PROJECT ACRONYM: **C3HARME**

PROJECT TITLE: **Next generation ceramic composites for combustion harsh environments and space**

Deliverable 2.7

Summary of D2.1, 2.2, 2.3, 2.4

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1	[02/05/2018]	Production of the document	Diletta Sciti, Luca Zoli, Marius Kütemeyer, Jon Binner, Achim Schoberth
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Table of Contents

Table of Figures

1. Executive summary

This deliverable collects the activity performed in the first two years of the project in the frame of WP2, which considers different technologies for the obtainment of UHTCMCs.

The objectives of WP2 include:

- processing of UHTCMCs at the laboratory scale through different techniques;
- methodology set-up for nanoparticles dispersion to impart self-healing behaviour;
- preparation of samples with desired microstructure requirements for thermomechanical testing;
- preliminary assessment of processing route to be scaled up;
- process optimization to improve the quality of UHTCMCs.

Deliverable 2.7 is a summary of the contributions of deliverables 2.1, 2.2, 2.3, 2.4, presents the various processing routes adopted to produce UHTCMCs, with the aim of defining the best processing route to produce the prototypes for Near ZERO - Erosion nozzle inserts (application 1) and Near ZERO - Ablation thermal protection systems (application 2) that will be scaled up within WP4.

Overall, within WP2 more than 200 items have been produced, investigating:

- different types of carbon fibres fabrics (UD, 2D, 2.5D, 3D),
- different fibre volumetric amounts (20-70 vol. %),
- different matrix compositions (with SiC, SiC-free, addition of self-healing phases, addition of sintering agents),
- four different technologies: Spark plasma sintering (SPS), reactive melt infiltration (RMI), polymer infiltration and pyrolysis (PIP), Radio Frequency-Chemical vapour deposition (RF-CVI),
- scale up from 30x30x3 mm^3 samples to discs with diameter 150 mm height 5 mm, or cylinders with 50 mm diameter and 40 mm height,

and all the data of composition and process details, physical properties, mechanical properties, are stored in a newly created DATABASE.

Multiple cross-activities performed amongst the units were carried out to improve/minimize limits of each single technique and to explore new methods.

2. C³HARME Project

The main purpose of the C³HARME project is the design, development, manufacturing and testing of a new class of Ultra High Temperature Ceramic Matrix Composites (UHTCMCs) based on C or SiC fibre fabrics combined with ultra-refractory ceramics (UHTC) suitable for application in severe aerospace environments.

The project will bring the Proof-of-Concept of these new materials into two main applications:

- Application 1: Near **ZERO - Erosion nozzle inserts** that can maintain dimensional stability during firing in combustion chambers of high performance rockets.
- Application 2: Near **ZERO - Ablation thermal protection systems (tiles)** able to resist the very high heat fluxes in strongly reactive gases and thermo-mechanical stresses found at launch and re-entry into Earth's atmosphere.

The goal of C³HARME is to introduce a significant improvement in the performance of the existing materials in terms of increased capability to withstand severe environments, achieving also efficiency, reliability, cost-effectiveness and scalability. The C³HARME project will reach this goal by introducing innovative material solutions whilst adapting existing and well-established processing techniques. In this sense, the project represents a well-balanced mixture of innovative and consolidated technology for new and very demanding applications, mitigating the level of risk intrinsic in top-quality research and innovative development.

