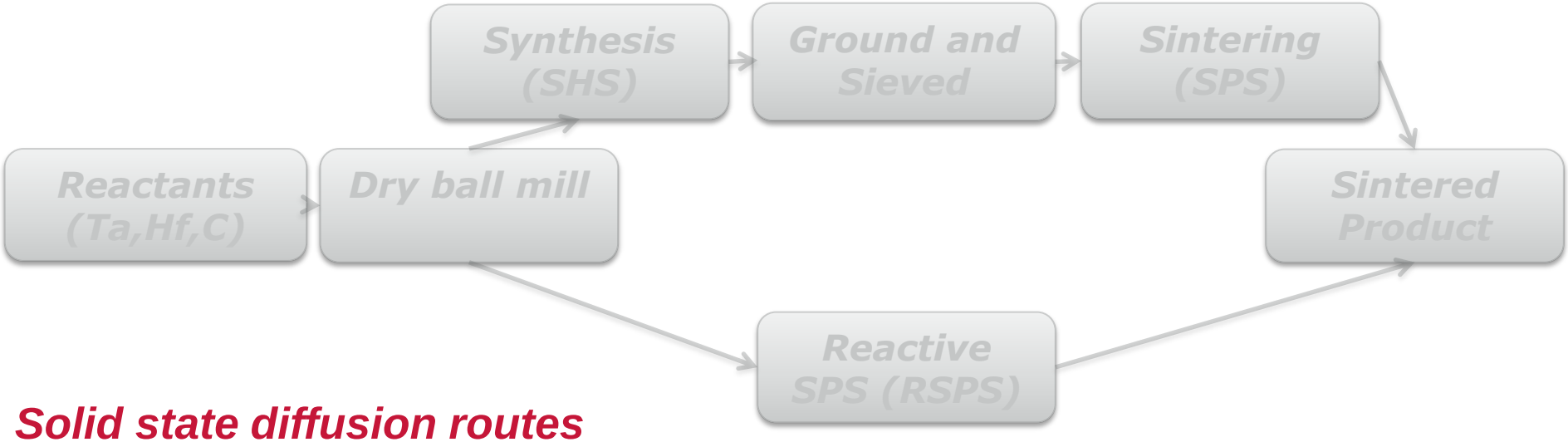
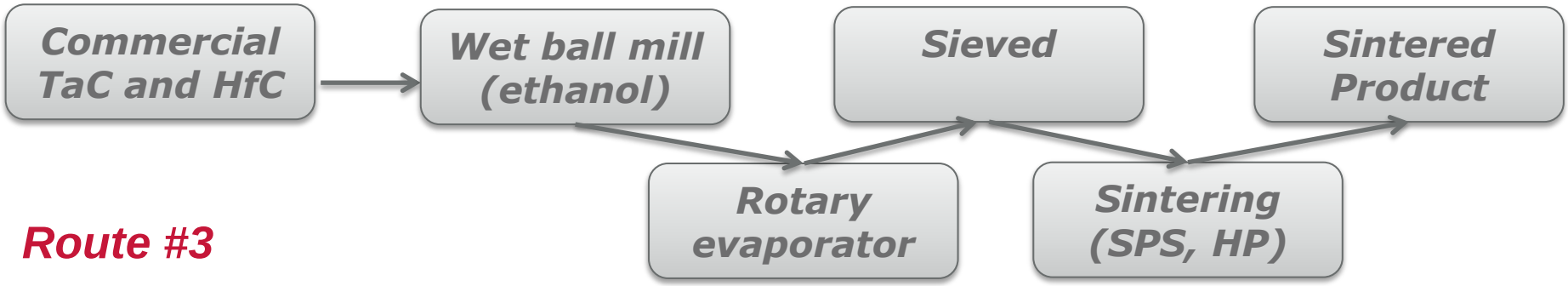
Processing Routes

Reactive routes



Solid state diffusion routes



Route #3

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Characterisation of 4TaC-1HfC fabricated by SPS

- **Commercial powders of $TaC_{0.94}$ (-325 mesh, ABCR) and $HfC_{0.94}$ (-325 mesh, ABCR) used.**
- **4TaC-1HfC composition sintered at different temperatures (2050-2450°C) for 20 min and 30 MPa**
- **Solid solution formation evaluated by XRD, SEM, EDS and TEM.**

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Density and MGS of 4TaC-1HfC after SPS for 20 min and 30 MPa

Sintering temperature (°C)	Bulk density (g/cm^3)	Relative density (%)	Mean grain size MGS (μm)	Pore size (μm)
2050	10.94 ± 0.02	77.7 ± 0.18	-	0.48 ± 0.37
2150	12.01 ± 0.02	85.2 ± 0.17	-	0.56 ± 0.32
2250	13.10 ± 0.02	93.0 ± 0.16	3.2	1.17 ± 0.47
2350	13.28 ± 0.05	94.5 ± 0.38	5.1	1.61 ± 0.88
2450	13.35 ± 0.02	94.8 ± 0.17	6.2	1.79 ± 0.77

Maximum density after SPS ≥ 2350°C.

