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Zr-, Hf- and Ta-based Ultra High Temperature Ceramics for Thermal Protection Systems

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Introduction

Ultra High Temperature Ceramics (UHTCs) based on transition metal (Zr, Hf, Ta, etc.) diborides and carbides are considered to be quite interesting due to the unique combination of suitable chemical-physical and mechanical properties:

- **melting point above 2700°C**
- **high hardness**
- **good electrical and thermal conductivity**
- **chemical inertness**
- **good thermal shock resistance**
- **resistance to ablation in oxidizing environments**

Introduction - 2

Starting powders

Conventional techniques
(furnace, solution methods, etc.)

Low sintering ability

Consolidation methods

classical HP

Severe sintering conditions:

- Temperature (> 2000°C)
- Processing times (hours)

- Coarse microstructure
- High production costs

Typical approach

- Introduction of appropriate sintering aids
  - Examples: SiC, Si_3N_4, $MoSi_2$, $TaSi_2$, etc.

Alternative options

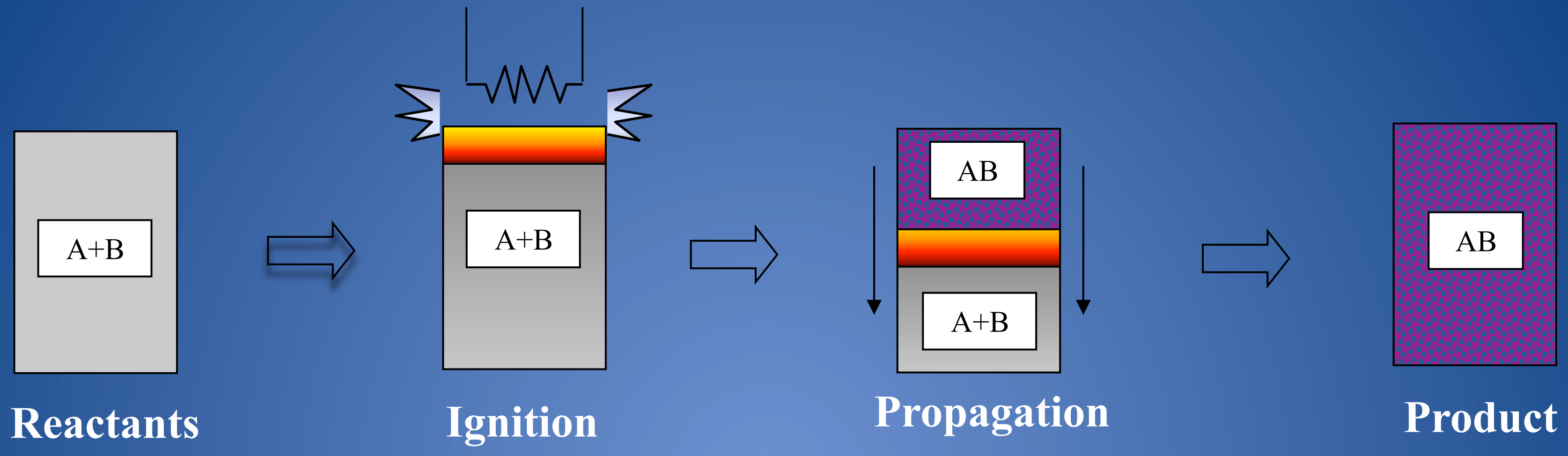
- Starting powders with improved sinterability

- More efficient consolidation methods

In this work

- Convenient route for obtaining powders with improved sinterability
  - Self-propagating High Temperature (SHS)
- Innovative consolidation method
  - Electric Current Assisted Sintering or Spark Plasma Sintering (SPS)

SHS and its process parameters



Burning velocity	**0.1–20 cm/s**
Combustion temperature	**2300–3800 K**
Heating rate	**10^3 - 10^6 K/s**
Induction time for ignition	**0.2–1.2 s**
Ignition temperature	**800–1200 K**

Sintering ability of SHS powders

Mishra et al., *J. Mater. Res.* 15 (2000) 2499-2504
Mishra et al., *Mater. Sci. Eng.* A364 (2004) 249–255

ZrB_2 powders prepared by three different techniques:

a) self-propagating high-temperature synthesis (SHS)
   - $ZrO_2 + B_2O_3 + 5Mg \rightarrow ZrB_2 + 5MgO$
   - MgO removal using diluite HCl

b) replacement reaction process (RRP)

c) carbothermic reduction process (CRP)

sintered in a graphite furnace for 1 h at 1800°C

	SHS	**RRP**	**CRP**
Relative density	**93-94%**	86%	87%

Sintering ability of SHS powders
Motivation

- TEM :
  - Significant differences in defect concentrations (dislocations, stacking faults and twins):

	SHS	RRP	CRP
Defect density	**~10^{12} cm^{-2}**	~10^{8} cm^{-2}	~10^{8} cm^{-2}

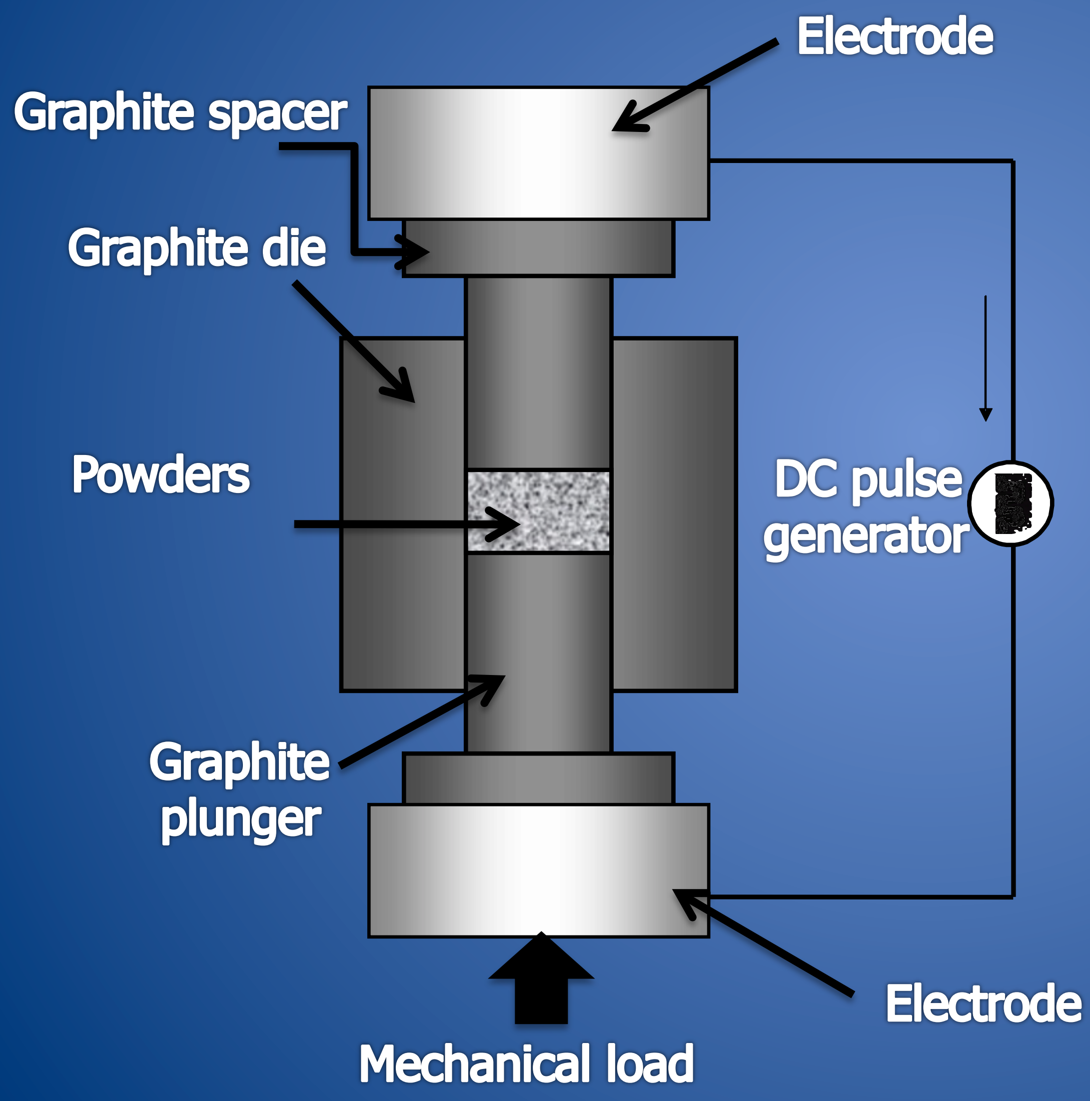
Rapid heating (240000 K/min) and cooling (1600 K/min) rates during SHS