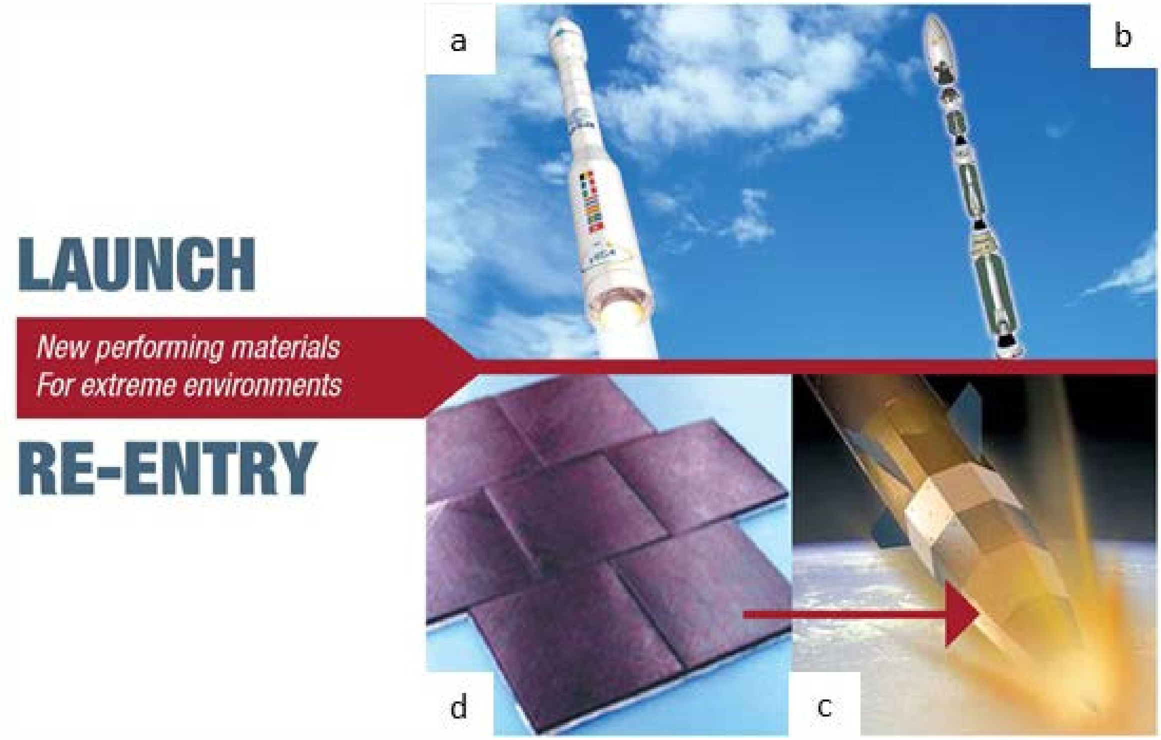

Figure 1: a) Vega launcher and b) sketch of the various stages of launch, indicating the position of nozzles for civil aerospace rockets c)SHEFEX I re-entry experiment (courtesy of DLR) d) CMCs tiles for thermal protection systems.

The project will start from a TRL of 3-4 and then focus on TRL 6 thanks to a strong industrial partnership that includes RTOs, SMEs and large companies as end users.

To reach TRL 6, rocket nozzles and TPS tiles with realistic dimensions and shape must be fabricated, assembled into a suitable system and tested in a relevant environment (environment centred testing).

Twelve consortium partners from different industries, countries and company sizes are working collaboratively ensuring an innovative approach and result of the project: 6 research institutions, 3 large end-users, 3 Small and Medium-sized Enterprises (SMEs).

The project objectives are pursued through 8 different work packages. Amongst them WP2 investigates all the aspects of processing of UHTYCMCs. Different technologies are considered in the project, such as spark plasma sintering (SPS), or chemical vapour infiltration (CVI), the reactive melt infiltration (RMI) and the polymer infiltration and pyrolysis (PIP). The C³HARME consortium is also considering hybrid approaches that are based on an integration of two of these techniques.