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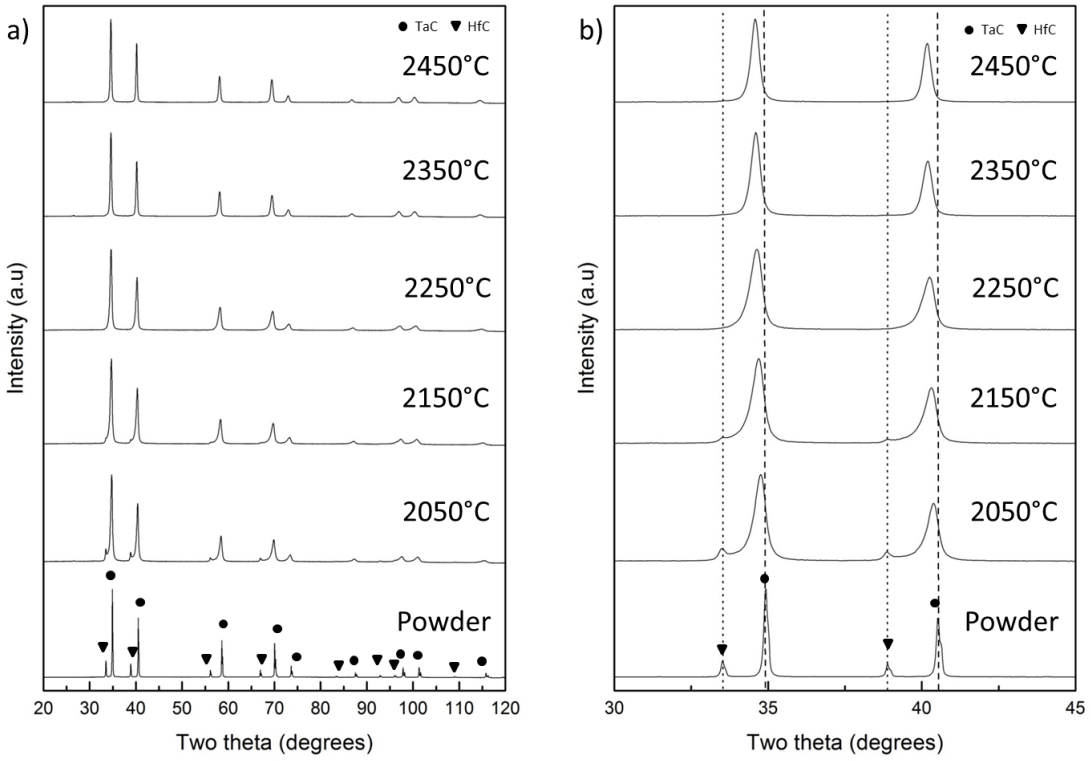
XRD & lattice parameter measurements 4TaC-1HfC

4TaC-1HfC



Sample	Lattice parameter (Å)
Starting TaC (powder)	4.459
2050°C	4.461
2150°C	4.468
2250°C	4.473
2350°C	4.483
2450°C	4.484

Single phase solid solution after sintering ≥ 2350°C.

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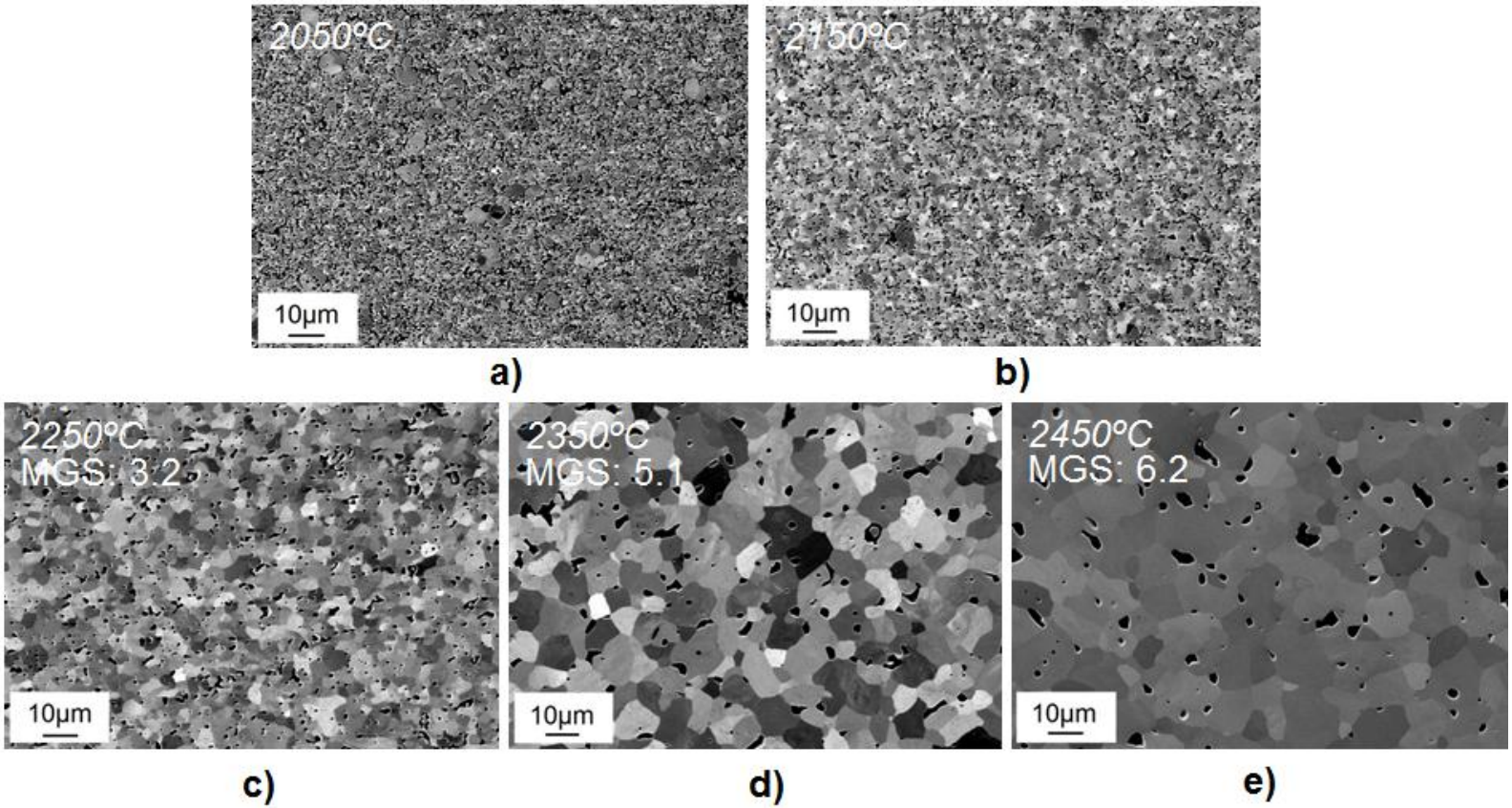
Microstructural evolution of SPS'd 4TaC-1HfC