Sintering of SHS powders: Examples

System	Sintering Method	Reference
AlN	Microwave Sintering	*Hsieh et al, 2007*
Al_2O_3-TiC	Pressureless Sintering, Hot Pressing	*Lee et al., 2001*
γ-alon	Hot Pressing	*Zientara et al., 2009*
CoAl	Spark Plasma Sintering	*Takano et al., 2001; Hirota et al., 2001*
Cr_2AlC matrix composites	Hot Pressing, Spark Plasma Sintering	*Jaworska et al., 2013*
HfB_2	**Spark Plasma Sintering**	***Musa et al., 2013***
HfB_2-$HfSi_2$	**Spark Plasma Sintering**	***Musa et al., 2014***
HfB_2-SiC, HfB_2-HfC-SiC	**Spark Plasma Sintering**	***Licheri et al., 2009***
La_x-$Sr_{1-x}TiO_3$	Spark Plasma Sintering	*Kikuchi et al., 2010*
$La_{0.7}Sr_{0.3}MnO_3$	Spark Plasma Sintering	*Yan et al., 2011*
$MoSi_2$	Spark Plasma Sintering	*Shimizu et al., 2002*
NbC–NbB_2	Spark Plasma Sintering	*Tsuchida and Kakuta, 2006*
NiAl	Spark Plasma Sintering	*Kitaoka et al., 2000; Hirota et al., 2001*
β-Si_3N_4	Hot Pressing, Spark Plasma Sintering	*Bai et al., 2007*
α-Sialon	Hot Pressing	*Chen et al., 2002; Smirnov, 2009*
$Sr_{1-x}R_xTiO_3$	Spark Plasma Sintering	*Zhang et al., 2007*
TaB_2-SiC, TaB_2-TaC-SiC	**Spark Plasma Sintering**	***Licheri et al., 2010a, Licheri et al., 2010b***
Ti-Al_2O_3-TiC	**Hot Pressing, Spark Plasma Sintering**	***Musa et al., 2009a***
Ti_2AlC	Hot Pressing	*Chlubny et al., 2010*
Ti_2AlN	Hot Pressing	*Chlubny et al., 2012*
TiB_2	Pressureless Sintering	*Khanra et al., 2007*
$TiC_{0.7}$-TiB_2	**Spark Plasma Sintering**	***Musa et al., 2009b***
TiC-Si_3N_4	Spark Plasma Sintering	*Bai et al., 2008*
TiN	Hot Pressing	*Russias et al., 2007*
TiN/Y-(α/β)-Sialon	Pressureless Sintering	*Xu et al., 2006*
Ti-Si-C	High Temperature High-Pressure	*Jaworska et al., 2005*
ZrB_2	Pressureless Sintering	*Mishra et al., 2000; Mishra et al., 2004*
ZrB_2-SiC, ZrB_2-ZrC-ZrC	**Spark Plasma Sintering**	***Licheri et al., 2007; Licheri et al., 2008***

Spark Plasma Sintering

***R. Orrù** et al., Consolidation/Synthesis of Materials by Electric Current Activated/ Assisted Sintering, Mater. Sci. Eng. R, **63(4-6)**, 127-287 (2009)*

