Spring 5-14-2012

Sintering and densification of UHTCs

Diletta Sciti
Institute of Science and Technology for Ceramics

Laura Silvestroni
Institute of Science and Technology for Ceramics

Stefano Guicciardi
Institute of Science and Technology for Ceramics

Frederic Monteverde
Institute of Science and Technology for Ceramics

Sintering and densification of UHTCs

Diletta Sciti, Laura Silvestroni, Stefano Guicciardi, Frèdèric Monteverde

Institute of Science and Technology for
Ceramics, Via Granarolo 64,
I-48018 Faenza, ITALY.

ECI

istec

Aknowledgements

- AFOSR: Contract FA8655-12-3004
- ISTEC Staff: A. Bellosi, D. Dalle Fabbriche, C. Melandri, L. Pienti, G. Celotti
- M. Nygren, Arrhenius Lab, Univ. Stockholm.

Outline

- Introduction
- Densification of Borides
  - Effect of additive on HT Strength
- Present issues: Fiber-reinforced composites
  - Fiber evolution during densification
  - Mechanical properties
- Conclusions
- Densification of Carbides
- Advantages of SPS

Introduction

Borides and carbides are difficult to sinter…

Strategies:

- Proper selection of sintering aids
- Pressure-assisted densification techniques (HP, SPS, RHP..)
- Processing of starting powders (milling, SHS…)

Purpose:

- Full density (with low sintering temperatures and short processing time)
- Fine microstructure for RT properties
- **Maintain properties at high temperature**

Focus on sintering aid: affects the materials properties especially at high temperature

Additives and temperatures

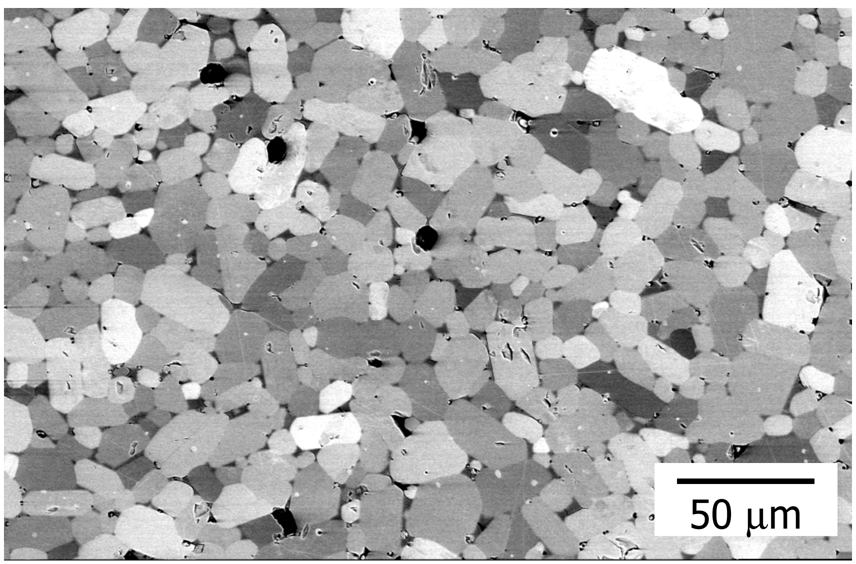
	ZrB_2	HfB_2
$ZrSi_2$(<10%)	HP 1550°C	HP 1600°C
Si_3N_4 (5%)	HP 1650-1700°C, SPS 1500°C, PLS 2150°C	HP 1800°C
$MoSi_2$ (5-15%)	HP 1700-1750°C, SPS1600°C PLS 1850°C	HP 1900°C, SPS 1750°C, PLS 1950°C
$TaSi_2$ (5-15%)	HP 1850°C	HP 1900°C, SPS 1750
Ni (2-3%)	HP 1850°C	HP 1750°C
AlN (5%)	HP 1850°C	-
Oxides (Al_2O_3+Y_2O_3)	HP 1900°C	-
C, B, B_4C ,WC, SiC	HP1900-2000°C PLS	HP 1900-2000°C

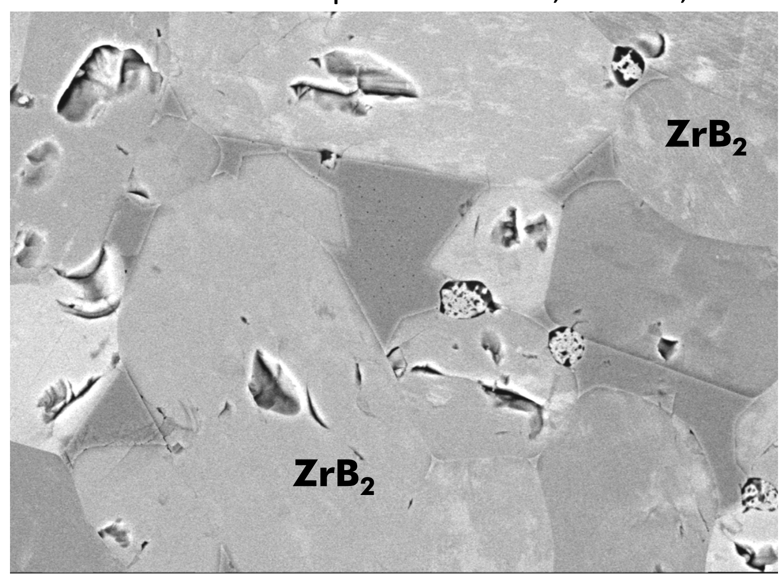
ZrB_2/HfB_2 + metals

In the past: Fe, Cr, Ti.. additions
Densification by liquid phase.

More recently: Ni additions allow ZrB_2 full density at 1850°C.
Drawback: large mean grain size (20 µm), low melting phases in the system
HfB_2 only reached 93% at 1750°C , grain coarsening

Secondary phases: Ni_2B
G. b. phases: Zr-B-O, Zr-Ni-O, Zr-O

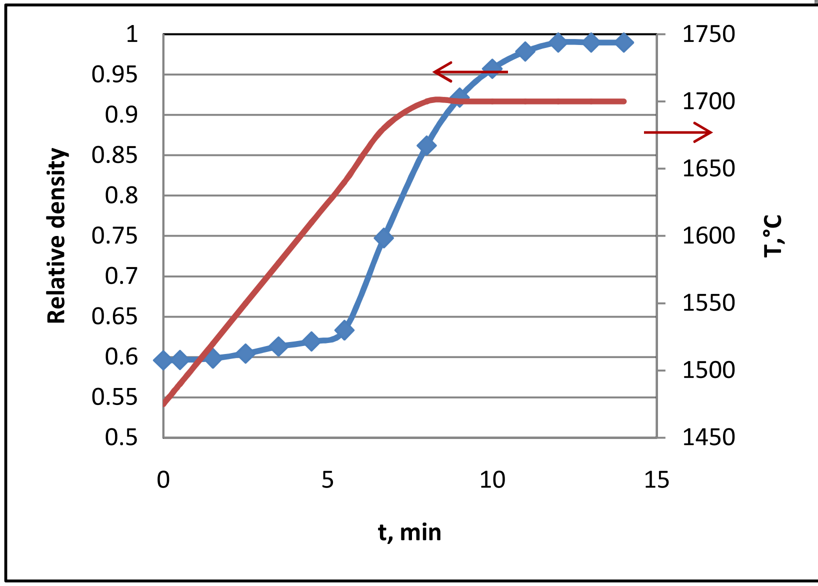


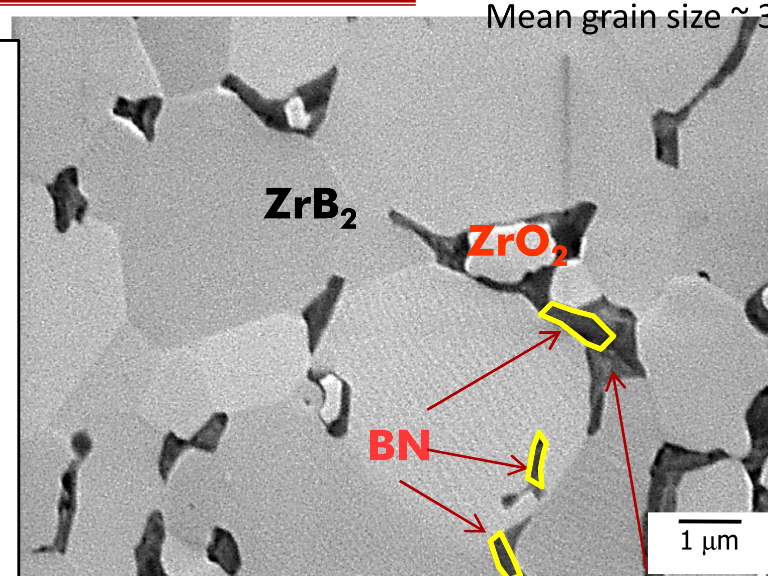


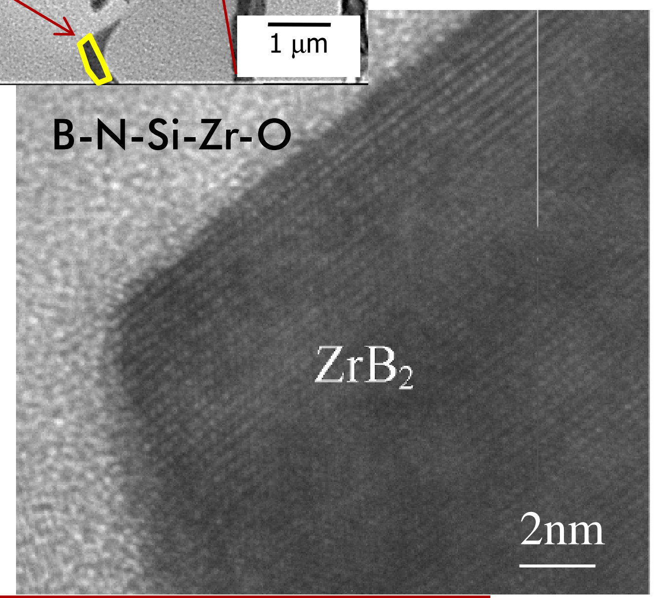
Additives: Nitrides

Borides + 1-5 % Si_3N_4

Nearly Full density by HP at 1700°C/1800°C, for ZrB2/HfB2
Mean grain size ~ 3 µm







Liquid phase formation: $Si_3N_4 + B_2O_3 \rightarrow$ liquid Si-O-B-N

Liquid phase sintering: rearrangement + coarsening

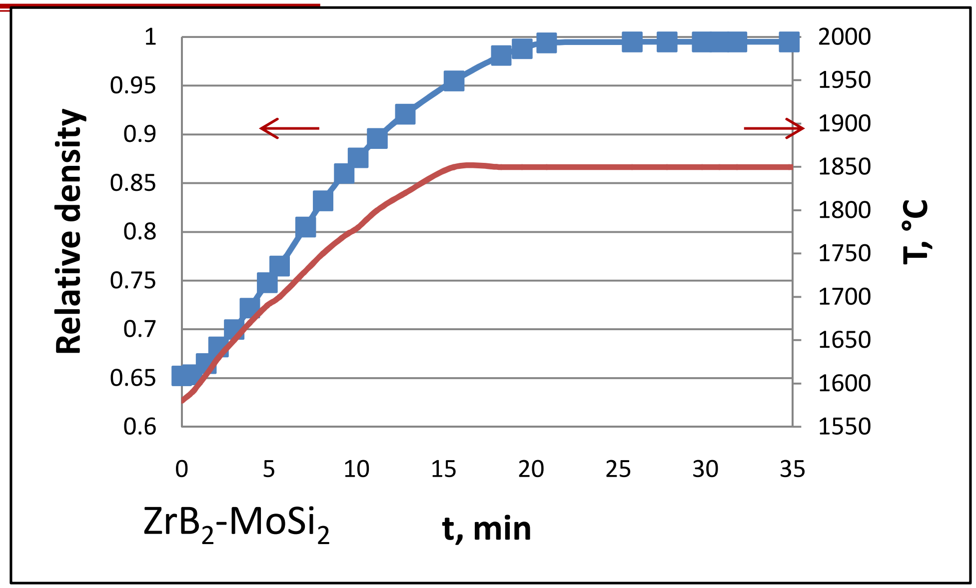
During cooling: precipitation of BN from the liquidus

Remainder of liquid originates the Zr/Hf-Si-B grain boundary phase

(Similar mechanisms for AlN additions: Al2O3 + BN+ liquid)

Borides with silicides

- Effective with many borides
- High melting point>2000°C (except $ZrSi_2$)
- Protective phases for oxidation
- PS possible with $MoSi_2$ (10%)

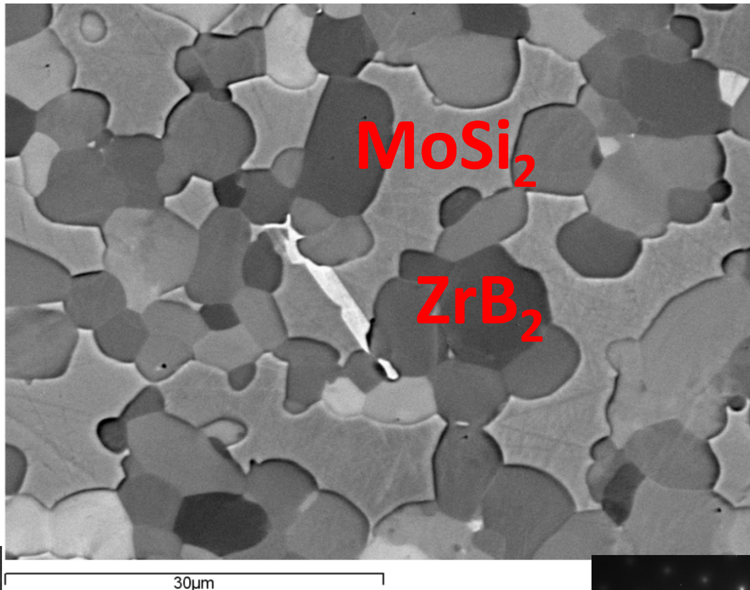


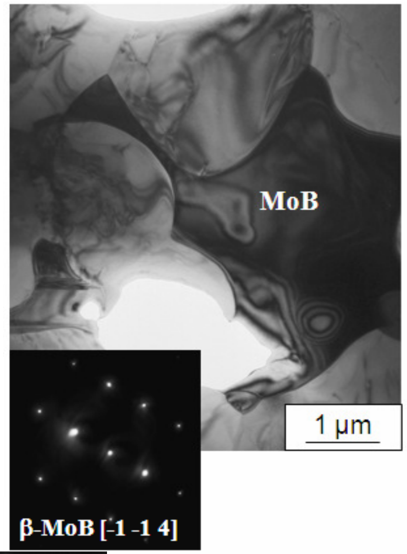
HP Temperature (°C)	ZrB_2	HfB_2	TaB_2
$ZrSi_2$	1550	1550 (SPS)	-
$TaSi_2$	1870	1900	-
$MoSi_2$	1750/PS:1850	1900/PS:1950	1680
WSi_2	1930	-	-

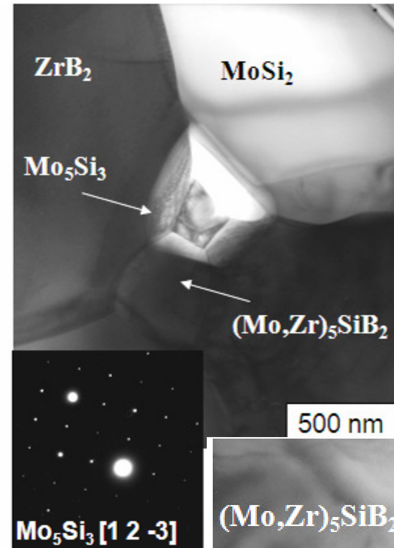
Additives: silicides

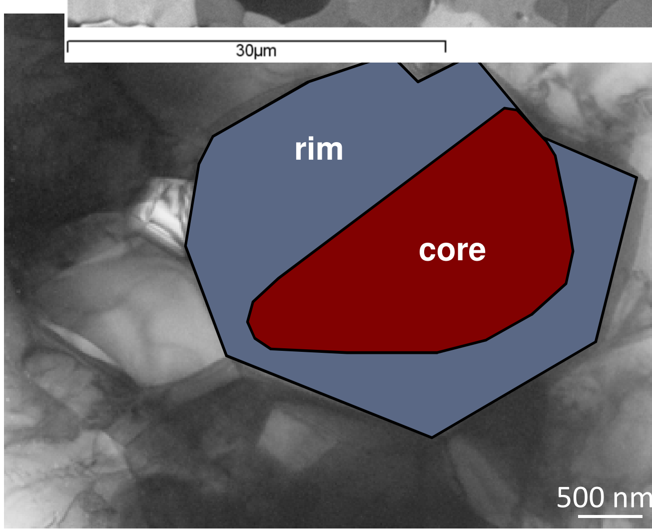
ZrB_2 + (1-15)% $MoSi_2$

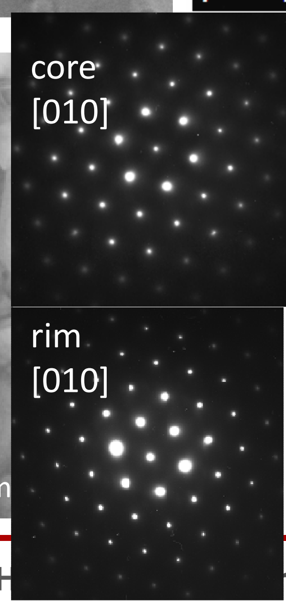
Full density at 1750°C, 10 min
Mean grain size ~ 2.5 µm
Secondary phases: MoB, Mo_5Si_3, $(Mo,Zr)_5SiB_2$



