NOVEL CERAMICS AND COMPOSITES PROCESSING TECHNOLOGIES FOR ENERGY-INTENSIVE APPLICATIONS

27 SEPTEMBER, 2024

CEM-WAVE

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MW-CVI production of large SiC-based CMCs for energy intensive industries: a challenge won?

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Summary

1) Introduction

    a) Energy-intensive industries & steelmaking decarbonization pathways;
    b) CMCs application in steelmaking sector;
    c) CMCs manufacturing methods;

2) MW-CVI process background

    a) Design & Improvements of the MW-CVI pilot plant
    b) Challenges and Upgrades

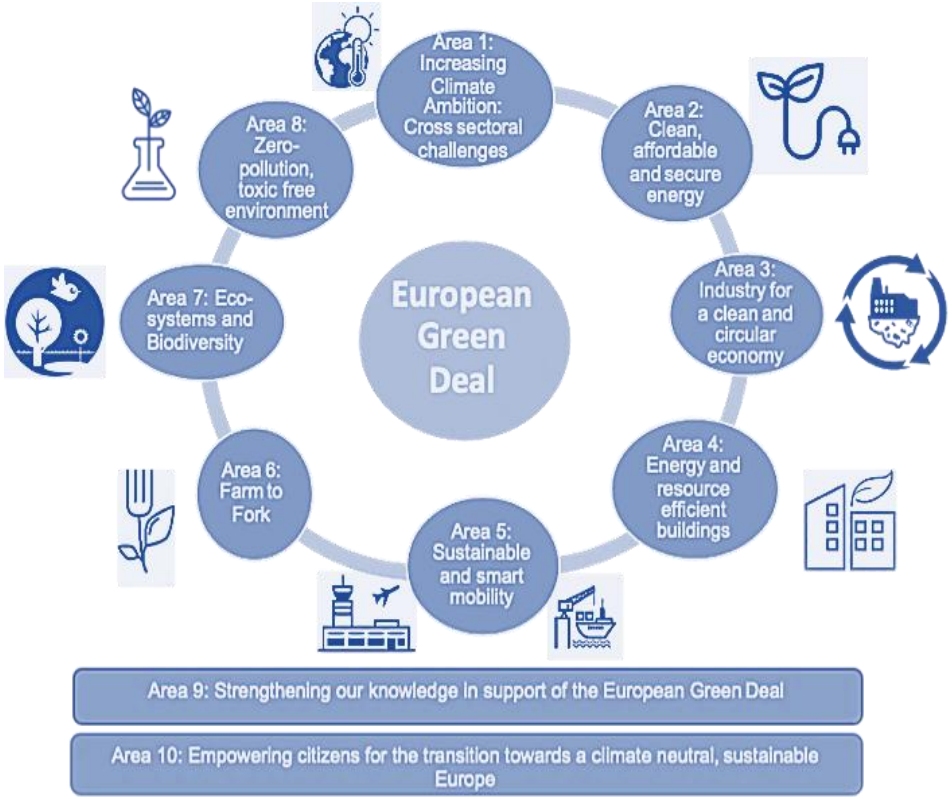
3) MW-CVI processing of large SiC-based CMCs

    a) MW-CVI processing of SiC_f/SiC square-shaped preforms
    b) MW-CVI processing of SiC_f/SiC tubular-shaped preforms

4) Conclusions

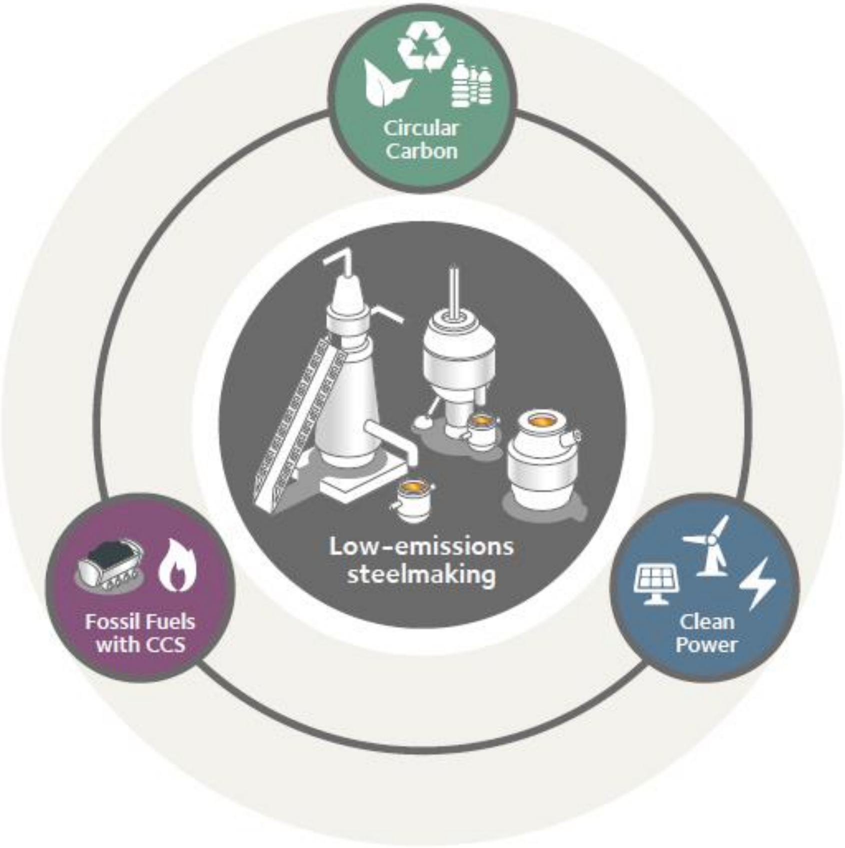
1. Introduction

❖ Over the last century an increasing need to develop stronger, tougher and more chemically resistant structural materials has been observed



https://eur-lex.europa.eu/resource.html?uri=cellar:b828d165-1c22-11ea-8c1f-01aa75ed71a1.0006.02/DOC_1&format=PDF

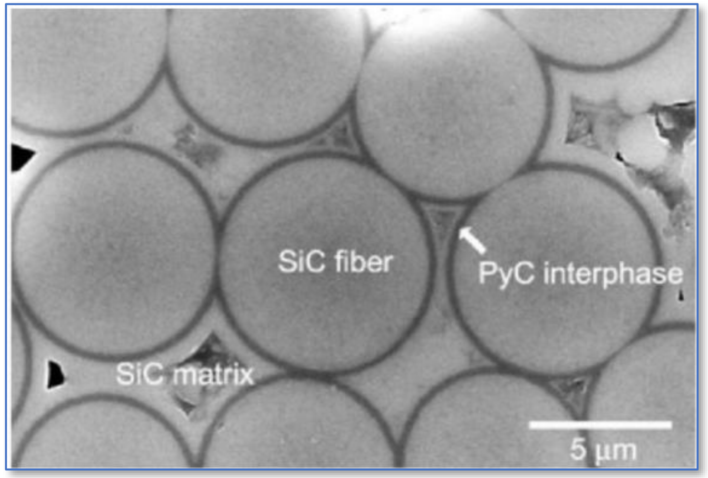
❖ Steelmaking industries will need to follow one or more low carbon emissions pathways



https://automotive.arcelormittal.com/news_and_stories/blog/2019PathToLowCarbonSteelmaking

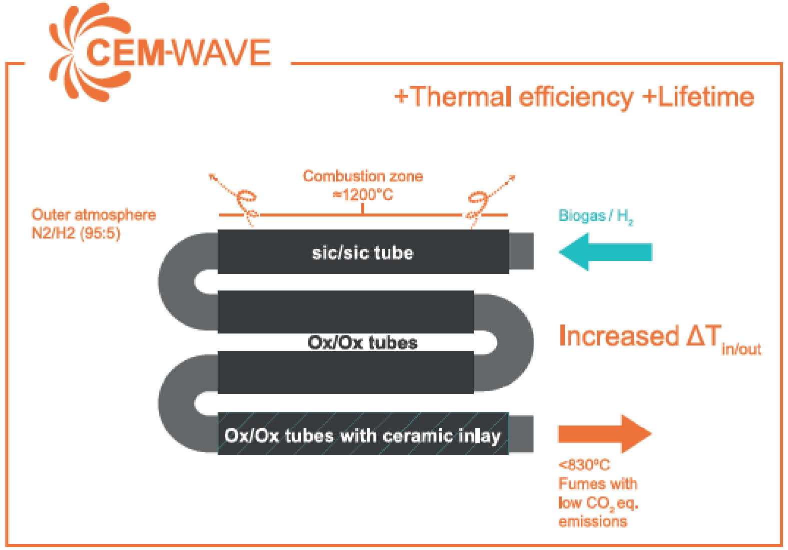
❖ **SiC_f/SiC CMCs** are promising materials for thermo-structural applications in various strategic sectors (i.e. aerospace, energy) due to their:

- Good high-temperature mechanical properties
- Low density
- High toughness
- High oxidation resistance



❖ In the framework of the **EU CEM-WAVE project**, the application of SiC_f/SiC has been proposed for the replacement of Inconel superalloys in the hottest section of ***radiant tube furnaces*** for steelmaking applications:

- T^{MAX} ~ 900-1000°C
- Average lifetime ~ 4 years

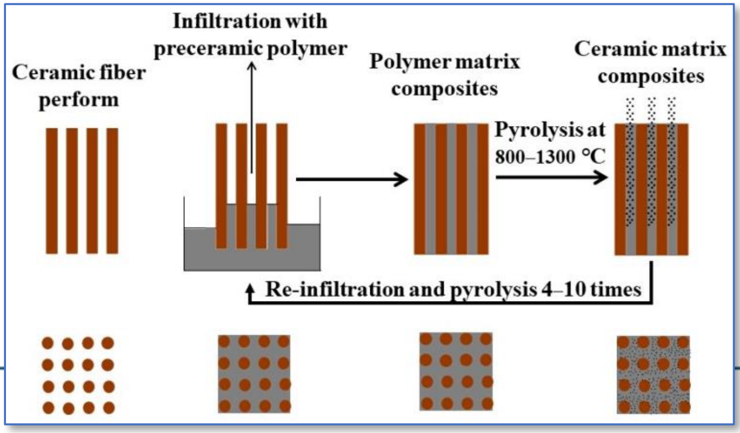


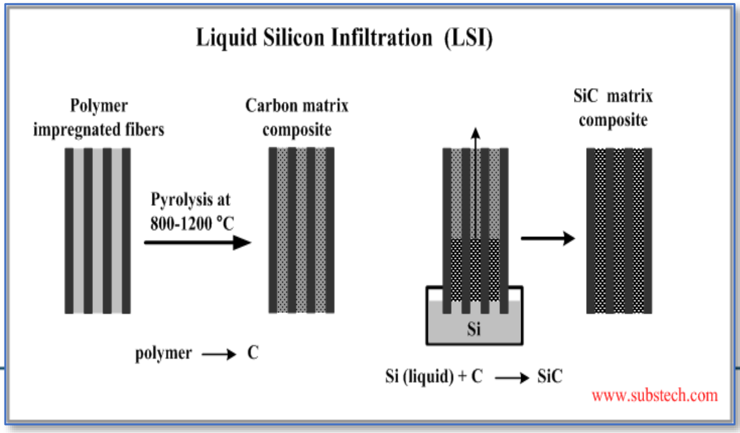
Simplified SiC matrix synthesis processes are needed to reduce production costs