2.1. Spark plasma sintering (SPS)

This paragraph summarizes the activity performed from M0 to M24 in the frame of WP2-Task2.1, that considers the spark plasma sintering as the Key technology for the obtainment of UHTCMCs. The main partners involved are CNR and TECNALIA that have intensively collaborated for the entire period. Spark Plasma Sintering (SPS) is a key sintering technology in the processing of nanostructured, composite and gradient materials. The process is based on a modified hot pressing (HP) setup in which a pulsed electric current runs directly through the graphite pressing mould and the component. By means of the pulsed electric current, which can lead to extremely rapid heating and high pressures used, short process cycles (a few hours including cooling) can be achieved. SPS technology is particularly suited for the industrial production of UHTCs since it guarantees fast sintering rates and the cost-competitive post-processing of pre-sintered CMCs. In addition, as a result of the negligible grain growth during densification, SPS could open the possibility of consolidating the matrix preventing coarsening of nanosized phases added into the UHTC matrix for imparting self-healing properties. Currently, one limitation of SPS is linked to the maximum size of the samples that can be processed without introducing heterogeneities in the microstructure of sintered products due to thermal gradients produced by the radial heat loss in the moulds.

A large number of composites reinforced with short or continuous fibres have been produced, see Figure 2. Thermal cycles have been firstly optimised by HP at CNR, and then transferred to the various SPS facilities available in the consortium (TECNALIA and NANOKER).

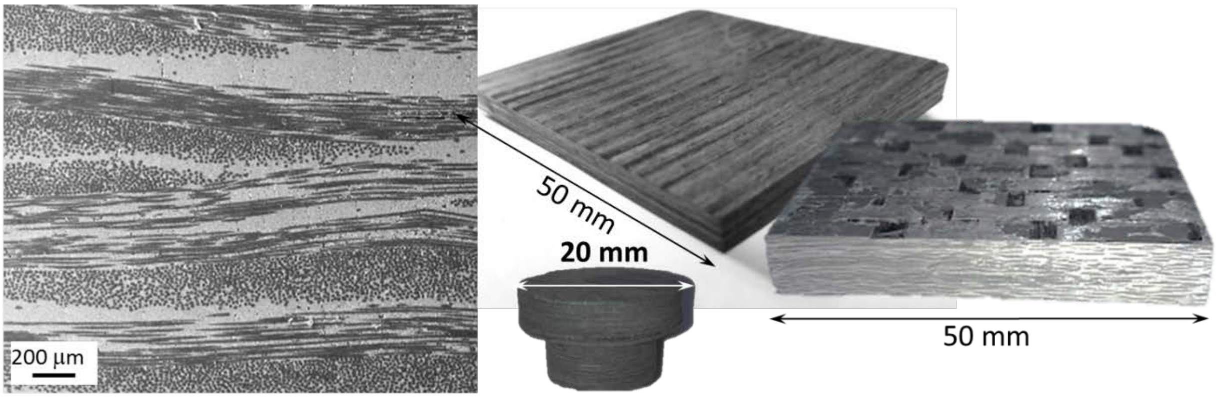

Figure 2: Microstructural features of pellets and small prototypes produced by HP and SPS.

For the material optimization we have explored several aspects:

i) Type of fibre, fibre architecture;

ii) Type of matrix, matrix composition;

iii) Effect of self-healing phases;

iv) Effect of fibre coatings on the process and properties of the final material;

v) In addition to the UHTC based materials, that are the baseline of the project, some other materials are being investigated in a more fundamental stage. MAX phases are very interesting for high temperature applications due to their combination of mechanical properties and oxidation resistance.

Among these activities, we can state that this technology (sintering by HP/SPS) is rather advanced and promising. Large pellets have been obtained and machined for the final application.

Generally speaking, independently on the used method, optimization in the matrix include introduction of the suitable dopants for densification, healing at low temperature and ultra-high temperature.

Collaboration amongst the partners has been essential to enable meaningful advancements in all explored technologies.