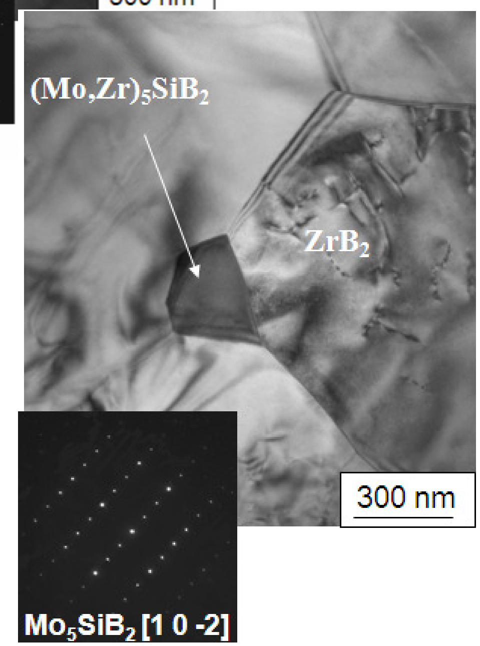








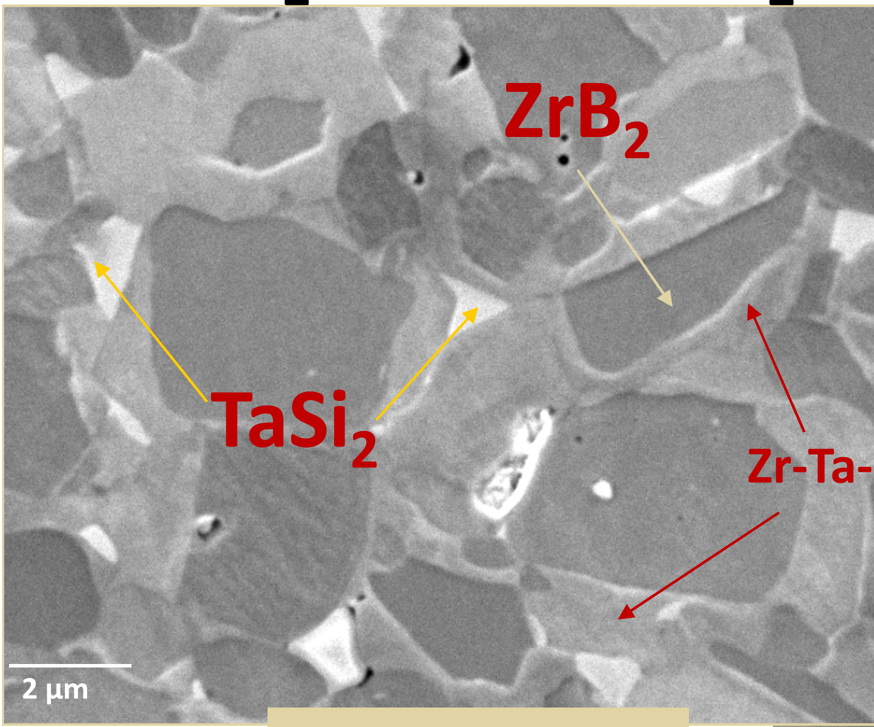
- Crystalline phases
- Clean grain boundaries
- Core: Zr, B
- Rim: Zr, Mo, O, B
- Epitaxy between core and rim



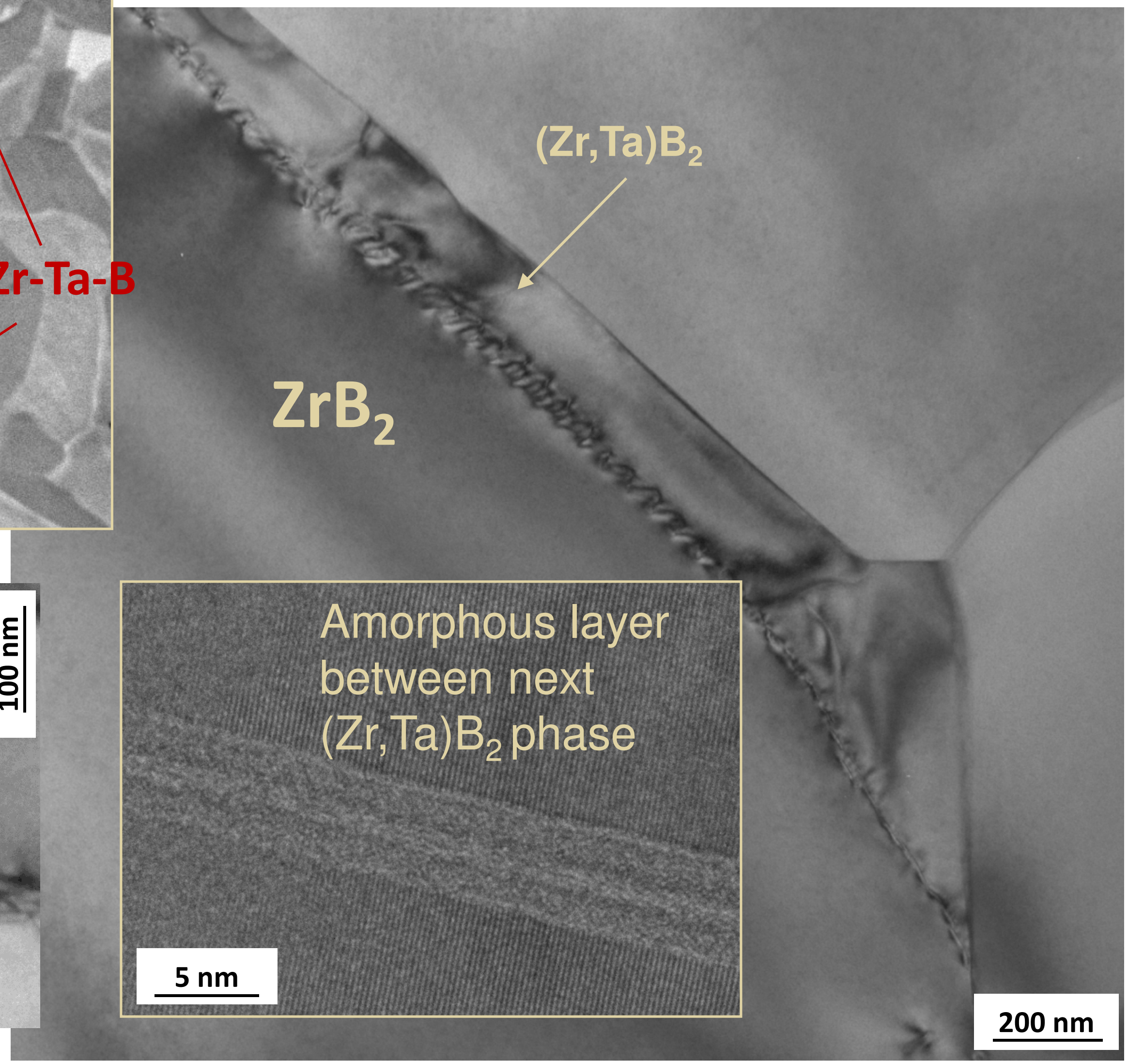
Additives: silicides

ZrB_2-(3-15)% $TaSi_2$

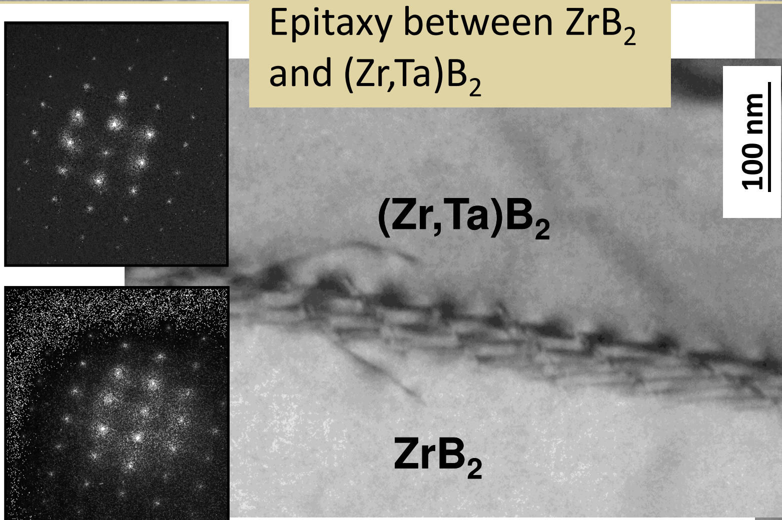
Full density at 1850°C, 10 min
Mean grain size ~ 2 µm
Secondary phases: ZrO_2, Zr-Ta-C, SiC, SiO_2



Partial decomposition of $TaSi_2$ and formation of solid solution $(Zr,Ta)B_2$

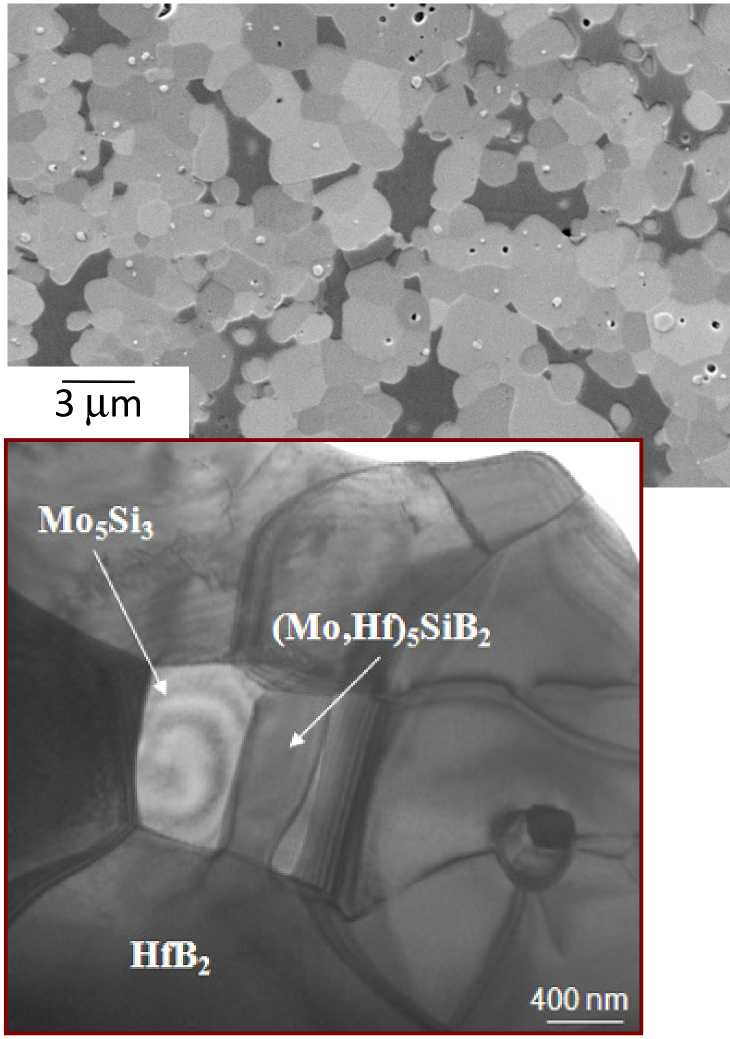


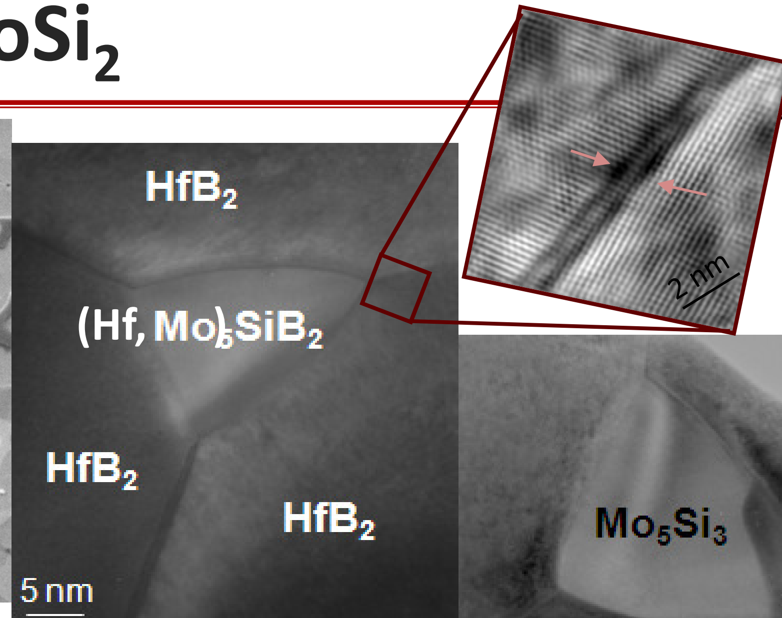
Epitaxy between ZrB_2 and $(Zr,Ta)B_2$



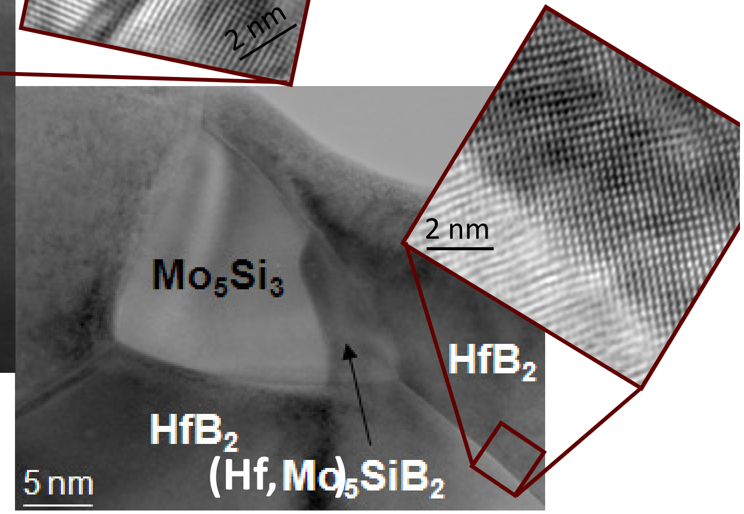
Additives: silicides

HfB_2 + (1-15)% $MoSi_2$





Full density at 1900°C
Mean grain size ~ 1.0 µm
Secondary phases:
HfO_2, HfC, Mo_5Si_3, (Mo,Hf)$_5SiB_2$

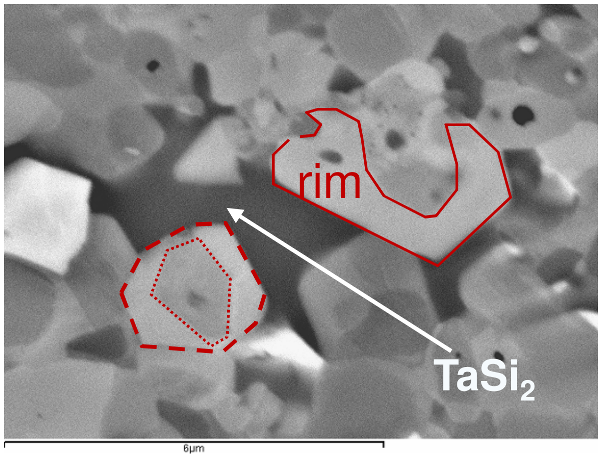


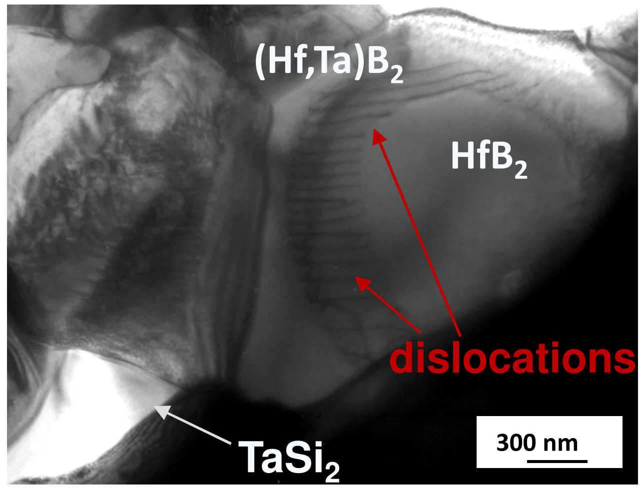
- Triple points: Mo_5Si_3, (Mo,Hf)$_5SiB_2$
- Wetting of HfB_2 by (Mo,Hf)$_5SiB_2$ liquid
- Not al the HfB_2/HfB_2 interfaces are wet
- Core – shell difficult to observe