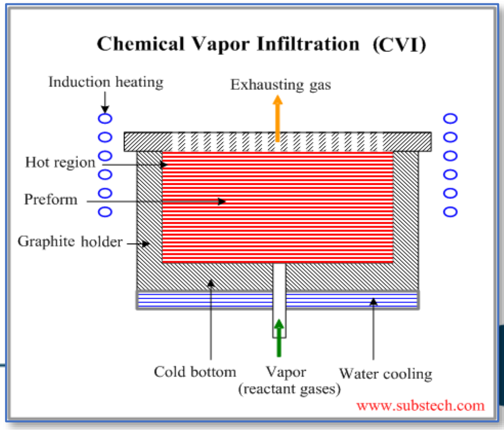
Kim, Daejong & Kim, Weon-Ju & Park, Jeong Yoon. (2012). Compatibility of CVD SiC and SiCf/SiC Composites with High Temperature Helium Simulating Very High Temperature Gas-Cooled Reactor Coolant Chemistry

1.1 SiC_f/SiC CMCs manufacturing by infiltration methods

	Polymer Infiltration and Pyrolisis (PIP)	Liquid Silicon Infiltration (LSI)	Chemical Vapor Infiltration (CVI)
Advantages	• Low temperature (prevents fiber damage) • Good control of microstructure and composition • No free silicon in the matrix	• Low cost • Short production time • Low residual porosity	• High purity matrices • Low temperature (prevents fiber damage) • Excellent mechanical properties • Often smooth process surfaces
Disadvantages	• Multiple infiltration-pyrolysis cycles • High production cost • High residual porosity • Poorly SiOC, SiCN crystalline matrices	• High temperature and highly corrosive metal melt (may damage fibers) • Residual free silicon • Low mechanical properties • Rough surfaces need machining with diamond tools	• Very slow process (~several weeks) • High residual porosity (15-20%) due to crusting • High capital and production costs



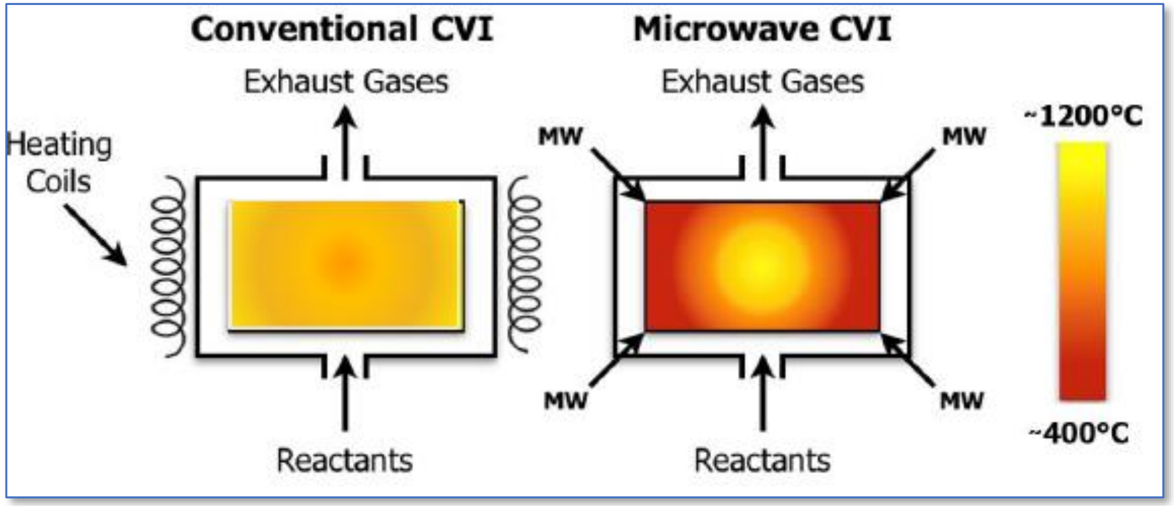




1.2 MW-CVI process: Advanges & challenges

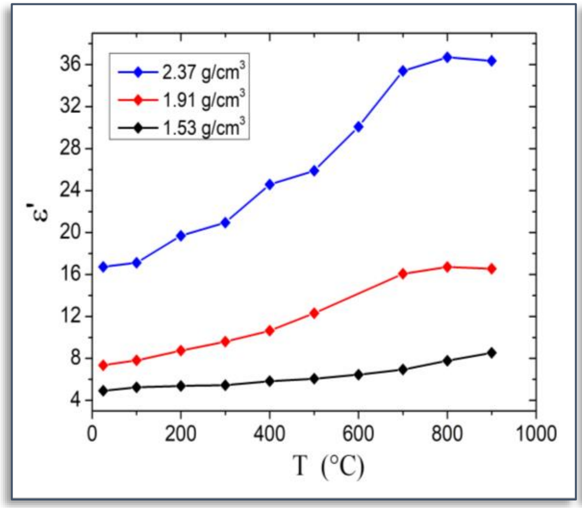
- The Microwave-assisted CVI (**MW-CVI**) is an attractive alternative to manufacture SiC-based CMCs due to:

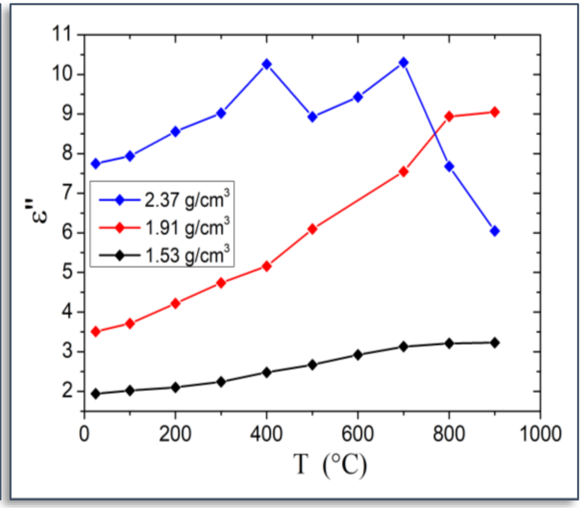
  - Sample volumetric heating (Inverse T profile)
  - Faster processing
  - Significant cost reduction

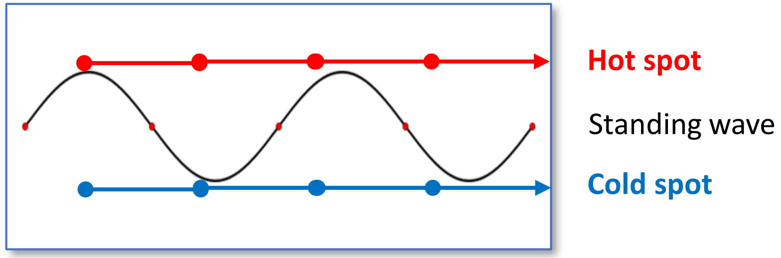


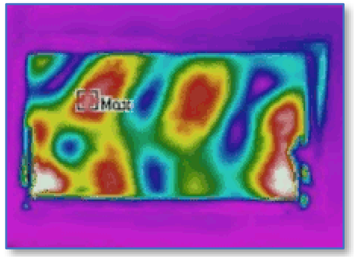
- Among the major challenges of MW-assisted processes there are:

  1) Non-uniform heating
  2) Plasma occurrence
  3) Control and optimization of the MW-heating with dielectric properties change





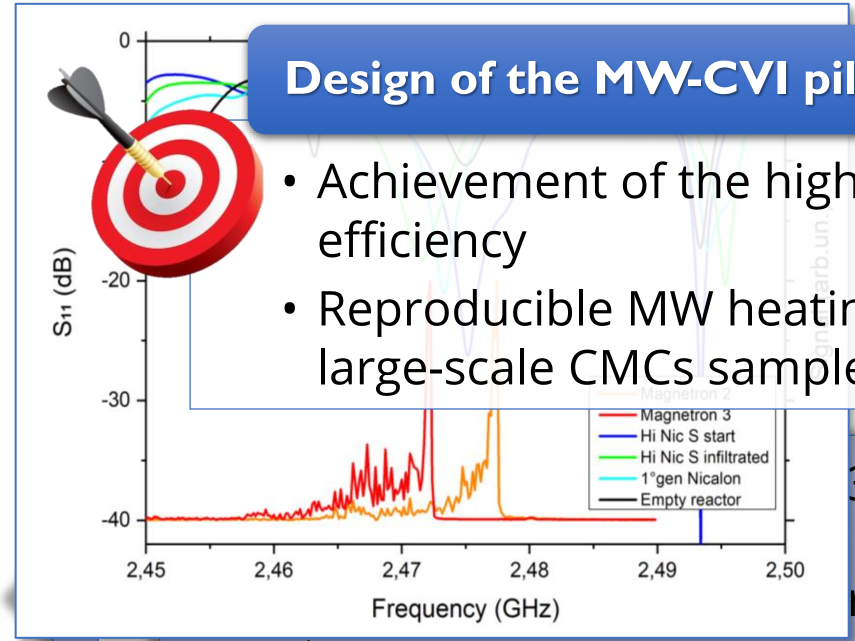




D'Angió, A. "Microwave enhanced chemical vapour infiltration of silicon carbide fibre preforms." (2018).

2. MW-CVI reactor: Design & Improvements

- **Duration:** 48 months (2012-06-01 to 2016-05-31)
- **Total cost:** EUR 10,285,626
- **EU contribution:** EUR 7,151,000
- **Programme acronym:** FP7-NMP
- **Subprogramme area:** NMP.2011.4.0-1
- **Contract type:** Large-scale integrating project



Design of the MW-CVI pilot plant in Pisa:

- Achievement of the highest MW heating efficiency
- Reproducible MW heating of relatively large-scale CMCs samples

3 **Magnetrons**, each

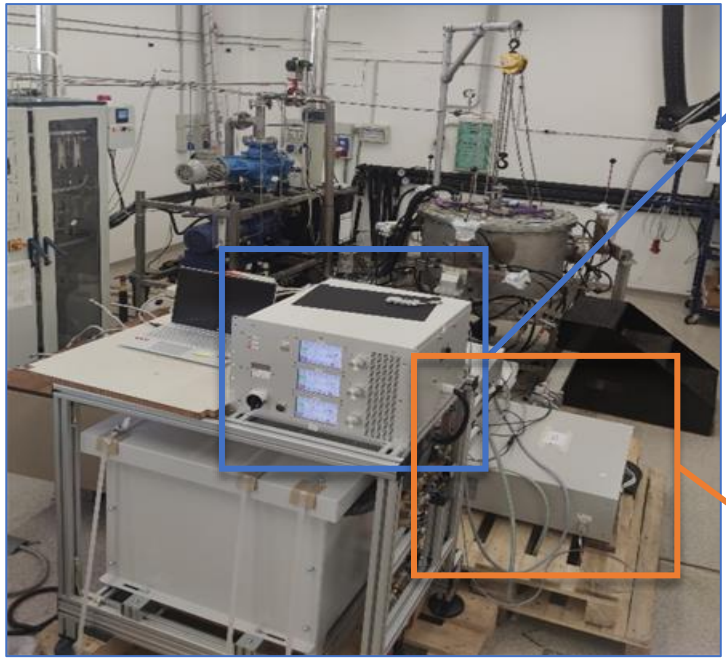
requency band 2,4 ÷ 2,5 GHz

- 3 kW power

❖ A MW **Solid-State source** system has been developed by Fricke und Mallah (Peine, Germany):

- 3 x 2kW Solid-State Generators (SSGs)
- 2400 – 2500 MHz ISM band (1 MHz step)
- 3 x 3 kW isolator

