

 Contenu archivé le 2024-06-18



MULTIFUNCTIONAL COMPONENTS FOR AGRESSIVE ENVIROMENTS IN SPACE APPLICATIONS

Rapports

Informations projet

SMARTEES

N° de convention de subvention: 262749

Projet clôturé

Date de début

1 Janvier 2011

Date de fin

31 Decembre 2013

Financé au titre de

Specific Programme "Cooperation": Space

Coût total

€ 2 688 900,10

Contribution de l'UE

€ 1 971 938,00

Coordonné par

FUNDACION TECNALIA
RESEARCH & INNOVATION



Spain

Ce projet apparaît dans...

Final Report Summary - SMARTEES (MULTIFUNCTIONAL COMPONENTS FOR AGGRESSIVE ENVIROMENTS IN SPACE APPLICATIONS)

Executive Summary:

The aim of this proposal was the development of ceramic composites structures which are required for applications in aggressive environments (oxidative) and high temperatures, such as hot parts of space vehicles for orbital re-entry (reusable launcher vehicles, RLVs). The solution was focused on re-usable systems. As expressed by the European Commission a non-dependent access to the critical space technology is required at European level. Therefore the strategy was to focus on materials systems able to be in a medium term independent from the technologies that already exist outside Europe (mainly in USA, China and Russia). The technical approach was focused on the development of multilayer concept based on high temperature ceramics (HTCs) and ultrahigh temperature ceramics (UHTCs) with multiple tailored properties. Their joining processes to conventional structural ceramic matrix composites (CMCs) or novel porous sandwich structures, and the final attachment to metallic structures and frames was carried out.

The MULTIFUNCTIONAL COMPONENT can be broken down at three levels:

- 1st Level: This was composed of multilayers. The point was to design each layer to form a system with multiple properties (i.e. an external layer with resistance to oxidation at re-entry, an intermediate layer with high thermal conductivity to eliminate hot-spot and distribute the heat homogeneously and an inner layer with insulation properties).
- 2nd Level: This was composed by conventional CMCs with structural or insulating properties (such as endless fibre reinforced Cf/SiC). Novel CMC-SiC foam sandwich structures integrating SiC foam able to grant additional thermal insulation were developed in the frame of the project, but also qualified CMCs were also manufactured and provided for comparison.
- 3rd Level: This was composed by the metallic structural frames, such as those based on Nickel superalloys or Titanium alloys.

A proof-of TPS technology sample design was provided by the end-user Aerospace companies participating in the project. Furthermore the system design was aided by material's modelling and simulation via conventional methods and computed tomography was used to obtain a real FEM model of each part of the system. The physical, mechanical and thermal characterisation of this part were also

carried-out over different temperatures ranges. This helped to obtain an accurate and realistic simulation of the insulation capability of the system. The output was employed to determine critical parameters such as thicknesses and geometries.

Finally the technology sample was tested in a relevant ground facility simulating the re-entry conditions. The testing at sample level determined the fundamental performance and the degradation mechanisms. This final step has given insight into the overall performance of a TPS, identify possible modes of failure, and assess the efficiency of the thermal insulation and the heat fluxes into the sub-structure of a spacecraft. The ground testing results were reviewed in comparison with the outputs of TPS requirements and environment specifications. This resulted in the completion of the validation of the TPS performance and the assessment of achievement of a TRL 3-4.

Project Context and Objectives:

A non-dependent access to critical space technologies is required at European level. Therefore, the aim of SMARTTEES is the achievement of a European autonomous technology for thermal protection systems (TPS).

The solution is based on a novel reusable TPS architecture which can withstand the extreme environment conditions during atmospheric re-entry. A proof-of TPS design will be provided within the project. This will be the result of the completion of the validation of the TPS performance and the achievement of a Technology Readiness Level between TRL 4 and 5.

The design will incorporate advanced ceramic composites and porous structures and will be aided by material modelling. A computed tomography technique will be used to obtain a real model of each part of the system. The thermo-mechanical characterisation of this part will also be carried-out over different temperature ranges. This will help to obtain an accurate and realistic simulation of the insulation capability of the system. The output of this work will help to calculate critical design parameters. In a final stage the technology sample will be tested in a relevant ground facility simulating the re-entry conditions. The testing will determine the fundamental performance and the degradation mechanisms. This final step will give insight into the overall performance of the TPS, identify possible modes of failure, and assess the efficiency of the thermal insulation and the heat fluxes into the sub-structure of a spacecraft. The ground testing outputs will be reviewed in comparison with the outputs of TPS requirements and environment specifications.

The main objective of the proposed project is to develop a new reusable solution based on multifunctional hybrid concept with very high insulation and environmental protection capability during the atmospheric re-entry and the ability to reach a TRL level between 4 and 5 at the end of the project.

From this premise it was planned to achieve the following technical targets:

- Develop a multilayer concept with the ability to obtain multifunctional properties: high emissivity, insulation capability, oxidation protection, high toughness and damage tolerance.
- Suitable bonding/adhesion among the different parts and materials to form the technology sample solutions.
- Proof-of technology sample concept to satisfy the needs of TPS end users.
- Validate the technology sample in a ground testing, which simulates and reproduces with high accuracy the space re-entry.
- Obtain a solution able to survive at least to 10 re-entries with minor repairs.

- Reduced maintenance and failure probability during the re-entry, due to the substitution of stand-offs and bolts by bonded joints.
- Achieve a technology readiness level (TRL) between 4 and 5 after the complete testing of the technology sample.