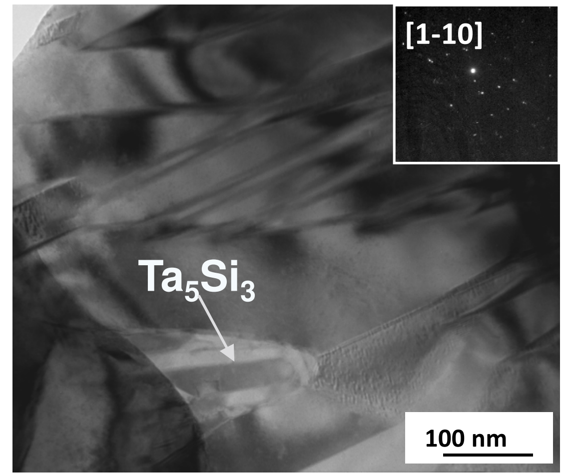
Additives: silicides

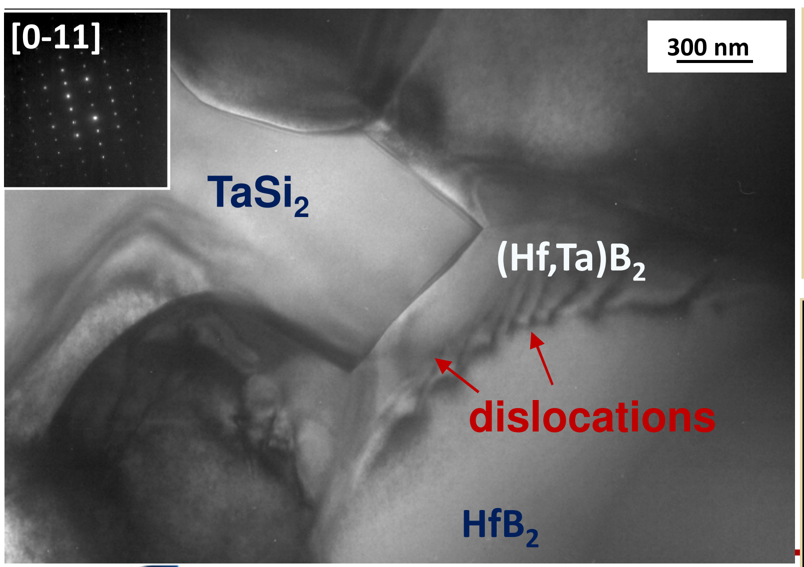
HfB_2 + (3-15)% $TaSi_2$

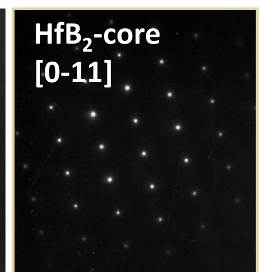
Full density at 1900°C, 10 min
Mean grain size ~ 1 µm
Secondary phases: HfO_2, TaSiB

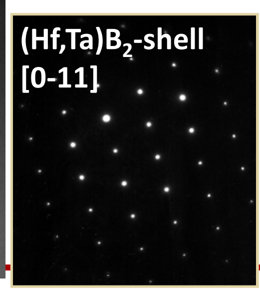


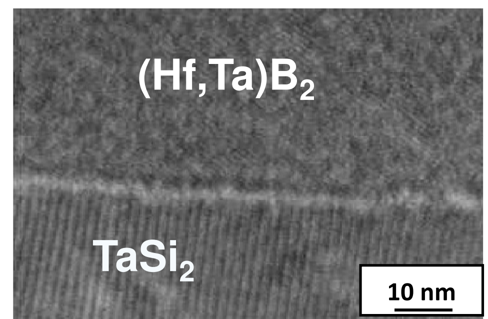








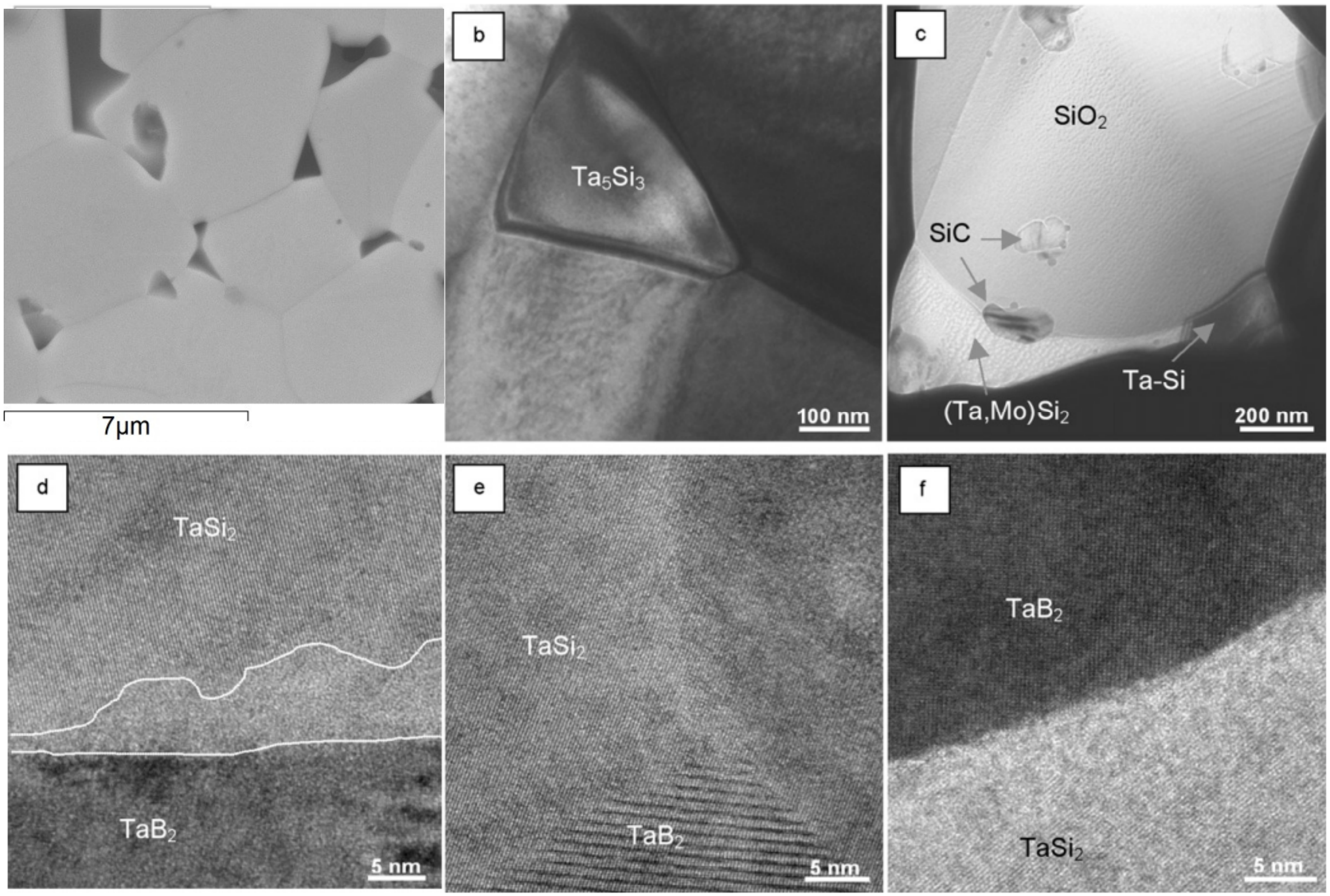




- Core: HfB_2
- Rim: $(Hf,Ta)B_2$
- Triple junctions: $(Hf,Ta)Si_2$, $(Hf,Ta)_5Si_3$
- Wetted grain boundaries
- Partial decomposition of $TaSi_2$
- Epitaxy between core and rim

TaB_2 + 10% $MoSi_2$

Full density at 1680°C
Mean grain size ~ 3.5 µm



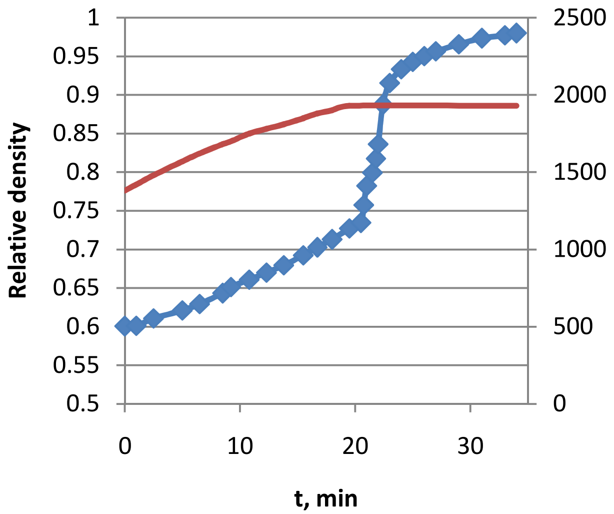
- ❖ Triple points: Ta_5Si_3, (Ta, Mo)Si_2
- ❖ Wetting of TaB_2 by (Ta-Si-O-B) liquid
- ❖ SomeTaB_2/$TaSi_2$ interfaces are wet
- ❖ Core – shell difficult to observe

Densification mechanisms

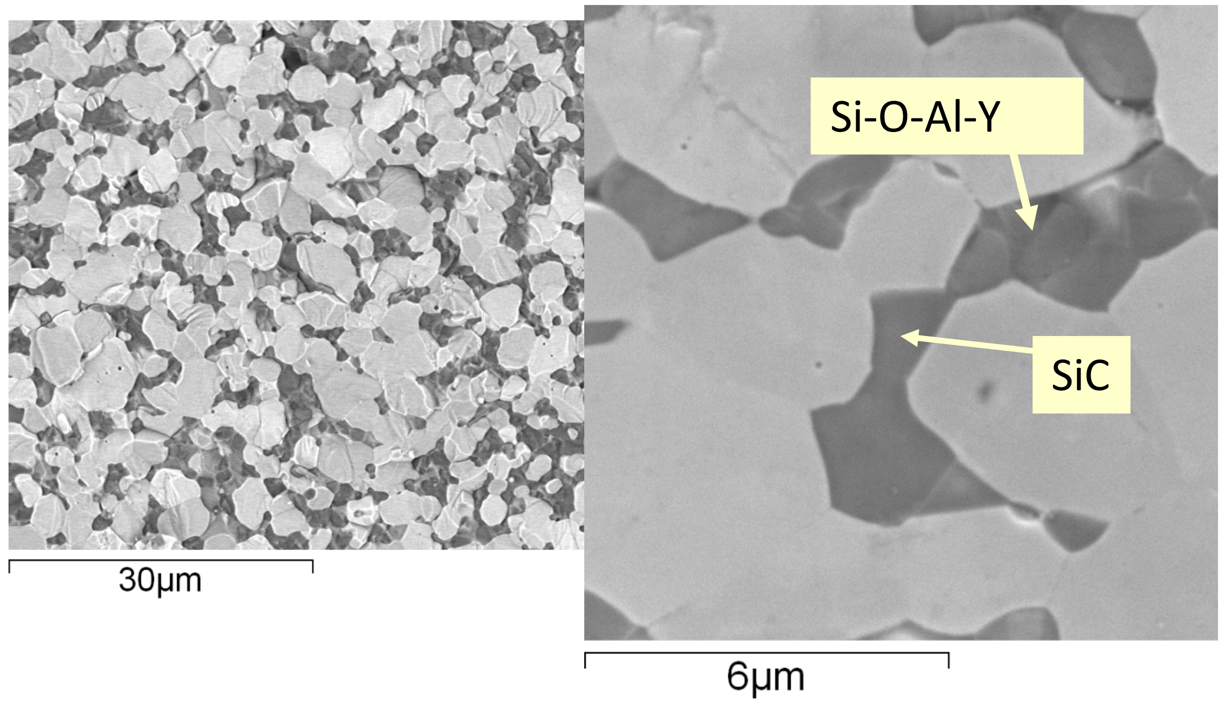
- **Low dihedral angles** in final ceramics indicate that $MoSi_2$/$TaSi_2$ have a high affinity for diboride ceramics
- During heating, **transient liquid phases** form due to reaction between silicide and surface oxide impurities on the diboride particles.

  $Mo/TaSi_2 + B_2O_3 \rightarrow$ Mo/Ta-Si-B-O liquid
- Densification assisted by **liquid phase:**
  - Borides: wetting Ta/Mo-Si-B-O liquid;
  - ZrB_2, HfB_2 are partially soluble in Ta/Mo-Si-B liquid phases.
- Solution - reprecipitation: formation of **core-shell** diboride grains. $(M,Mo/Ta)B_2$ shells grow **epitaxially** on pure MB_2 cores during densification as the transient liquid phase solidifies.
- During cooling the liquid phase solidifies, resulting in formation of and Mo/TaB, Mo/Ta_5SiB_2 crystalline phases.
- Few residual integranular films, can be removed calibrating the sintering cycle

ZrB_2-SiC + 5vol%(Y_2O_3+Al_2O_3)



HP 1900℃



- During heating, **liquid phase** form due to eutectic between Al_2O_3-Y_2O_3 (1780°C) and silica
- Promotes sintering for ZrB_2 and SiC
- Classical solution-reprecipitation of SiC – SiC grain growth

Solid state sintering

- Additions of C, WC to pure ZrB_2, HP 1900°C (UMR)
- Additions of WC to ZrB_2-SiC, HP 2000°C (SIC-CAS)
- Carbides: cleaning of the boride surface from residual oxides