Fricke und Mallah Microwave Technology

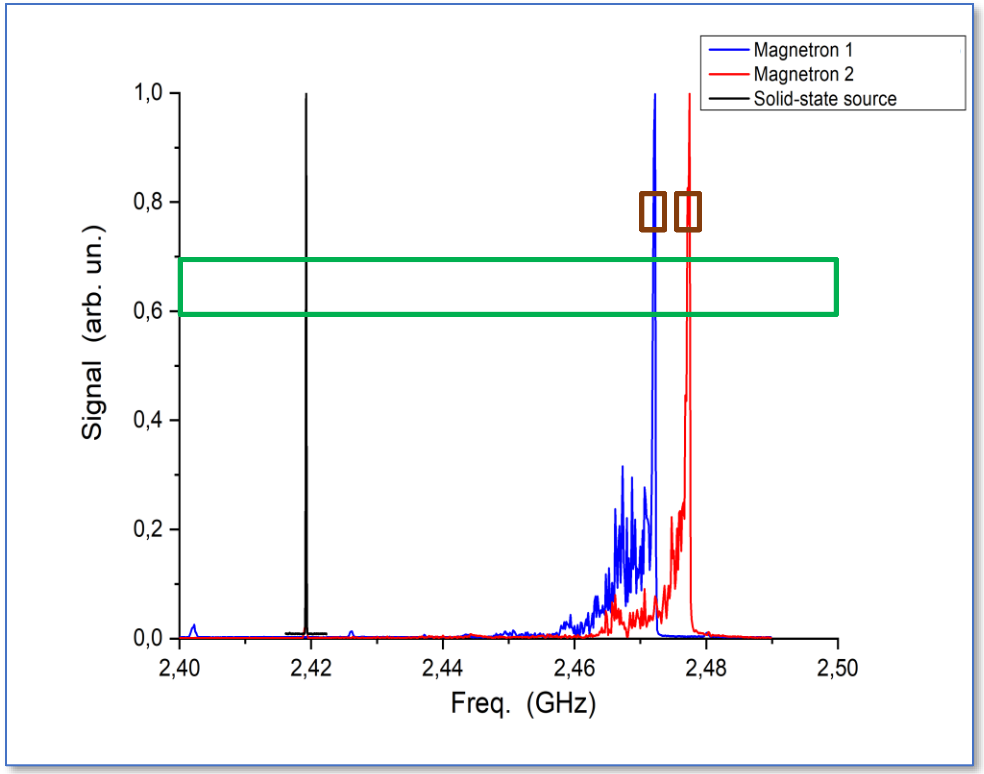


Control unit interface

2 kW SSG + isolator

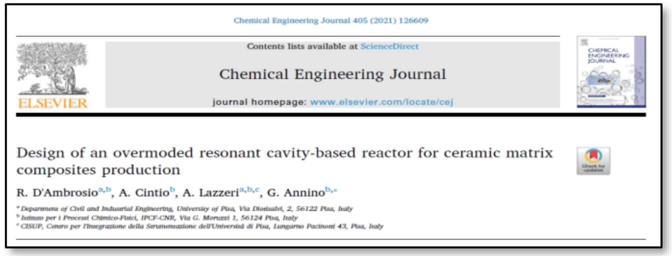
Frequency interval covered by magnetrons

Frequency interval covered by s.-s. sources



EM Design of the MW-CVI reactor

- Design of a high quality **Overmoded** resonant cavity
- **Multiport** excitation scheme



Chemical Engineering Journal 405 (2021) 126609

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Design of an overmoded resonant cavity-based reactor for ceramic matrix composites production

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Original Article

Design of a pilot-scale microwave heated chemical vapor infiltration plant: An innovative approach

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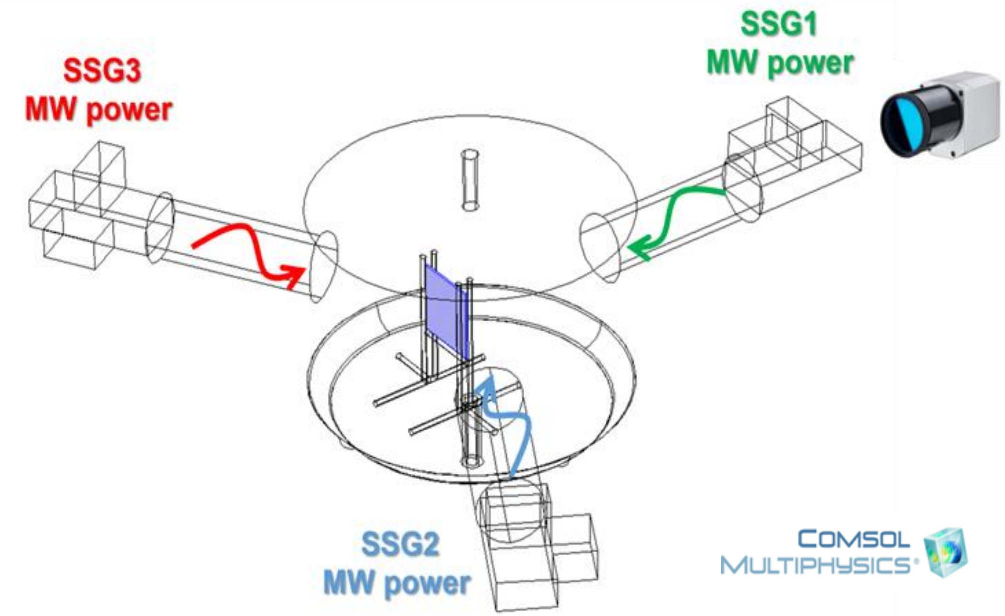
Optris PI 1M overview

Temperature range	Spectral range	Frame rate	Detector
500 to 1800°C	0,85-1,1 µm	Up to 1 kHz	CMOS, 764x480 px @ 32 Hz

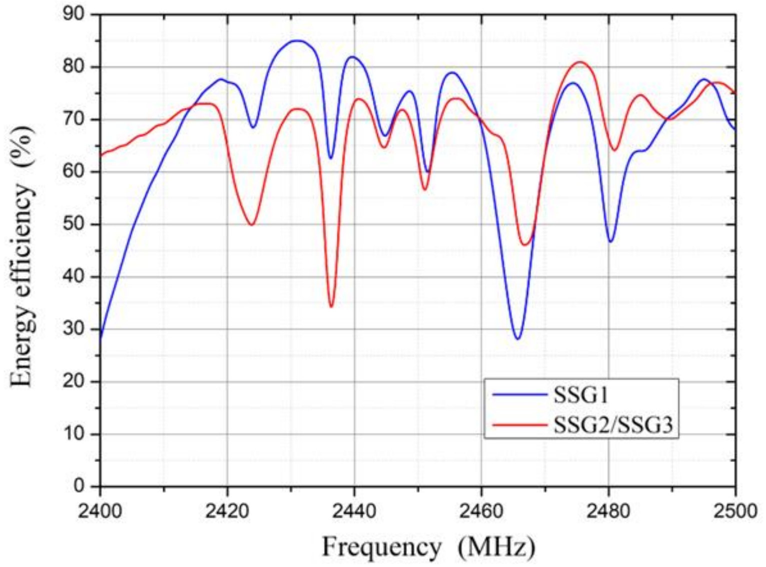


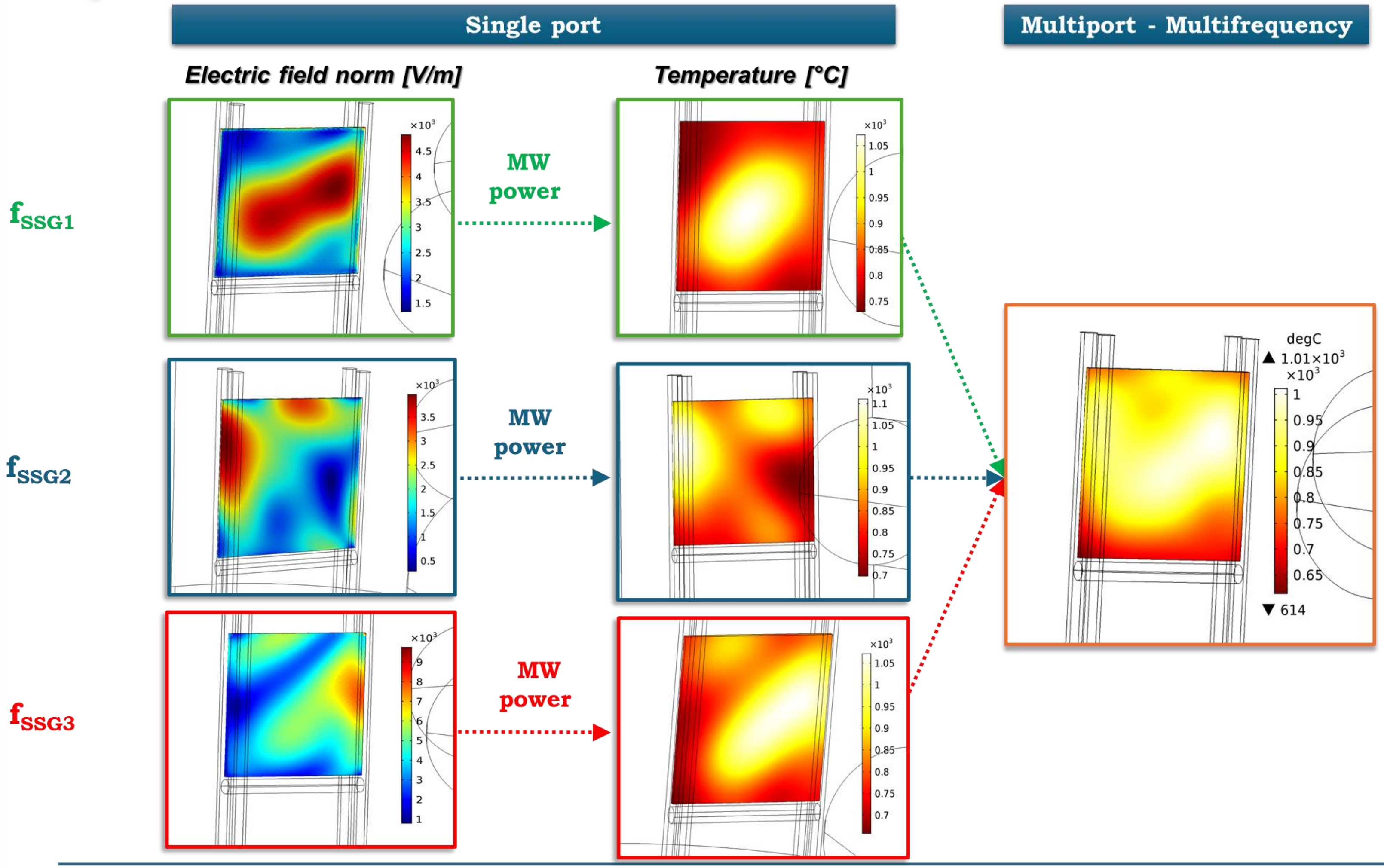
- A **Multiport-Multifrequency** approach has been developed, whose main benefits are:
  1) Higher degree of electric field homogeneity;
  2) Reduced risk of plasma formation;
  3) Reduced risk of unwanted MW coupling between the different channels (cross-coupling) with higher process energy efficiencies;