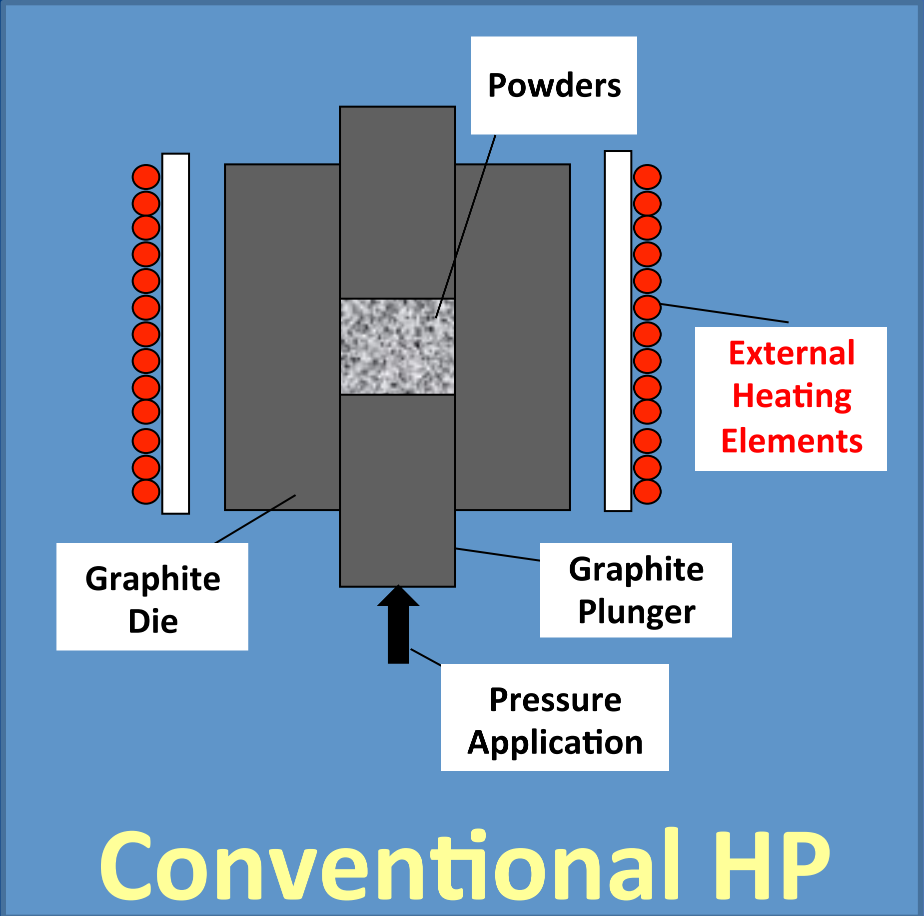


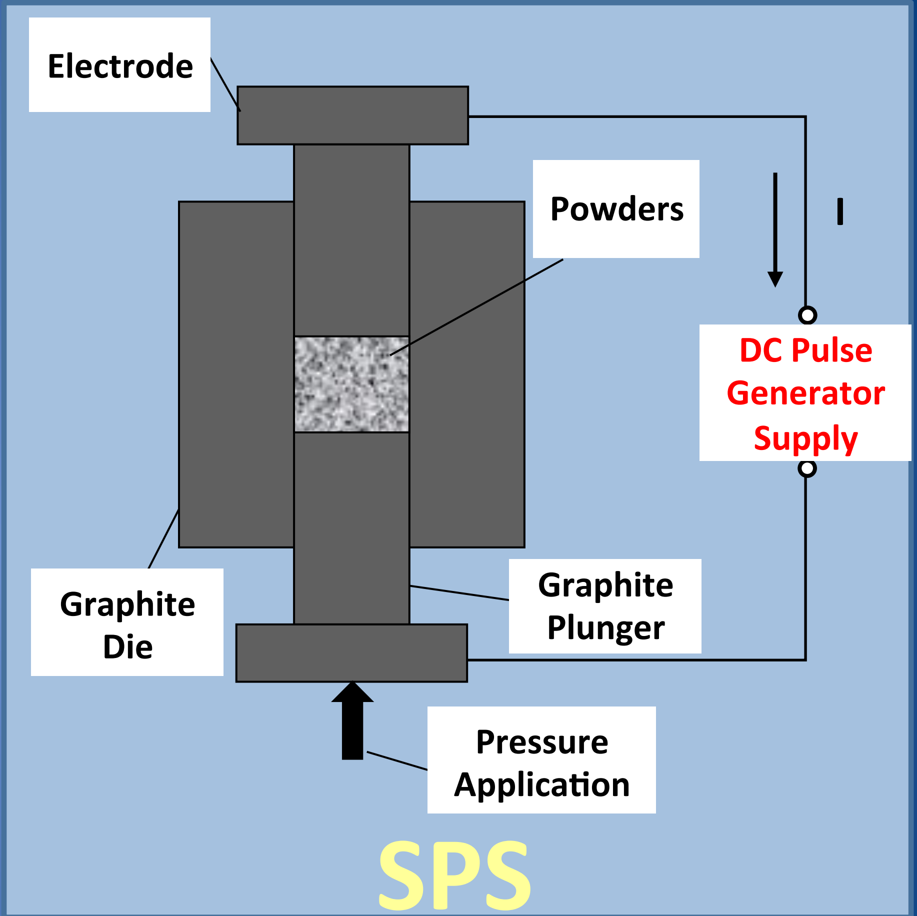
Electric current
(Joule + other effects)
+
Mechanical pressure

Dense products

- Classical sintering purposes
- Reactive Sintering (RSPS)

SPS vs Conventional HP

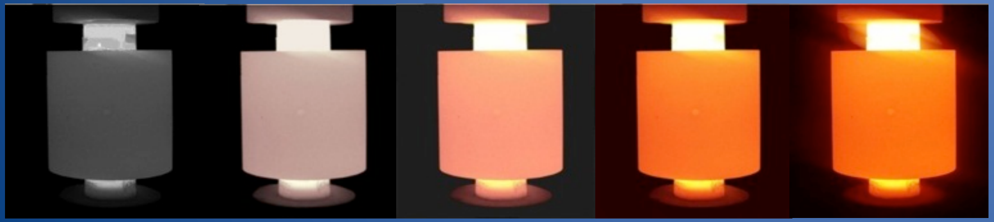




- **Main difference:** external or direct powders/die heating
- **Increased heating rates:** ➔ Sintering phenomena are promoted
  ➔ Processing times significantly reduced
  ➔ Finer microstructure

SPS experiments

SPS apparatus 515S model , Sumitomo Coal Mining Co. Ltd, Japan



I=1500 A
Mechanical load= 50kN

Vacuum (10-20 Pa)

Measured parameters

- Temperature of the die surface
- Electric current
- Voltage
- Sample Displacement (δ)

The case of Ti-Al_2O_3-TiC: Results

Musa et al., J. Cleaner Prod. 17(9), 877-882 (2009)

Sintering conditions

Technique	T (°C)	Pressure (MPa)	t_D (min)	t_T (min)	ρ (g/cm^3)	ρ_{rel} (%)
SPS	1100	20	4	7	4.14	94.5
SPS	1150	20	4	7	4.24	96.8
SPS	1200	20	2	5	4.52	>99.9
HP	1200	40	60	~295	4.22	96.3
HP	1250	50	60	~305	4.39	>99.9
HP	1300	25	60	~315	4.50	>99.9

- Lower T, applied P and shorter processing times

Energy consumption

Method	Total energy consumed (J)	Specific energy consumed (J/g)	Specific energy consumed (kWh/g)
SPS	$(1.15 \pm 0.15) \times 10^6$	$(3.83 \pm 0.50) \times 10^5$	0.10 ± 0.01
HP	$(1.97 \pm 0.12) \times 10^7$	$(6.57 \pm 0.39) \times 10^6$	1.83 ± 0.11

- Energy saving of the order of 90-95%

Material properties

Method	E (GPa)	H_K	H_{V1}	Thermal shock (°C)	Wear rate (mm^3/Nm)	Friction coefficient μ	K_{IC} (MPa × m$^{1/2}$)
SPS	286	1290	1846	250	$6.7 > \times 10^{-6}$	0.76	4.20
HP	293	1330	1454	275	9.6×10^{-6}	0.85	4.35

- Improved Vickers hardness and wear rate

SHS - SPS: recent results

- Several near fully dense UHTC products:

MB_2, MB_2-SiC, MB_2-MSi_2 and MB_2-MC-SiC (M=Zr, Hf, Ta)

Applications:

- aerospace industry
- solar absorber
- molten metal crucibles
- cutting tools
- electrodes, etc.



The case of ZrB_2-ZrC-SiC

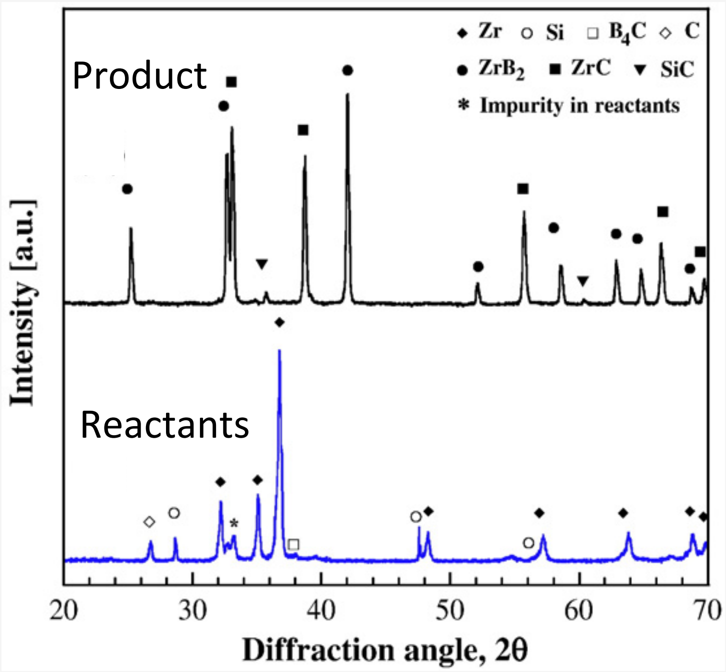
Licheri et al., Combination of SHS and SPS Techniques for Fabrication of Fully Dense ZrB_2-ZrC-SiC Composites" *Mater. Letters* **62**, 432–435 (2008)

Powders Synthesis by SHS

$$8Zr + 2B_4C + 1.5Si + 3.5C \rightarrow 4ZrB_2 + 4ZrC + 1.5SiC$$

Self-propagating behaviour: T_C= 2200°C, v_f = 8 mm/s

Complete reactants conversion



Commercial ZrB_2-ZrC-SiC powder mixture with the same nominal composition also processed by SPS