Other non-technical objectives are of high interest as well:

- To disseminate the results of the project through publications in the most relevant journals, the creation of a webpage, organization of a workshop and roundtables and other tools like blogs, social networks and so on, participation to relevant conferences, fairs and exhibitions.
- To elaborate a use plan of the technology for the exploitation of the results achieved in the frame of the project.
- To reduce the dependence of Europe on the TPS systems (mainly US, Japan and Russia), by the development and exploitation of the technologies resulting from the project.

Project Results:

WP1: TPS design

The envisaged concept of the SMARTTEES project was based on the integration of conventional and non-conventional parts to create a TPS technology sample with multifunctional properties such as oxidation protection, thermal protection, thermo-structural functionality, adjustable surface emissivity, insulation capability and in-plane controlled thermal conductance. This was planned to be carried out by the integration of materials at three levels, as depicted in Figure 1.1 left. The preliminary design was based on the integration of three main parts: ceramic multilayer system (SiC or ZrB₂/SiC multilayers), thermo-structural part (CMC/foam/CMC sandwich structure) and metallic frame (titanium alloy). The way of joining of these three parts is brazing technology (1st and 2nd level bonding). Considering the three described material layers and procedure for a multifunctional SMARTTEES TPS sample a first preliminary design concept was suggested, illustrated in Figure 1.2.

Fig. 1.1. Schematic TPS concept in an early stage (left) and preliminary design (right)

For the SMARTTEES development work specification and requirements were selected and defined from ARV (advanced Reusable Vehicle) project which foresees implementation of a cargo transportation capability with the objective of being used for ISS cargo upload and download in support of ISS operations beyond 2016 (Figure 1.2 left). The concept retained for ARV shall not prevent nor impair its subsequent evolution towards a genuine crew transportation capability. A crew transportation version could become available in the 2025 timeframe. Within ARV project an APOLLO-type shape was selected and the heat shield was subdivided in two parts (see Figure 1.2 right): front shield with thermally high loaded areas and back shield which is moderately loaded.

Fig. 1.2 ARV Cargo version (left) and ARV capsule with heat shield locations (right)

Two material options were available for the exposed multilayer level to be designed and developed with respect to different load case scenarios from ARV mission profile: SiC multilayers (suitable for temperatures $T < 1700$ °C) and ZrB₂/SiC multilayers (suitable for temperatures $T > 1700$ °C). Because of the nature of these two material options for the exposed outer surface layer two control points from ARV load case (LC) scenarios were selected for the design of the samples. Load Case 1 (LC1) is for a control point at the back shield where the corresponding heat fluxes and thermal loads (sizing trajectory) are moderate

and therefore offer an interest for the SiC based materials. The temperature is approx. 1300 °C and heat flux around 0.3 MW/m². Load Case 2 (LC2) is at the front shield with high heat fluxes and thermal loads (sizing trajectory) and therefore interesting for ZrB₂/SiC materials. The corresponding temperatures are approx. 1700-1800 °C and heat fluxes around 0.8 MW/m². Considering the selected load case scenarios and defined TPS relevant requirements (thickness, aerial mass, emissivity, temperatures, thermal insulation capability, maximum temperature on vehicle structure, mechanical & thermo-mechanical stability under load conditions etc.), two solutions for LC1 and LC2 were designed. TPS technology sample size was defined first to 50x50mm² for development and second 150x150mm² for upscale. For LC1 a SiC multilayer without ZrB₂ and for LC2 a SiC/ZrB₂ multilayer with ZrB₂ layers intercalated among SiC layers (POLITO) was selected for the exposed top layer. For the integrated CMCupper skin-SiSiC foam-CMClower skin sandwich structure a continuous carbon fiber reinforced Cf/SiC material (SiCARBONTM from EADS) with a 2D-0°/90° architecture and a customized SiSiC foam (ERBICOL/SUPSI) with a defined pore size and orientation was used for both LC1 and LC2. The metallic stand-off was based on Ti6Al4V alloy (TECNALIA). The joints for SiC multilayer/CMCupper skin and CMClower skin/metallic stand-off were realized by brazing technology (TECNALIA/NCSR D). For thermal insulation a fibrous ceramic phase was selected to be filled into in the SiSiC foam (ERBICOL/SUPSI). Figure 1.3 shows the 3D models of the fully assembled technology samples for LC1 (left) and LC2 (right), illustrating the top SiC multilayer, the upper CMC skin, the SiSiC foam, the lower CMC skin and the metallic stand-offs (from the top to the bottom).

Figure 1.1: 3D model for LC1 design (left) and LC2 design (right), top view

WP2: Materials development and manufacturing

Three kinds of materials and the relevant manufacturing processes/technologies were developed during the project:

1. Ceramic laminates based on SiC (or SiC plus ZrB₂) mainly designed for oxidation protection
2. SiC-based foams (filled in by silica fibres) designed for thermal insulation
3. CMCs suitable to act as skin of SiC foams in a sandwich structure and designed for providing toughness and strength

1. Ceramic laminates based on SiC (or SiC plus ZrB₂) mainly designed for oxidation protection

A manufacture technology for multilayer ceramics was developed with the aim of granting to the part of TPS facing the atmosphere the following properties: oxidation and thermal shock resistance; high emissivity; thermal management capability; suitable strength, stiffness and hardness.