Operating frequencies selection

- Highest energy efficiency
- Mode characteristics
- Minimum cross-coupling

$$\eta = \frac{P_s}{P}$$





3. MW-CVI processing of large SiC-based CMCs

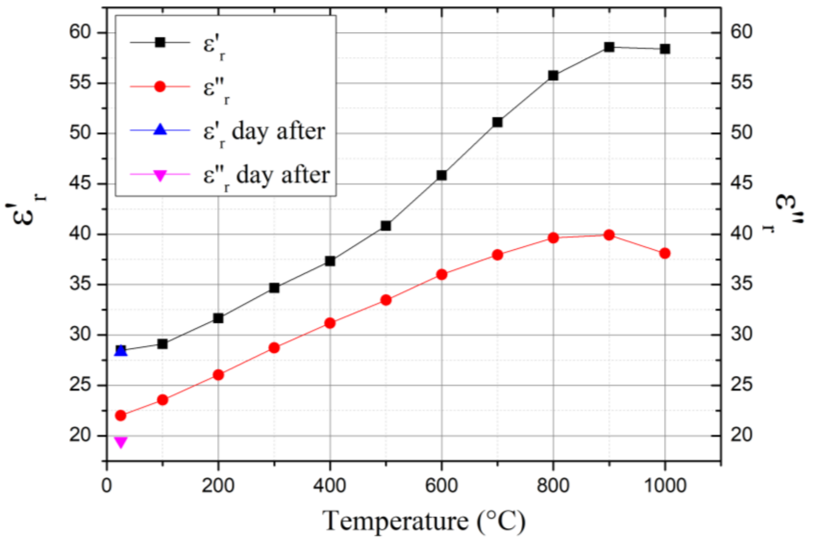
Fraunhofer ISC

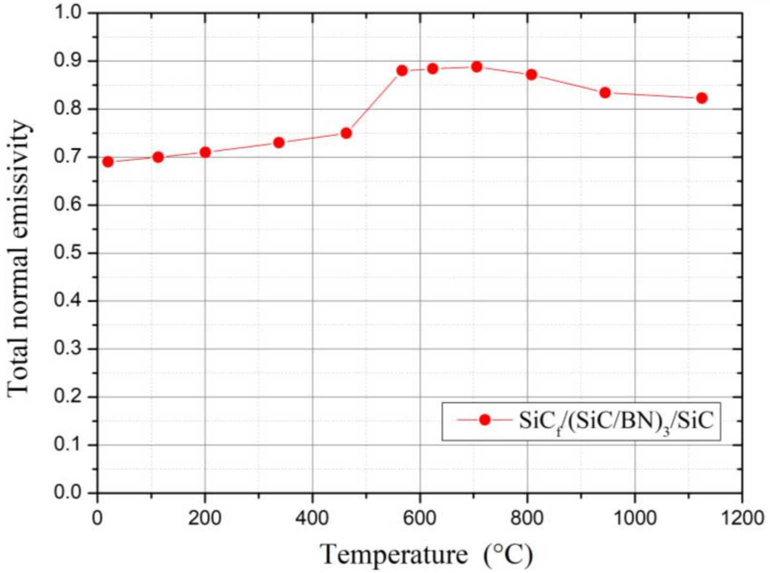
- ❑ Two square-shaped and one tubular-shaped $SiC_f/(SiC/BN)_3/SiC$ preforms have been successfully infiltrated by the MW-CVI process;
  - The $SiC_f/(SiC/BN)_3/SiC$ preforms have been manufactured by Filament Winding method by Fraunhofer ISC (Bayreuth, Germany)
- ❑ The Multiport-Multifrequency approach has been employed to tailor the SiC_f/SiC preforms temperature profile exploiting the frequency tunability of MW Solid-State sources;
- ❑ The choice of the most suited excitation frequencies has been guided by rigorous numerical modeling of the reactor loaded by the sample of interest;

#ID sample	SiC_f/SiC-1	SiC_f/SiC-2
Roving	200 tex	200 tex
Green body matrix	Epoxy	Epoxy
Pyrolised matrix	Carbon	Carbon
Porosity [%vol]	40.0	40.0
Density [g/cm³]	1.19	1.19
Geometry [B x L x T, cm]	10×10×0.26	10×10×0.27

- The dielectric properties have been determined as a function of the temperature up to 1000°C by a facility available at **IPCF-CNR** premises
- The total normal emissivity has been determined as a function of the temperature up to 1000°C by **CEMHTI** laboratory (Orléans – France)
- The SiC matrix densification pattern and porosity levels distribution in the sample volume post-infiltration have been characterized by a high-resolution micro-focus computed tomography (µCT)

CT Scan parameters V|TOME|X M 300	Square-shaped samples
Voltage/current	150 kV / 170 µA
Filters	0.5 mm Cu
Focus-to-Object Distance (FOD) - Focus-to-Detector Distance (FDD)	102.640 - 808.217 mm
Voxel size	26.02 µm
Exposure time	250 ms
Averaging/Skip	1/0
Sensitivity	0.5

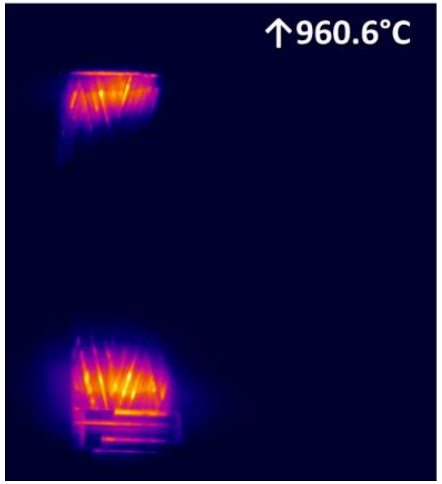




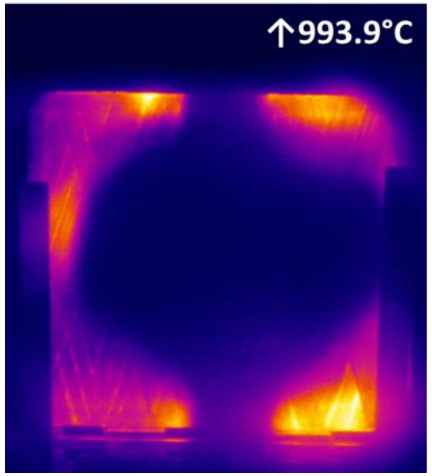
- Both the investigated samples, underwent a 10 h infiltration cycle
- The CMC sample temperature distribution matched quite well with that determined by numerical modelling along WP2 (~5 MHz difference)
- Along the infiltration process, the CMC regions at the infiltration temperature steadily expanded towards the center
- The surface-to-core temperature difference in the CMC sample, estimated by numerical modelling, was of about 80°C

MW-CVI final Results & Parameters						
Pressure [mbar]	Temperature [°C]	Average MW transmitted Power [W]			Average deposition rate [g/h]	Average Chemical Efficiency [%]
		SSG1 2428 MHz	SSG2 2443 MHz	SSG3 2470 MHz		
200	900-1000	473	548	470	0.72	4.50

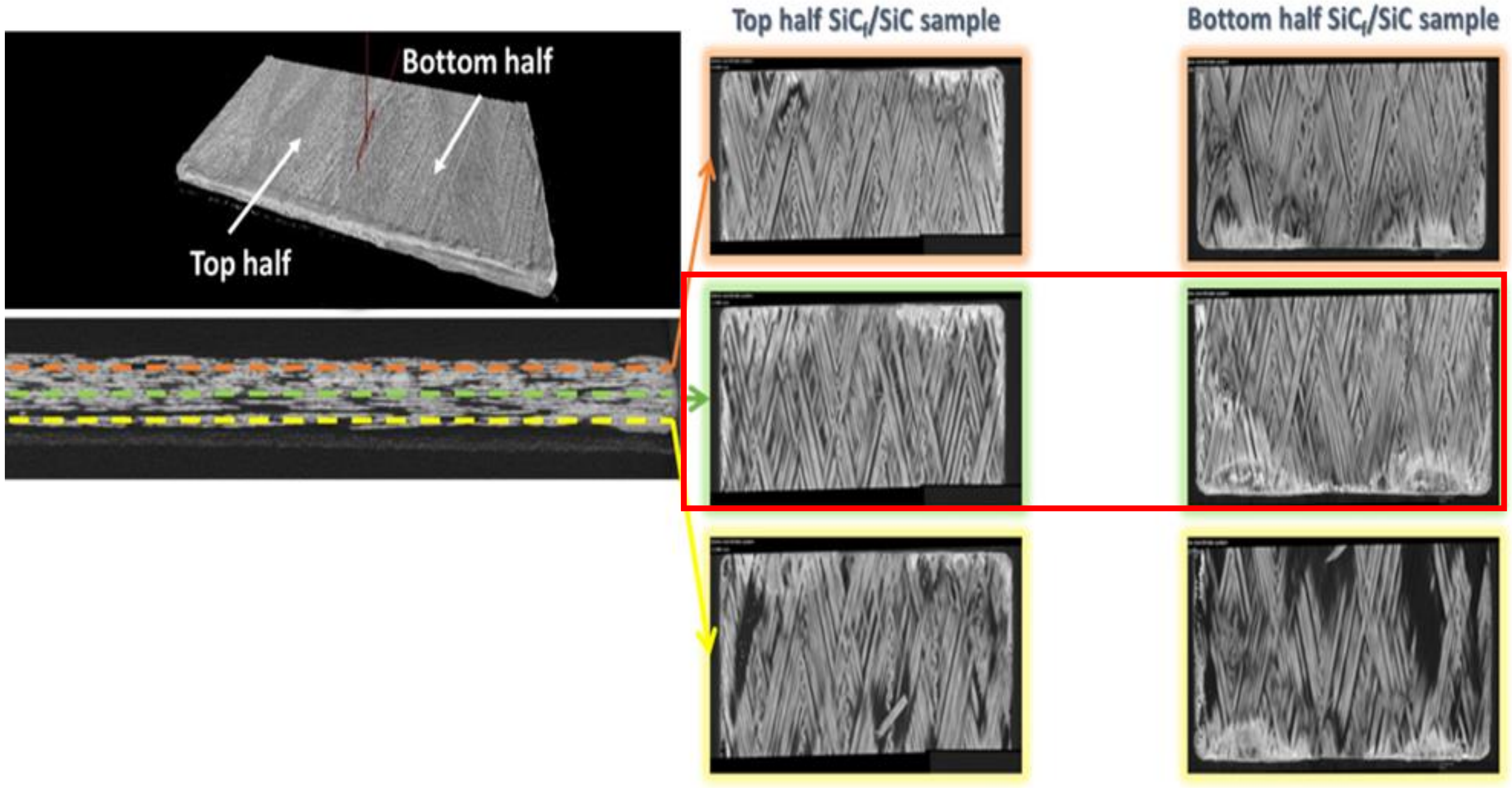
T profile – Infiltration start



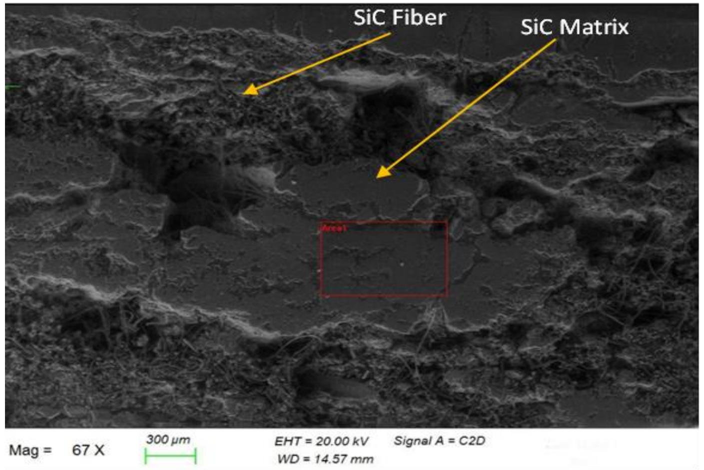
T profile – After 10 h infiltration



- The obtained results confirmed the inside-out densification pattern, expected from the sample volumetric heating