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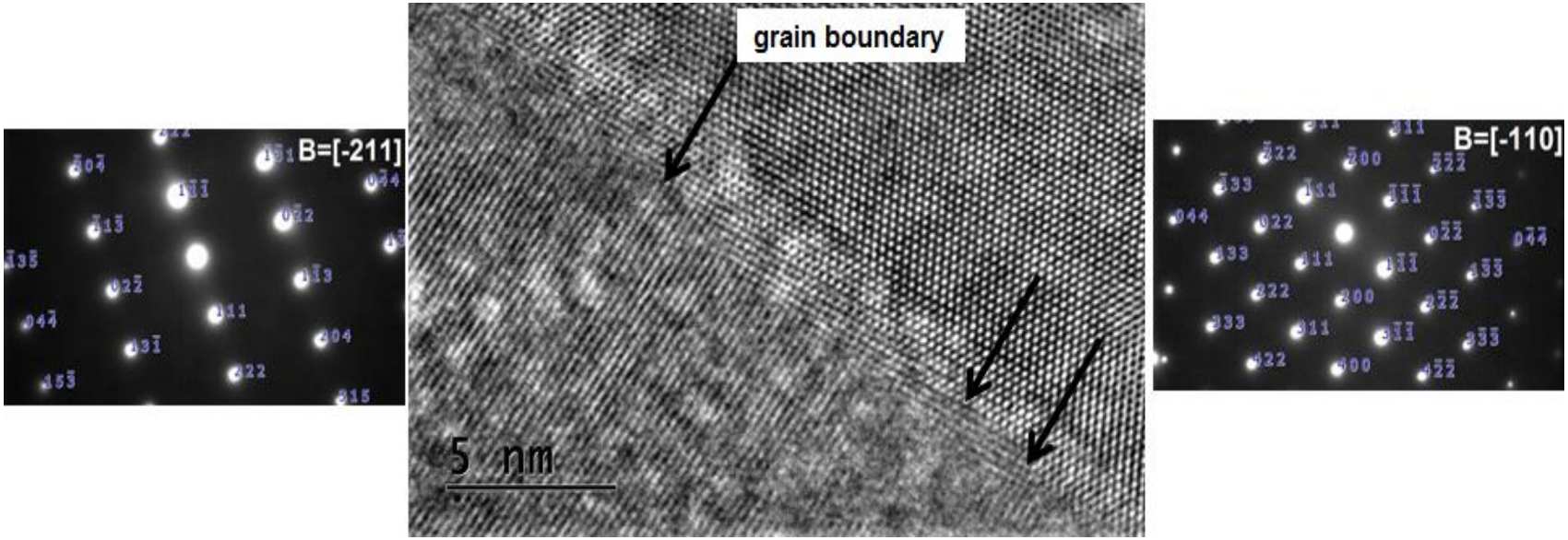
HRTEM of 4TaC-1HfC after SPS

4TaC-1HfC after SPS at 2450°C, 20 min and 30 MPa



Clean grain boundary with no glass suggesting solid state sintering and SAED index as cubic crystals.

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Characterisation of TaC, HfC and TaC-HfC solid solutions

- Commercial powders of $TaC_{0.94}$ (-325 mesh, ABCR) and $HfC_{0.94}$ (-325 mesh, ABCR) used.
- TaC, HfC and TaC-HfC solid solutions (4TaC-1HfC, 1TaC-1HfC and 1TaC-HfC) sintered using a two-step sintering schedule:
  i) 2100°C for 30 min and 55 MPa for high density
  ii) 2350°C for 20 min and 30 MPa for solid solution.
- A high-density single-phase solid solution material was desired.
- Characterisation by XRD, SEM, EDS and TEM.
- Mechanical and thermal properties measured and T_m via laser melting.

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Density, relative density, MGS and pore size after SPS

Sample	Bulk density (g/cm^3)	Relative density (%)	Mean grain size (μm)	Pore size (μm)
TaC	14.25 ± 0.02	98.3 ± 0.14	6.2	0.58 ± 0.13
4TaC-1HfC	13.77 ± 0.02	97.7 ± 0.09	8.5	1.83 ± 0.09
1TaC-1HfC	12.94 ± 0.03	95.7 ± 0.29	4.2	1.35 ± 0.63
1TaC-4HfC	11.31 ± 0.03	87.0 ± 0.26	4.4	1.26 ± 0.32
HfC	10.81 ± 0.01	85.3 ± 0.10	1.8	1.01 ± 0.72

HfC difficult to sinter, small grain size.

