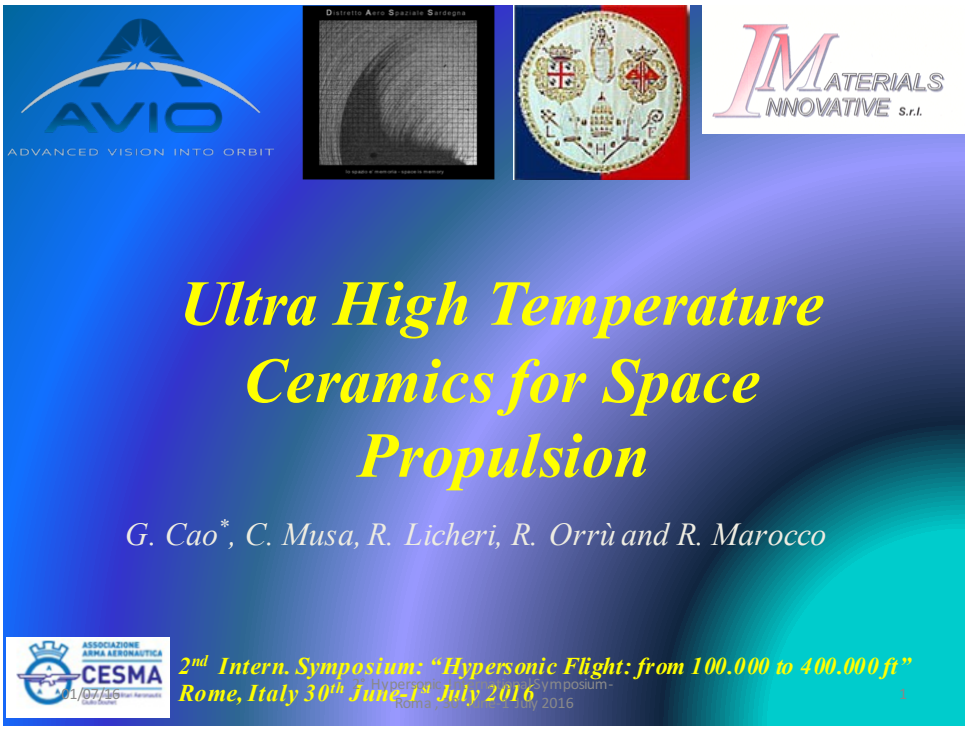
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Ultra High Temperature Ceramics for Space Propulsion
G. Cao*, C. Musa, R. Licheri, R. Orrù and R. Marocco
ASSOCIAZIONE ARMA AERONAUTICA
CESMA
2nd Intern. Symposium: "Hypersonic Flight: from 100.000 to 400.000 ft"
Rome, Italy 30th June-1st July 2016
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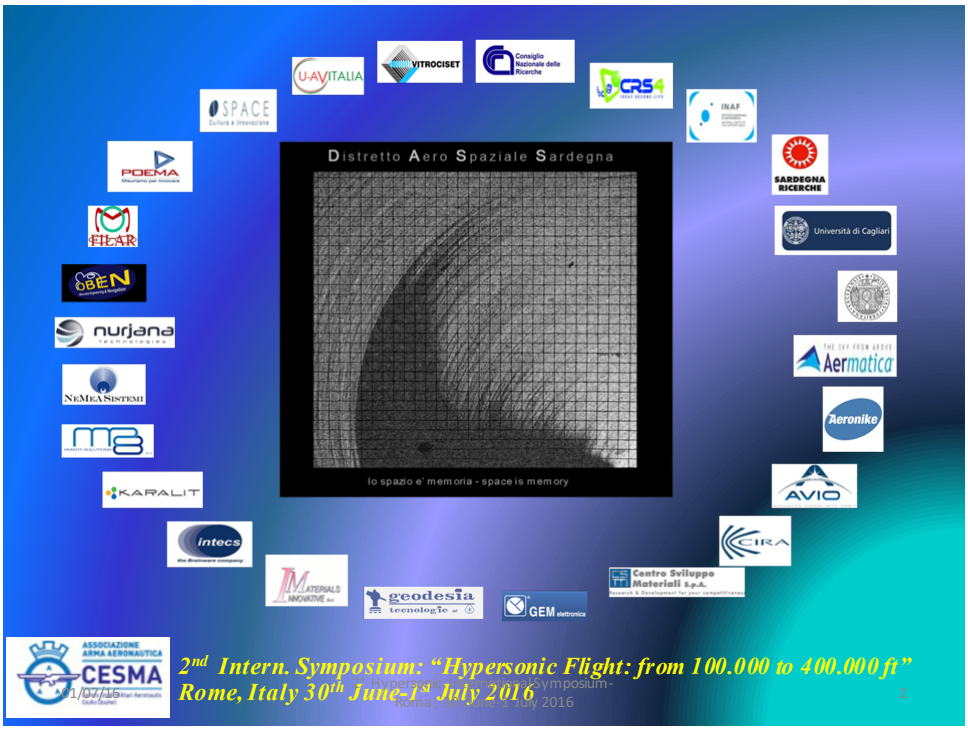
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2