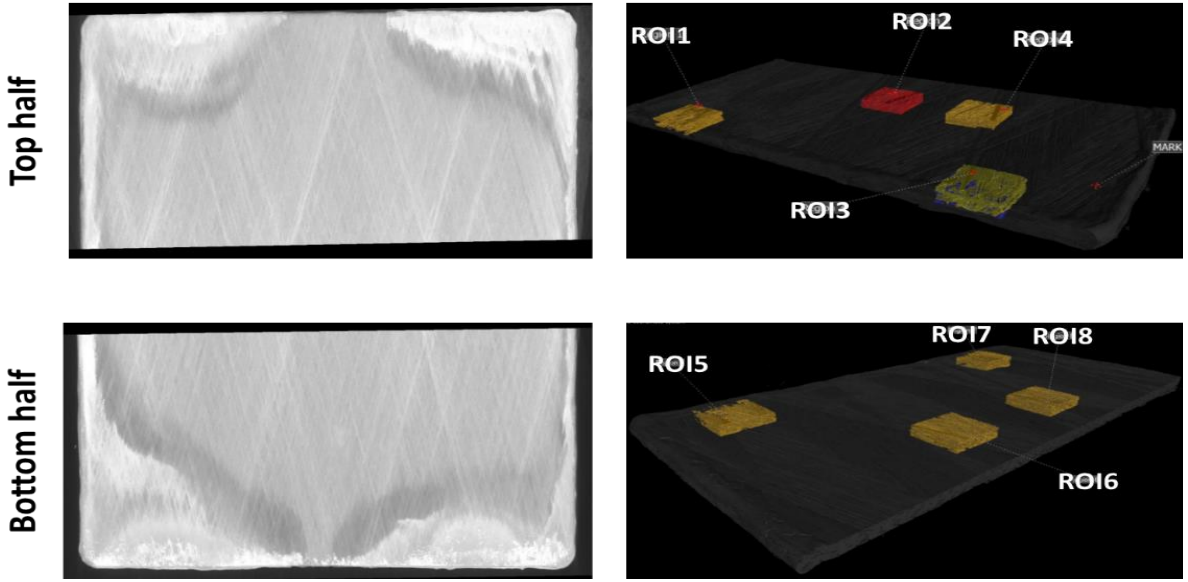
- SEM-EDS analysis confirmed the presence of a homogeneous SiC matrix (Si:C ratio of 0.8)



Element	Atomic No.	Atom Norm. [%]
C	6	51.83
O	8	7.5
Si	14	40.67

- A consistent reduction in porosities across the targeted regions, compared to the starting values, has been observed

- The results of these activities have been reported in a recent joint paper on JECS, recently accepted for publication.



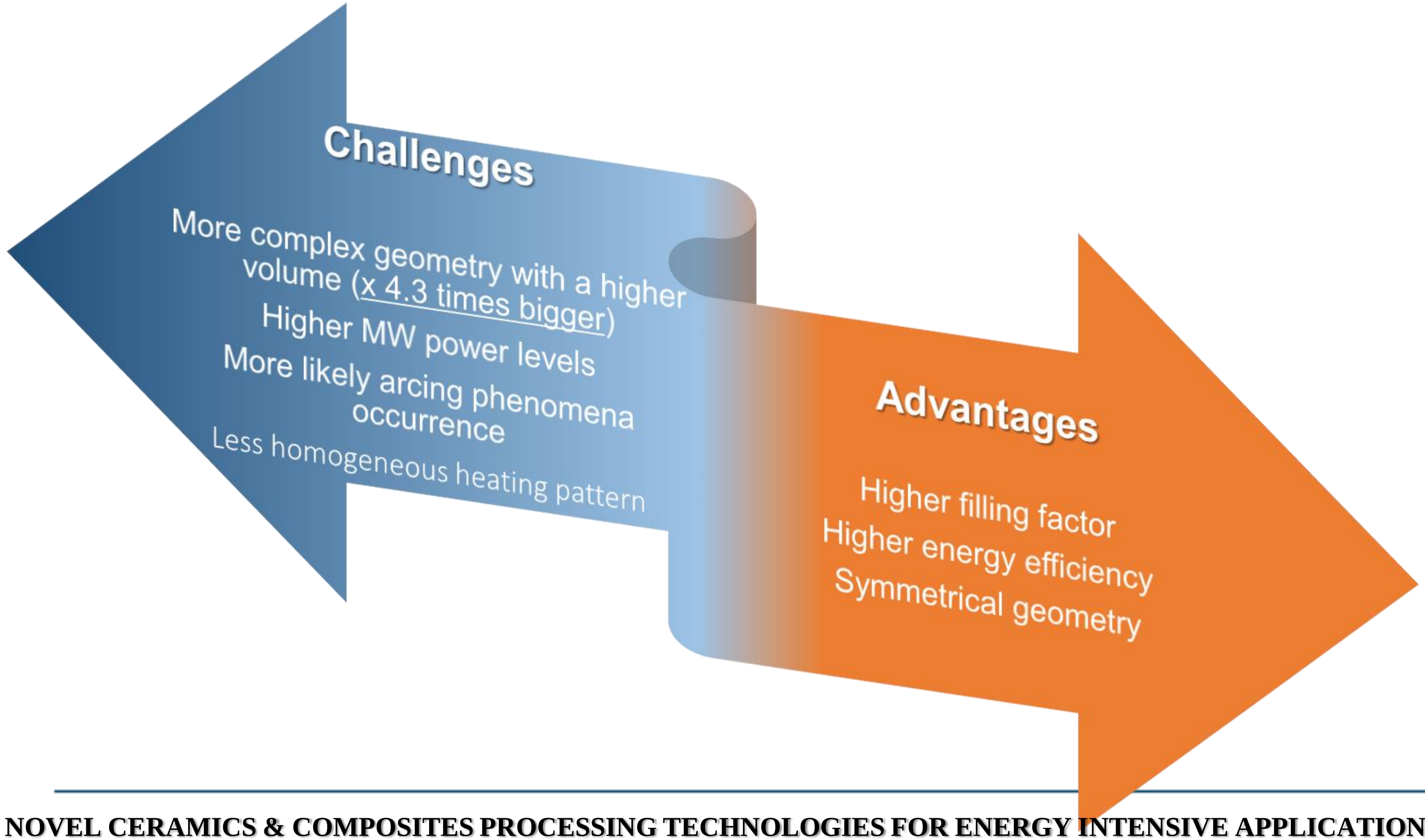
	Top half SiC_f/SiC sample				Bottom half SiC_f/SiC sample			
ROI	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Volume [mm³]	173	161	221	158	223	181	243	165
Porosity [%]	**29**	39	**27**	37	**15**	27	**20**	31

3.1 MW-CVI processing of SiC_f/SiC tubular preforms

- The selection of the optimal MW heating parameters was guided by the rigorous numerical modelling of the loaded reactor;

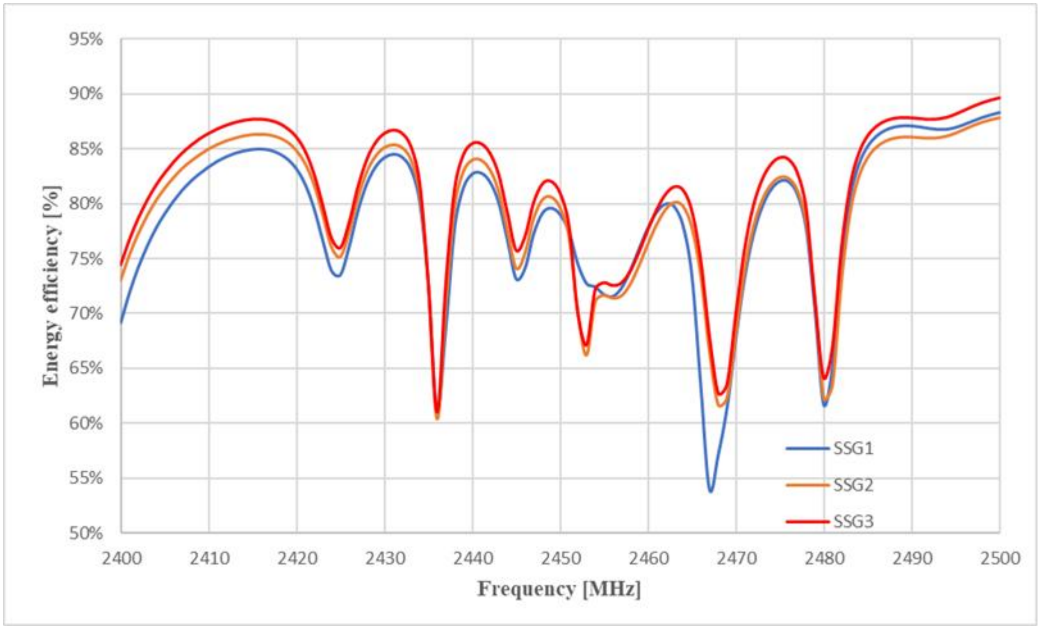
- The Multiport-Multifrequency approach has been employed during the MW-CVI trials.

#ID sample	SiC_f/SiC-C2
Roving	200 tex
Green body matrix	Epoxy
Pyrolised matrix	Carbon
Porosity [%vol]	50.2
Density [g/cm^3]	1.42
Geometry [D x L x T, cm]	10×**12.7**×0.3



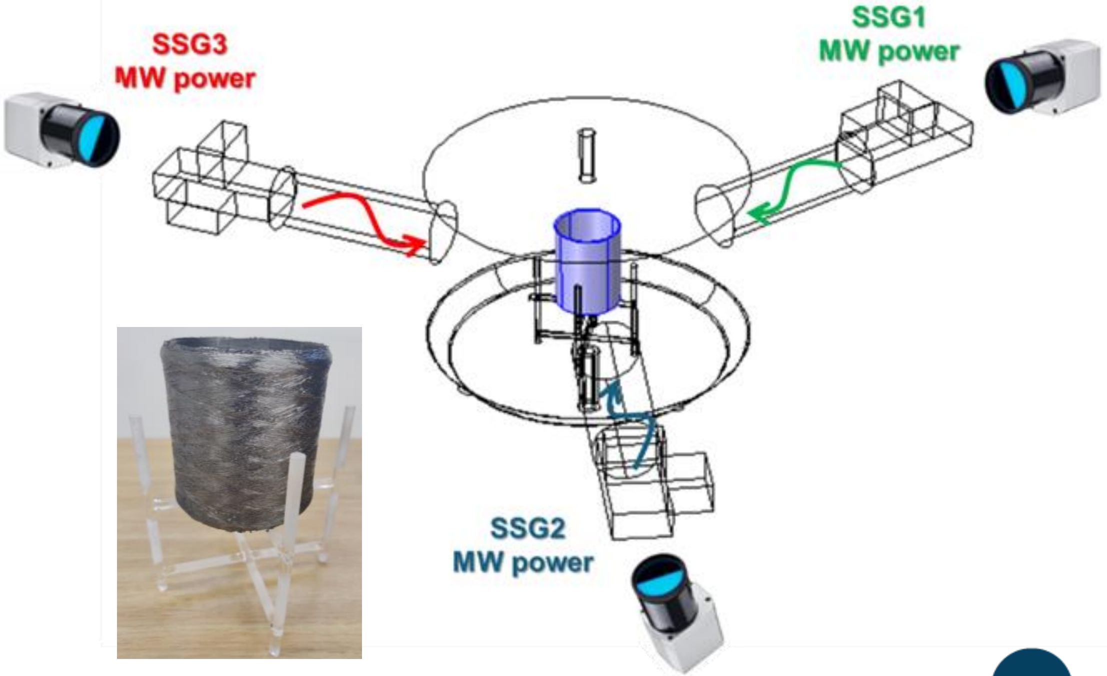
EM assessment of the loaded MW-CVI reactor

- ❑ The modes distribution is independent from the excitation port
  - The identification of the optimal operating frequency, in the electromagnetic models, is simplified;
  - More stable behavior in frequency during the MW-CVI process due to the reduced modes density with resonance curves characterized by larger linewidths.