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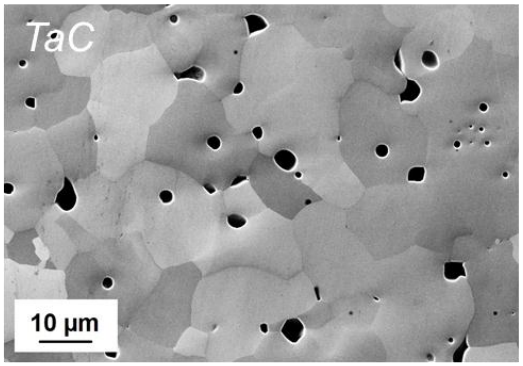
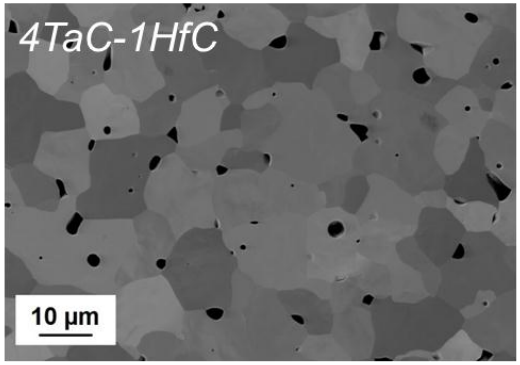
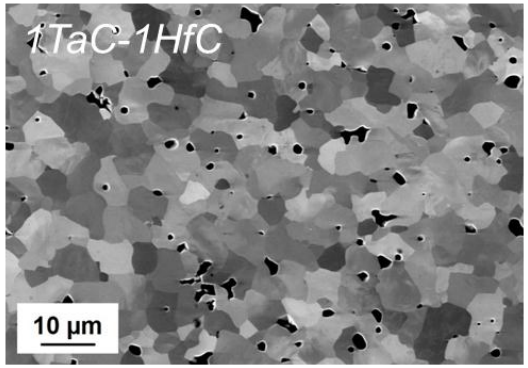
SEM of TaC, HfC and TaC-HfC solid solutions after SPS



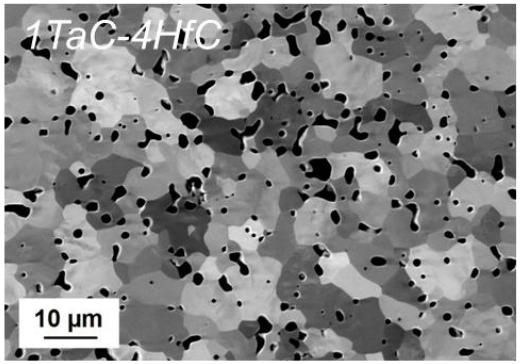
a)



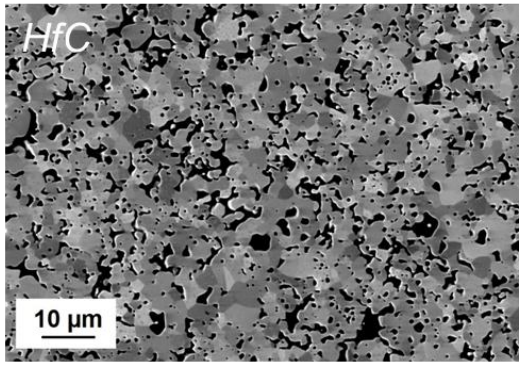
b)



c)



d)



e)

- Grains plus trapped pores.
- Smaller grains with HfC.
- EDS shows even distribution of Hf and Ta in solid solutions.

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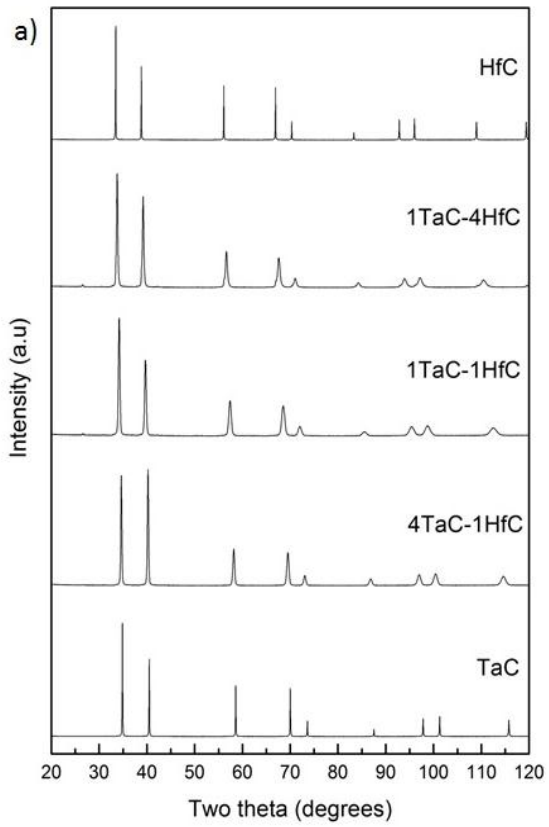
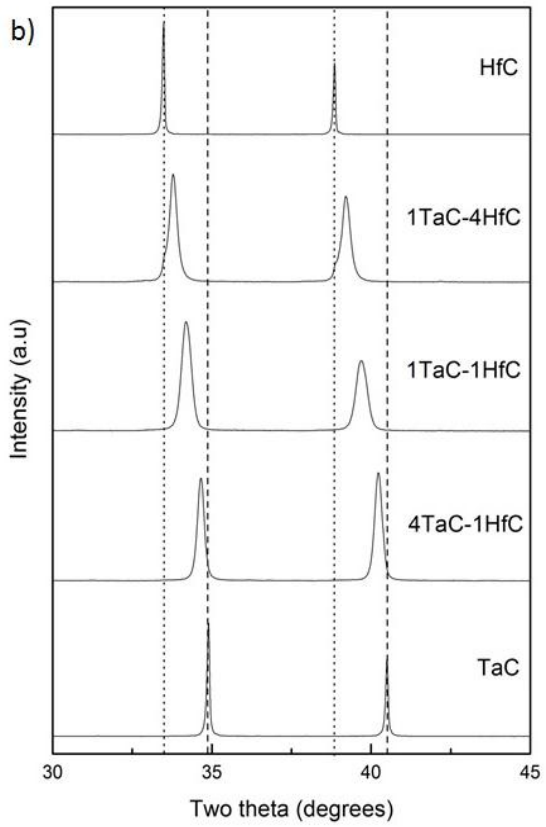
XRD and lattice parameter measurements