$$ZrO_2 + B_2O_3 + C \rightarrow ZrB_2 + CO(g)$$

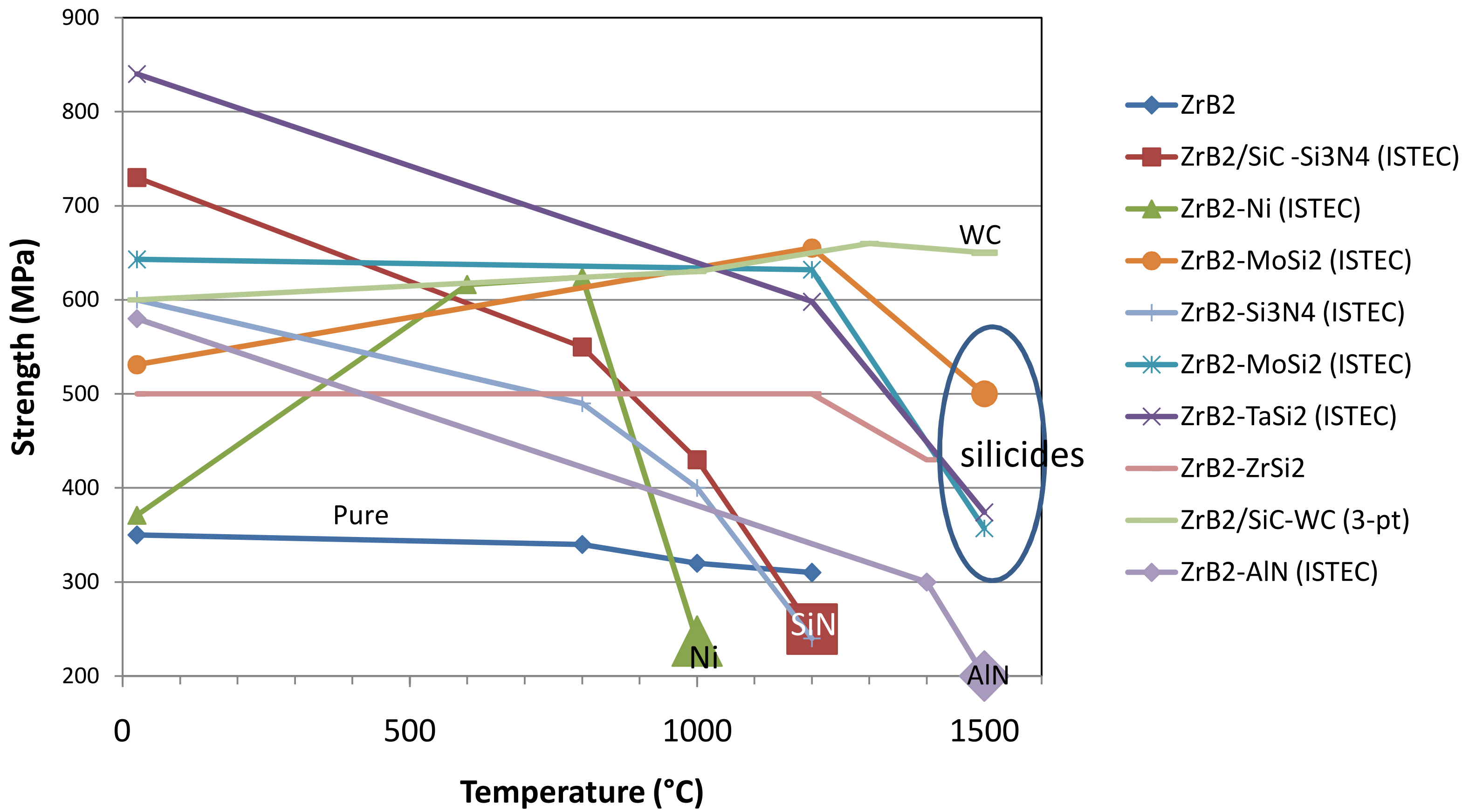
$$ZrO_2 + C \rightarrow ZrC + CO(g)$$

$$3\,WC + ZrO_2 \rightarrow ZrC + 3W + 2CO(g)$$

- Clean grain boundaries by TEM

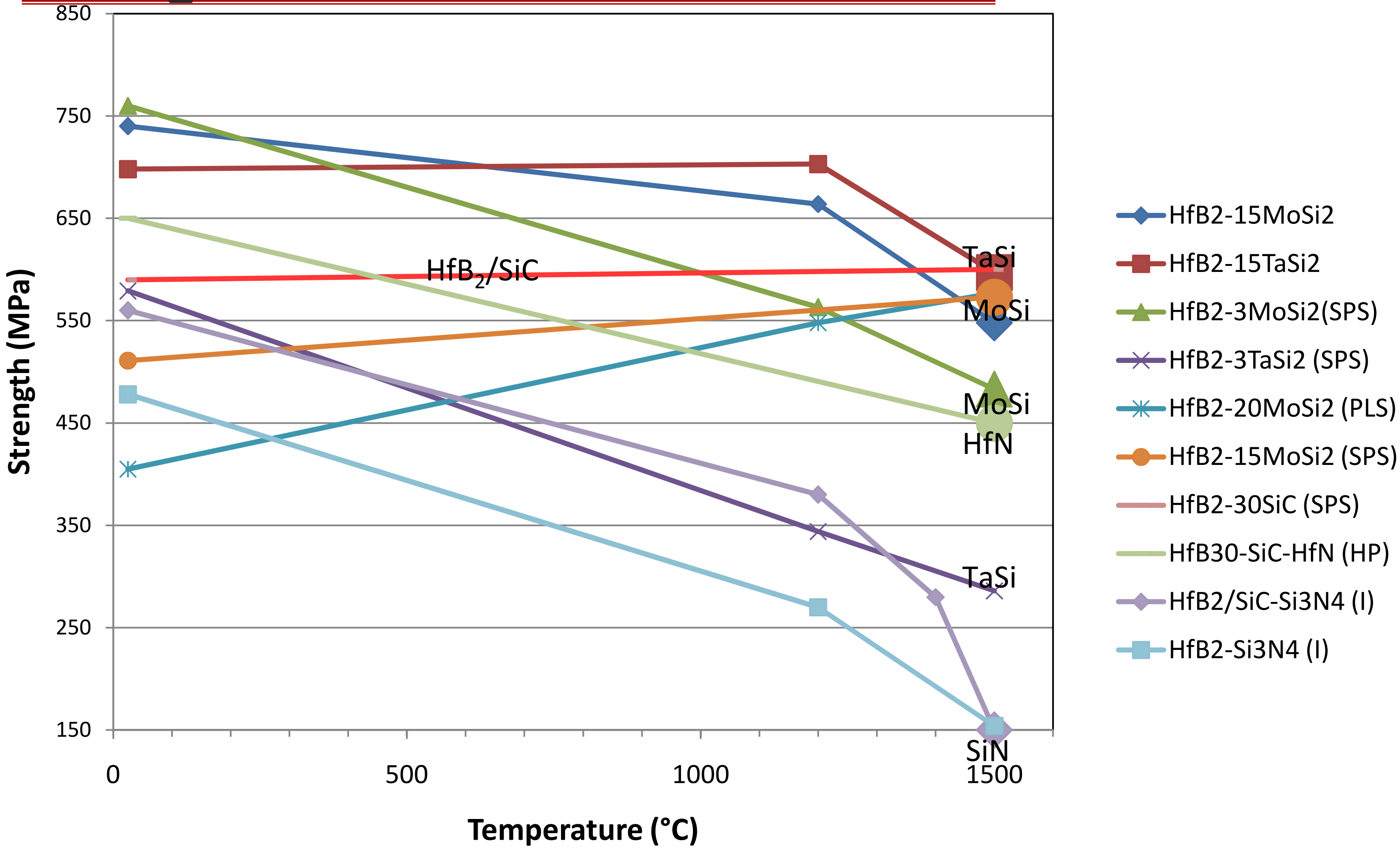
M. J. Thompson et al., Elevated temperature thermal properties of ZrB_2 with carbon additions, JACS, 95, 1107 (2012) , J. Zou, Strong ZrB_2-SiC-WC Ceramic at 1600°C, JACS, 95, 874 (2012)

ZrB_2 Strength in air



Nitrides, Metals: strength degradation at high temperature
Silicides: $MoSi_2$ ok > $TaSi_2$ > $ZrSi_2$
Carbides: WC ok

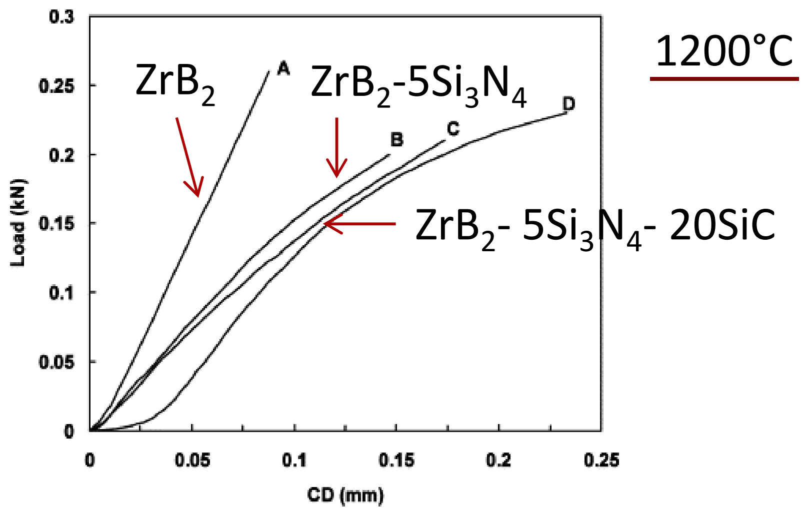
HfB_2 Strength in air

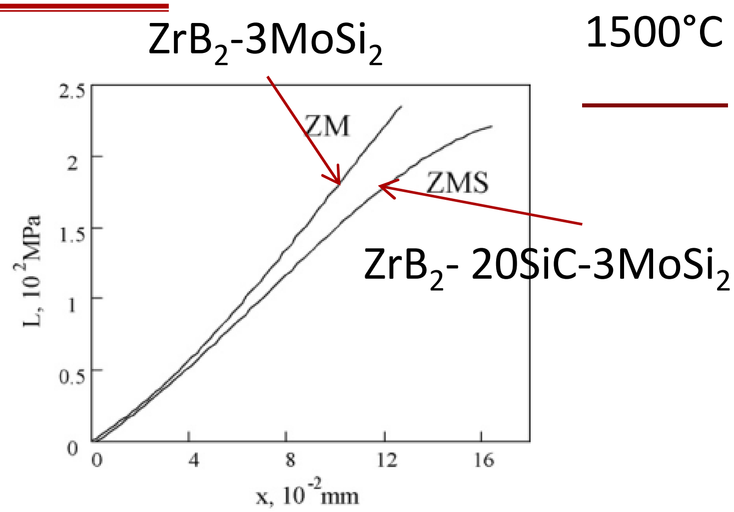


Nitrides: strength degradation at high temperature

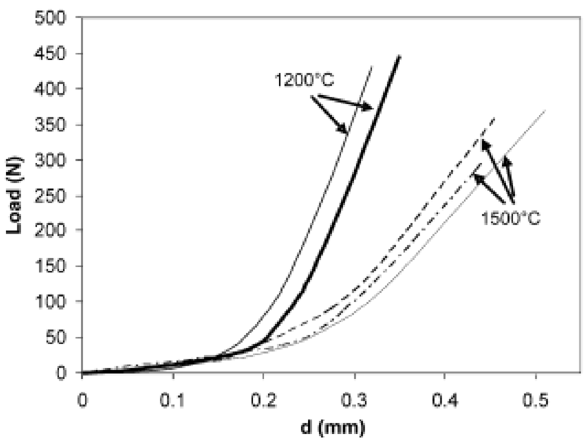
Silicides: $MoSi_2$ ok

Load-displacement curves

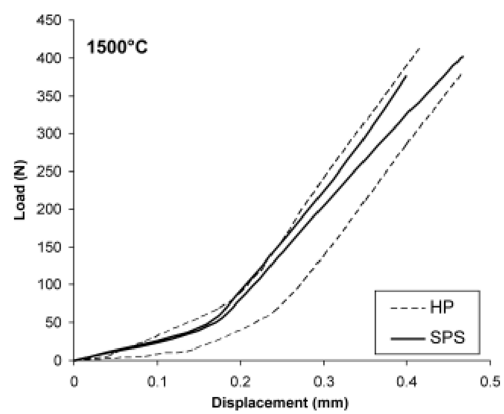




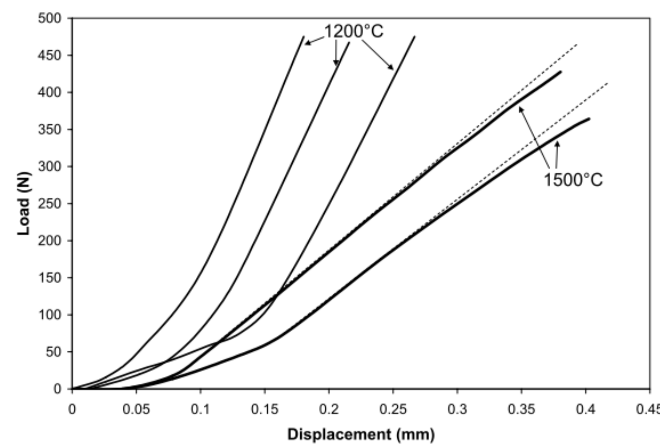
ZrB$_2$-MoSi$_2$, PS



HfB$_2$-MoSi$_2$, HP/SPS



HfB$_2$-TaSi$_2$, HP



Summary of densification mechanisms

- Liquid phase sintering (metals, nitrides, oxides)

  -advantages: fast material transfer (low sintering temperature)

  -drawback: residual amorphous phases

- Transient liquid phases sintering (silicides) + solid solution formation

  -advantages: few or no residual amorphous phases;

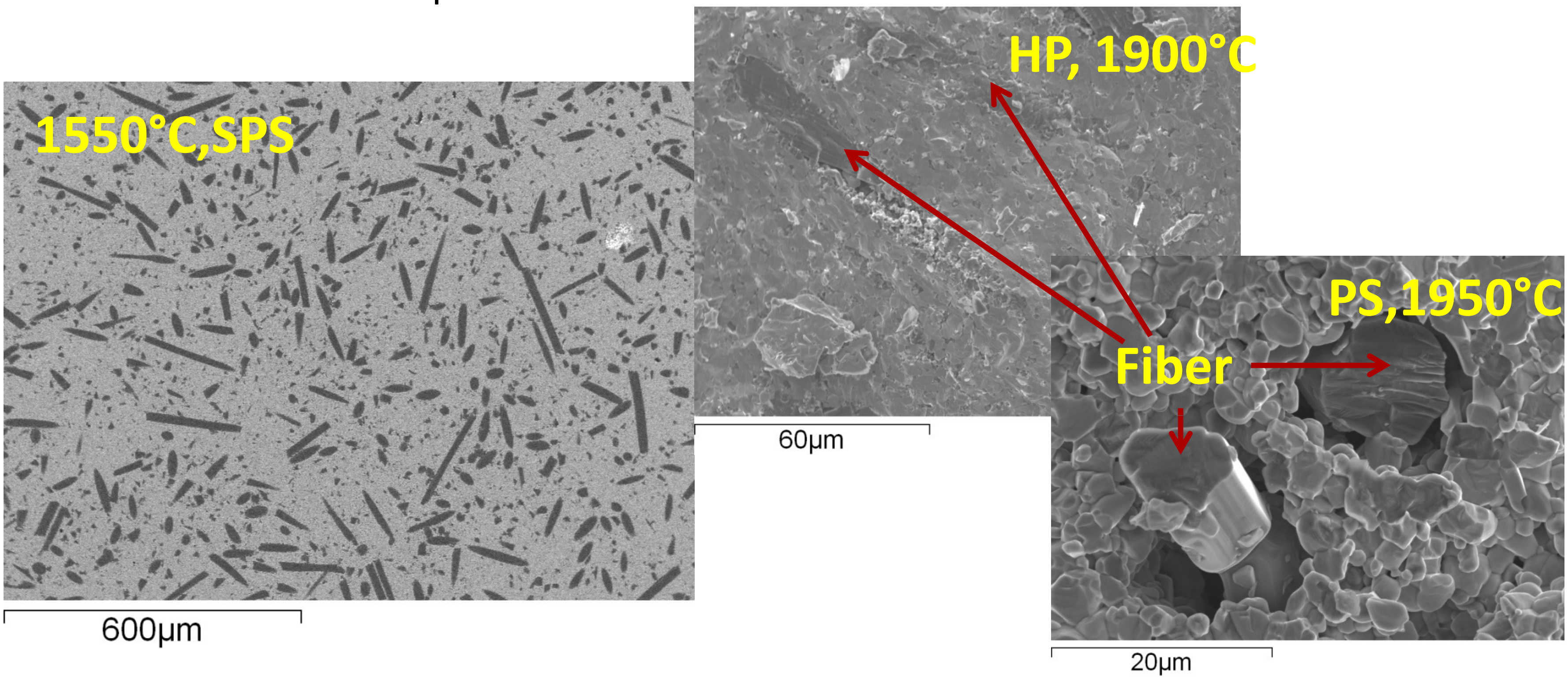
- Solid state sintering (activated by carbide phases)

  -advantages: no residual amorphous phases

  -higher sintering temperatures: 1900°C

Densification issues for reinforced materials

Short Fiber-reinforced composites -5.5 MPa m0.5



ZrB_2-SiC fibers could sinter at 1850°C-1900°C, with no sintering aids, by HP.

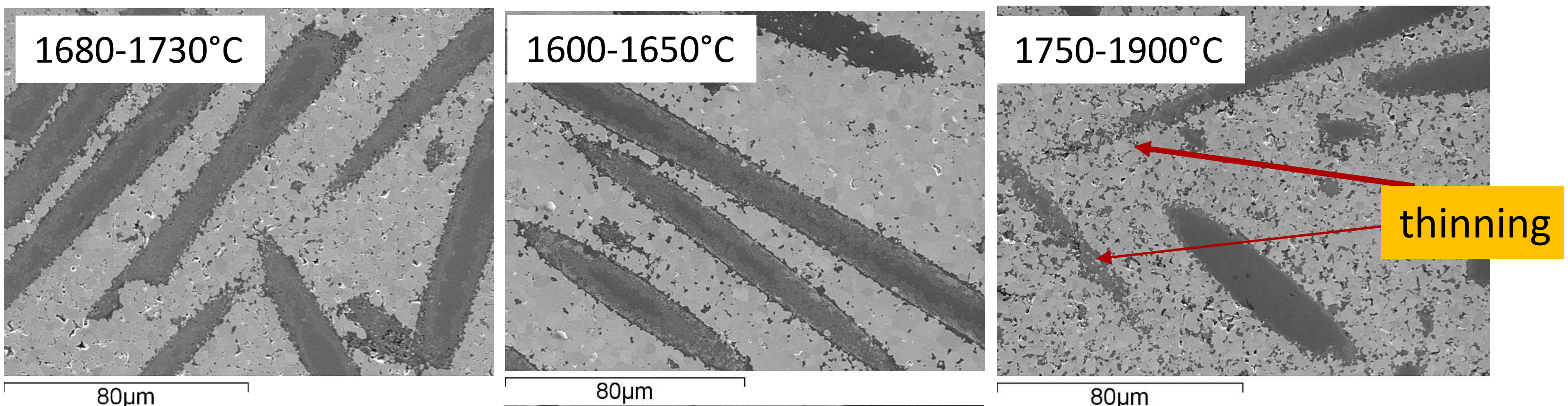
Hi-Nicalon fibers do not withstand these temperatures.