Sample heating configuration selection

- ❑ A temperature monitoring configuration to obtain an almost 360° view of the sample heating pattern has been implemented
  - 75% of the overall SiC_f/SiC-C2 surface could be monitored with the defined material configuration in the reactor;
  - The heating pattern uniformity has been evaluated by an in-house developed Python code.

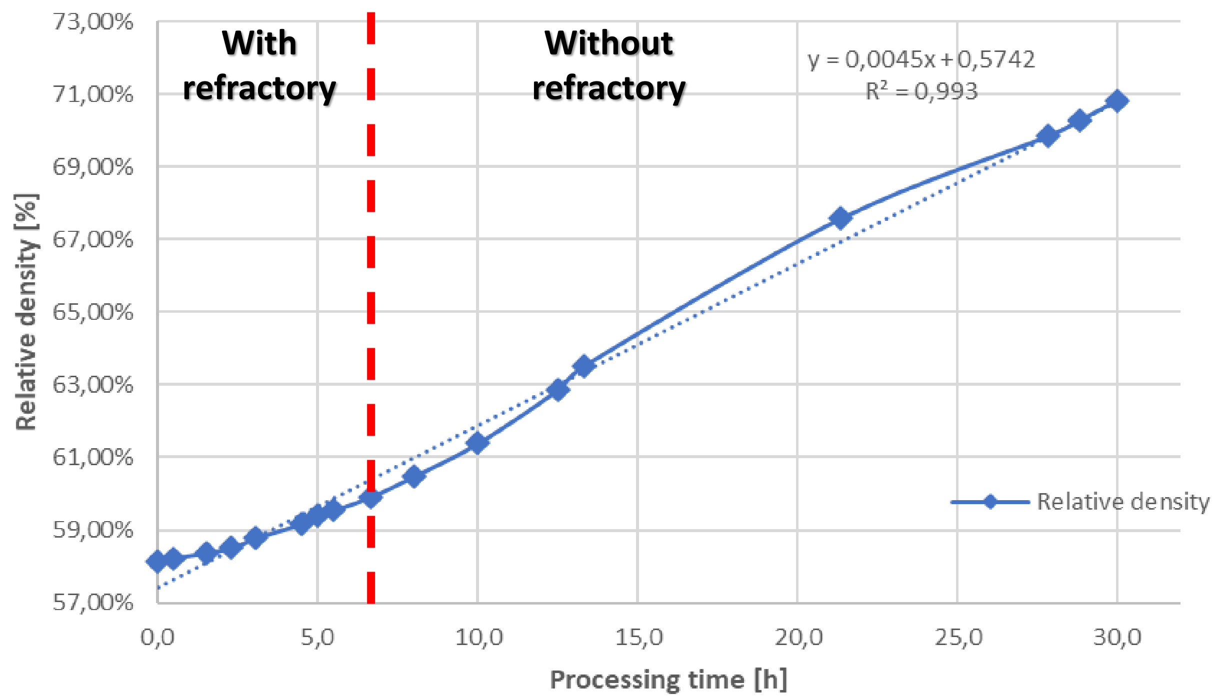


- SiC_f/SiC-C2 sample underwent a total of 30 h of MW-CVI processing
  - The MW-CVI reactor proved quite robust in terms of resonance frequency shift with the SiC_f/SiC sample dielectric properties variation during the process;

MW-CVI tests SiC_f/SiC tube: Average operating parameters

Pressure [mbar]	Temperature [°C]	Average MW transmitted Power [W]		
		SSG1 2480 - 2487 MHz	SSG2 2484 - 2487 MHz	SSG3 2476 - 2484 MHz
200	836.6 ± 19.3	1404	1413	1270

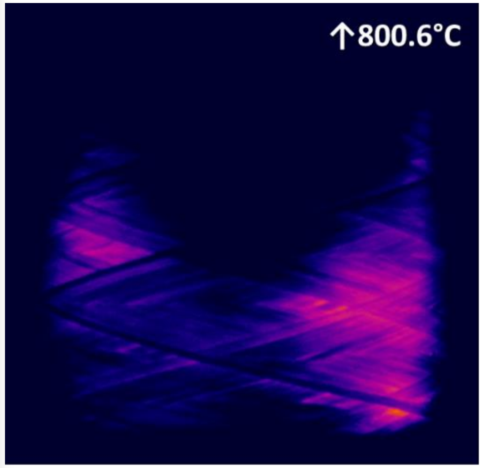
- The relative density increased from 58% to 71% (density 2.4 g/cm³ – residual porosity of 15-20 %vol)
- The densification process has been not straightforward due to:
  - Presence of a 10 %wt C matrix;
  - Presence of the mullite-based refractory.

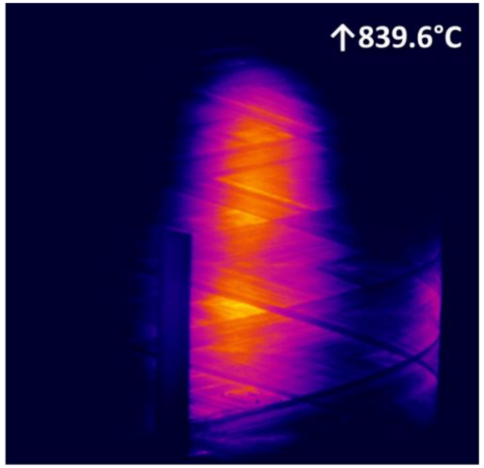


MW-CVI trials with refractory

- Tubular-shaped mullite-based refractories have been employed during first MW-CVI trials to:
  - Minimize the MW power requirements while improving the heating pattern uniformity
- The starting sample temperature distribution was characterized by only small regions at the infiltration temperature

T profile – Infiltration start (Channel 1+2 view)





Uniformity ($T_{threshold}$ =800 °C) = 0 %   Uniformity ($T_{threshold}$ =800 °C) = 0.95 %

Altraform KVS 184-400 (Rath, Germany)	
Geometry [D x L, cm]	8 × 10; 6 × 10
Composition [% wt]	Al_2O_3 78%
	SiO_2 22%
Max application temperature [°C]	1800
Density [g/cm³]	0.4

- Mullite, as well as other silica (SiO_2) based refractories, reacts with H_2 at temperatures of about 1400°C [1]:

$$SiO_{2\,(s)} + H_{2\,(g)} \rightleftharpoons SiO_{(g)} + H_2O_{(g)}$$

[1] M. Ribeiro Gomes, T. Leber, T. Tillmann, D. Kenn, D. Gavagnin, T. Tonnesen, J. Gonzalez-Julian, Towards H2 implementation in the iron- and steelmaking industry: State of the art, requirements, and challenges for refractory materials, J. Eur. Ceram. Soc. 44 (2024) 1307–1334. https://doi.org/10.1016/j.jeurceramsoc.2023.10.044.

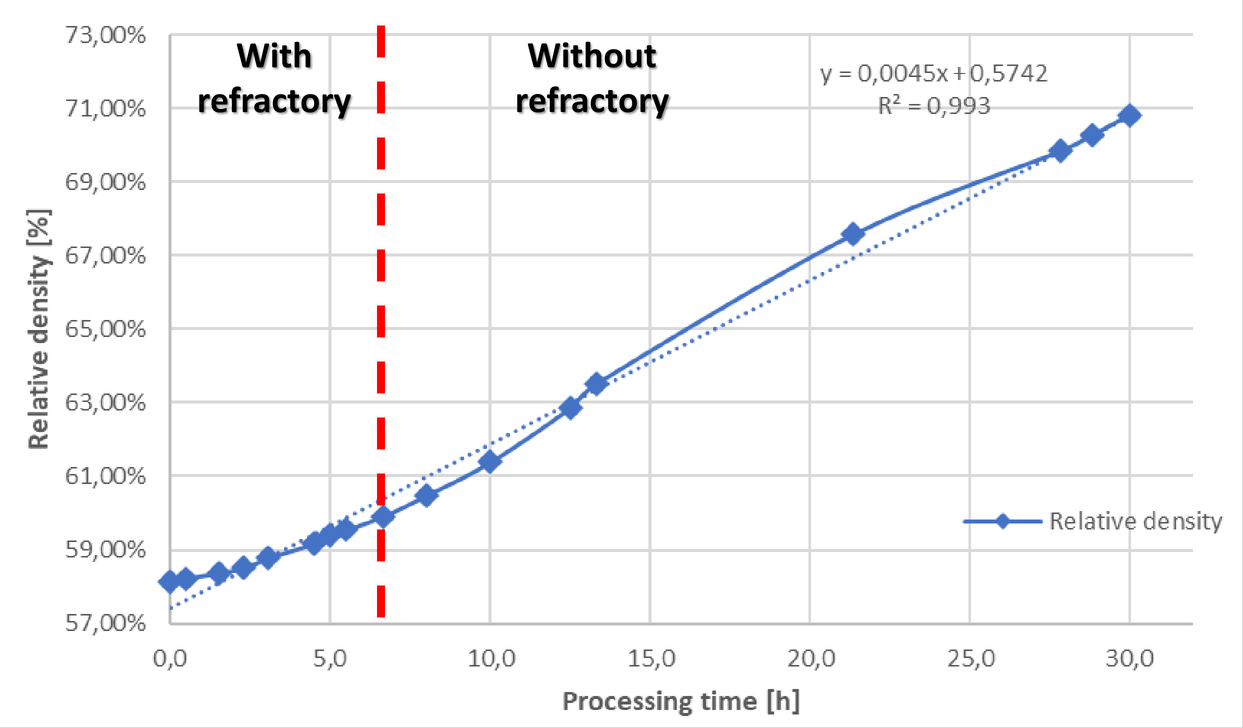
- The latter reactor configuration forced us to daily MW-CVI trials with durations among 30 to 90 minutes
- After 6.5 hours of MW-CVI processing, corresponding to the SiC_f/SiC tube weight increase (i.e. SiC matrix increase) of 3.26 g (1.32 %vol)

  - A comparable heating pattern with respect to the starting point, but without the refractory, has been obtained as a result of the material dielectric properties improvement

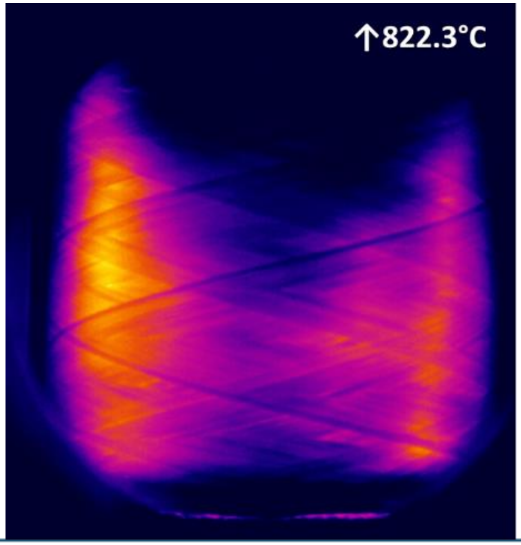
- MW-CVI runs of about 8 hours, split among three different days, without the need to open the reactor

  - Due to the lack of the reactor stainless steel lateral wall water cooling system, we had to limit daily runs to max 3.5 hours;

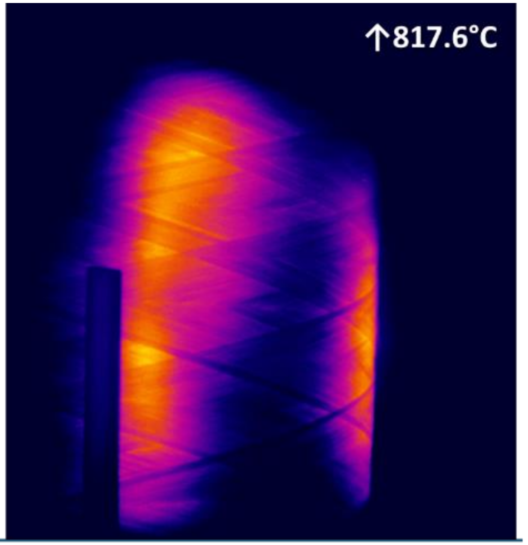
  - The possibility of performing 8 hours long continuous process run has been proved.