The processing path (Fig. 2.1) consisted of the following steps: green tape production by tape casting a suitable ceramic slurry containing proper sintering aids (E. Padovano, C. Badini, et al. "Pressureless sintering of ZrB₂-SiC composite laminates, using boron and carbon as sintering aids", *Advances in Applied Ceramics*, 112, n°8 (2013) 478-486); formation of the green multilayer by stacking green tapes; de-binding thermal treatment; final sintering without the help of pressure.

The processing method based on tape casting allowed to developed several kinds of laminates (either with similar or dissimilar layers):

- a) SiC multilayer
- b) SiC-ZrB₂ composite multilayers showing different SiC:ZrB₂ ratios ranging from 100%SiC to 100% ZrB₂.
- c) SiC laminates integrating porous layers for improving thermal insulation.
- d) Hybrid laminates with Cf/SiC composite layers put in between SiC layers showing not-isotropic thermal

conductivity (higher in the plane and lower through the thickness).

e) Hybrid laminates with alternate layers made of SiC and ZrB₂-SiC composite designed for alternating materials that are expected to display the best oxidation resistance in different temperature ranges (SiC up to 1600 °C and ZrB₂-SiC composites over 1700 °C).

Some mechanical features of different kinds of ceramic laminates are compared in table 2.1.

Fig. 2.1. Ceramic laminates processing path

Samples composition

[% Vol.] Elastic modulus [Gpa] Bending strength [MPa]

100% SiC 339 324

40%SiC-60%ZrB₂ 408 284

20%SiC-80%ZrB₂ 444 277

100% SiC with 2 porous layers out of 10 240-270* 200-260*

SiC-Cf/SiC multilayer

(2 composite layers out of 10) 288 288

20%SiC-80%ZrB₂ / SiC multilayer

(2 composite layers out of 10) 310 263

*Depending on porosity degree in the porous layers

Tab. 2.1 Strength and stiffness of ceramic laminates.

The main results achieved for each multilayer concept developed in the frame of SMARTTEES project are summarized in the following.

a) SiC multilayer: very good oxidation resistance in the temperature range 25-1600 °C owing to the formation of a very thin and effective silica passive layer on the surface, quite good emissivity (C. Badini, et al “Oxidation behavior of laminate ceramics belonging to SiC-ZrB₂ system” in proc. 7th Workshop on Thermal Protection Systems and Hot Structures, Noordwijk, 8-10 April 2013 ESA ESTEC).

b) SiC-ZrB₂ composite multilayers: formation of a passive layer in every case but oxidation resistance in the temperature range 25-1600 °C worsening with the ZrB₂ content increase; very high emissivity due to ZrB₂, even better than that displayed by SiC multilayer; expected better oxidation resistance over 1700 °C due to the formation of ZrO₂ which does not melts up to 2700 °C, contrary to silica which melts and then evaporates over 1700 °C.

c) SiC laminates integrating porous layers: the presence of porous layers can halves the thermal conductivity through the thickness.

a) SiC laminates with Cf/SiC composite layers: composite layers provide enhanced conductivity in the plane and decrease of conductivity through the thickness (Fig. 2.2; W.S. Yang, C. Badini et al. “Thermophysical properties of short carbon fiber/SiC multilayer composites prepared by tape casting and pressureless sintering”, Int. J. Appl. Ceram. Technol., (2013) DOI: 10.1111/ijac.12149).

d) Laminates with alternate layers made of SiC and ZrB₂-SiC: the ZrB₂-SiC composite layers are integrated in the multilayer structure with the aim of delaying the oxidation when temperature exceeds 1700 °C and therefore the recession of SiC layers occurs; nevertheless the oxidation resistance up to 1600 °C is well assured by the SiC skin (Fig. 2.3).

Fig.2.2 Thermal conductivities of SiC multilayer and Csf/SiC multilayer composites in Z direction from 30 to 1500 °C (a) before and (b) after oxidation treatment at 1500 °C.

Fig.2.3. TGA curves under flowing air up to 1600 °C: passive layer formation after the first heating run. The manufacture process of these ceramic laminates has been based on tape casting technology because this technology has been adopted at industrial plant level since many years and it is well suitable for processing hybrid laminates with layers showing different microstructure and composition. Anyway in the frame of SMARTTEES project the processing method parameters were adjusted in order to perform the up-scaling required for the production of the TPS at the technological sample level (WP5, Fig. 2.4).

Fig. 2.4. Tiles 150X150X1.8 mm³, ten SiC layers.

In addition to the pressure-less sintering, other alternative process for the sintering of multilayers is the Spark Plasma Sintering. Spark plasma sintering (SPS) is found to compact powders satisfactorily through the simultaneous application of direct current pulses of high intensity and pressure. The electric current induces a temperature elevation within the sample by Joule's effect. The whole process lasts just a few minutes.

The consolidation experiments were performed at TECNALIA in a FCT Spark Plasma Sintering furnace (model S8451). This equipment can supply a direct current of 10000 A of intensity under a maximum tension of 10 V. The DC current was applied with pulse time of 10 ms and a pause time of 5 ms. The powder was filled in a graphite die between two graphite punches. The diameter of the samples was 20 or 30 mm. During the tests, the chamber was maintained under vacuum (10⁻² Pa). Temperature was controlled by a pyrometer that measures the temperature in the interior part of the graphite punch. The maximum temperature was between 1700-1900 °C during 1 min of holding time. The load (50 MPa) was applied during the heating.

A B

Fig. 2.5. SPS samples A) Diameter 20 mm, B) Diameter 30 mm.