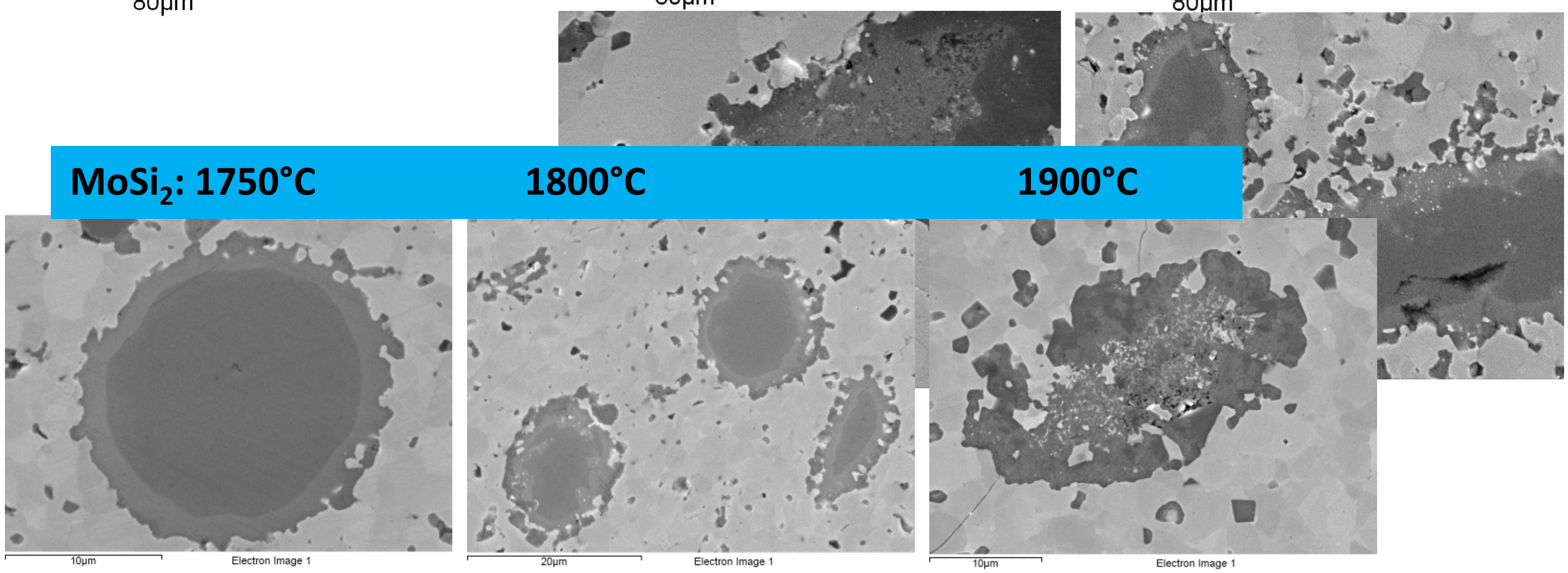
Sintering temperature < 1750°C ⟶ Sintering additive needed

S. Guicciardi, et al., Journal of the American Ceramic Society, 93, 2384(2010)

Sintering aids (<1750 ℃)

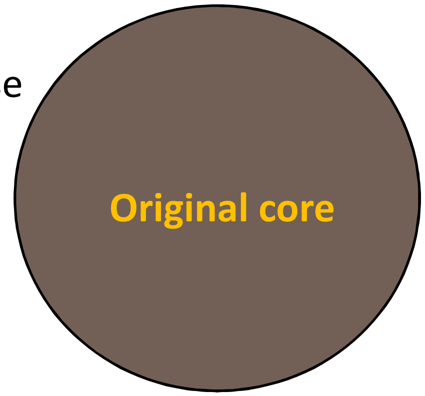
$ZrSi_2$ Si_3N_4 $MoSi_2$

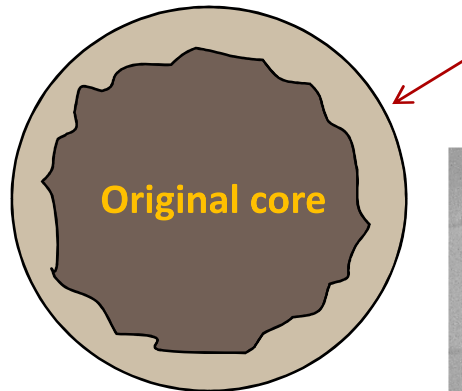




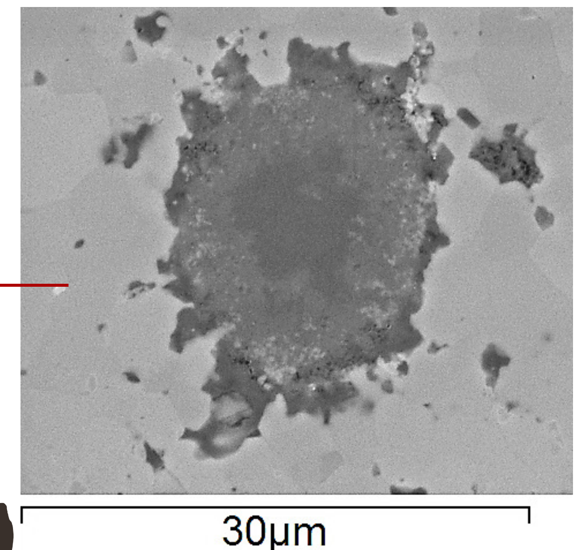
ZrB_2 - SiC fiber : Fiber evolution around 1700°C

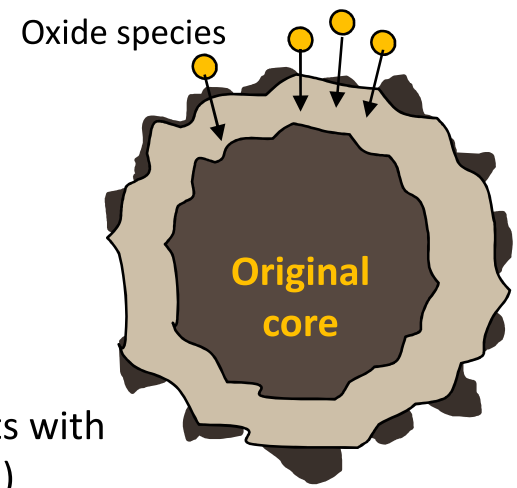
I
Original fiber:
-5-20 nm SiC crystallites
-SiOC intergranular phase
-C

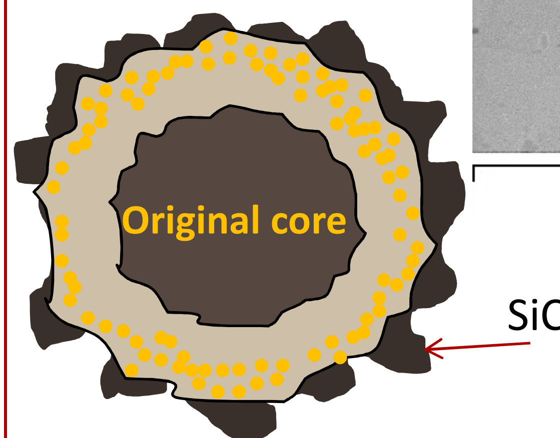




II
-SiC grain coarsening,
-SiOC softening and
migration outward



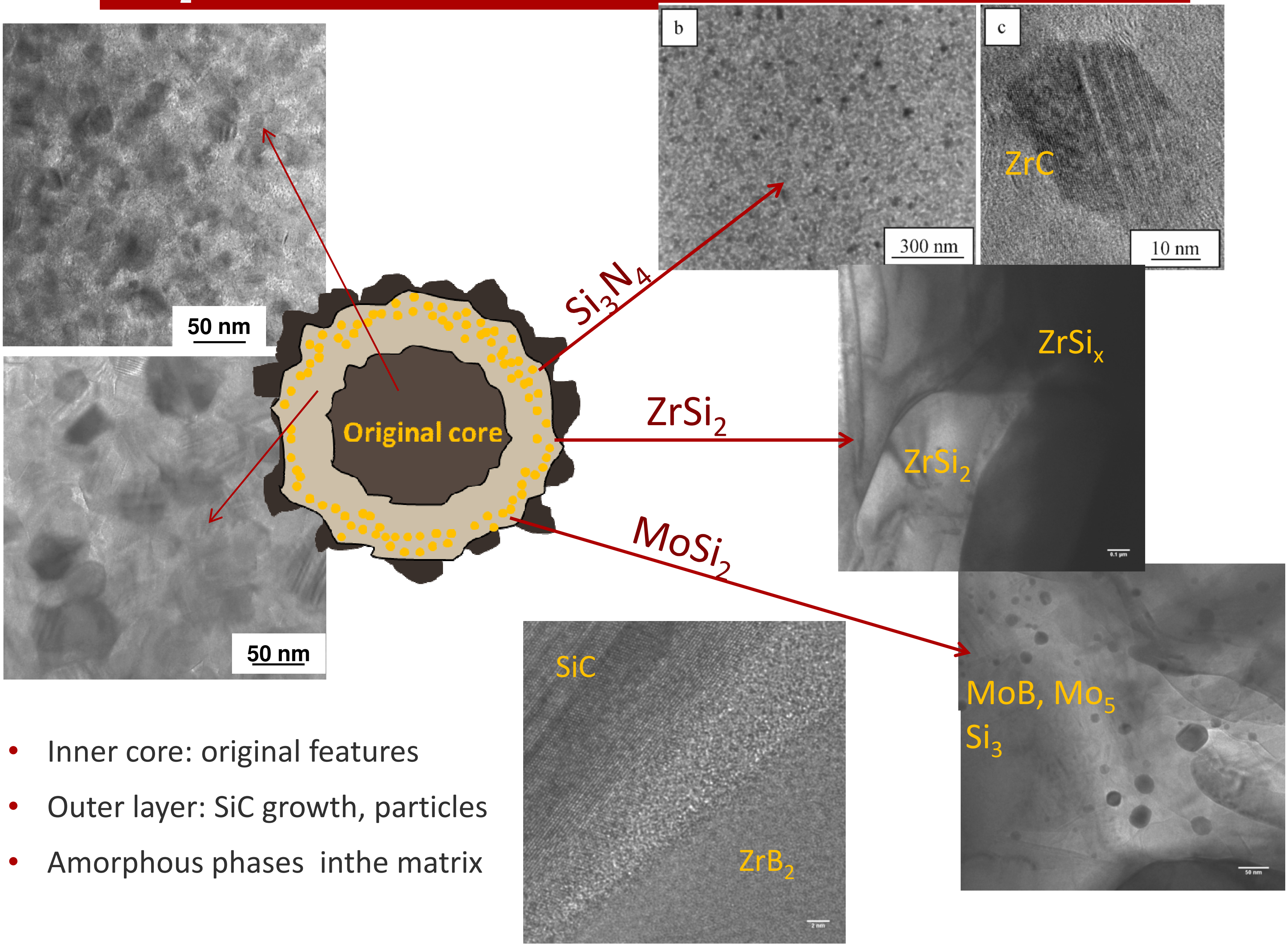




III
SiOC liquid interacts with
oxide species (ZrO_2)
and/or other liquid phases

IV
Squeezing of liquid
phase, Recrystallizatio
n of SiC particles
Partial Carburization
of oxide particles

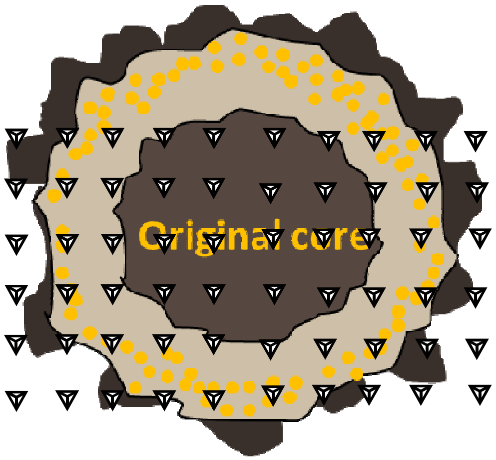
ZrB_2 - SiC fiber: fiber evolution

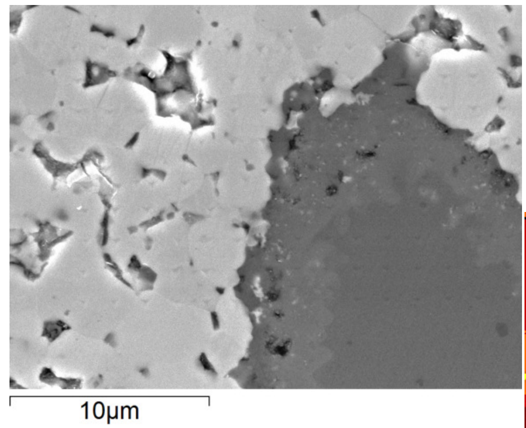


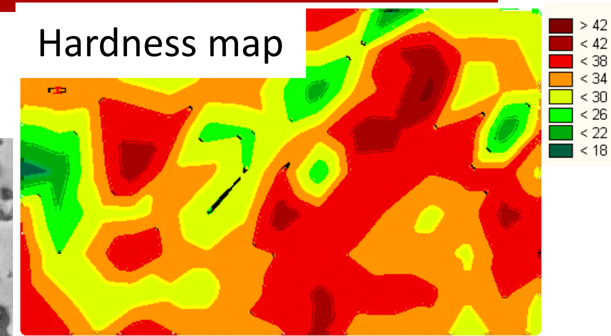
- Inner core: original features
- Outer layer: SiC growth, particles
- Amorphous phases inthe matrix

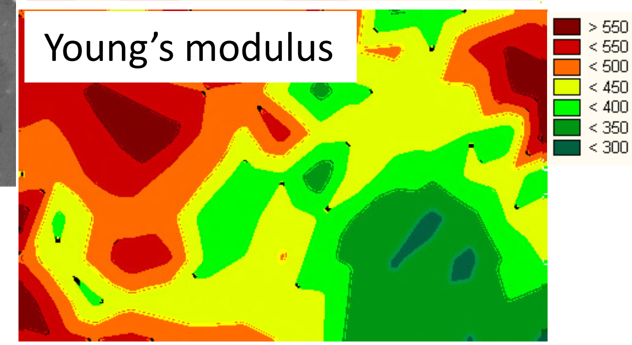
ZrB_2 - SiC fiber

5 mN nanoindentations









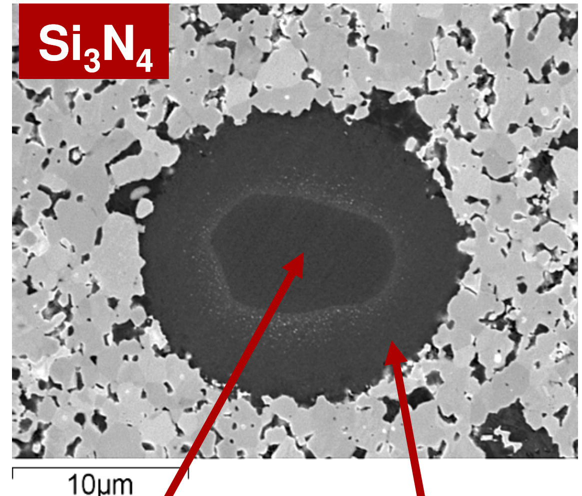
Sample	**Matrix**	**Rim**	**Core**
Sintering additive	**H (GPa)**	**H (GPa)**	**H (GPa)**
Si_3N_4	33.1 ± 3.6	35.6 ± 4.7	32.0 ± 2.7
$ZrSi_2$	38.7 ± 3.5	42.5 ± 3.1	30.6 ± 2.1
$MoSi_2$	32.8 ± 5.0	38.6 ± 7.1	33.3 ± 2.2
	E (GPa)	**E (GPa)**	**E (GPa)**
Si_3N_4	511 ± 38	417 ± 32	313 ± 18
$ZrSi_2$	579 ± 52	488 ± 30	329 ± 26
$MoSi_2$	526 ± 52	407± 31	332 ±14

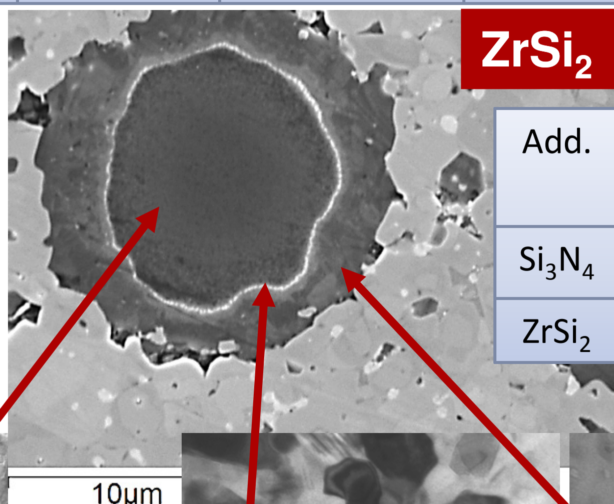
- Fiber Starting properties:
  E = ~300 GPa, HV= 30 GPa
- H, E (rim) > H, E (core) (elimination of intergranular glassy phase)
- RIM ($ZrSi_2$)>RIM ($MoSi_2$, Si_3N_4)
- Significant differences in the matrix

K_{Ic}	Si_3N_4	$ZrSi_2$	$MoSi_2$
$MPa{\cdot}m^{0.5}$	5.7	6.2	4.7

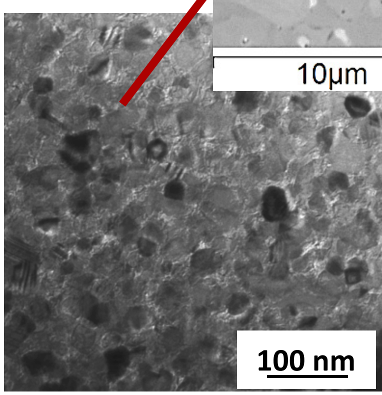
Issue: effect of sintering aid on strength and toughness