Sample	Lattice parameter (Å)
TaC	4.459
4TaC-1HfC	4.484
1TaC-1HfC	4.536
1TaC-4HfC	4.594
HfC	4.636

Lattice parameter follows Vegards law

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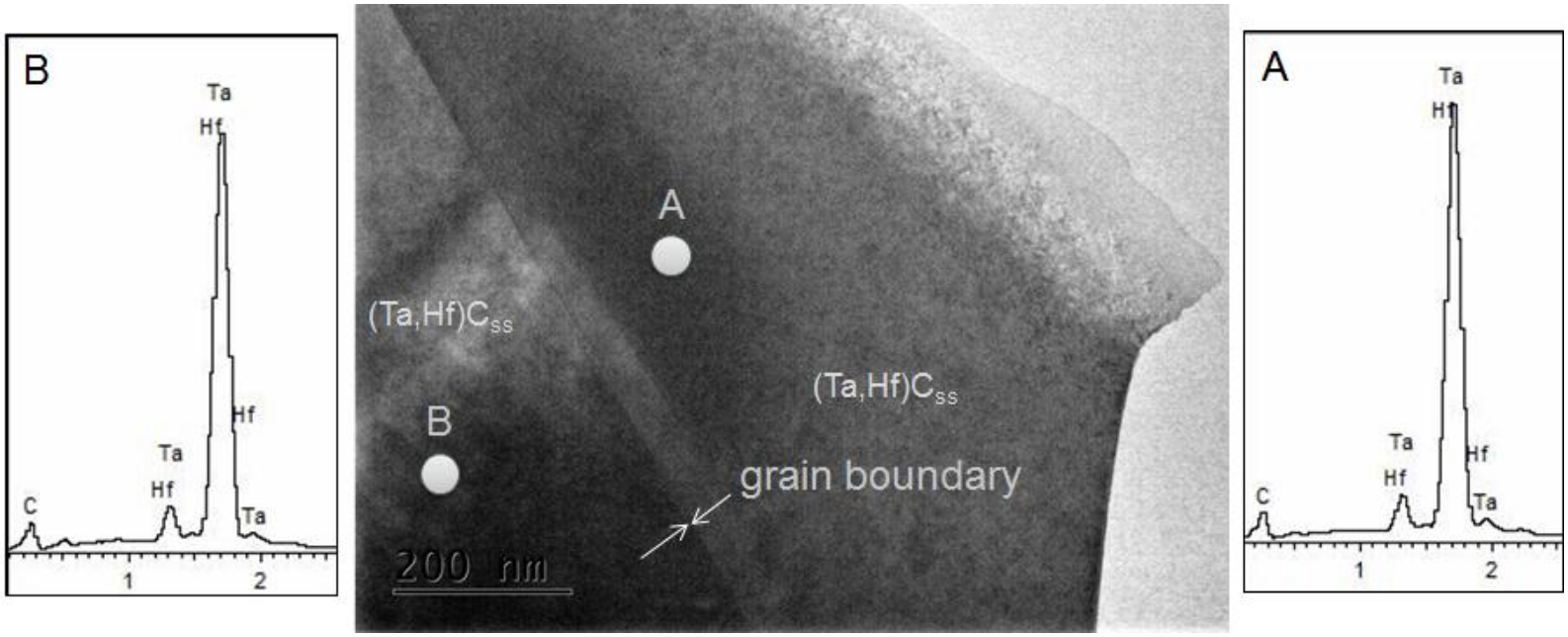
TEM of 4TaC-1HfC after SPS



4TaC-1HfC SPS'd @ 2450°C, 20 min and 30 MPa

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Mechanical properties of TaC, HfC and TaC-HfC solid solutions after SPS

Composition	Vickers hardness (HV1)	Nanohardness (GPa)	Elastic modulus *E* (GPa)	K_{IC} (MPa*$m^{1/2}$)
TaC	13.9 ± 0.7	13.3 ± 0.73	458 ± 6.6	2.72 ± 0.30
4TaC-1HfC	17.1 ± 1.2	19.3 ± 1.33	459 ± 5.8	2.92 ± 0.91
1TaC-1HfC	20.4 ± 2.3	22.1 ± 1.87	549 ± 11.2	2.98 ± 0.77
1TaC-4HfC	15.0 ± 0.5	16.73 ± 3.00	438 ± 17.8	3.43 ± 0.63
HfC	10.2 ± 0.7	10.52 ± 1.04	283 ± 9.6	2.91 ± 0.51