2.2. Radio Frequency- Chemical vapour infiltration (RF-CVI)

This paragraph summarizes the activity performed from M0 to M24 in the frame of WP2-Task2.2, that considers RF-CVI as Key technology for the obtainment of UHTCMCs. The main partner involved is University of Birmingham (UoB). Conventional CVI is a well-understood technology for the manufacture of both Cf-C composites (e.g. for aircraft brakes) and SiCf-SiC composites for aerospace applications. The latter has not been extensively utilised because conventional CVI is slow. The process relies on heating a porous (typically fibre-based) preform and passing a gas through it whilst hot; the gas breaks down and deposits the matrix within the porosity of the preform, e.g. methane is used to create a C matrix. Conventional heating leads to problems with deposition at the surface (where the preform is hottest), forming a ‘crust’. This requires periodic machining off to reopen the channels to the interior of the preform. The consequence is that it can take 2 – 3 months to make components (though for products such as aircraft brakes many can be made simultaneously in very large chambers). The long duration can make parts too expensive for many applications, however. In this programme, heating of the carbon fibre preforms is accomplished using an RF system; this allows an inverse temperature profile to develop, i.e. the centre of the preform is the hottest location, so deposition occurs from the inside out. This significantly reduces the time required to make components and, hopefully, therefore, the cost.

Despite the loss of the postdoc at the end of Nov 2017 and the fact that it took until Apr 2018 to recruit a successor, a large number of 2.5 D and 3D composites made using continuous C fibres and containing significant quantities of ZrB_2 powder have been produced. The inverse temperature profiles developed during heating have been measured and controlled and components made with the densities illustrated below in Figure 3. Ongoing work is seeking to increase the final densities to >90% of theoretical.

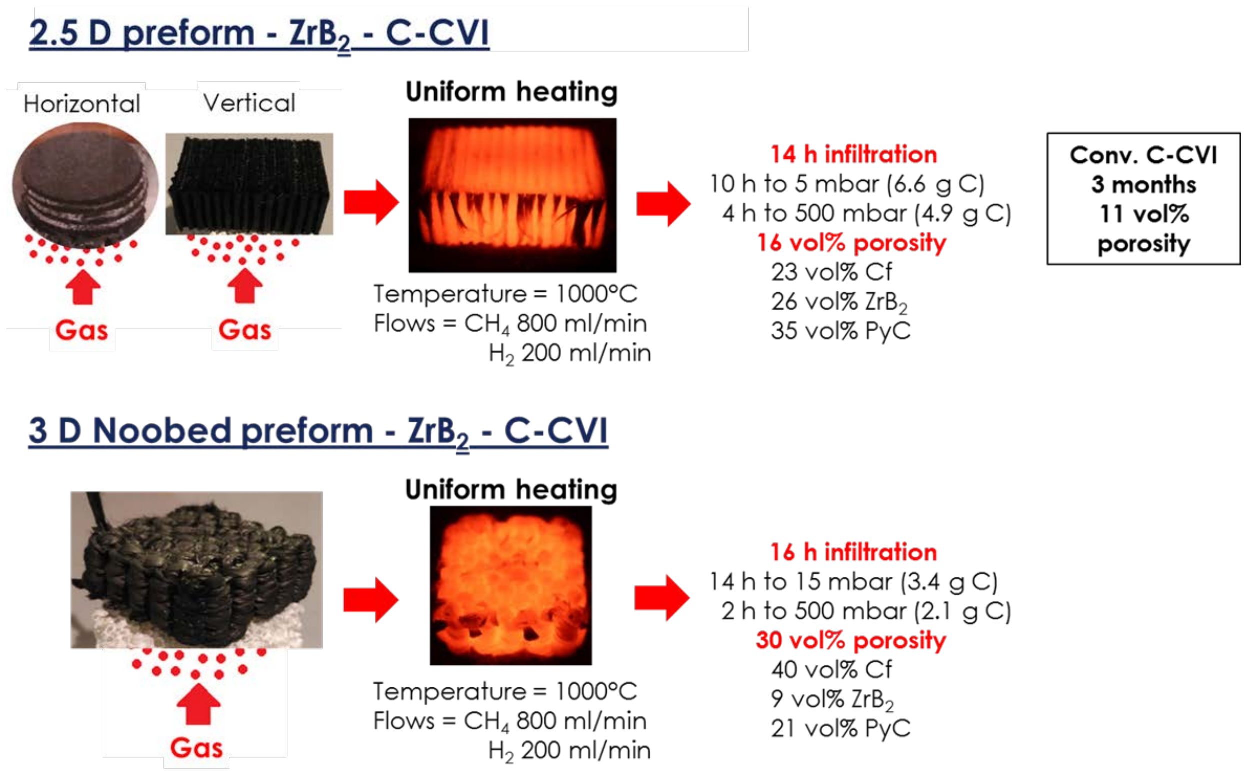

Figure 3: Illustrations of the preforms, heating and current densities achieved using RF-CVI of C matrix