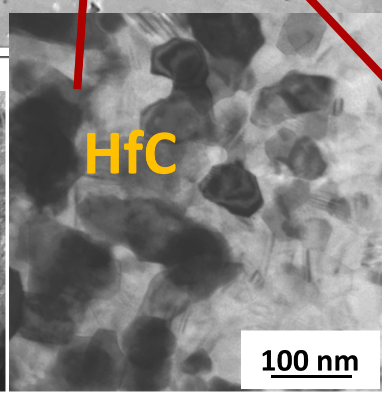
HfB_2	Add.	T sint (°C)	K_{Ic} ($MPa \cdot m^{1/2}$)	σ (MPa)	σ (MPa) **1200°C**
20f	Si_3N_4	1700	4.7±0.1	680±20	400±10
20f	$ZrSi_2$	1550	5.4±0.1	400±40	290±20

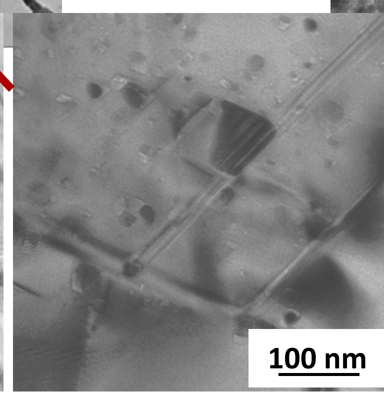


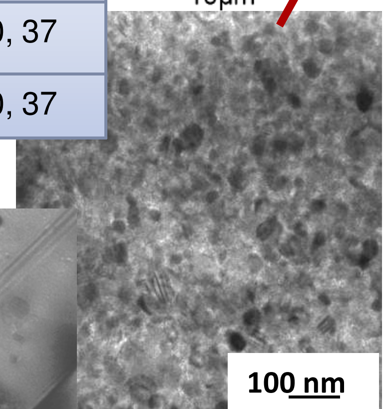


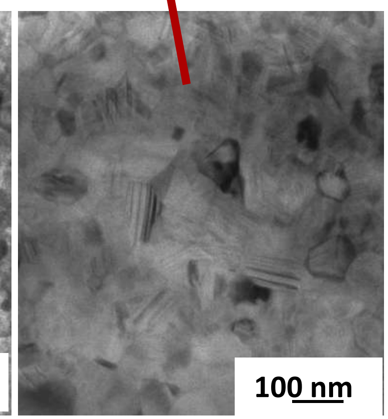
Add.	**Core** **E, Hv**	**Rim** **E, Hv**
Si_3N_4	300, 25	450, 37
$ZrSi_2$	290, 25	450, 37











Conclusions

- Many ways to densify UHTCS
- Sintering in presence of a liquid phase is more convenient
- Sintering aid: affects HT properties
- Silicides are a good option:
    - Pressureless Sintering
    - No strength degradation up to 1500°C in air
- Addition of carbides (WC) very promising

- For fibers-reinforced composites, sintering aid is needed
- Sintering agents affect fiber chemistry and its local properties
- Efficient processing route to avoid introduction of amorphous phases still has to be found

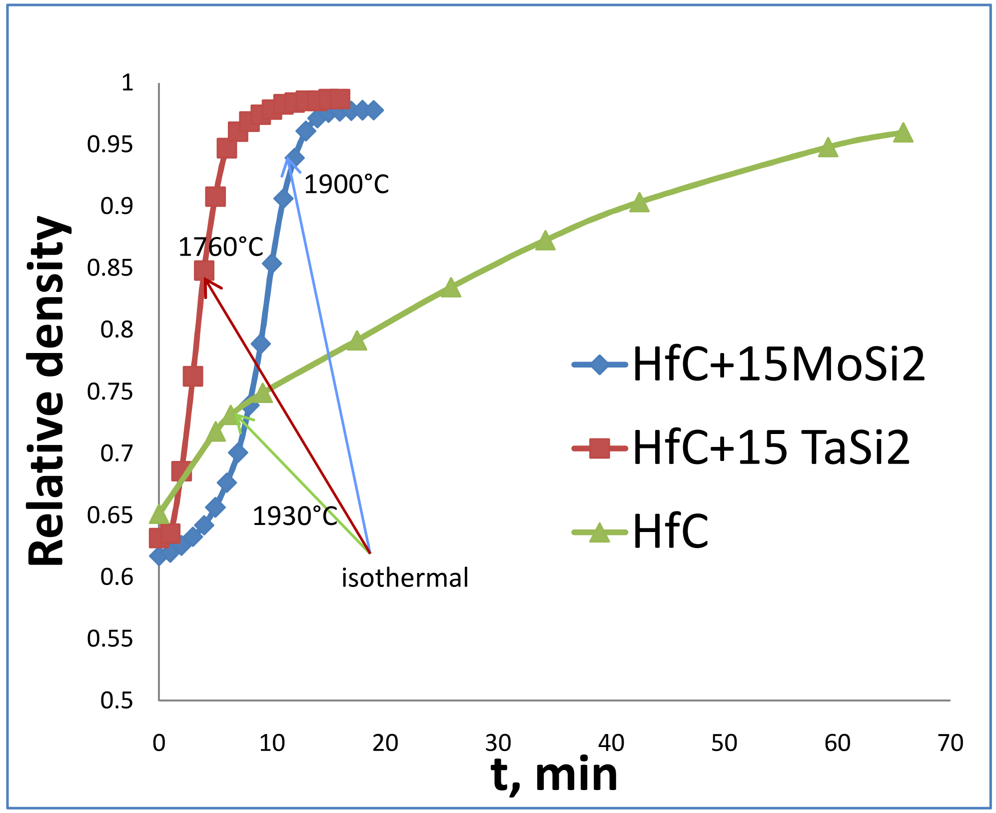
Carbides

- Less data available for carbides
- Sintering aids: B, C, B_4C (Solid state sintering)
- Silicides work well with carbides
- Similar densification mechanisms:
  - -Transient liquid phase for $MoSi_2$
  - -Transient liquid phase + SS for $TaSi_2$/$ZrSi_2$

PS with $MoSi_2$

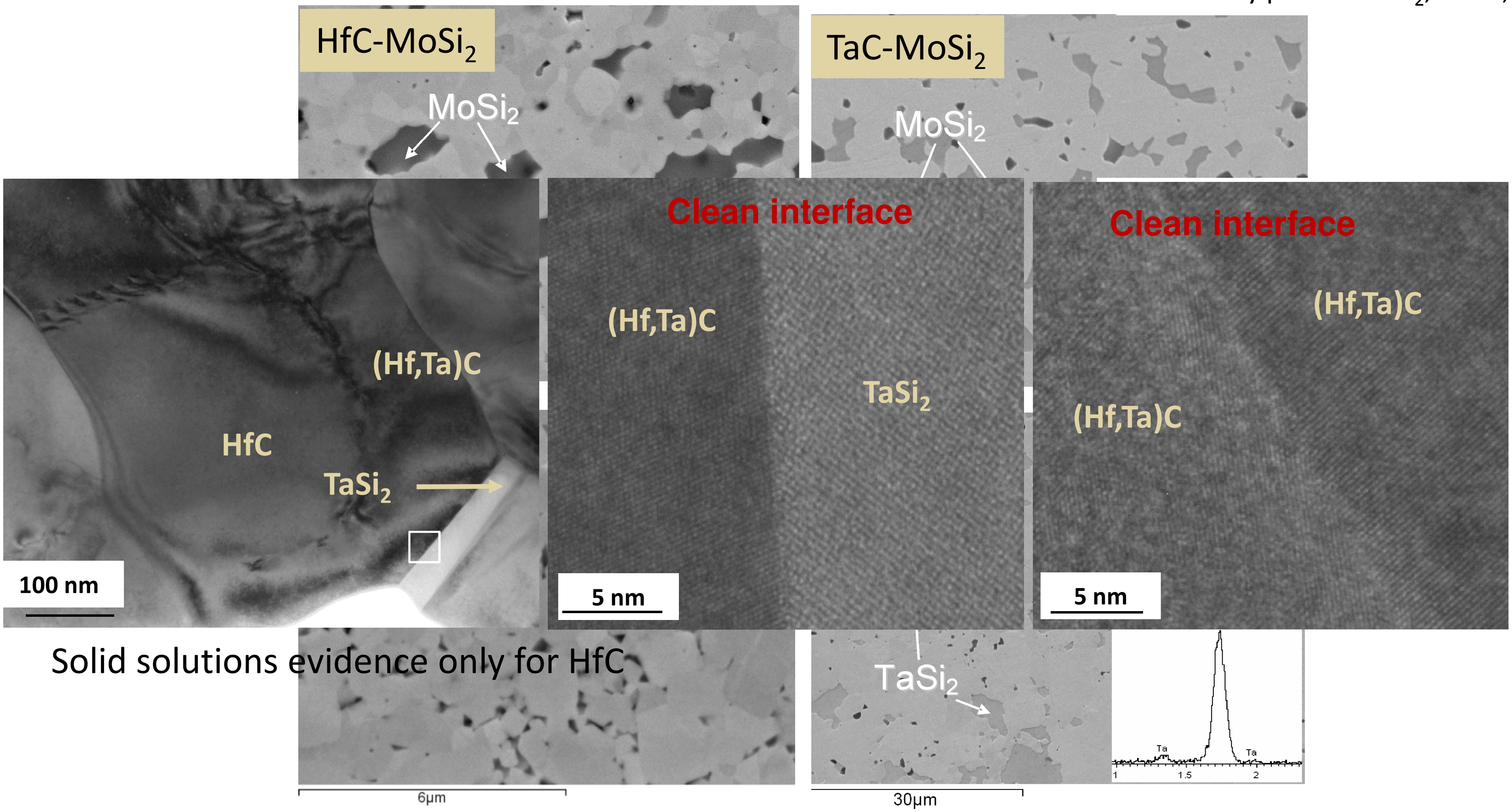
HP Temperature (°C)	ZrC	HfC	TaC
5-15 $ZrSi_2$	-	1750*	1700
5-15 $TaSi_2$	1700	1760	1750
5-15 $MoSi_2$	1900	1900	1850

*final density: 90%



Carbides

Sintering T: 1700-1900°C
Mean grain size ~ 1 µm
Secondary phases: HfO_2, TaSiB,



Solid solutions evidence only for HfC

Carbides

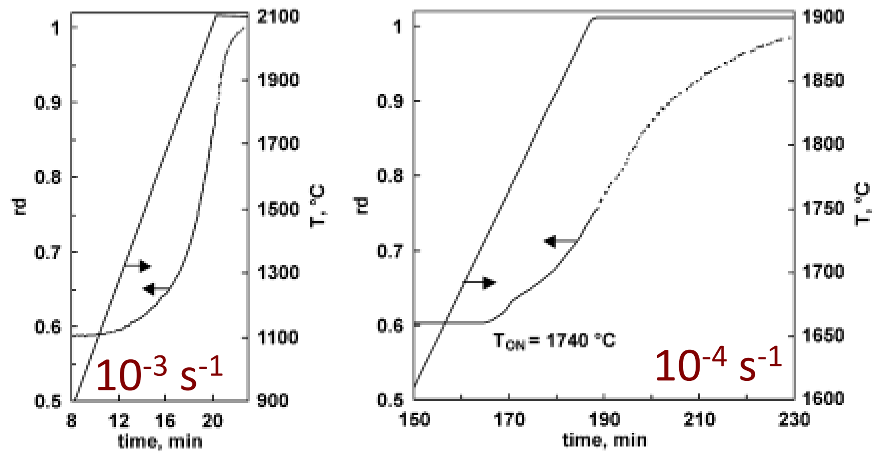
Composizione (Vol%)	Sinterizzazione (°C/min/MPa)		Densità rel. (%)	Mgs (µm)	H_V 1.0 (GPa)	E (GPa)	K_{Ic} ($MPa\ m^{1/2}$)	σ_{RT} (MPa)	$\sigma_{1200°C}^{\#}$ (MPa)	$\sigma_{1500°C}^{\#}$ (MPa)	Rif.
100HfC	PLS	1900/60	~70	1.5	-	-	-	-	-	-	6
100HfC	SPS	2200/3/65	98.0	20	25	464	-	470	-	-	27
HfC+(1,3,9)$MoSi_2$	SPS	1750-1900/3-5/100	98.0-99.7	2.2-0.8	27	484-498	-	868-510	-	-	27
HfC+(5,10,20)$MoSi_2$	PLS	1900/60	96.5-98.1	4	15	434-385	3.5	465-383	350-410	240-300	6
90HfC+10$MoSi_2$*	PLS	1900/60	99.1	2	16	-	-	540	-	-	6
85HfC+15$MoSi_2$	HP	1900/10/30	99.9	~1.2	20	450	3.8	420	300	-	10
85HfC+15$TaSi_2$	HP	1760/10/30	98.6	~0.8	18	490	3.6	470	400	-	10
100TaC	PLS	1900/60	~91	6	-	-	-	-	-	-	6
TaC+(5,10,20)$MoSi_2$	PLS	1900/60	92.9-98.4	5-7	12	480	3.8	590	-	-	6
95TaC+5$MoSi_2$**	HP	1900/5/30	94	2.8	14	-	3.5	585	-	300	11
85TaC+15$MoSi_2$	HP	1850/3/30	93.3	~1.2	14	490	4.7	900	580	-	10
85TaC+15$TaSi_2$	HP	1750/9/30	97.3	~2.5	14	490	4.7	680	430	-	10
80TaC+20SiC	SPS	1800/5/404	99.3±1.6	-	20	510	6.4	680	640	680	24
90TaC+10TaB_2 wt	HP	2100/-/30	98.6	-	20	545	3.4	600	-	-	26
TaC+(1,2)B_4C wt	HP	2100-2300/45/-	98-99	-	15-16	468-470	3.2	-	-	-	18
99TaC+1B_4C wt	SPS	1850/10/100-255-363	97-fully	0.7-1.2	22-25	364-510	-	-	-	-	23
96TaC+4CNTs wt short	SPS	1850/10/100-255-363	94-fully	1.6-1.9	11-18	258-331	-	-	-	-	22
96TaC+4CNTs wt long	SPS	1850/10/100-255-363	94-fully	0.6-1.2	13-23	288-395	-	-	-	-	22

Advantages of Spark plasma sintering

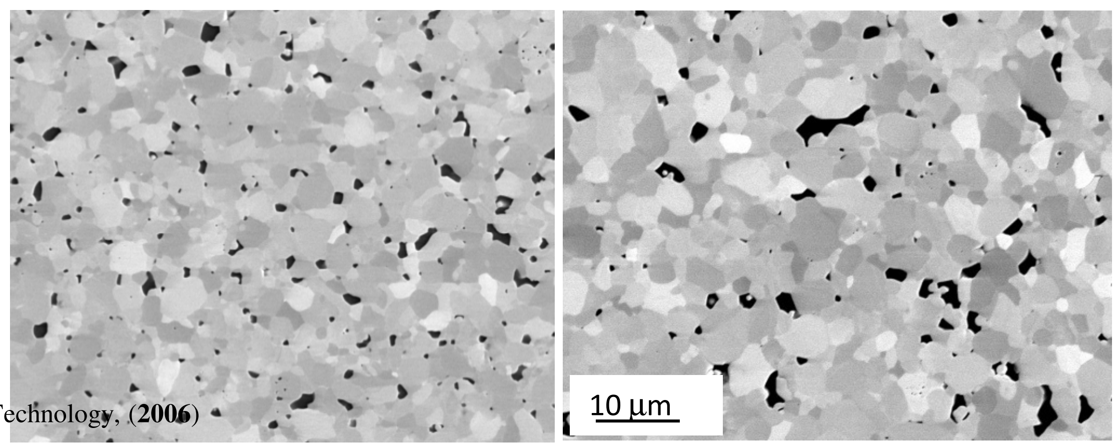
High heating rates, short processing times, minimization of grain growth $\rightarrow$ improvements of the materials' properties

- Monolithic HfC, ZrC, ZrB_2 densified to 98-99% at 2100-2200°C (HfB_2 only 80%)
- Sintering rates: 10^{-3} s^{-1}