Ultra High-Temperature Ceramics (UHTCs)

UHTCs are based on metal refractory borides and carbides such as ZrB_2 (T_m=3323 K), ZrC (T_m=3805 K), HfB_2 (T_m=3523 K), HfC (T_m=4103 K), TaB_2 (T_m=3373 K), TaC (T_m=3500 K) which make them suitable for high temperature applications in harsh environments such as Thermal Protection Systems (TPS) and Components for Solid Propellant Engines

Addition of silicon carbide (SiC) to these materials strongly improves their oxidation resistance at high temperature as well as room temperature strength

AIM OF THIS WORK

Development and Testing of Innovative UHTCs for Nozzle Components in Small Scale Solid Propellant Engines

General requirements

Suitable combination of : density, thermal expansion coefficient, thermal diffusivity, specific heat, thermal conductivity, mechanical strength and capability to withstand severe environment (CO_2, N_2, H_2, CO, etc.) and temperatures (up to 3000 K)

DEVELOPED STRATEGY

- Fabrication of fully dense small size samples of various UHTC systems
- Screening of UHTC candidates by means of TGA under different conditions (CO_2, N_2, air)
- Fabrication of relatively large size samples for standard testing
- Performing ablation test
- Evaluation of thermophysical properties (Thermal diffusivity and conductivity, heat capacity, etc.)
- Thermo-mechanical properties
- Fabrication of Small Scale Nozzle Components (Prototype)
- Prototype validation under operating conditions of Solid Propellant Engines

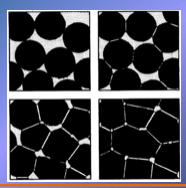
Fabrication of dense UHTC materials
Critical features

Consolidation methods

Pressure-Less Sintering (PLS) or classical Hot Pressing (HP)

Severe sintering conditions:
- *Temperature (> 2000°C)*
- *Processing times (hours)*

- *Coarse microstructure*
- *High production costs*



Sintering stages
(German R.M., "*Sintering Theory and Practice*" Ed. Wiley-Interscience, 1996)

Fabrication of dense UHTC materials

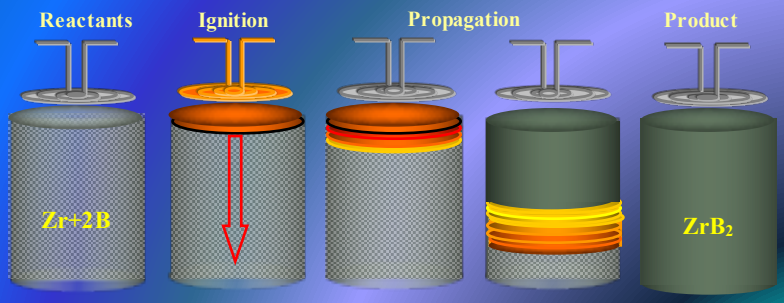
Use of efficient synthesis/sintering methods