Main conclusions of the SPS tests are:

e) With monolithic materials (pure SiC, pure ZrB₂ and SiC with carbon fibres), the temperature to obtain the maximum density depends on the composition. For SiC and SiC + Cf, this maximum densification (around 92 % of the theoretical density) was obtained at around 1850 °C, however, for pure ZrB₂ was necessary to reach 1900 °C. As sintering aids B₄C, TiC, C and B were used and it was not observed significant different between them. In all cases the porosity was very small and well distributed. In the case of the SiC with carbon fibres, the interface between the fibre and the SiC was very good, due to the fact that it is not possible to observe cracks or porosity between both materials.

f) Different configurations of multilayers were successfully obtained (see figure 2.6). The most important problem was the presence of cracks after the sintering. The reason of this cracks are the stresses produced by the difference in CTE during the fast cooling. The most successful way to avoid the cracks was the change of the load cycle. It was necessary to release the pressure at high temperature, to release the stresses produced by the difference in CTE.

g) The density of the composites was higher than the 90 % of the theoretical value. Small cracks were

observed in the ZrB₂/SiC layers. These cracks were perpendicular to the application of the load and it is believed that they are produced by the contraction of the layers during the fast cooling.

A B

C

Fig. 2.6. Different configurations of multilayers consolidated by SPS

2. SiC-based foams (filled in by silica fibres) designed for thermal insulation

For TPS applications, some carbides (e.g. SiC) are, for their outstanding thermo mechanical properties, the most appropriate. Reticulated SiC foams have an open pore structure with an interconnected network of cells, whose edges are made of solid struts. These foams can withstand long oxidative exposing conditions with low material degradation. The production method allows obtaining a microstructure composed of crystalline SiC and residual silicon with an open porosity smaller than 1%.

The material demonstrates high temperature stability up to 1400 °C (air), resistance to acid and basic conditions, high thermal conductivity and thermal shock resistance.

The Erbicol standard foams are composed of 70% of SiC and 30% of free Si with pore size of 10 PPI. Erbicol, for the SiSiC foams production, uses a method called Schwarzwaldler (Figure 2.7) which consists of the impregnation of a sacrificial polymeric template. The green body is then pyrolyzed in inert atmosphere and liquid silicon infiltrated under vacuum, which transforms the residual carbon in SiC.

Figure 2.7. Section of a foam strut after impregnation, pyrolysis, densification and LSI.

In the table 2.2 material properties of standard 10 PPI foams are reported.

During the project, Erbicol produced different type of foams, optimizing material properties both at a microscopic and macroscopic level, aiming at producing the most performing and reliable product TPS application.

Property Value

Foam Density [gcm⁻³] 0.323

Normalized Density 0.114

Macroporosity [%] 88.6

Surface Area [m² m⁻³] ~ 500

Av. Strut Thickness [mm] 0.9

Flexural Strength [MPa] 4

Compression Strength [MPa] 3

Thermal Conductivity [Wm⁻¹K⁻¹] ~ 7

Young module [GPa] 2-3

Table 2.2 SiC foam properties (ErbiSiC foam, 10 PPI, source: Erbicol SA)

Erbicol produced foam samples with different cell orientation because it is well known that cell orientation affects both thermal conductivity and mechanical properties, which are important properties for application of foams in TPS. Enough material for tests and analysis was provided to the partners. Other samples with dimensions of 30x30x15 mm, 10 PPI, to study the adhesion between the CMC skins and foams and for re-entry tests simulations were produced. A better interface between foams and CMC was facilitated smoothing the edges of the foams.

Subsequently, Erbicol reduced the content of free silicon in foams, optimizing the microstructure but keeping mechanical and thermal properties above the threshold. Excess free silicon can cause material degradation at high temperature, given his relatively low melting point of 1414°C.

Figure 2.8. Calculation for standard Si-SiC foams

The optimization of the silicon content in the end product took into account the reaction bonding, the amount of silicon needed to form the matrix, thermal and mechanical properties. Following pictures show different sample after the LSI optimization.

Figure 2.9. Foams with different content of silicon and carbon

After the products were validated at Supsi, EADS and POLITO, parameters were fixed and Erbicol manufactured the samples needed for the assembly with the CMC skins at EADS. These foams were produced using pure silicon (99.8% of purity) to further optimize the quality of the product.

a) b) c)

Figure 2.10. a) pure silicon; b) LSI preparation ; c) final result

It was found that a thermal stabilization treatment for the final product was beneficial for its stability during the subsequent assembly step. Therefore all products were stabilized by performing thermal shocks over a porous burner.

Figure 2.11. 50x50x10-15 mm samples during thermo shock;

To increase the insulation capacity of SiC cellular structure, a production method for hierarchical foams was developed. As a second insulating phase Fibremax™ bulk fibres (UNIFRAX Niagara Falls USA) were utilized. Fibres characteristics are reported in Table 2.3.

Fibre

Fibre diameter [μm] 4-6

Composition:

Al₂O₃ 72%

SiO₂ 27%

Fe₂O₃ Trace 0.02%

TiO₂ Trace 0.001%

MgO 0.05%
 CaO 0.05%
 Na₂O₃ 0.10%
 Specific heat [J kg⁻¹ °C⁻¹] 1172
 Felt
 Density 0.13
 Thermal Conductivity [Wm⁻¹K⁻¹]
 @ 800 0.18
 @ 1000 0.25
 @ 1200 0.36

Table 2.3 Physical properties of the oxide fibre insulating phase (Fibremax®) from product datasheet.