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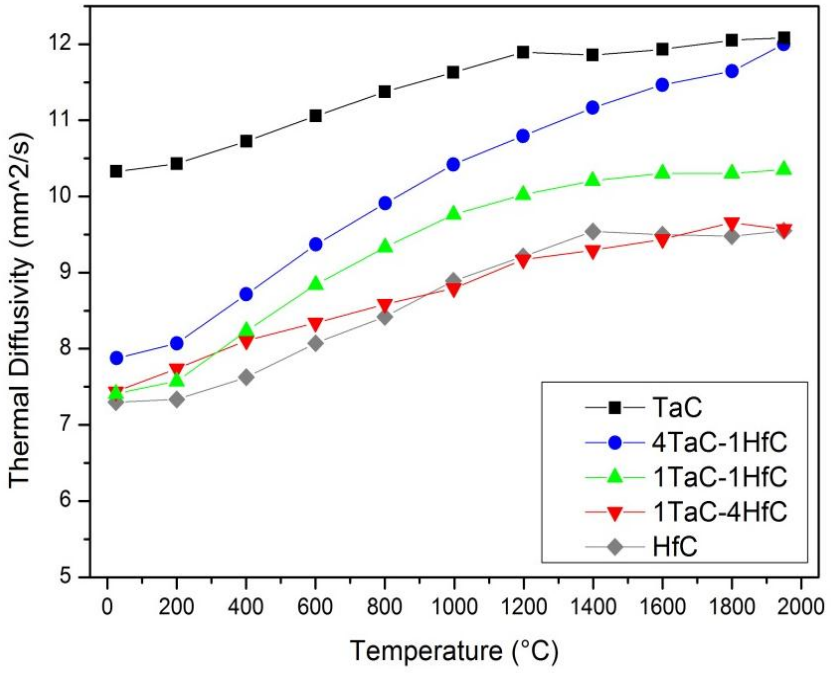
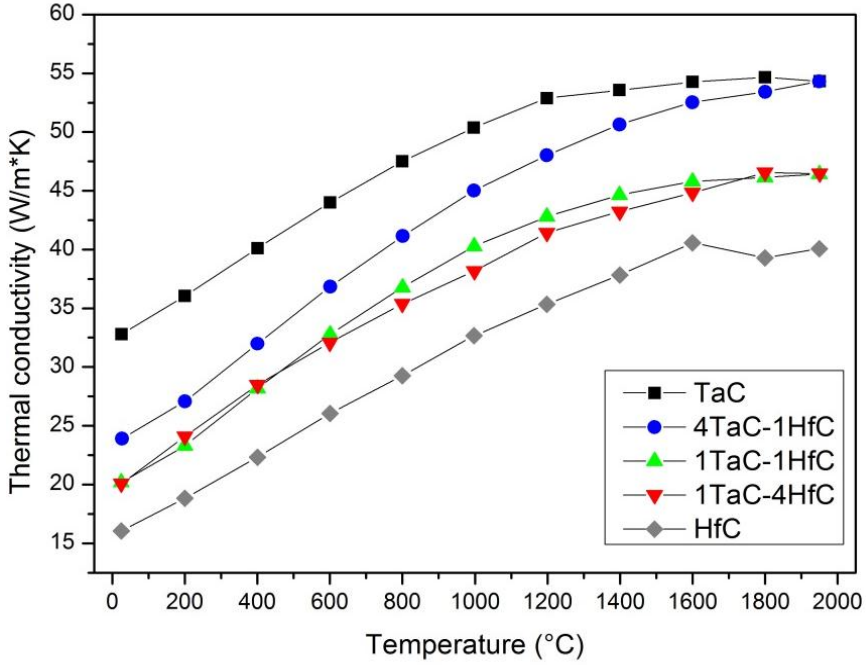
Thermal diffusivity and conductivity





- **Thermal conductivity normalised to 100%TD using Maxwell-Eucken equation to remove effect of porosity.**

Thermal expansion (CTE)

Composition	Coefficient of thermal expansion (CTE) (10^{-6}/K)	Temperature range (°C)
TaC	7.08	25-2000
4TaC-1HfC	7.24	25-2000
1TaC-1HfC	7.41	25-2000
1TaC-4HfC	7.59	25-2000
HfC	7.66	25-2000

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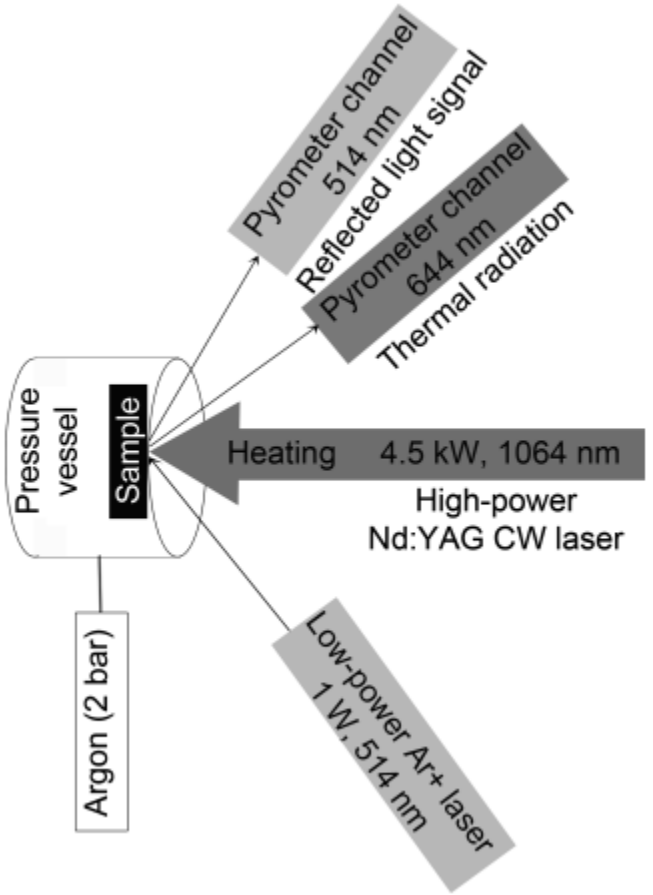
Laser melting of TaC, HfC and TaC-HfC solid solutions

- **Laser melting experiments at ITU (Karlsruhe, Germany).**
- **Samples heated using a 4.5 kW Nd:YAG CW laser.**
- **Surface temperature and intensity of reflected light recorded.**