SHS (Self-propagating High-temperature Synthesis)
for highly sinterable powders

SPS (Spark Plasma Sintering)
for nearly full dense materials

Self-propagating High-temperature Synthesis

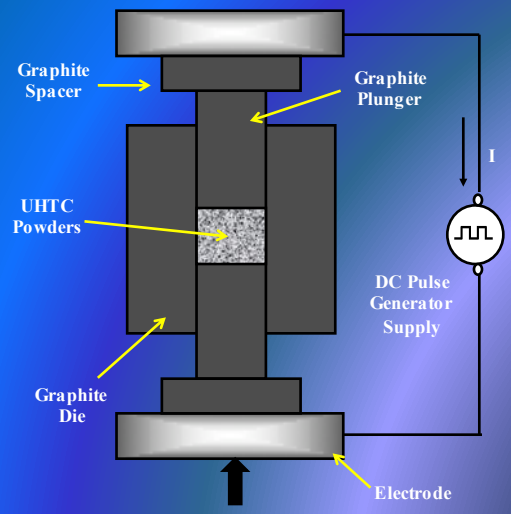
SHS refers to a solid-solid process where an highly exothermic reaction occurs between reactants in powder form (ex. $Zr+2B \rightarrow ZrB_2$, (- H^o)= 323 kJ/mol)



ADVANTAGES

- Extremely rapid process
- High quality of products
- No use of solvents
- Extremely simple process
- Energy saving
- Good sinterability

Spark Plasma Sintering Technology



Simultaneous application of a pulsed electric current and a mechanical load (Joule effect)

Advantages

- Relatively short times (< 1 h)
- Lower temperatures
- Energy efficient

with respect to traditional hot sintering technologies (Hot Pressing)

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SPS equipments

SPS 515S Sumitomo

Small samples

SPS-FCT HP D 25

Large samples

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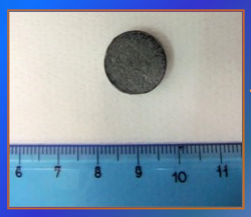
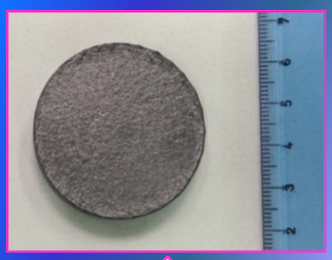
UHTC Systems Investigated

Monolithic		Binary Composites	Ternary Composites
Borides	Carbides		
ZrB_2	ZrC	ZrB_2 - SiC	ZrB_2 - ZrC - SiC
TaB_2	TaC	TaB_2 - SiC	TaB_2- TaC - SiC
HfB_2	HfC	HfB_2 - SiC **(1)**	HfB_2- HfC - SiC
		HfB_2 - SiC **(2)**	
		HfB_2 - SiC **(3)**	

UHTC Samples Produced



TGA and Thermophysical Properties

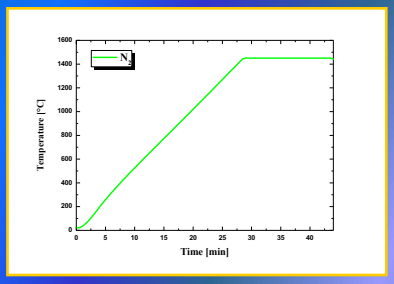


Thermo-mechanical Characterization

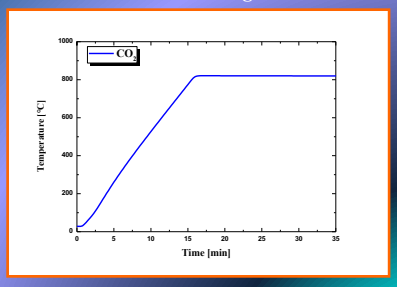
Ablation test

TGA

1) Operating gas: N_2
Maximum operating Temperature: 1450°C
Heating schedule: 50°C/min
Step under isothermal conditions: 15 min
Free cooling