For the material optimization we have explored several aspects:

i) Fibre architecture (2.5D and 3D);

ii) Quantity and distribution of the impregnated UHTC powder;

iii) Matrix composition (C matrix and UHTC matrix)

Microstructures, mechanical and thermo-ablative properties have been characterised on a range of samples made to date and the results are have been promising, especially for the thermal protection system target component. Collaboration with the other partners has been essential, both to progress some aspects of the work described above and to enable meaningful advancements in the creation of hybrid technologies.

2.3. Reactive Melt Infiltration (RMI)

This paragraph summarizes the activity performed from M0 to M24 in the frame of WP2-Task2.2, that considers Reactive Melt Infiltration (RMI) as Key technology for the obtainment of UHTCMCs.

For the continues development of UHTCMCs manufactured using RMI, the influence of three different melt alloys and two preform routs on mechanical behaviour and melt infiltration is investigated. Contact angle and viscosity measurement are performed to describe the melt infiltration process. The purpose of these experiments is to further understand the RMI process and increase the mechanical performance of the material. The infiltration height of molten metals within capillary systems depends on the measured contact angles and viscosity as well as the different phases present in the preform, matrix and fibre coating. In order to successfully maintain mechanical performance, minimal reactivity between the melt and coating/fibres is desired.

RMI using different Zr-alloys have obtained promising results regarding mechanical strength and oxidation resistance. Limiting factors concerning upscaling of UHTCMC fabricated by RMI are the furnace diameter and the expenses to coat the carbon fibres with TiB_2. Hence further work will concentrate on modifying the RMI process to dispense the need for a fibre coating.
Similar to Liquid Silicon Infiltration (LSI), a ZrB_2 formation with Zr-based melts, requires attention of the following aspects, forming a porous B containing preform utilizing a capillary system for the liquid melt. It is necessary to produce a powder based slurry which can be infiltrated into fibre bundles and act as a boron source. Additionally, the composition of the Zr-based melts needs to be taken into account. Different alloy compositions do influence contact angles, viscosity, phases forming and melting temperature. The three step process, is described in Figure 4.