Figure 2.12 shows the process employed to fill the foam. A dispersion of short fibres was forced to pass through the foams' pores. Fibres were stopped at the bottom of the foam by a filtering medium. To obtain the dispersion, 0.06 wt% of surfactant (Triton X100, Aldirch D) was diluted in distilled water, then short oxide fibres (5.7 wt.%) were added and dispersed by ball milling for 80 minutes.

Figure 2.12 SiSiC foam filling via forced sedimentation: fibres dispersion pouring, water draining and fibres sedimentation and further pouring. The procedure was repeated till reaching the complete filling of the MRC body.

Foams were laid on a filter paper and a metallic net placed at the bottom of a metallic case surrounding the foam. The dispersion was then poured into the case and forced to pass by gravity through the SiSiC foam and the filter. The fibres, stopped by the filter, started to compact from the bottom of the foam. This forced sedimentation let the fibres layer grow inside the foam. The dispersion was poured several times until the entire foam was filled with short fibres.

Figure 2.13 On the left a 50x50 [mm] sandwich tile produced filling reticulated SiSiC with oxide fibres. On the right a close view of the foam showing the complete filling of the macroporosity.

The fibres amount into the dispersion and the filter pore size were optimized in order to fill the foams with the fibres (Figure 2.13). For the following thermal loading tests, six samples were produced, their properties are reported in Table 2.4.

foam Oxide fibres system
 sample # Mass
 [g] L
 [mm] w
 [mm] t
 [mm] ρ
 [g cm⁻³] ρ
 10⁻⁴ [g cm⁻³] w%

[-] ?

[g cm⁻³]

1	5.18	30.02	29.94	15.20	0.38	3.27	0.43	0.66
2	5.28	30.00	30.20	14.75	0.40	2.69	0.37	0.63
3	5.59	30.04	30.10	15.04	0.41	1.96	0.29	0.58
4	4.92	30.00	30.00	15.25	0.36	2.84	0.41	0.61
5	5.91	30.06	29.86	14.93	0.44	1.96	0.27	0.61
6	5.69	30.20	30.18	15.12	0.41	2.12	0.31	0.59
Average	5.43	30.05	30.05	15.05	0.40	2.47	0.35	0.61

Table 2.4 MRC, FRGI and HCC weights volumes and related properties before and after the forced sedimentation process.

3. CMCs suitable to act as skin of SiC foams in a sandwich structure and designed for providing toughness and strength

Within the SMARTTEES novel technological applications were turned out with respect to joining of ceramic matrix composite (CMC) materials to ceramic foams. With Cf/SiC and SiCf/SiC two different types of CMC materials have been evaluated. Furthermore different SiSiC ceramic foam types with respect to varying (tailored) Si content were used for the development of integrated CMCupper skin - SiSiC foam - CMClower skin sandwich structures and its optimization in terms of achieving best mechanical performance and the criteria 'non-failure of the brittle SiSiC foam' over the complete assembly process and during loads. Finally a suitable process for the integration of CMCupper skin - SiSiC foam - CMClower skin sandwich structures with excellent mechanical performance (bending strength, tensile strength, bonding at interface CMC/foam) was developed, see Figure 2.14.

Fig. 2.14 Integrated Cf/SiC - SiC foam - Cf/SiC sandwich structure

The specific results refer to the following:

- Process development for joining dissimilar ceramic materials such as CMC materials with ceramic foam
- Ability to join dissimilar ceramic materials, in particular non-oxide CMC materials (Cf/SiC, SiCf/SiC) with SiC & SiSiC based ceramic foams of varying Si content
- Development of a suitable slurry in order to join non-oxide CMC materials with ceramic foams SiSiC by chemical reaction (reaction bonding) between CMC (here mainly Cf/SiC), slurry constituents (e.g. binder, Si, C, SiC, additives) and ceramic SiSiC foam with varying Si content
- Application of the slurry material in the interface between the CMC and the ceramic foam in order to achieve a sound joint
- Ability to improve the mechanical performance of the joint by surface modification of the CMC and/or the ceramic foam
- Development of a suitable curing process using autoclave technique in order to guarantee good and homogeneous connection between CMC and ceramic foam
- Development of an high temperature treatment process based on Liquid Silicon Infiltration (LSI) technology in order to achieve chemical reaction between CMC (here mainly Cf/SiC), slurry constituents (e.g. binder, Si, C, SiC, additives) and ceramic SiSiC foam with varying Si content
- Improvement of LSI process and its parameters (atmosphere, gas flow, temperatures, temperature ramps, end temperature, time, sample placement including tooling etc.) in order to guarantee best

mechanical performance of the CMC (here mainly Cf/SiC) / ceramic SiSiC foam (with varying Si content) joint

- Ability to fabricate CMC (here mainly Cf/SiC) / ceramic SiSiC foam joints and integrated CMC (here mainly Cf/SiC) / ceramic SiSiC foam / CMC (here mainly Cf/SiC) sandwich structures
- Ability to characterize the CMC (here mainly Cf/SiC) / ceramic SiSiC foam joints and integrated CMC (here mainly Cf/SiC) / ceramic SiSiC foam / CMC (here mainly Cf/SiC) sandwich structures, e.g. mechanical testing (bending, tensile)
- Ability to up-scale the developed process for the fabrication of CMC (here mainly Cf/SiC) / ceramic SiSiC foam joints and integrated CMC (here mainly Cf/SiC) / ceramic SiSiC foam / CMC (here mainly Cf/SiC) sandwich structures

WP3 Joining processes

The activities carried-out in WP3 refer to the definition, development and application of the bonding processes for the joining of the different parts of the Thermal Protection System (TPS) structure, i.e.

a) joining of a ceramic matrix composite material (CMC) that consists of carbon fibers embedded in a silicon carbon matrix a SiC matrix (Cf/SiC) to SiC based ceramic multilayers (SiC ML) for the external part of the TPS structure.

b) joining of the CMC to the metallic part for the internal part of the TPS.

c) the integration of SiC multilayer, CMC and metallic frame by joining for the whole TPS.