T profile – After 6.5 h (Channel 1+2 view)



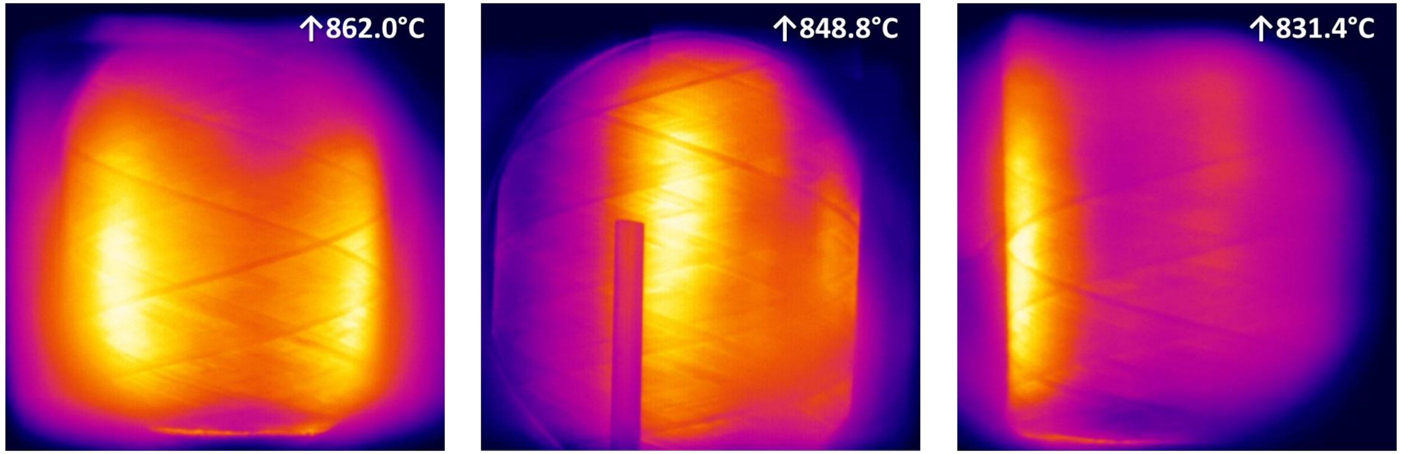
Uniformity ($T_{threshold}$ =800 °C) = 0.25 %



Uniformity ($T_{threshold}$ =800 °C) = 0.19 %

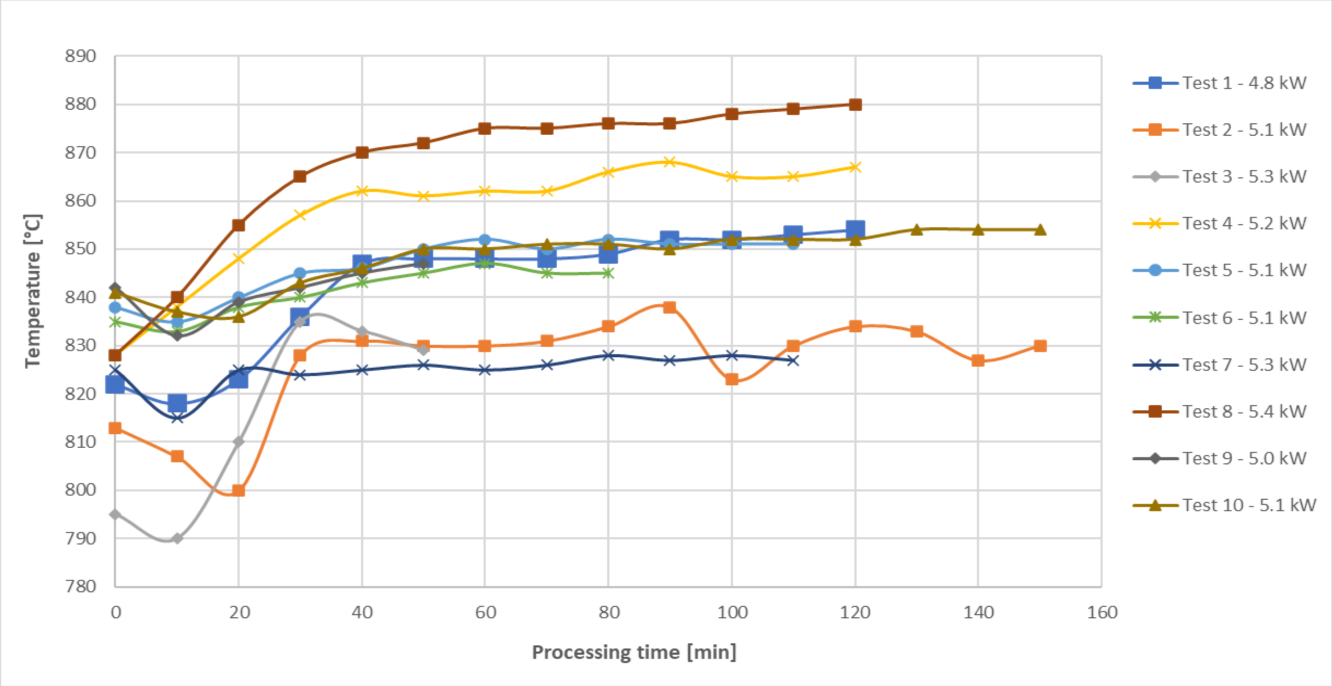
- Longer MW-CVI runs have been realized in the subsequent trials collecting additional 23.5 hours, corresponding to the SiC_f/SiC tube weight increase (i.e. SiC matrix increase) of additional 20.15 g (9.48 %vol)
  - Remarkable increase of the sample heating pattern uniformity

T profile – After 30 h (Channel 1+2+3 view)

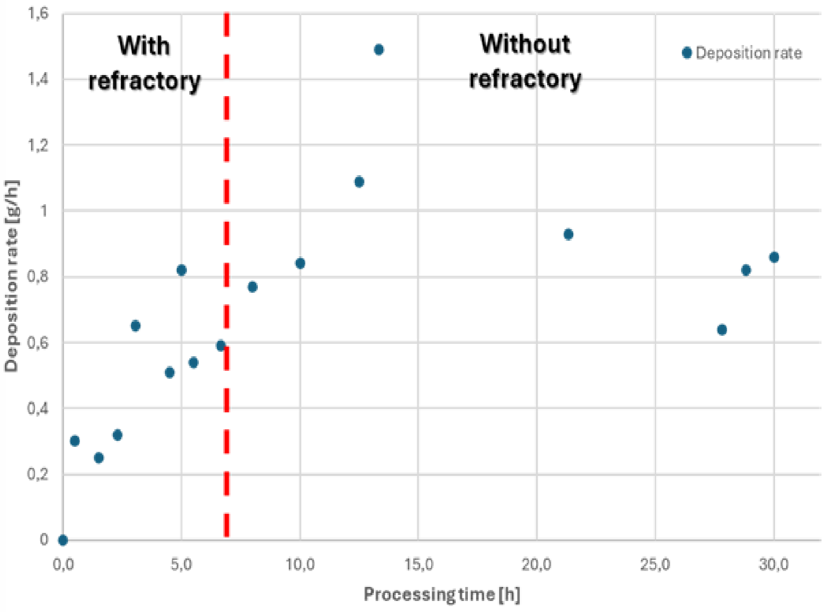


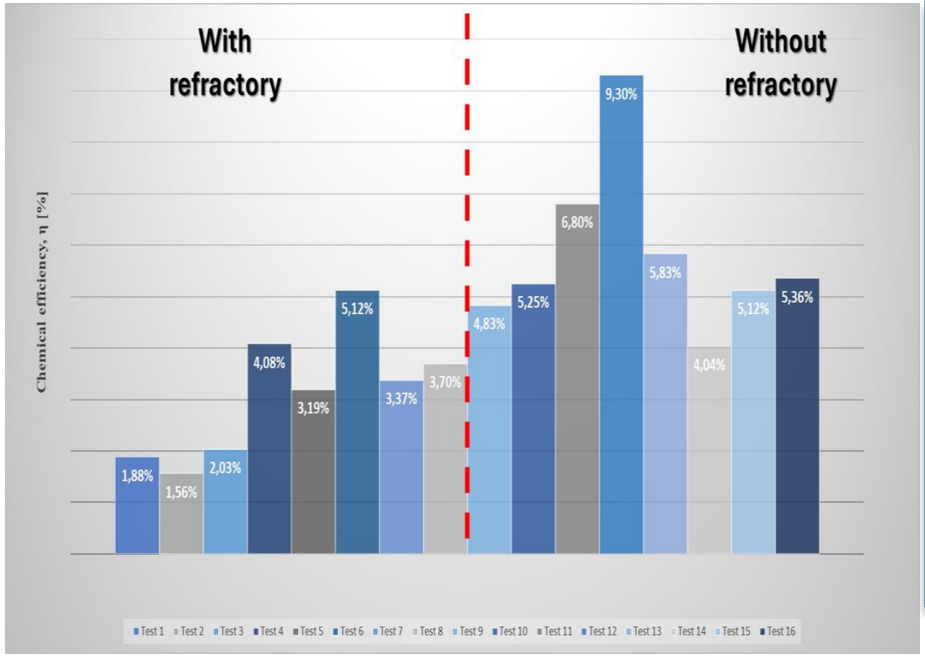
Uniformity ($T_{threshold}$ =800 °C) = 15.00 % Uniformity ($T_{threshold}$ =800 °C) = 9.68 % Uniformity ($T_{threshold}$ =800 °C) = 3.26 %

- Another point of interest is represented by the temperature evolution during each trial:
  - During each test, T increased at constant MW power differently from previous literature studies;



- These results translated in an increase of the SiC matrix deposition rates and thus of the process chemical efficiency (max value of **9.3%** with a deposition rate of **1.5 g/h**)





- An average deposition rate of **0.93 g/h** has been computed without the refractory:

$$t_{miss} = \frac{\Delta M_f}{M_i} * \frac{1}{V_{SiC}} = \mathbf{51\ h}$$

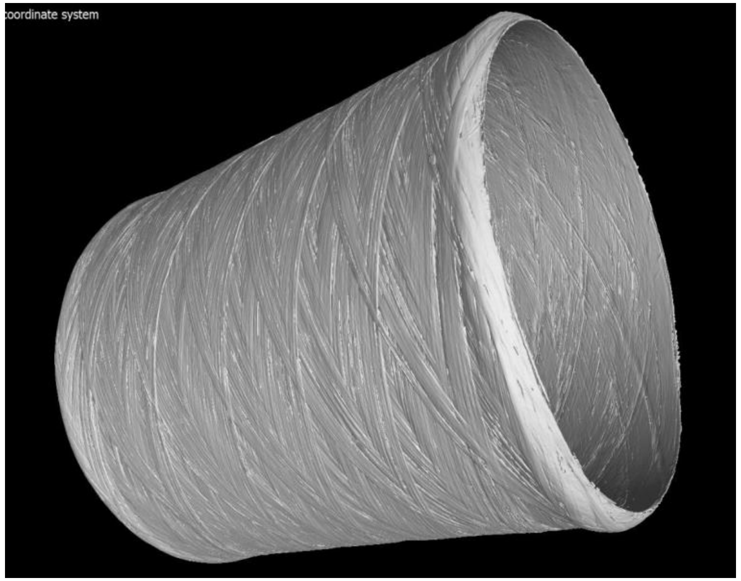
- A total MW-CVI processing time of **81 h** has been estimated!