The case of ZrB_2-ZrC-SiC

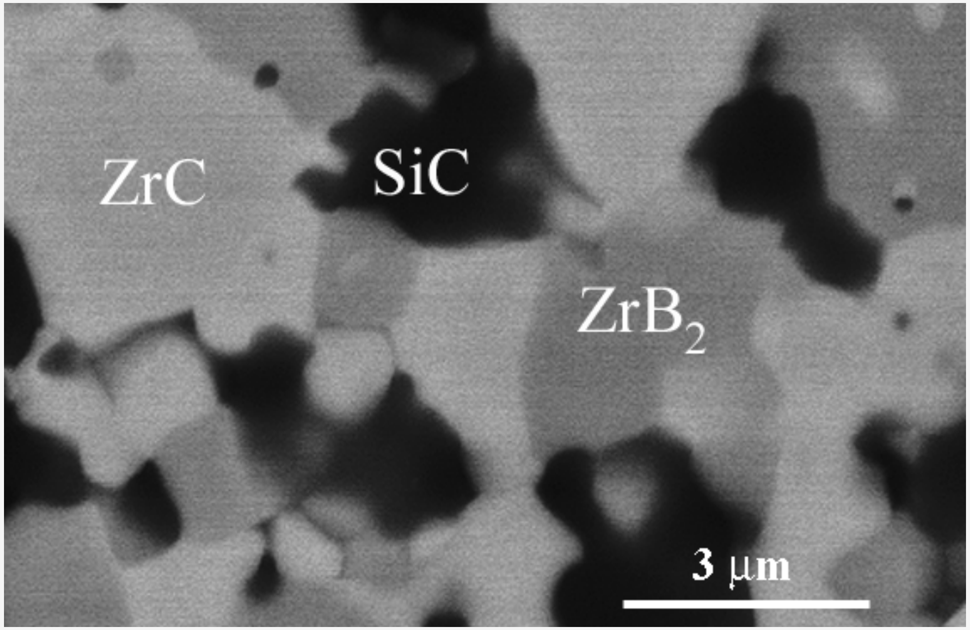
Spark Plasma Sintering of SHS Powders

Sintering conditions: T_D= 1800 °C, P=20 MPa, t_D =10 min

SHS powders

- Fully dense products

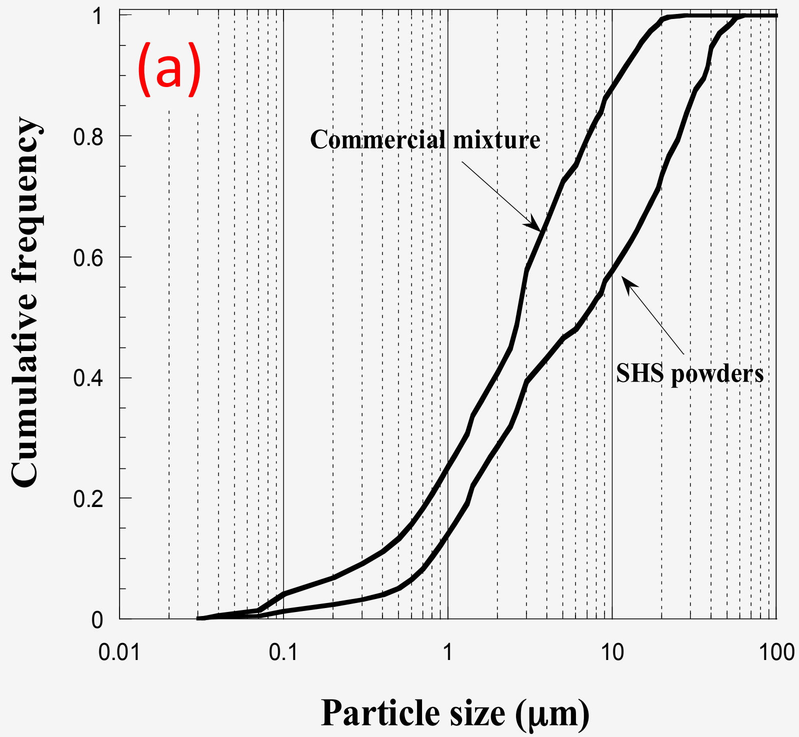
- Mechanical and oxidation resistance properties comparable to the best results reported in the literature

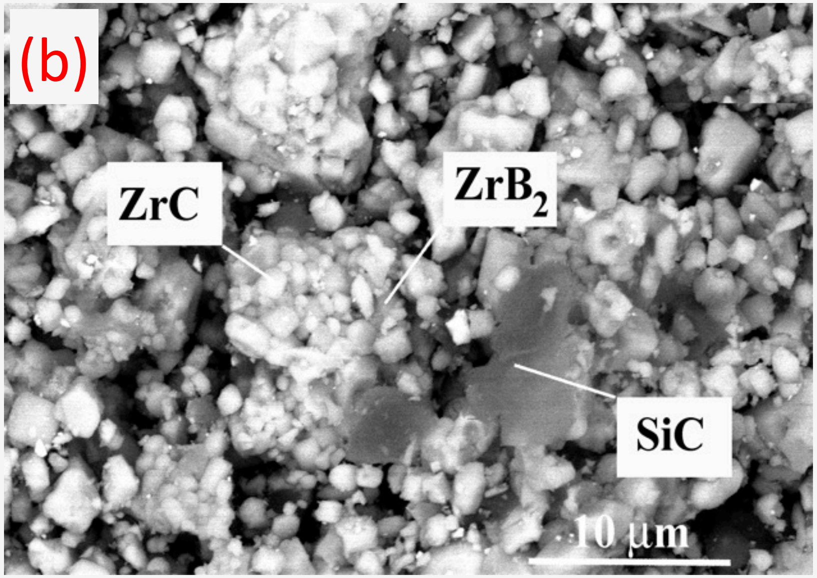


Commercial powders → Only 90.6±1.4% dense materials

The case of ZrB_2-ZrC-SiC

Motivation





- Relatively coarser SHS powders

- Each SHS particle consists of various ZrB_2 and ZrC grains

Strong interfaces between phases

Reduced diffusion distances

The case of HfB_2-$HfSi_2$

Musa et al., Synthesis, Sintering and Oxidative Behaviour of HfB_2-$HfSi_2$ ceramics, Ind. Eng. Chem. Res., **53**, 9101–9108 (2014)

Powders Synthesis by SHS: two options

Single step synthesis: the two components are synthesized in one stage

$$(1+\alpha)\ Hf + 2.2\ B^{*} + 2\alpha Si \rightarrow HfB_2 + \alpha HfSi_2 + B_2O_3 \uparrow$$