SPS HP

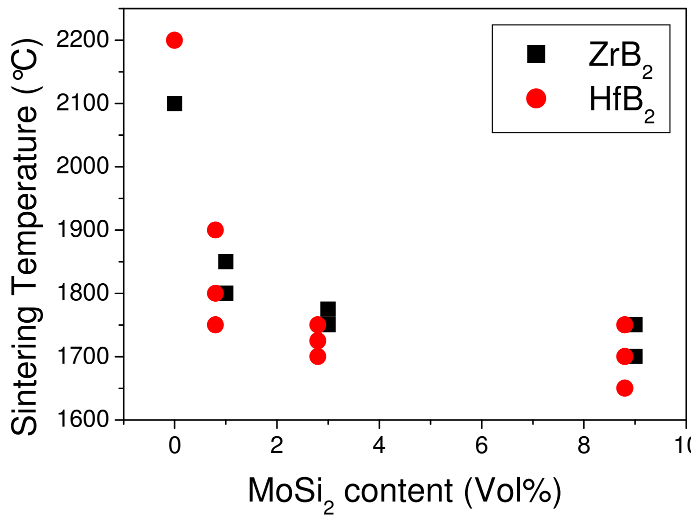


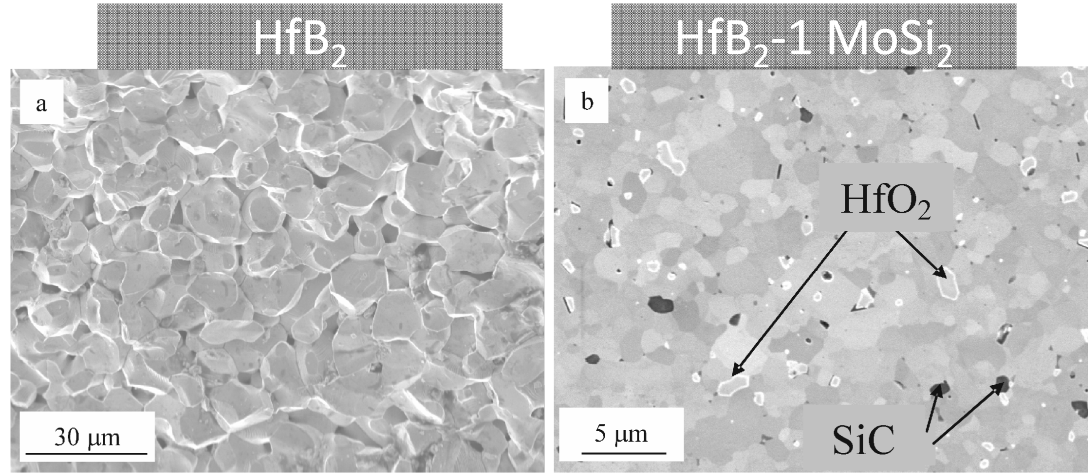
ZrB_2-$MoSi_2$

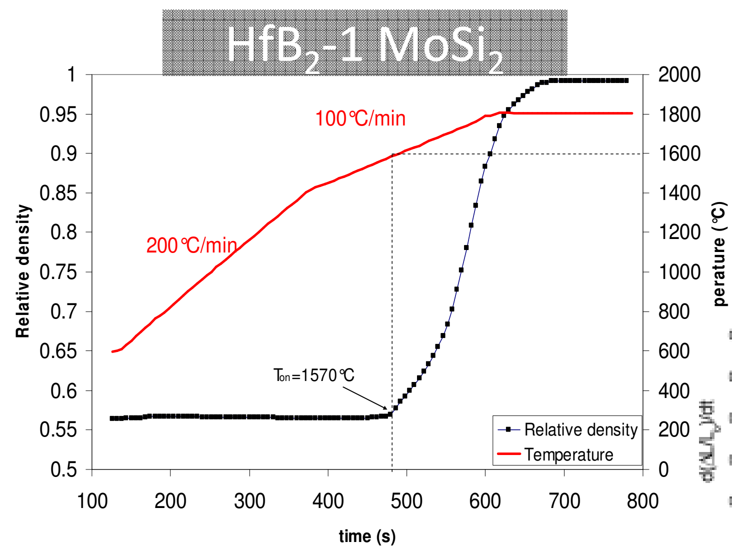


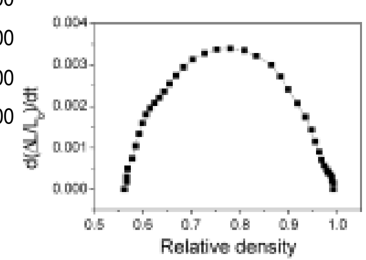
A.BELLOSI, et al, International Journal of Applied Ceramic Technology, (**2006**)

Borides with 0-9% $MoSi_2$









1 vol % $MoSi_2$ is already efficient in:

-Improving the sintering

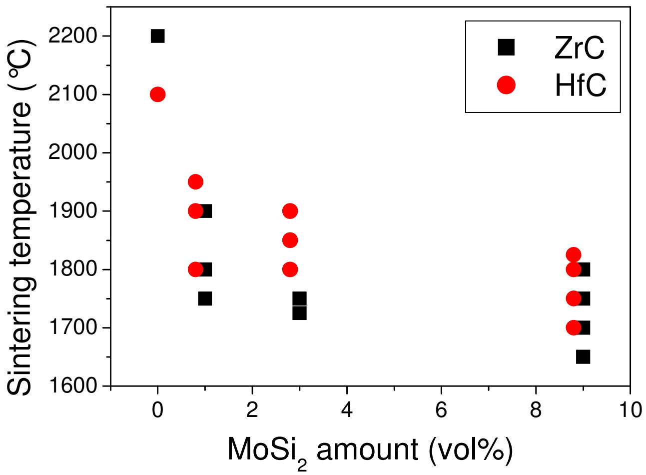
-Decreasing sintering Temperature

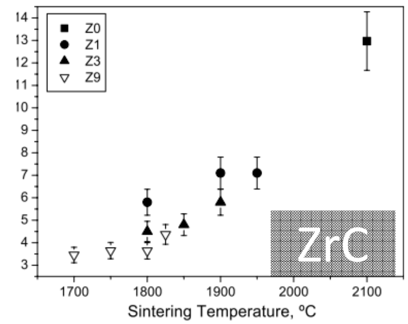
-Refining micorstructure

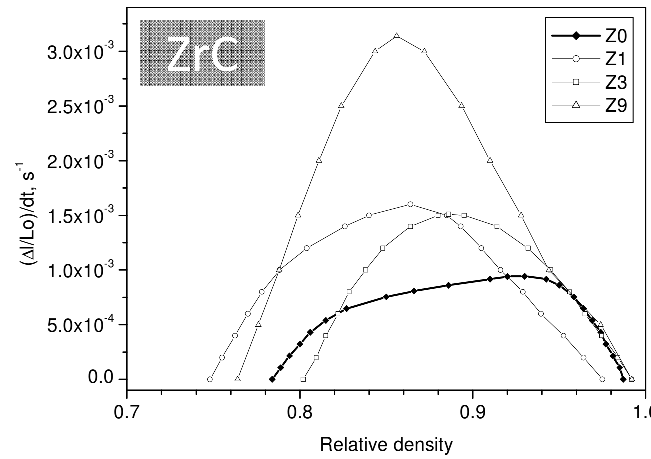
For SPS: 3 vol% silicides is OK

D. Sciti, et al, Journal of the American Ceramic Society, 91(2008) 143

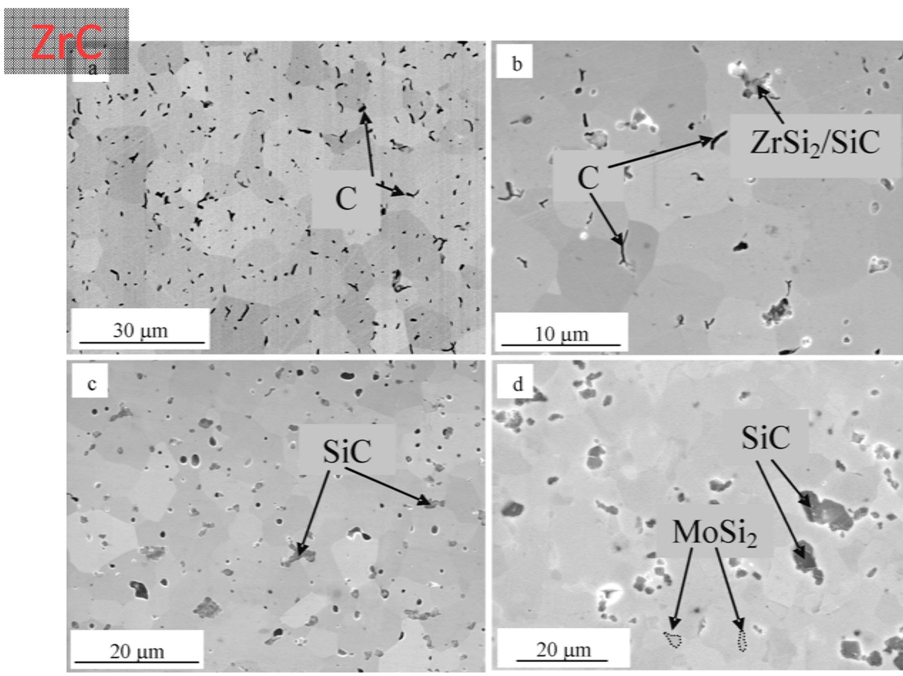
Carbides with 0-9% $MoSi_2$

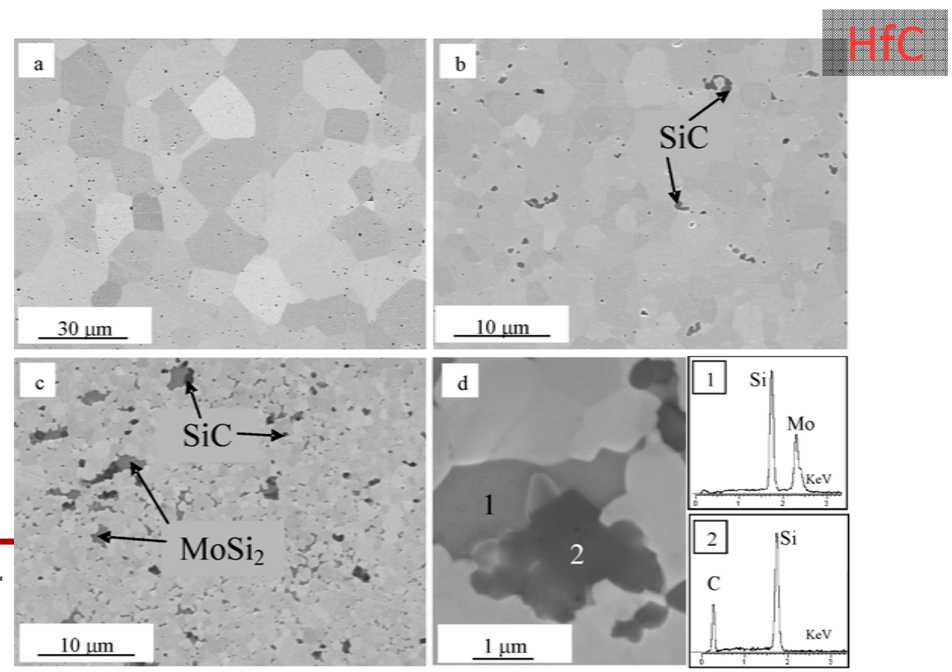






D. Sciti,et al, Scripta Materialia 59 (2008) 638





SPS for fiber reinforced

- SPS is a preferential technique (lower temperature, shorter times)

ZrB_2-20f	Sintering cond.	K_{Ic} MPa m0.5	σ MPa	σ (1200°C)
HP	1700°C/50MPa	5.7	413	335
SPS	1500°C/50MPa	5.5	370	450

HfB_2-20f	Sintering cond.	K_{Ic} MPa m0.5	σ MPa	σ (1200°C)
HP	1700°C/50MPa	4.2	330	290
SPS	1500°C/50MPa	4.7	680	400

Thank you for your attention!

Mechanical properties vs additive

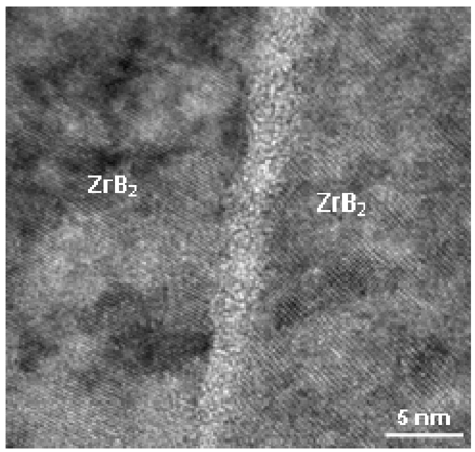
Sample	Composition	Sintering Temperature	Relative density	K_{Ic}	σ_{RT}
	Vol%	°C	%	$MPa \cdot m^{0.5}$	MPa
ZS	$ZrB_2+Si_3N_4$	1700	100	3.75±0.10	600±90
ZS20f	ZS+20 SiCf	1700	97.7	**5.65±0.30**	413±17
ZZ	ZrB_2+ZrSi_2	1600	98.5	4.25±0.04	808±31
ZZ20f	ZZ+20SiCf	1650	100	**6.24±0.35**	385±13
ZM	ZrB_2+MoSi_2	1750	97.6	3.50±0.60	780±87
ZM20f	ZM+20SiCf	1750	100	**4.73±0.13**	378±15

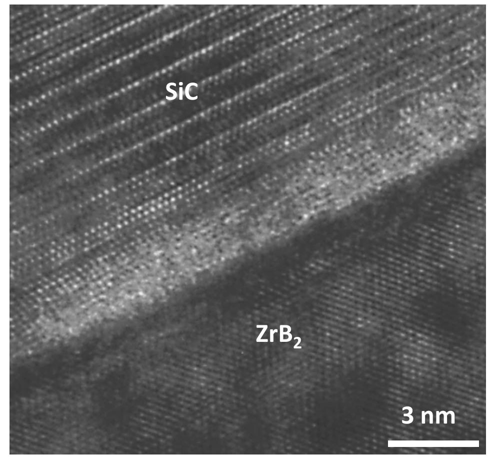
ZrB_2- SiC platelets: matrix/platelets interface

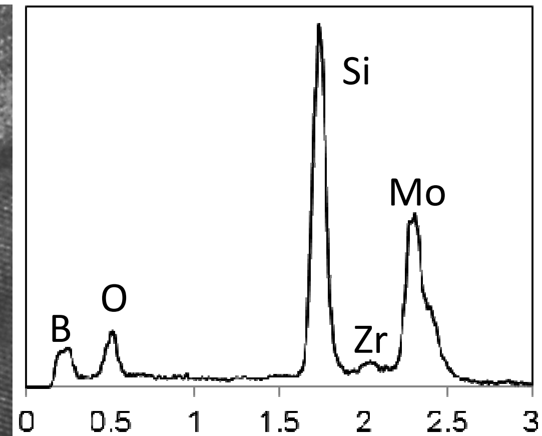
	Add.	K_{Ic} (MPa m$^{1/2}$)	σ (MPa)	$σ_{1200°C}$ (MPa)
ZrB_2- βSiC	$MoSi_2$	5.0±0.1	410±40	380±30
ZrB_2- βSiC	Si_3N_4	3.8±0.1	300±40	-