Schematic of laser-melting system

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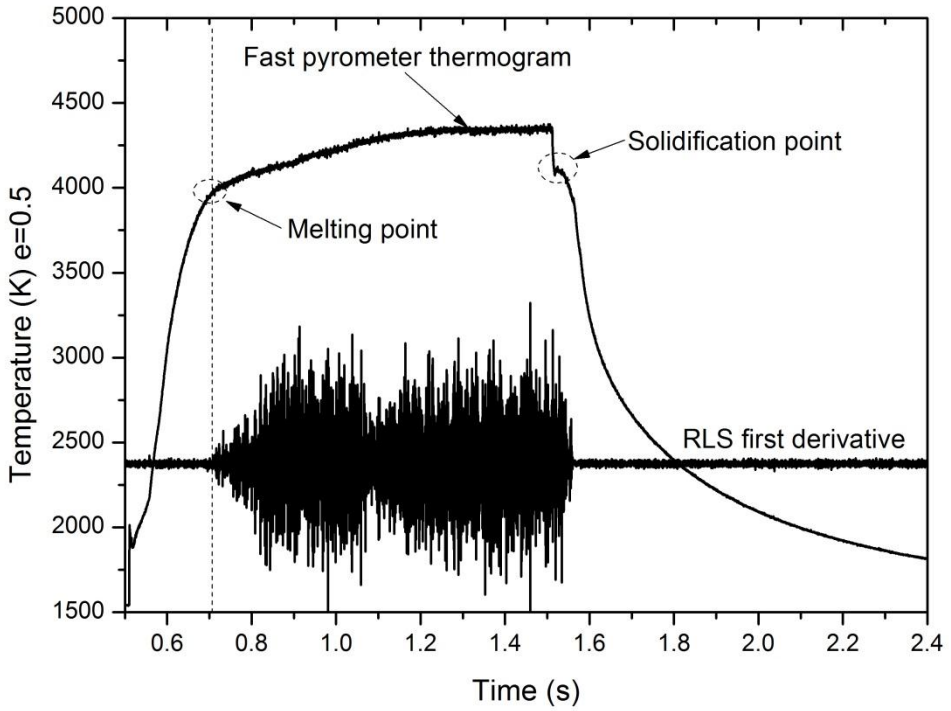
Melting behaviour of HfC



$T_m = 3959^oC$

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Reported melting points and comparison with this work

		Melting temperature T_m (°C)				
Authors	Year	TaC (C)	4TaC-1HfC	1TaC-1HfC	1TaC-4HfC	HfC (C)
Agde and Alterthum	1930	3877	3940	3900	3881	3887
Rudy	1965	3983 (0.88)	3965	3945	3934	3928 (0.94)
Andrievskii et al.	1967	3840 (0.98)	3990	-	-	3750 (0.97)
Gusev et al.	1985	4002	3960	3917	3937	3948
Okamoto	1998	3969 (0.88)				
Okamoto	2001	-	-	-	-	3942 (0.94)
This work	-	3768 (0.94)	3905	3803	3847	3959 (0.94)

- **Highest melting temperatures ever measured with such high accuracy.**

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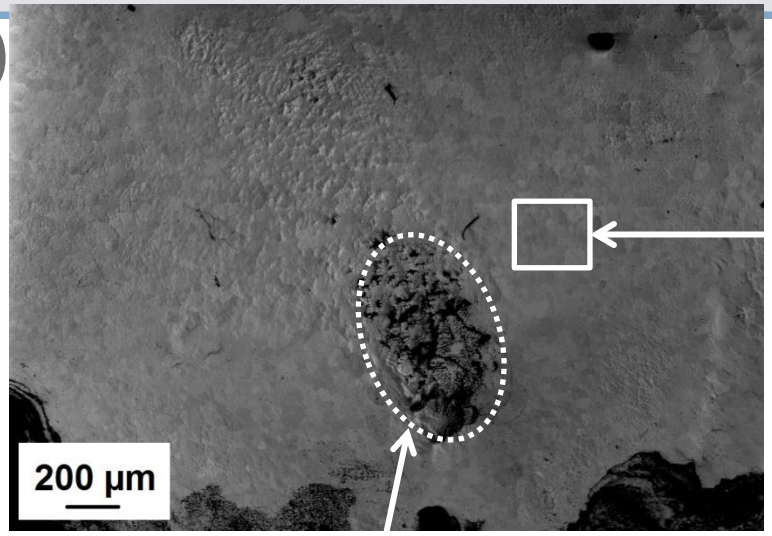
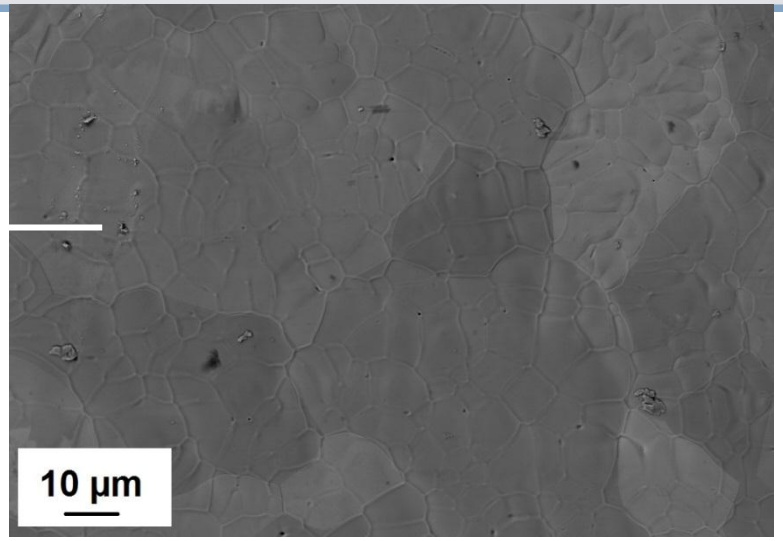
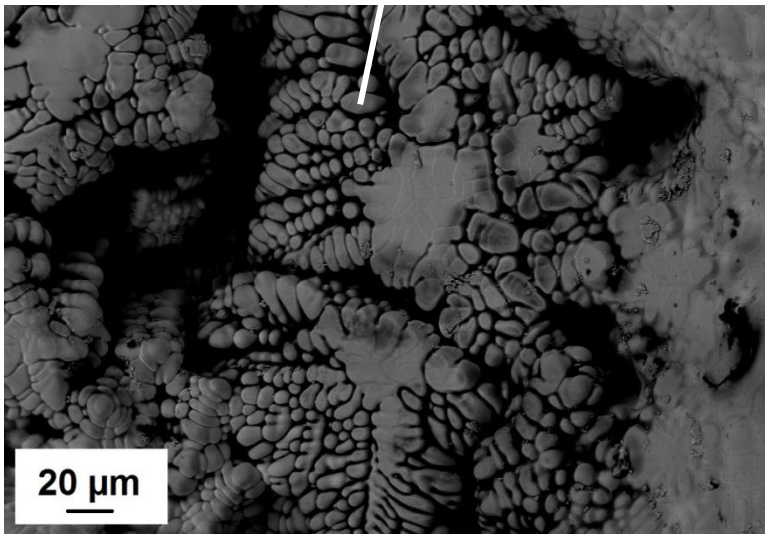
Microstructural characterisation of laser-melted HfC