Two steps synthesis: the two components are synthesized separately

$$Hf + 2.2\ B^{*} \rightarrow HfB_2 + B_2O_3 \uparrow$$

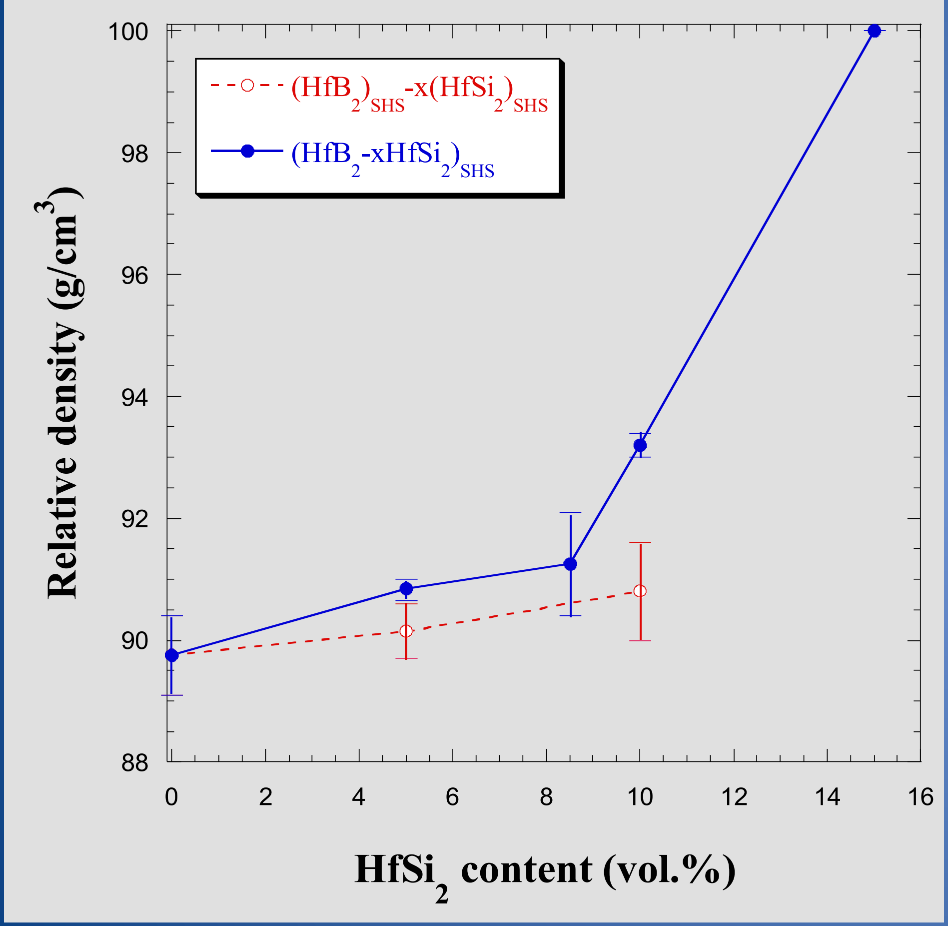
$$Hf + 2Si \rightarrow HfSi_2$$

*Excess of Boron required to compensate its partial loss during the occurrence of the SHS reaction

- Complete reactants conversion
- SHS powders → Similar particles size

The case of HfB_2-$HfSi_2$

Spark Plasma Sintering



- $HfSi_2$ acts as a sintering aid during the SPS process for the densification of HfB_2

- A major effect is displayed when starting from powders where the two constituent phases are simultaneously obtained *in-situ*

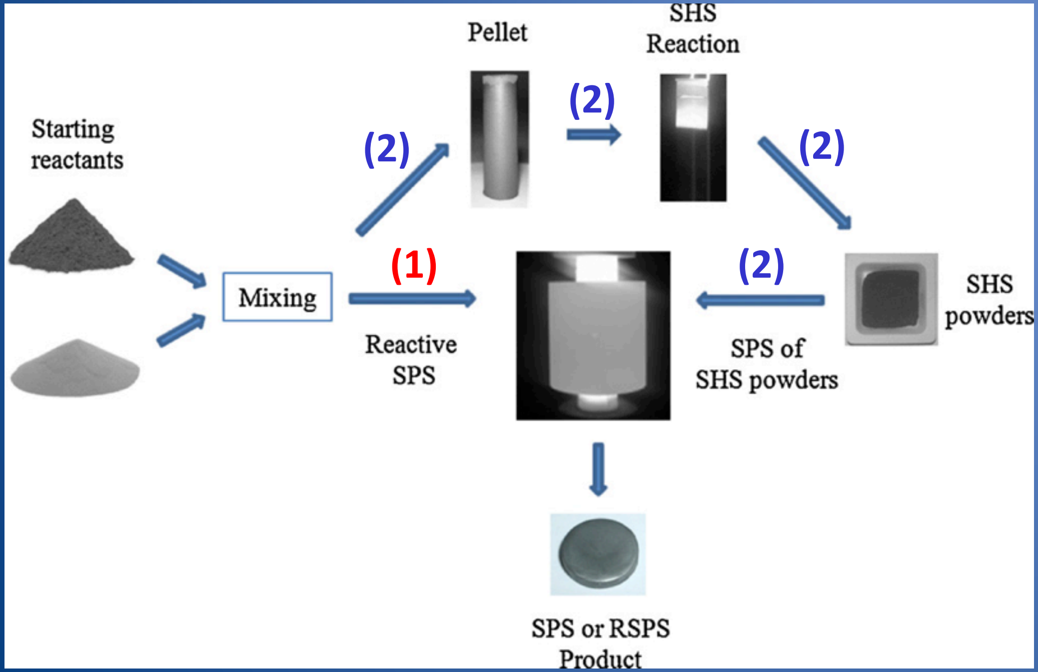
Importance of interface formation during SHS

The case of ZrB_2-SiC

Licheri et al., Efficient Synthesis/Sintering Routes to obtain Fully Dense ZrB_2-SiC Ultra-High-Temperature Ceramics (UHTCs) Ind. Eng. Chem. Res. 46 9087-9096 (2007)

Two processing routes

$$2Zr + B_4C + Si \rightarrow 2ZrB_2 + SiC$$

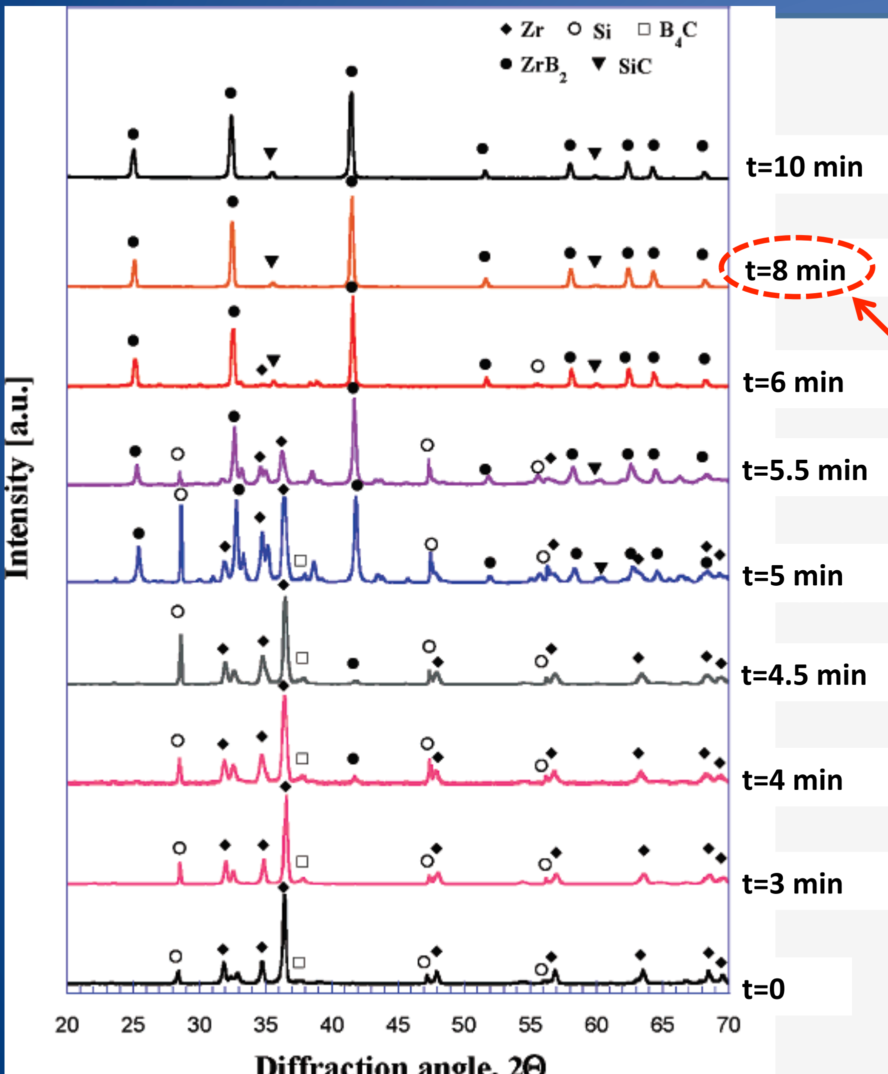


1) RSPS (Reactive SPS): Synthesis and simultaneous consolidation of the material

2) SHS-SPS (SPS of SHS powders): The composite material is first synthesized by SHS and then consolidated by SPS