The output of this work was used for the construction of the technology samples in WP5.

The selection of the bonding processes, in order to comply with the TPS requirements investigated under WP1 and the environmental specifications and technology sample basic design, was carried out under WP3.1 and the outcome is described in deliverable D3.1 document.

The investigations that have been carried out so far give the following conclusions regarding the definition of the bonding processes

1) SiC ML multilayer to CMC joining

A number of routes have been selected and investigated for joining the CMC to SiC based ceramic multilayer for the external part of the TPS that can withstand temperatures as high as 1500 °C.

From the investigated routes the diffusion bonding process employing TiSi_{1.5}C₂ as powder filler metal was selected as the most promising one. A series of joints were fabricated for various fabrication parameters, metallographically and structurally characterized and selected joints were mechanically and thermally tested for their performance. The optimization of the bonding process referred mainly a) to the proper pressure selection for the diffusion bonding process and b) to the elimination of cracks that appear on the surface of the SiC ML and extend from the filler area up to the free SiC surface, vertically to the joint interface. Reduction of cracks was achieved and their existence was proven not to be detrimental for the performance of the TPS under ground field relevant conditions. The optimised joining process gives sound joints which have, for the envisaged application, the appropriate thermomechanical properties at temperatures as high as 1794 °C. Fig. 3.1 depicts the cross section of the SiC ML-Cf/SiC fabricated using 25 MPa pressure.

However, the upscaling of the joining process to the size of 150x150 mm² for the technological sample resulted in warping of the joint at the periphery. For that reason an alternative route, based on graphite high temperature adhesive accompanied by appropriate surface modification of the surfaces to be joined, was investigated and used as an alternative solution. The cross section of the adhesive bonding of the SiC

M to CMC s depicted in Fig.3.2.

Fig.3.1. SEM micrographs of the cross section of the SiC ML-Cf/SiC joint fabricated at 25 MPa at magnification $\times 100$ (left) and $\times 600$ (right).

Fig.3.2. SEM micrographs of the cross section of the SiC ML-Cf/SiC joint using high temperature adhesive depicting all the interfaces (left) and the adhesive-Cf/SiC (right).

2) CMC to Ti alloy joint

The CMC to metal frame joining refers to the internal part of the TPS and the requirement is to withstand temperatures up to about 700 °C maximum. The route that was selected within WP3.1 as the most promising one is based on brazing employing TiCuAg filler metal and perforation of the CMC. The joining process was optimized for the a) the brazing parameters (brazing temperature, holding time), b) the perforation geometry (hole diameter and depth) and c) filler type (foil, paste and powder). A series of joints were fabricated and metallographically investigated employing SEM with EDX analysis. Also the cross sections were structurally characterized by X-ray diffraction measurements. In general TiCuAg filler metal wets both parts and crack free brazed areas are produced. In most cases small cracks appear inside the CMC parallel to the interface, most often between the first and second interlayer. These cracks are always trapped between the vertical cracks, which are inherent in the CMC and which do not allow the propagation of the parallel to the interface cracks.

Two titanium alloys were investigated, Ti6Al4V-grade 5 and Ti-beta-21s. The latter, although it presents higher service temperature and enhanced oxidation resistance than Ti6Al4V, was rejected due to its beta transus at 800 °C (transformation from hexagonal to cubic phase), about 100 °C below the liquidus temperature of the TiCuAg filler metal. In addition the microstructural investigation of CMC/Ti-beta-21s joints have shown lengthy cracks in the first interlayer of the CMC.

Figs. 3.3 and 3.4 present the cross sections of the perforated CMC/Ti alloys joints.

Furthermore CMC/Ti alloys joints were fabricated for mechanical tests in the temperature range 25 to 600 °C and for thermal cycling tests under re-entry conditions at a maximum temperature of 840 and 675 °C. The maximum shear strength of 7.4 MPa achieved at 600 °C for the CMC to Ti alloy joint is adequate for the envisaged application and comparable to that of the CMC. In addition, the CMC/Ti joints survived 50 re-entry cycles with temperature at the CMC surface with no change in the microstructure of the joint (Figs. 3.5 and 3.6). Small cracks that are observed around the peripheral perforation of the CMC, in the post test analysis of the joints, are trapped in between the most peripheral holes and cannot propagate through the whole length of the joint.

Fig.3.3. Cross of the perforated Cf/SiC-Ti6Al4V joint. Fig.3.4. Micrograph of the cross of the perforated Cf/SiC-Ti6Al4V joint.

Fig.3.5. The CMC/Ti joints before the re-entry cycles.

Fig.3.6. The CMC/Ti joints after 50 re-entry cycles at two heat loads.

The integration of the two types of joints in the TPS structure is depicted in Fig. 3.7 which shows a SiC multilayer joint to the CMC skin. The SiC/CMC joint was subsequently used to bond the foam between

SiC/CMC upper structure with the lower CMC.