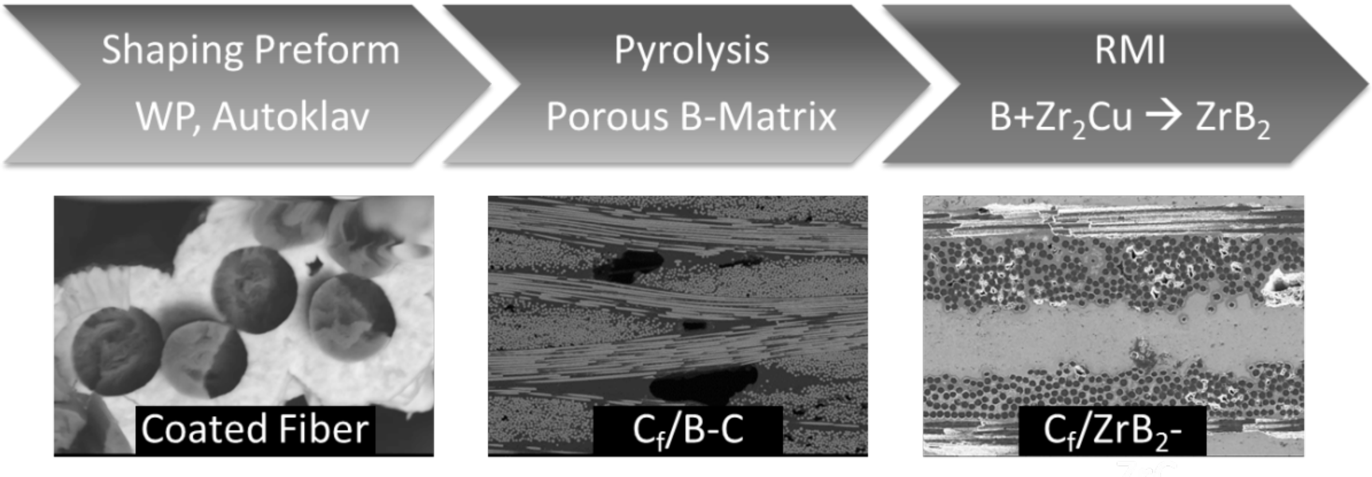

Figure 4: Schematic of RMI process.

2.4. Polymer-Infiltration-Pyrolysis (PIP)

The main partners involved are CRT (former AGI) and UoB that have intensively collaborated for the entire period.

The material development is based on the Airbus protected 2D (0°/90°) C-fibre reinforced C/SiC Ceramic Matrix Composite (CMC) material (SiCARBON™), prepared by the Polymer-Infiltration-Pyrolysis (PIP) process. This material is a qualified material standard for project partners Airbus (represented by CRT) and Ariane Group (former ASL – Airbus Safran Launchers). The process, described in Figure 5 , requires up to 6 re-infiltration and pyrolysis cycles to reduce porosity, which makes the process costly.

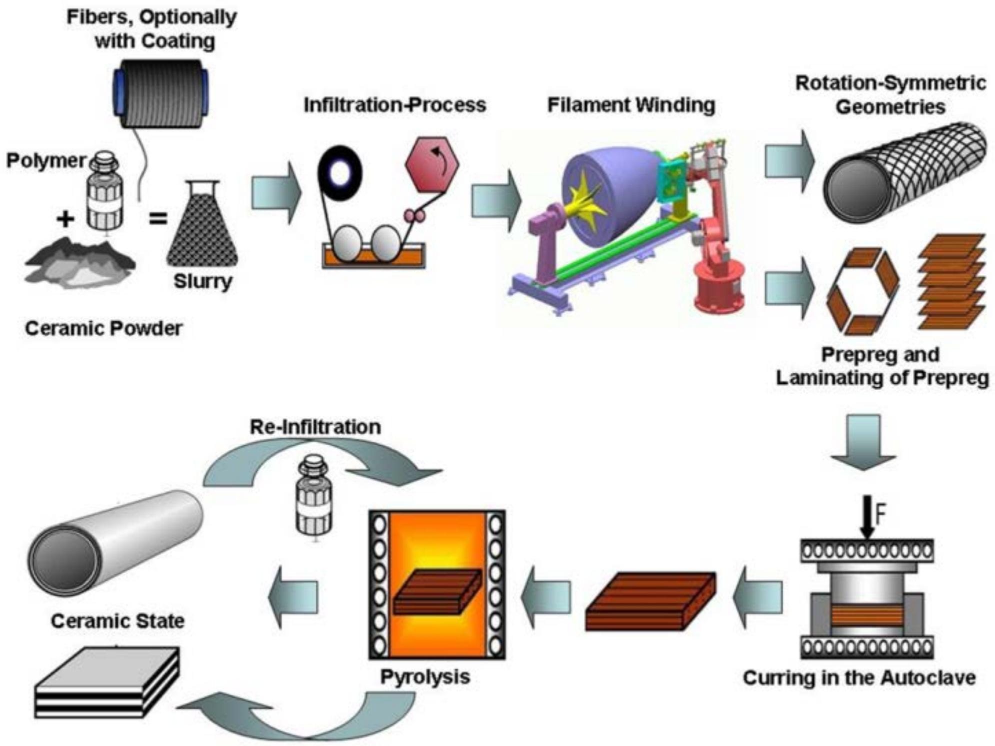

Figure 5: Polymer-Infiltration-Pyrolysis (PIP) process

For the material optimization towards higher oxidation resistance, several aspects have been explored:

i) effect of gradient ZrB_2 & TaC addition to the matrix, starting with the basic C/SiC material as core;

ii) effect of an additional gradient protection coating system containing refractory phases

iii) effect of nanoparticles impregnation to impart self-healing properties.