The case of ZrB_2-SiC

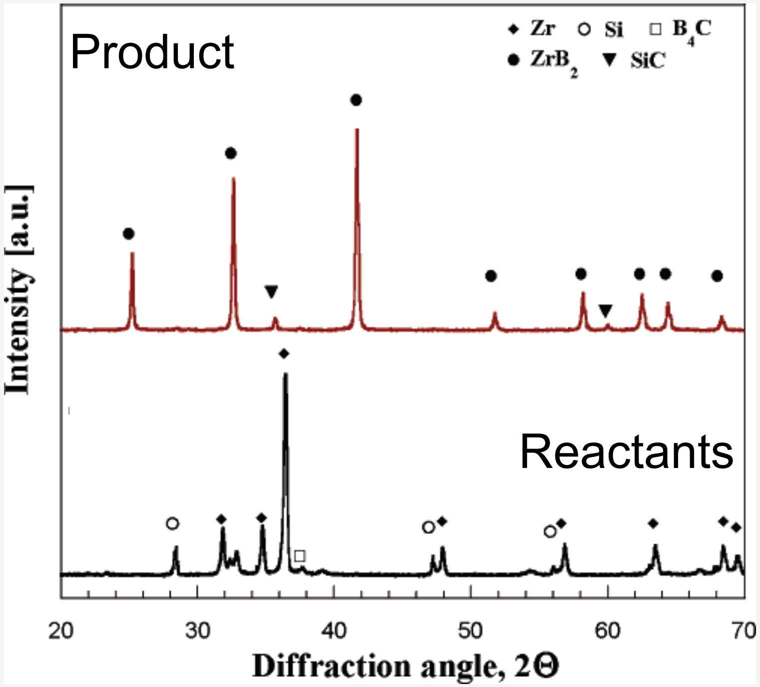
RSPS (T_D= 1900 °C, P=20 MPa)

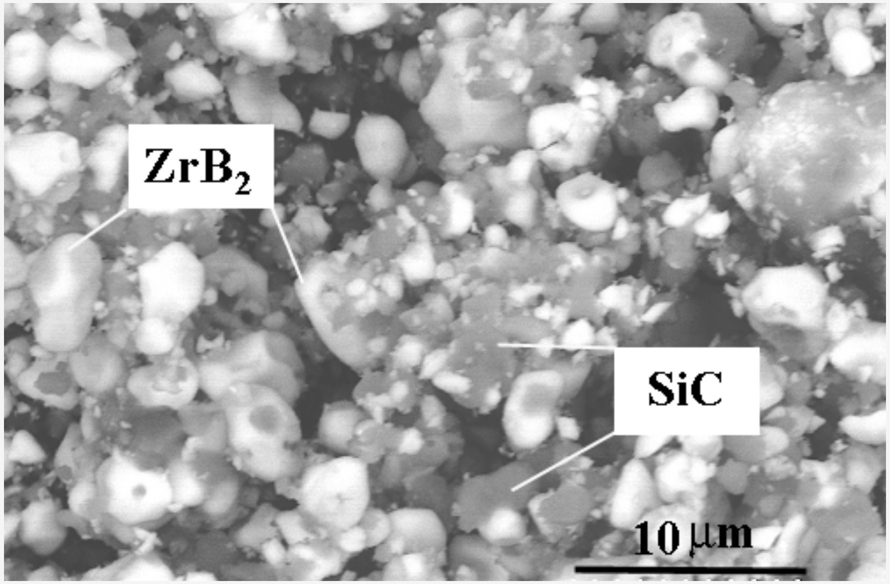


- Gradual solid-state mechanism
- Complete reactants conversion in 8 min
- Full densification (t_T =30 min)

The case of ZrB_2-SiC

SHS-SPS: Powders Synthesis by SHS

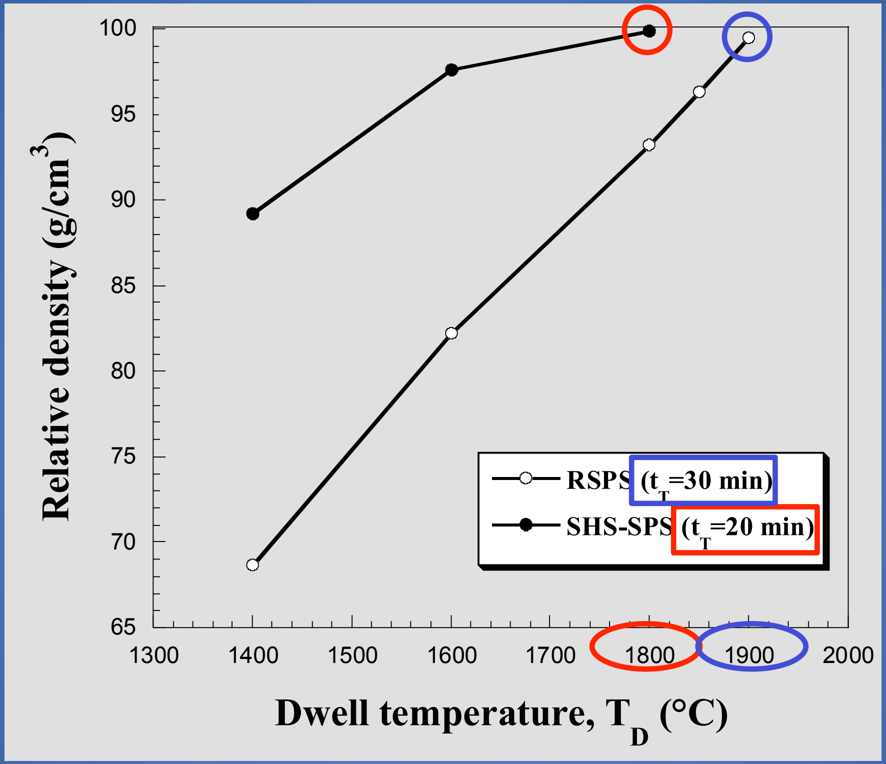




- Complete reactants conversion
- SHS particles → several ZrB_2 and SiC grains

The case of ZrB_2-SiC

RSPS and SHS-SPS: comparison



- SHS-SPS ➔ Relatively <u>milder sintering conditions</u> (1800 °C, 20 min)

- **<u>Different reaction mechanisms</u>**:

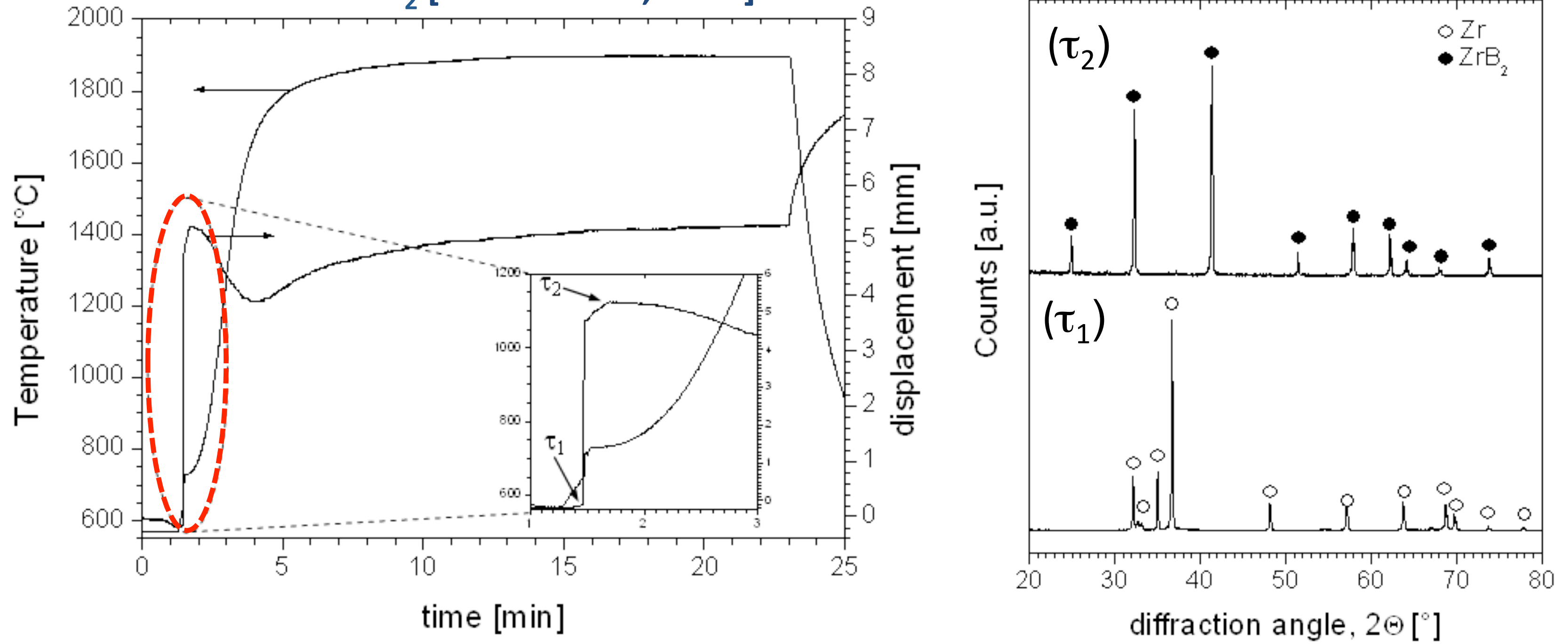
  combustion regime ➔ highly sinterable

Combustion synthesis during RSPS

Induced by:

- **Extremely reactive systems** (highly exothermic, mechanically activated, …)
- RSPS conducted at **high heating rates**

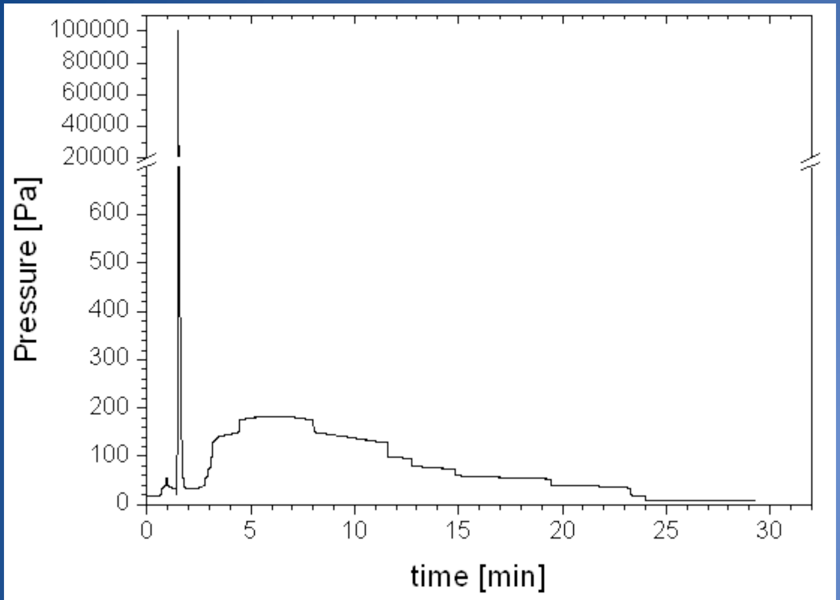
RSPS of ZrB_2 [Licheri et al., 2014]



- Sharp displacement → Combustion synthesis reaction

  Beneficial for powders consolidation

Combustion synthesis during RSPS Drawbacks



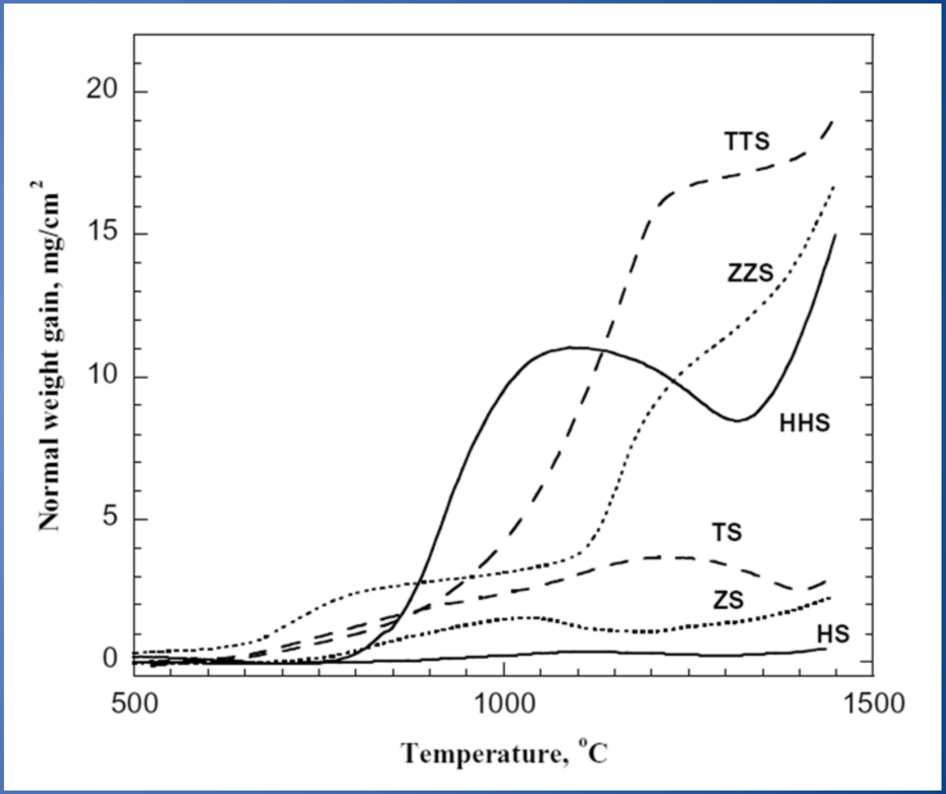
Marked gas pressure increase caused by volatile species (B_2O_3) developed during combustion synthesis (confined environment)