Fig.3.7. SiC/CMC/foam/CMC integration.

WP4 Simulation

In order to understand the mechanical behaviour of the sandwich for the TPS system, a X-Ray computed acquisition was performed on a sample. This was composed of an Erbicol Si-SiC foam and a SiCf/Si-SiC CMC. Reconstruction and segmentation is performed with AVIZO software.

Figure 4.1. XCT + image processing (AVIZO) was fundamental to better understand the skin to core bonding and the mechanism that provides the load transfer from the skins to the core.

First mechanical analysis

When subjected to the thermal loading during re-entry structures are locally bending. For this reason the design phase was started with a mechanical analysis under bending varying parameters like skins thickness and intrinsic stiffness (Young module) one at a time. This was done in order to understand how normal and shear stresses arise inside the sandwich in a similar loading condition at ambient temperature (Figure 4.2).

Figure 4.2. Bending set up Image shows the acquisition points for shear (1) and normal stresses

Figure 2 shows how shear stresses become dominant for stiffer ply configurations. Both elastic module and skin thickness (that act at forth power due to static moment of inertia) increase shear stresses into the system. This confirms the results obtained in experimental tests, were a prevalent shear failure mode is observed these structures..

Figure 4.3. Left: stress values inside the sandwich VS skins thickness, right sandwich failure because of shear stresses.

This work allowed us to minimize the range of this two parameters' values for the following phase

TPS design

The final TPS design was obtained with iterative thermo mechanical finite element analysis (COMSOL Multiphysics).

Simulation model Experimental set-up

Figure 4.4. Simulation calibration: model and experimental set-up

A calibration of the thermal insulation properties of the filled sandwich was executed crossing results from AAC's thermal tests, since in a first simulation campaign, a relevant mismatch between analytically obtained properties and experimental data was observed.

Figure 4.5. Model calibration with experimental results: a) Backside sample temperature profiles (load case 1) and b) Backside sample temperature profiles (Load case 2)

Thermal conductivity vs temperature behaviour was inferred by slight modifications of the specific heat

capacity (given volumetric quantities of the foam and filler). A “more insulating” solution was obtained leading to an optimization of the previous design. In order to reproduce real testing condition of the system, the insulating walls used at AAC were added to the model in order to duplicate also lateral heat dissipation (Figure 4.5).

In the present report two TPS solutions for Load Case 1 and Load Case 2 are proposed.

Load case 1 Load case 2

Figure 4.6. TPS final TPS configuration for the two load cases

Thermal insulation capability was the first design criteria for these final solutions. An important design constraint was also the areal mass that should be kept below mission requirements. For both load cases this requirement was not fulfilled taking into account the mass of each sub component. Insulation limitations were observed at the titanium-CMC interface where temperature has to be kept below the temperature of 816°C, and the surface of the vehicle structure temperature (150°C) (Figure 4.7).

Load case 1 Load case 2

Figure 4.7. Temperature profiles of the complete structure under load case 1 (left) and 2 (right)

Load case 1 Load case 2

Figure 4.8. Thermal analysis contours: iso-temperature surfaces and heat flux path arrows (logarithmic scaled) for the two load cases at the end of the heat flux loading.

In Load Case 2 the very slow heat dissipation of the system to the exterior of the TPS during the “cold” phase of the re entry, allowed heat to propagate through the TPS to the vehicle (temperature of 149°C after 10000[s]). Taking this into account the height of the standoffs separating the sandwich from the primary structure was fixed at 75[mm]. This solution impacted negatively on the areal mass and reduced the first eigen frequencies of the structure which became less rigid. On the other hand the temperature of the surface should be kept below a critical value. Thermal-stress simulations showed that stresses exceed the intrinsic limit in almost each component (Figure 4.9) , due to the relevant thermal expansion mismatches.

Load case 1 Load case 2

Figure 4.9. Von Mises stress contours in the ceramic foams for load case 1 (left) and 2 (right)

At the end of the project some materials properties, first taken from the literature, were made available after characterization (e.g. Emissivity). These were introduced into the model (as a function of the temperature) and simulations re-run.

Results in Figure 4.10 show that calculated temperature were previously over estimated giving further chances to obtain lighter and better performing solutions.

Figure 4.10 Temperatures distribution along the TPS before and after input properties modification.”

WP5 TPS technology samples assembly

Ti alloy stand offs using the commercial Ti6Al4V grade 5 alloy were fabricated for the two selected thermal load cases.

Fig. 5.1. The Ti stand off for load case 1 and 2.

In the upscaled technological samples having dimensions of 50[?]50 and 150[?]150 mm² the joining processes developed and optimised in WP3 were applied. Also filler metal Ti₃Si_{1.5}C₂ was fabricated for use in the upscaled SiC/CMC joints.

Specifically for the thermal load case 1 and 2 for samples having dimensions 50[?]50 mm² the joining processes for both SiC/CMC, CMC/foam/CMC and CMC/Ti alloy joints have been successfully applied as it is depicted in Figs. 5.2 and 5.3.

Fig.5.2. The technology sample 50 [?] 50 mm² for load case 1 showing the integration of all parts.

Fig.5.3. The technology sample 50 [?] 50 mm² for load case 2 showing the SiC/CMC interface (left) and the integration of SiC, CMC/foam/CMC sandwich (right).