The basic PIP technology is rather advanced and promising, because a scale-up towards large thin-walled plates is possible, which can be machined for the final TPS application.

No thruster application (application 2) is envisaged within this project.

However, the base material as well as each of the optimisation routes i) to iii) alone probably do not provide sufficient oxidation resistance to survive the harsh re-entry conditions. The combination of at least route i) and ii) and further development work are necessary steps to reach the target. Further improvement may come from the additional application of route iii) after successful selection of the right oxygen gettering nano-particles and the development of a suitable impregnation technique.

2.5. Cross Processing

Multiple cross-activities performed amongst the units were carried out to improve/minimize limits of each single technique and to explore new methods. The most important examples are reported below:

- CNR and TECNALIA have intensively collaborated to develop material combinations and to transfer the sintering technologies from HP to SPS;
- CNR and CRT (former AGI) collaborated in the setup of specific stages of the process to speed up the making of large components;
- CNR and DLR collaborated to set a new methodology for filling porosity in the composites and avoiding exaggerate interface reaction between matrix and fibre;
- TECNALIA and DLR to set a new methodology for filling porosity in the composites and avoiding exaggerate interface reaction between matrix and fibre;
- TECNALIA and CRT (former AGI) collaborated to improve the material consolidation;
- CRT (former AGI) and CNR collaborated for methodology set-up of nanoparticles dispersion in the ceramic matrix;
- UoB and DLR cooperated to create a new methodology for filling porosity in the composites, avoiding exaggerate interface reaction between matrix and fibre and increase UHTC content;
- CRT (former AGI) and DLR to set a new methodology for improving consolidation of the matrix and process cost reduction.

Some of these approaches were revealed to be particularly promising for the applications envisaged.

2.6. The most promising manufacturing routes

The C^{3}HARME team is actively investigating how to adapt existing and well-established technologies for the production of two prototypes made of the new UHTCMC material: TPS tiles and rocket nozzle inserts. The four selected techniques are generally used to produce either bulk ceramics like the spark plasma sintering (SPS), or ceramic matrix composites, like the chemical vapour infiltration (CVI), the reactive melt infiltration (RMI) and the polymer infiltration and pyrolysis (PIP). Hybrid approaches that integrate two of the selected techniques are also under investigation.

During the last two years, the preliminary results have suggested that at least 5 of the proposed technologies (2 hybrid and 3 pure) are suitable for the production of TPS tiles. For rocket nozzles, however, the shape and size make their production more challenging and, so far, we have identified two best solutions. The compositions have been screened up after intense work.

Future work will focus exclusively on the routes that prove to yield the required properties while being the most cost-effective solution.

3. Conclusions

This deliverable summarizes the activity performed from M0 to M24 in the frame of WP2, that considers the different technologies for the obtainment of UHTCMCs.

About 200 items have been produced by the consortium, investigating all the aspects of matrix composition, consolidation, type of fibres, type of preforms, addition of self-healing particles, effect of fibre coating, etc. We have also taken care of aspects related to the cost of single processes discarding those that may be non-cost-effective.

Cross processing amongst CNR, TECNALIA, UoB, DLR and CRT (former AGI) has been essential to enable meaningful advancements in all explored technologies and to set up hybrid processes.
Among these activities, we can state that some technologies are now rather advanced and promising. Large pellets have been obtained and machined in the form of nozzles and tiles. Other methodologies have been abandoned as they require further optimization.

COOPERATION BETWEEN PARTICIPANTS
Cooperation amongst partners is reported in par. 2.5