- Powders expulsion
- Products inhomogeneity
- Possible die breakage
- Safety

Problems with process scale up

Properties of bulk UHTC composites obtained by SHS-SPS

System	ρ [%]	Hardness [GPa]	K_{IC} [MPa $m^{1/2}$]
ZrB_2-SiC (ZS)	99.6	HV1 = 16.7±0.4	5.0±0.3
HfB_2-SiC (HS)	> 99.9	HV10 = 19.2±0.6	7.0±0.7
TaB_2-SiC (TS)	~ 96	HV10 = 18.9±0.4	8.4±0.8
ZrB_2-ZrC-SiC (ZZS)	98.7	HV10 = 16.9±0.2	5.9±0.5
HfB_2-Hf-SiC (HHS)	98.5	HV10 = 18.3±1.1	6.2±0.7
TaB_2-TaC-SiC (TTS)	~ 96	HV10 = 18.3±0.3	4.2±0.3



Rational

The observed oxidative behavior can be explained on the basis of several studies reported in the literature on this subject (Hinze et al., 1975; Monteverde and Bellosi, 2003; Monteverde and Bellosi, 2005; Wu et al., 2006). Briefly, the very volatile B_2O_3, obtained from the oxidation of MB_2, combines with SiO_2 formed from SiC oxidation to give a silica-rich borosilicate glass layer. The latter one reduces boria evaporation, other than acting as an oxygen diffusion barrier, thus providing improvement of oxidation resistance of the UHTC materials.

Concluding remarks

- The combination of the SHS and SPS techniques offers a promising opportunity for the consolidation in shorter processing times and milder temperature conditions of difficult-to-sinter ceramic powders

- The SHS route is able to rapidly provide highly sinterable UHTC powders
  - The severe heating and cooling rate conditions ➔ ➔ higher defect concentration in SHS product
  - A significant role is played by the stronger bonds established at the interfaces between the different phases formed *in-situ* during SHS

⬇

Sintering phenomena are promoted

Concluding remarks-2

- The direct passage of the electric current through the powders and the graphite die during SPS leads to very high heating rates, so that sintering phenomena are strongly accelerated

⬇

Processing times can be significantly shortened and sintering temperature lowered

- Comparison with RSPS:
  - Gradual solid-state mechanism → more severe sintering conditions are required with respect to SHS-SPS
  - Combustion regime → several inconveniences

Standard type	Dimension components [mm]	max. pressing force [kN]	max. voltage [V]	max. current [A]	max. heating power [kVA]
HP D 25	Ø 80	250	8	8000	60

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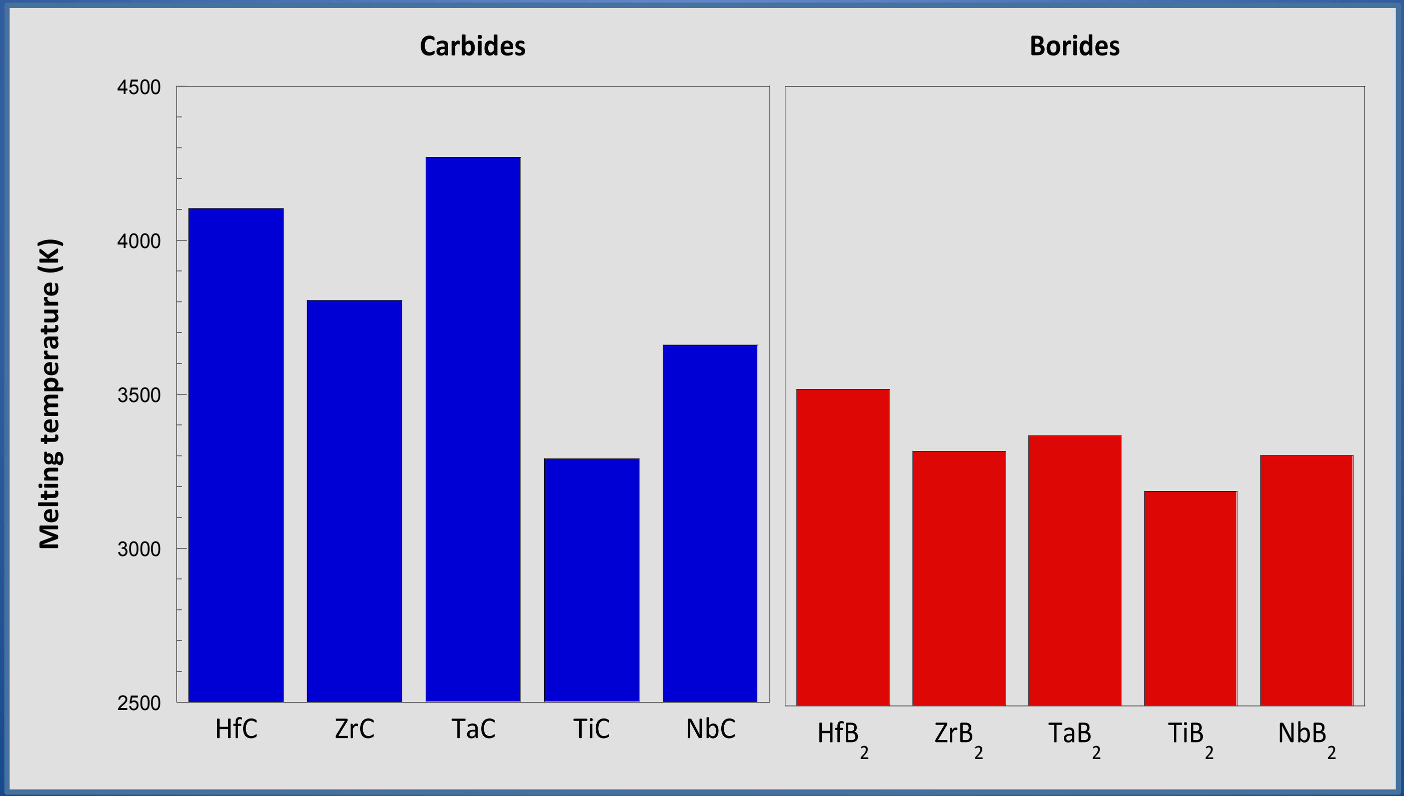
Introduction

- The diffusion and application of highly refractory materials such as transition metal (Zr, Hf, Ta, etc.) borides and carbides (**Ultra-high-temperature ceramics or UHTC**) is hindered by the difficulties for their fabrication in highly dense form



Introduction - 2

- **Bulk UHTCs are typically obtained in dense form by Hot Pressing (HP), through which commercially available powders are sintered**

- **Alternatively, the synthesis and simultaneous densification can be also accomplished by reactive HP using appropriate reaction promoters**

- **The critical aspect related to this processing route is represented by the high sintering temperatures, mechanical loads and, especially, prolonged processing times (on the order of hours), required to achieve acceptable relative density levels** (residual porosity and rather coarse microstructure)

The case of Ti-Al_2O_3-TiC

Musa et al., Energy efficiency during conventional and novel sintering processes: the case of Ti-Al_2O_3-TiC composites. J. Cleaner Prod. 17(9), 877-882 (2009)

Applications: wear parts, engine components, etc.

Powders Synthesis by SHS

$$0.9135\ Ti + 0.585\ TiO_2 + 0.780\ Al + 0.2485\ C \rightarrow$$
$$\rightarrow 1.250\ Ti + 0.390\ Al_2O_3 + 0.2485\ TiC$$

- **Sintering of SHS powders**: conventional **HP** vs **SPS**

HP experiments

HPW 150/200-2200/100-1 A apparatus, FCT Systeme GmbH
(Instituto de Cerámica y Vidrio, Madrid, Spain)