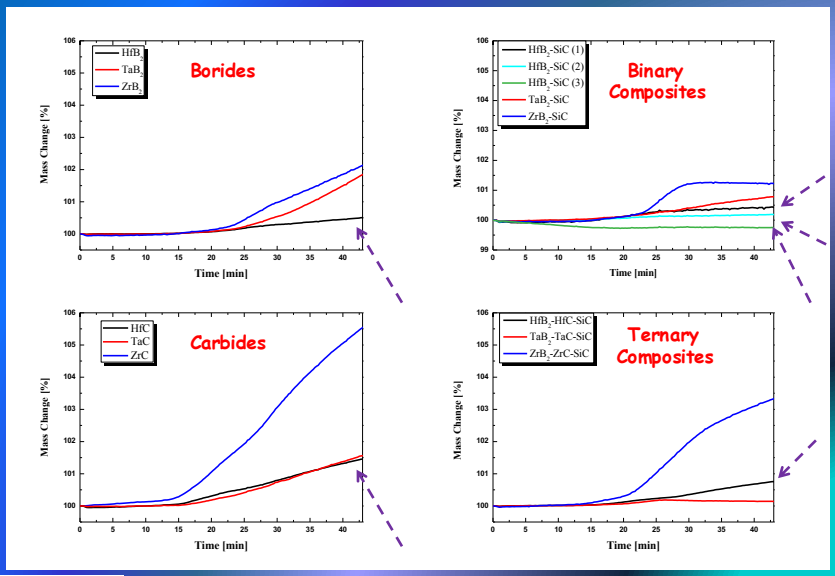


2) Operating gas: CO_2
Maximum operating Temperature : 800°C
(degradation of thermocouples at higher T)
Heating schedule : 50°C/min
Step under isothermal conditions: 20 min
Free cooling

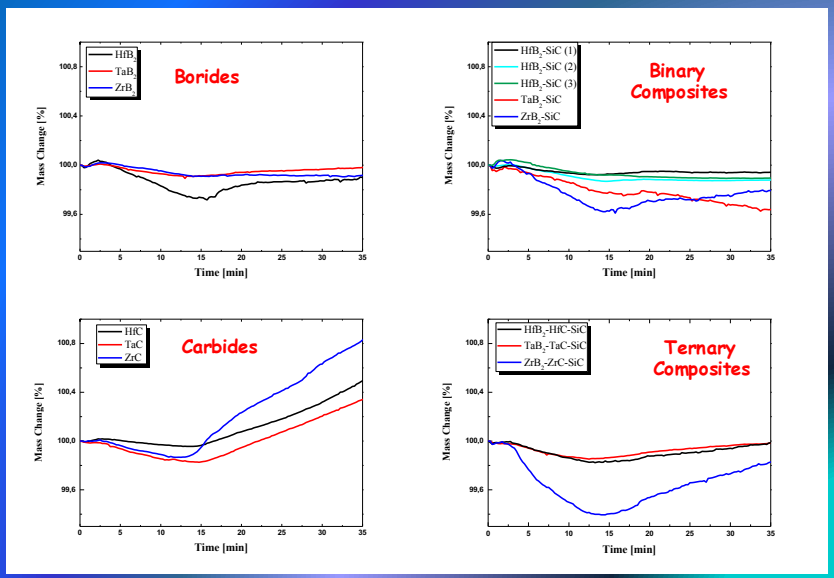


3) Operating gas: Air
Maximum operating Temperature: 1450°C
Heating schedule: 2°C/min
Free cooling

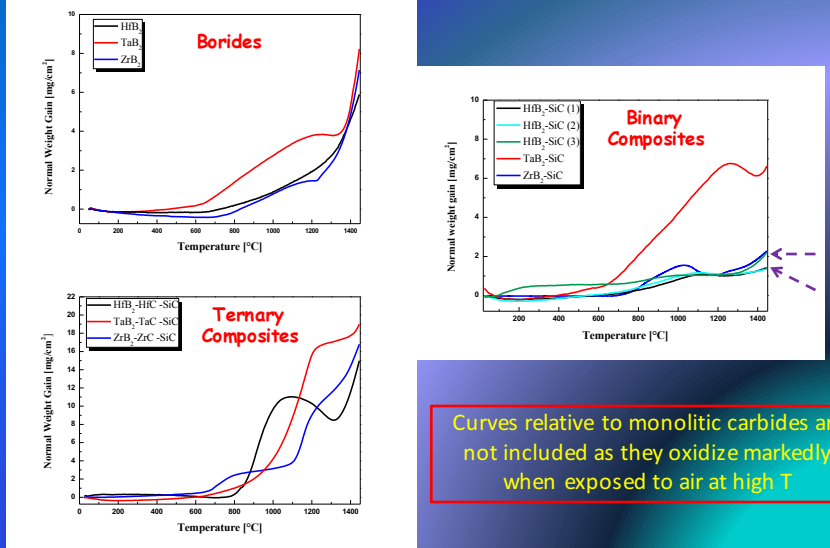
TGA in N_2_Results (1)