During the upscaling of the technology sample to the size of 150[?]150 mm² difficulties were faced at the level of

- a) Joining SiC multilayer to CMC. Warping of the joint prevented its use in the integration with the foam and the bottom part of the CMC
- b) Joining of the Ti stand offs due to the loss of the temperature control in the furnace used (a furnace outside the consortium partners was employed, due to technical problems in the brazing furnace at TECNALIA, and it proved to be inappropriate for the brazing process).

The above two problems were resolved as follows

- a) For the SiC/CMC joint the alternative route based on high temperature adhesives was applied
- b) The brazing process of the Ti stand offs was applied successfully at TECNALIA's furnace as can be seen in Fig. 5.4.

Fig.5.4. The technology sample 150 [?] 150 mm² for load case 2 after the brazing process of the Ti stand offs.

WP6 Ground testing and validation

The objective of this workpackage was the provision of ground testing facilities for representative load case for the selected flight application.

The overall work can be summarised as follows:

- In the 1st project year, improvements and adaptations of the test facility had to be performed, including test and calibration runs.
- Initial tests on SiC based foams delivered by ERBICOL performed under relevant thermal loads in order to assess the limits of these key components of the TPS

- In the 2nd project year, and based on these results, the open pore and filled foam samples from ERBICOL had been investigated, making clear that the pore filling enhances the suitability for TPS application substantially
- Joined Ti/CMC samples from DEMOKRITOS and TECNALIA were then investigated
- followed by tests on joined C/SiC / Multilayer Plates from DEMOKRITOS and TECNALIA
- Regarding the joined plates, no damage could be observed after applying heat fluxes equivalent to 1,391 °C and 1,794 °C. Further test were performed at a concentrated heat-flux (see description below).
- In the 3rd year, the improved joints of Ti/CMC delivered by DEMOKRITOS and TECNALIA were successfully characterised under all relevant load cases
- Joints of Multilayers (SiC based with and without ZrB₂ interlayers) joined to CMC had been tested, indicating thermally induced stresses in the multilayer. The applied thermal gradients were however too high and beyond the real load case in a TPS
- CMC/Foam/CMC sandwiches delivered by EADS-IW had been fully characterised, indicating that these joints are not undergoing relevant degradation even when tested under loads exceeding the initially defined design limits
- Finally, a full assembly (small sample for load case 1) had been successfully tested, and the suitability of the selected concept, the selected materials, and the applied joining technology had been demonstrated

Summarising all the aforesaid, it shall be concluded that the development of all the materials and processes was successful:

For the foams, substantial decomposition of the ceramic filler and partial melting of the foam itself is observed at the 2 highest thermal loads (equivalent to 2,053 °C and 2,163 °C) only. This is not to be regarded as detrimental for the application, as such temperatures are not expected for the load cases the TPS has been designed.

The substantial improvements of Ti/CMC joints, manufactured with different brazes and different mechanical pre-treatment of the CMC plates, had been demonstrated. While initial specimens revealed substantial scattering, the final ones showed good strength and reliability, even at temperatures beyond the design load.

Regarding the multilayers, a relevant flux gradient (calculated by the end user), concentrated in the central part of the sample was applied in order to load the samples under a realistic thermal gradients. The multilayers passed the test, even at low oxygen environment.

The multilayer/CMC samples also passed the same type of test.

No problems were found on the CMC/Foam/CMC sandwiches assemblies.

Regarding the CMC/Ti joints, and extrapolation with data from WP4 was employed to use the relevant heat flux/ temperatures corresponding to this part/height of the TPS and the temperature of the test was increased till failure occurred (above 800 °C).

Thus, at the end of the project, the SMARTTEES team had been able to deliver all necessary materials, processes, and joining technologies for a TPS panel. Though only a load case 1 subscale panel had actually been tested, it may be assumed from the test results that the project objectives may directly be transferred to the originally foreseen panel dimensions.

Potential Impact:

The efforts towards enable a strong impact of the project where not only addressed to the scientific

community (indexed paper and technical conferences and the EU citizen in general (webpage entries, short communication in newspapers, EU space conferences and brochures, but also to the space industry stake holders (technical workshops, news in Aerospace clusters and so on).

Concerning dissemination activities the following figures are highlighted:

- 10 sound paper at indexed journals
- 11 lectures at international technical conferences
- 11 dissemination activities to the public in general (news, poster, media, etc..)
- 2 Master/PhD thesis, arising from the results of the project and another 3 on going
- Scientific/technical workshop with relevant international experts and researchers.

Figure 1 shows figure and captions of few relevant dissemination activities the showcase in the 7th European Workshop on TPS & Hot Structures at ESA (2012, the poster at the 2nd FP7 space conference (2012) and the short news at the Spanish newspaper “La Razon” in 2013 and as an example of follow-up dissemination events a sample exposition at the kick off meeting for the new European Framework Programme for Research and Innovation “Horizon 2020”, in the frame of the incoming Greek Presidency of the European Council. SMARTEES was present at an exposition named “From Science to Technology”. Regarding the exploitation of the results

- Elaboration of an exploitation plan for each member of the consortium, also including non-space application.
- Specific use plan for the end user and industrial partners, including roadmaps, analysis of a value chain and technology transfer to other non-space products and applications (industry, energy, scientific infrastructure, etc...)

Documents connexes



final1-smartees-tecnalia-fspr-i0.pdf

Dernière mise à jour: 4 Novembre 2014

Permalink: <https://cordis.europa.eu/project/id/262749/reporting/fr>

European Union, 2025