ZrB_2- β-SiC+
5vol% $MoSi_2$

gb: **Mo**-Zr-Si-B-O

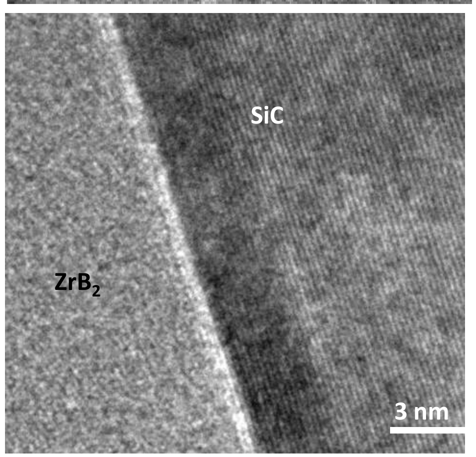


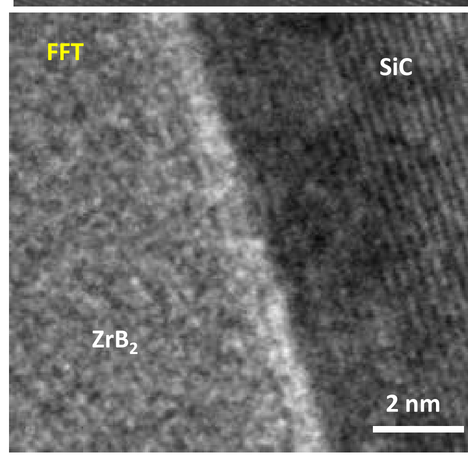


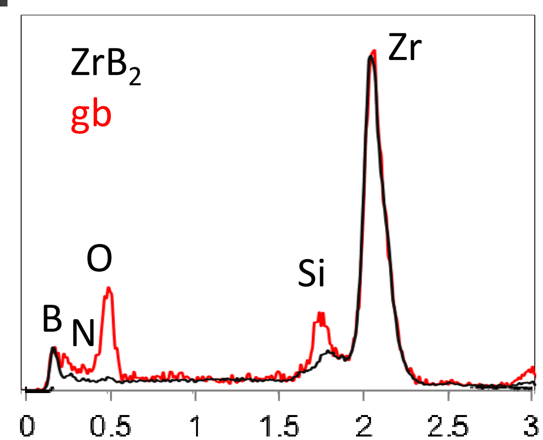


ZrB_2- β-SiC+
5vol% Si_3N_4

gb: Zr-Si-B-O-**N**



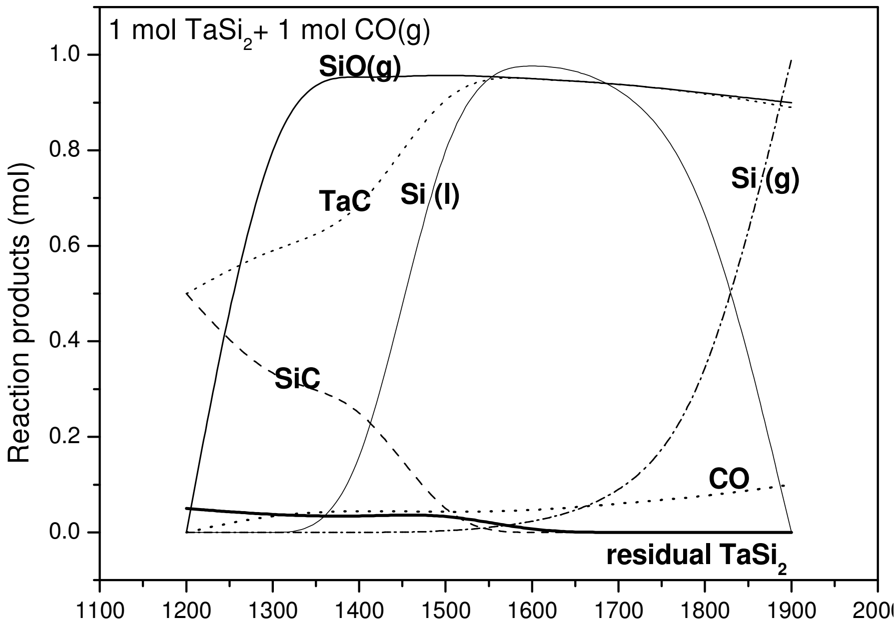


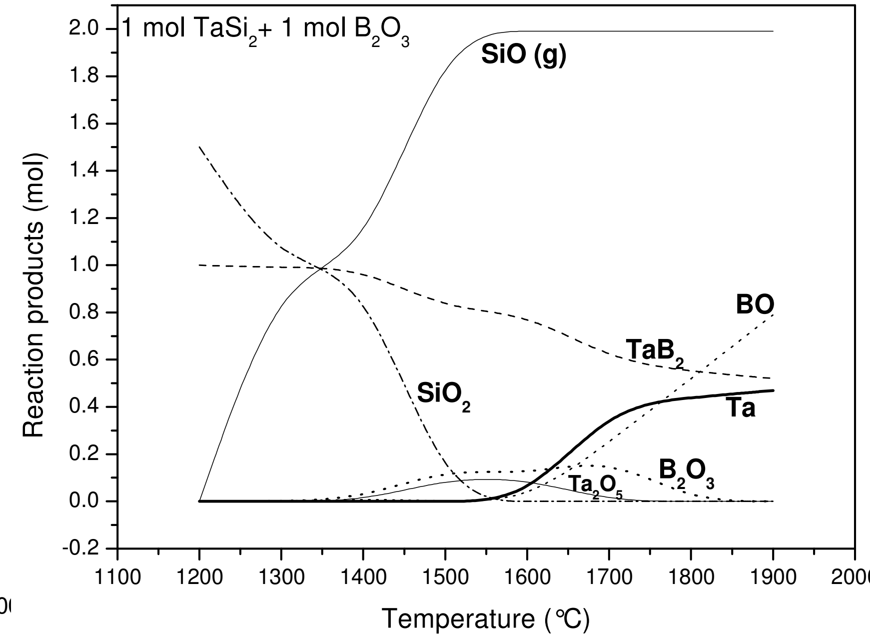


Solid solution formation and stability of silicides

Is SS formation necessary for densification? NO

Does densification take advantage of SS formation? In some cases lower sintering temperatures





a) 1mol $TaSi_2$+1mol B_2O_3:

Formation of:

SiO(g), TaB_2 at T≥ 1200°C and Ta at T≥ 1700°C.

b) 1mol $TaSi_2$+1mol CO (g):

Formation of:

SiO gas at T≥1300°C

Si(g) at T≥1450°C

TaC, SiC at T≥1200°C,

Liquid Si In the range 1450-1850°C

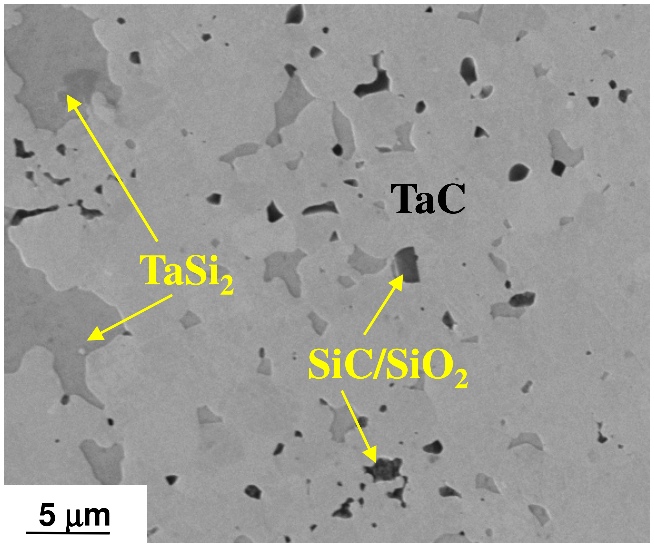
Molar content of the products deriving from the reactions:

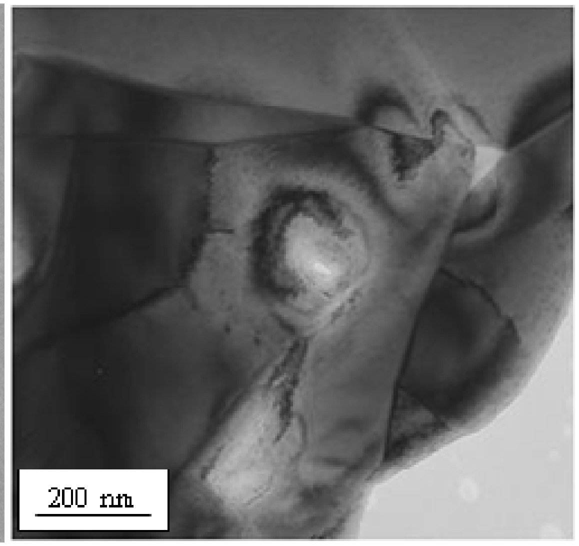
a) 1mol $TaSi_2$+1mol CO (g),

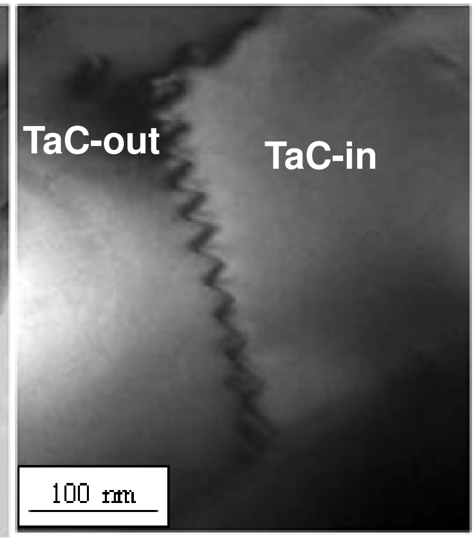
b) 1mol $TaSi_2$+1mol B_2O_3, as a function of the temperature and at constant pressure of 100 Pa. (pressure inside the furnace chamber)

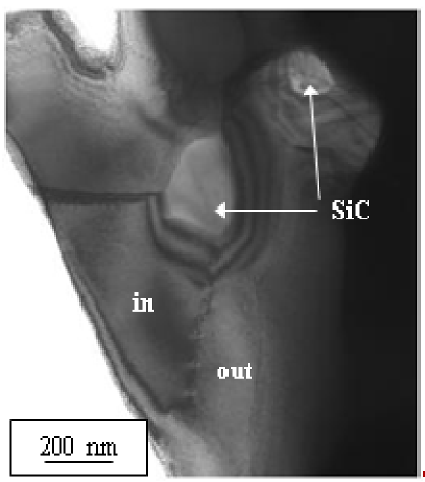
TaC + 15 $TaSi_2$

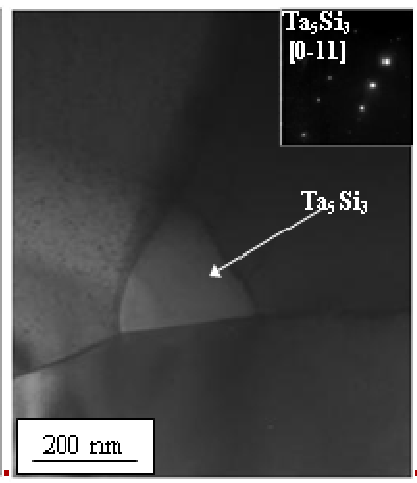
Full density at 1750°C, 30 min
Mean grain size ~ 2.5 µm
Secondary phases: $TaSi_2$, SiC, Si-O-C

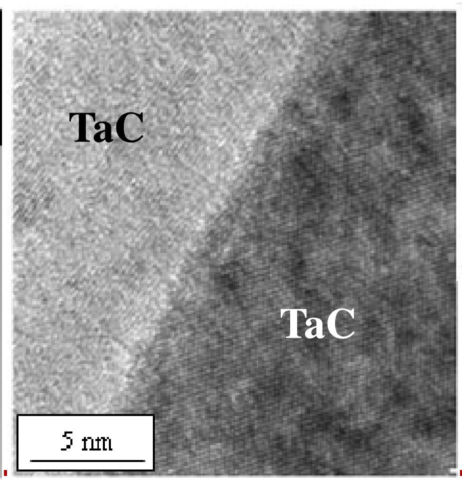


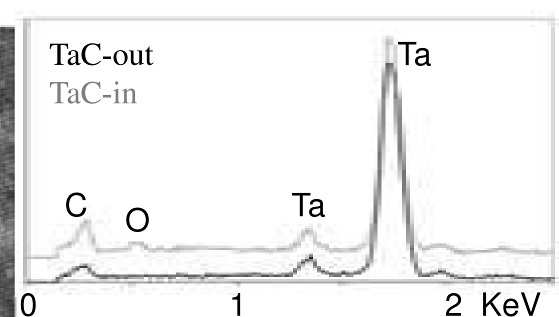






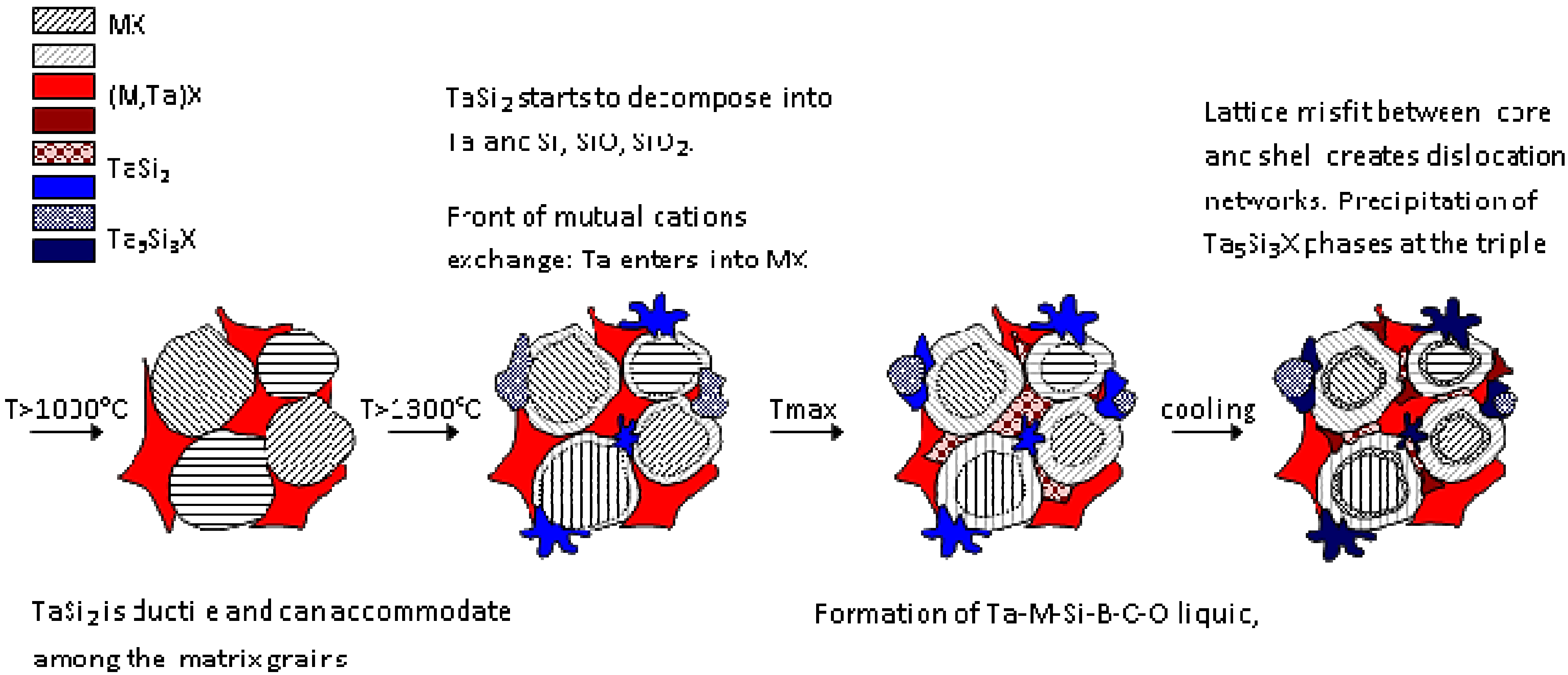






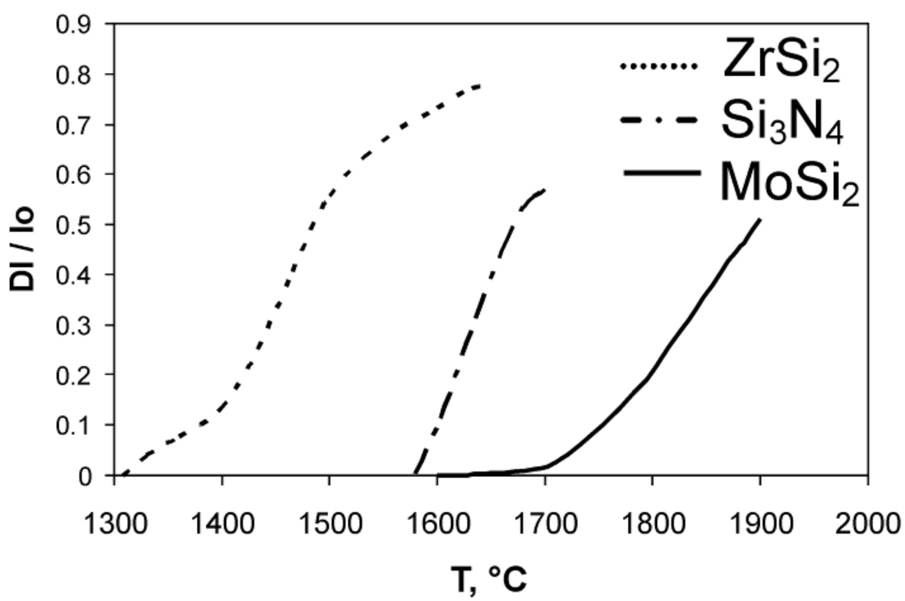
- Core: TaC
- Rim: TaxC
- Triple points: $(Hf,Ta)Si_2$, $(Hf,Ta)_5Si_3$
- Clean grain boundaries

Densification mechanisms: UHTCs + $TaSi_2$



Boride matrix: wetted grain boundaries
Carbide matrix: clean grain boundaries

Selected additives for SiC fiber reinforced

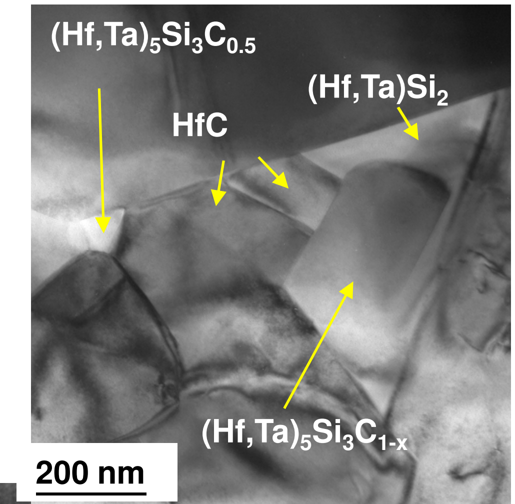


- Affects the sintering temperature of the matrix
- Reacts with the fibers

- Si3N4 allows densification at 1700°C
- ZrSi2 allows densification at 1550°C
- MoSi2 allows densification at 1750°C

Carbides

- Less data available for carbides
- Silicides work well with carbides
- Similar densification mechanisms:
  - -Transient liquid phase for MoSi2
  - -Transient liquid phase + SS for TaSi2/ZrSi2



HfC + 15 $TaSi_2$