TGA in CO_2_Results (2)



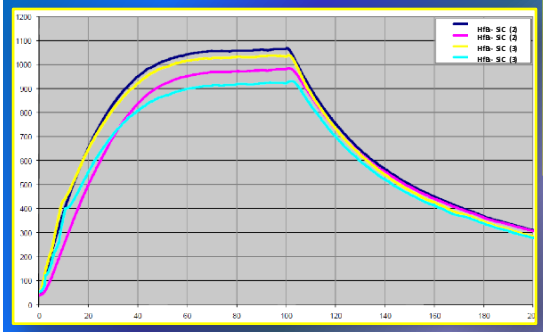
TGA in Air_Results (3)

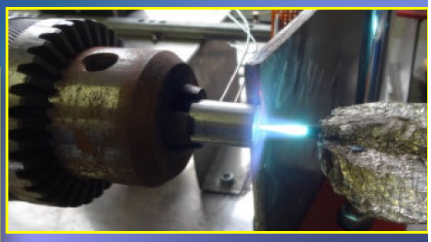


Curves relative to monolitic carbides are not included as they oxidize markedly when exposed to air at high T

Ablation Test

Beginning of the test





During the test

Ablation Test

Weight losses

		Virgin (g)	HF1 (g)	Delta W1 (%)	HF2 (g)	Delta W2 (%)	HF3 (g)	Delta W3 (%)
HfB_2- SiC (2)	1	28.88521	28.87780	0.02565	28.87673	0.02936		
	2	29.38954					29.38196	0.02579
	3	29.23627	29.23177	0.01539	29.22461	0.03988		
HfB_2- SiC (3)	1	29.20405					29.13924	0.22192
	2	29.38484	29.38183	0.01024	29.38136	0.01184		
	3	29.79464	2979442	0.00074	29.79479	-0.00050		

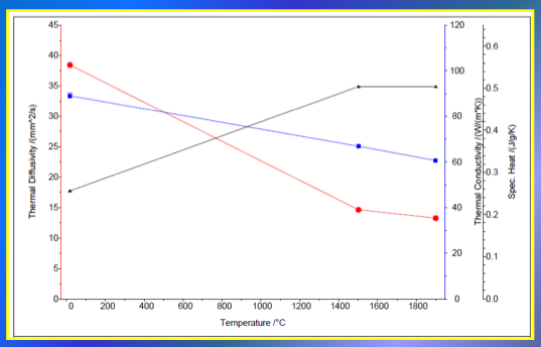
Heat Flux 1 (**HF1**) = 450 W/cm² for 120 s _ A/O ratio 1:1.3

Heat Flux 2 (**HF2**) = 1050 W/cm² for 80 s _ _A/O ratio 1:1.3

Heat Flux 3 (**HF3**) = 1250 W/cm² for 100 s _ A/O ratio 1:1.7

Weight losses of samples during ablation tests are negligible

Thermo-physical characterization



Thermal Diffusivity and Conductivity decrease up to 1900°C with the typical dependence for phonon conductors.

Temperature /°C	Thermal Diffusivity /mm²/s	Specific Heat /J/(gK)	Thermal Conductivity /W/(mK)
18	38,448	0,256	89,026
1500	14,653	0,504	66,880
1898	13,278	0,504	60,603

Conclusions

- UHTCs formulations identified and obtained in this work as fully dense products are very promising for High Temperature applications in aggressive environments.
- In particular, based on the results obtained with TGA tests conducted with different gaseous environments, the HfB_2-SiC system was selected for the fabrication of small size nozzle components
- The capability of HfB_2-SiC system to withstand harsh conditions was confirmed by the additional characterizations carried out:
  - Ablation tests conducted under different heat fluxes
  - Evaluation of thermophysical properties at high T

Work in progress and future plans

- Thermo-mechanical characterization at high T
- Fabrication of Small Scale Nozzle Components
- Prototype validation under actual operating conditions of Solid Propellant Engines
- Future work: Process scale-up for the fabrication of larger sized components