a) Molten pool of HfC,
b) Grain texture of melted HfC
c) Dendritic microstructure at laser spot centre.

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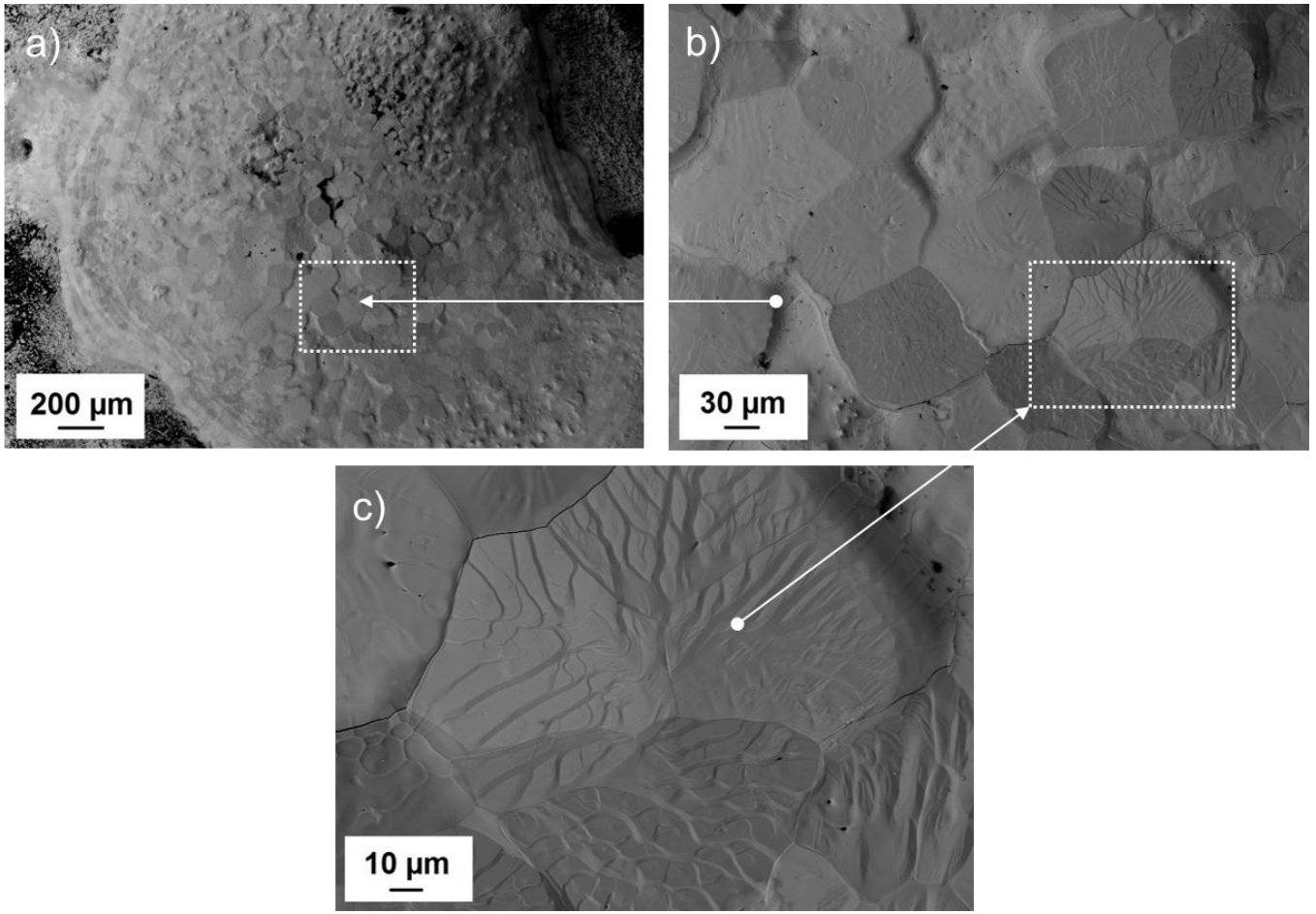
SEM analysis of laser melted TaC



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TEM of a FIB section of laser melted TaC

TEM analysis shows only TaC_{1-x} grains and SAED confirms only cubic crystals on TaC after laser melting.

Conclusions

- **Examined a range of processing routes and demonstrated it is possible to make (Hf,Ta)C solid solutions from commercial powders via SPS.**
- **Basic thermal and mechanical properties measured and shown largely to be suitable for UHTC applications.**
- **Measured ultra high melting temperatures with high degree of accuracy.**

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Acknowledgements

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Centre for Advanced Structural Ceramics Imperial College London

EPSRC Material Systems for Extreme Environments programme grant (EP/K008749/1, XMat)