- The overall SiC_f/SiC-C2 composite components content variation during each stage have been evaluated

- The overall sample porosity had been reduced of about 9.5% in 30 h

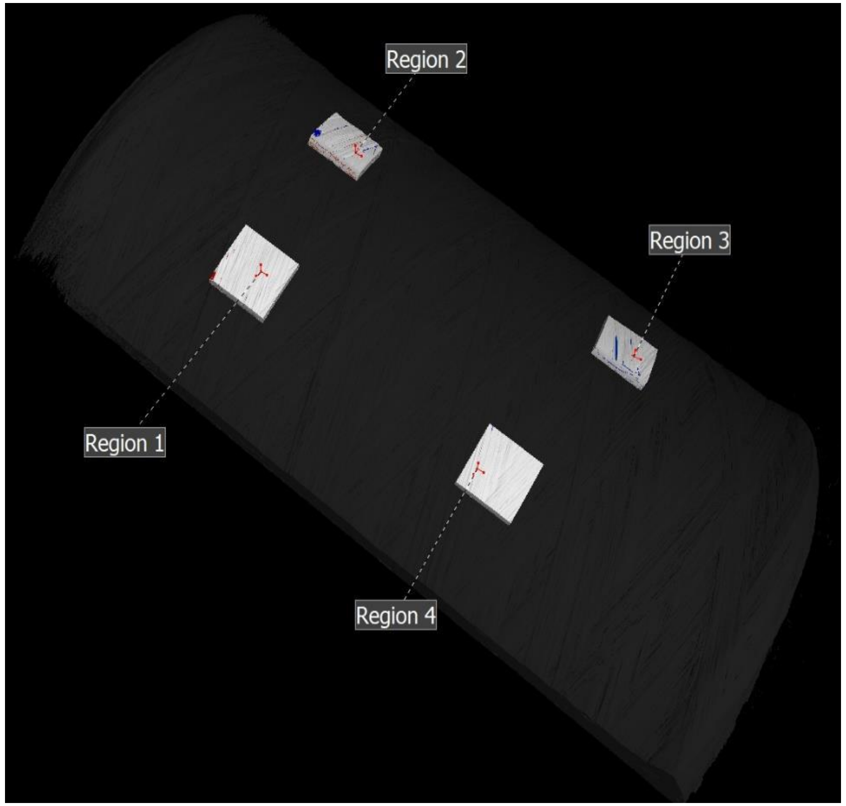
	Start	After MW-CVI processing with Refractory	After MW-CVI processing without Refractory
SiC fibers [%vol]	42,20%	42,20%	42,20%
C matrix [%vol]	7,61%	7,61%	7,61%
SiC matrix [%vol]	0,00%	1,32%	9,48%
Porosity [%vol]	50,18%	48,86%	**40,70%**

- Finally, the **SiC_f/SiC-C2** sample densification has been evaluated through μCT analysis
- Due the more complex geometry and dimensions of the sample, a lower resolution has been reached
  - The porosity values determined from the tomographic scans differed of about 20% with respect to the values experimentally measured.



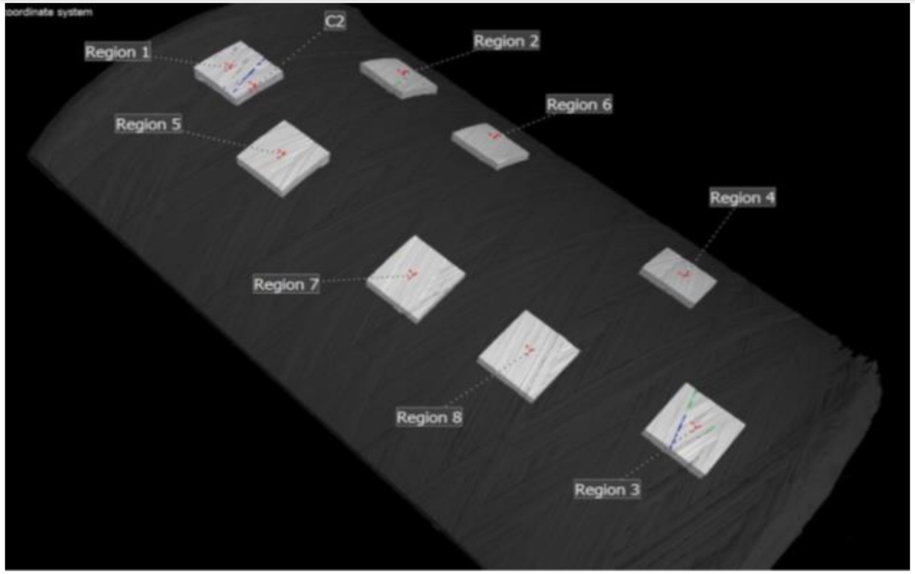
CT Scan parameters V|TOME|X M 300	Tubular-shaped samples
Voltage/current	120 kV / 180 μA
Filters	No filters
Focus-to-Object Distance (FOD) - Focus-to-Detector Distance (FDD)	141.704 - 808.196 mm
Voxel size	35.06 μm
Exposure time	150 ms
Averaging/Skip	3/1
Sensitivity	0.5

μCT analysis before MW-CVI trials

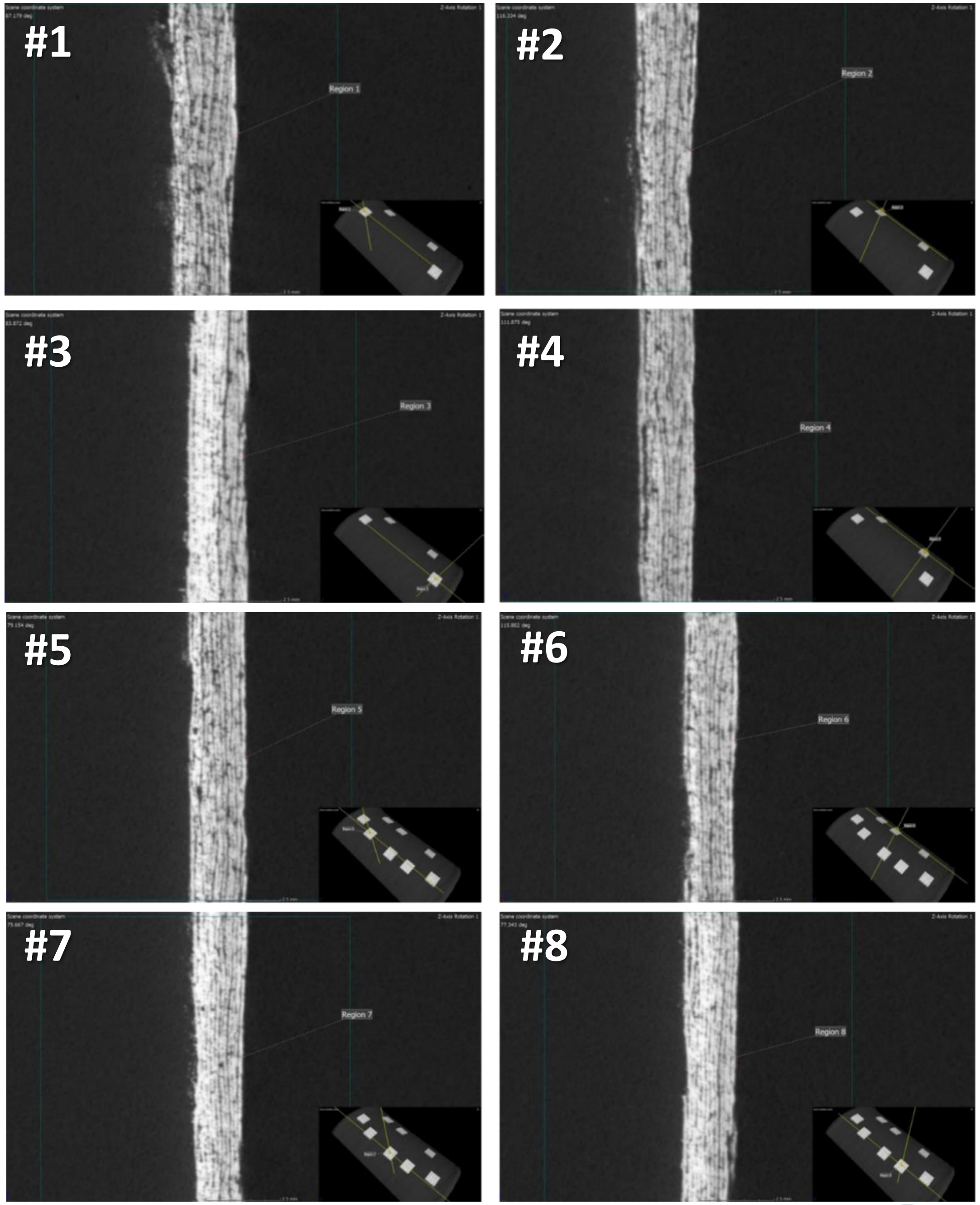


Area	Porosity [%vol]
Region #1	28
Region #2	27
Region #3	15
Region #4	17

- ❑ A homogeneous porosity reduction of about 10 %vol has been observed
- ❑ Most of the regions evidenced a densification front moving from the inner to the outer sample walls (surface-to-core temperature difference of about 30°C)



Area	Porosity [%vol]
Region #1	11
Region #2	15
Region #3	10
Region #4	19
Region #5	9
Region #6	7
Region #7	6
Region #8	6



4. Conclusions

- Both SiC_f/SiC preforms geometries have been successfully infiltrated by MW-CVI process:
  - In the infiltrated regions, a consistent porosity reduction has been observed with values comparable to those obtained by conventional I-CVI;
  - Potential reduction of about one order of magnitude in the processing times;
  - Tailored temperature gradients have been obtained resulting in densification fronts without crusting phenomena;

- Replacement of the starting C with SiC matrix to obtain more favourable starting dielectric properties
- The possibility of automatically maximize the heating pattern uniformity will result in significant steps ahead in view of the possible industrial scale-up of the MW-CVI technology

NOVEL CERAMICS AND COMPOSITES PROCESSING TECHNOLOGIES FOR ENERGY-INTENSIVE APPLICATIONS

27 SEPTEMBER, 2024

THANK YOU

CEM-WAVE

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