



"8th European Workshop on

Thermal Protection Systems and Hot Structures

19 - 22 April 2016

ESA-ESTEC, Noordwijk, The Netherlands + updated with some DGA (Delgation Generale de l'Armement) study results

Inexpensive, fast, green and easy to build TOUGHCERAM ® for TPS & nozzle





TOUGHCERAM ® RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN RAW MATERIALS reinforcing agents

PATENTED TOUGHCERAM @ macro reinforcing fibers can be :

- a. Glass fibers,
- b. Silica fiber,
- c. Quartz fiber ,
- d. Carbon fiber,
- e. Basalt fibers,
- f. Silicon carbide fiber,
- g. Ceramic fiber,
- h. Zirconium fibers
- i. Polysilazanes fibers

PATENTED TOUGHCERAM @ reinforcing and interlocking micro particles aggregate can be any dendritic material as:

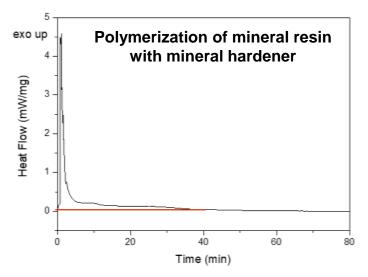
- a. Metallic oxides,
- b. Metalloid oxides (silica, boron etc)
- c. Nonmetal (carbon black)



TOUGHCERAM in DSC measurement.

Like in the case of organic polymerization;

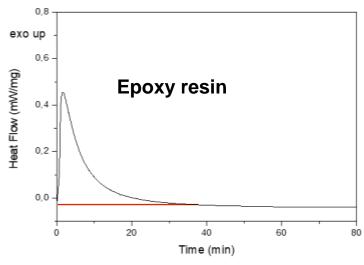
We observe an exothermal pick after 5 minutes of polymerization, and after 40 minutes à 60°C the material is fully polymerized & is perfectly stable,



Isotherm - @ 60°C

TOUGHCERAM polycristalization is complete after 40 min at 60°C

Enthalpy: 314 J/g



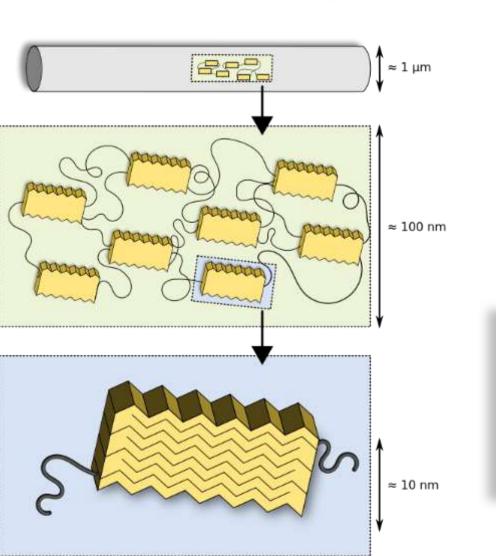
Isotherm - @ 190°C

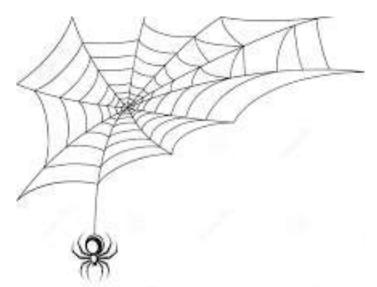
Reticulation is complete after 35 min at 190°C

Enthalpy: 338 J/g



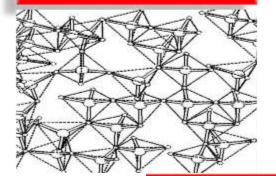
Principle of TOUGHCERAM ® flexibilized:





The spider
Toughening strategy





Flexible molecules

Typical mechanical properties

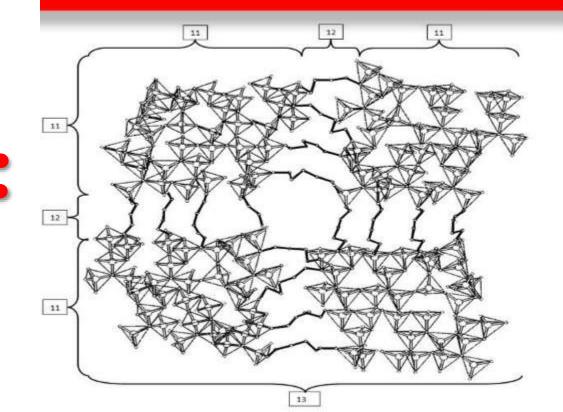


Maximum operating temperature +300 °C

Minimum operating temperature -120 °C



Flexibilized TOUGHCERAM @ polymerized



Benefit are high: Springiness Toughness Damage tolerance

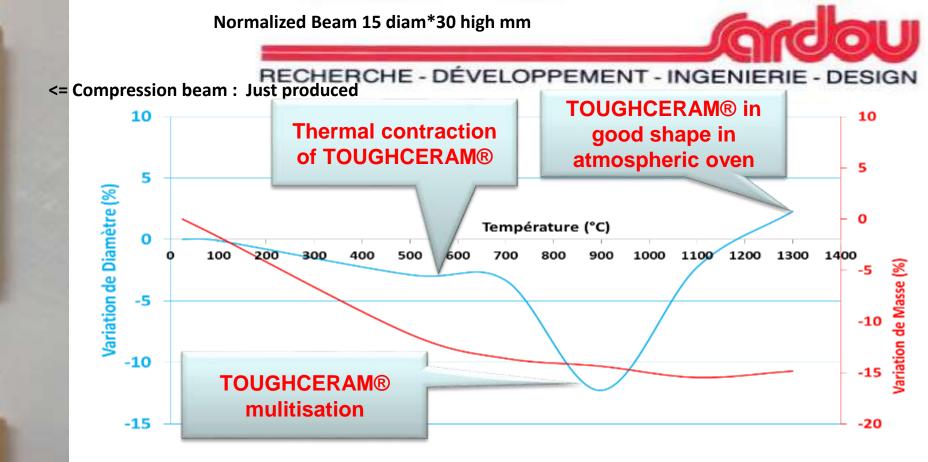
12= flexible molecules

11= ceramic domain

UNIQUE DESING!



TOUGHCERAM ® Unique mechanical properties



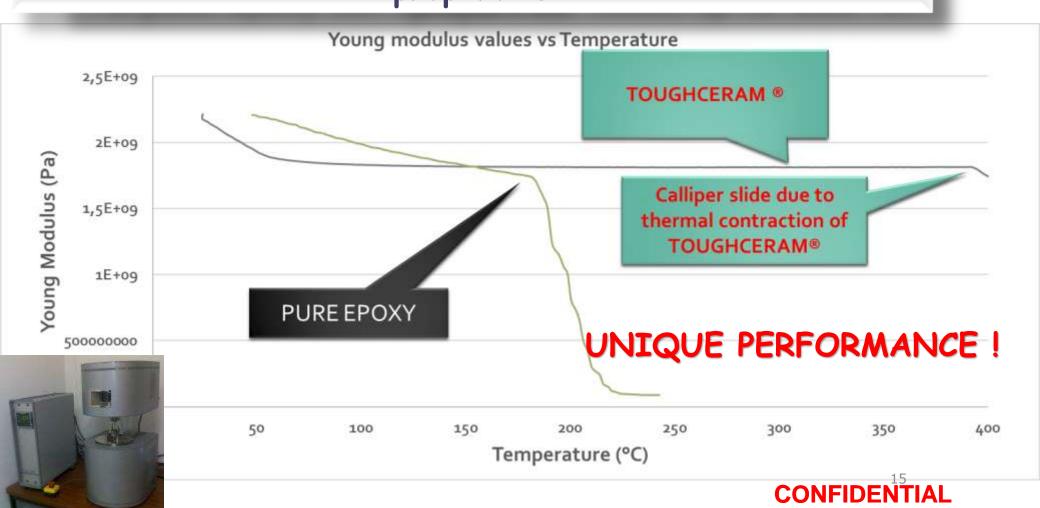
	STRESS MPa	Modulus	DL/L à 50MPa	DL/L Max
	maximum	Gpa	%	%
JUST PRODUCED	79	9,1	0,56	1,03
AFTER 1 HOUR AT 650°C	78	8,8	0,55	0,93

<= Compression beam : after 1 hour at 650°C</p>

Flexibilized TOUGHCERAM @ development campaign

DMA "traction-compression" test:

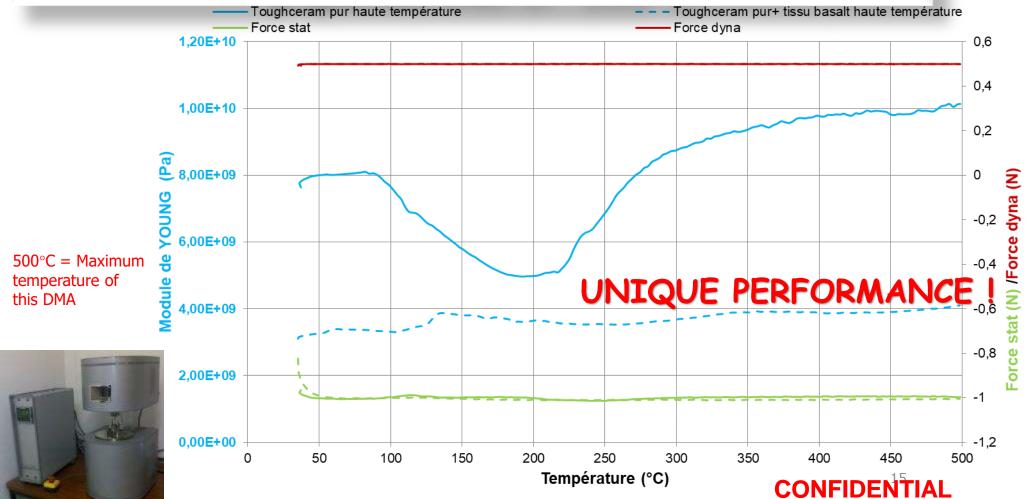
TOUGHCERAM @+basalt fibers give good mechanical
properties



Flexibilized TOUGHCERAM @ development campaign

RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN

DMA 3 points test : TOUGHCERAM @ and TOUGHCERAM @+basalt fibers give good mechanical properties even at 500°C!





Ultimate 3 points test

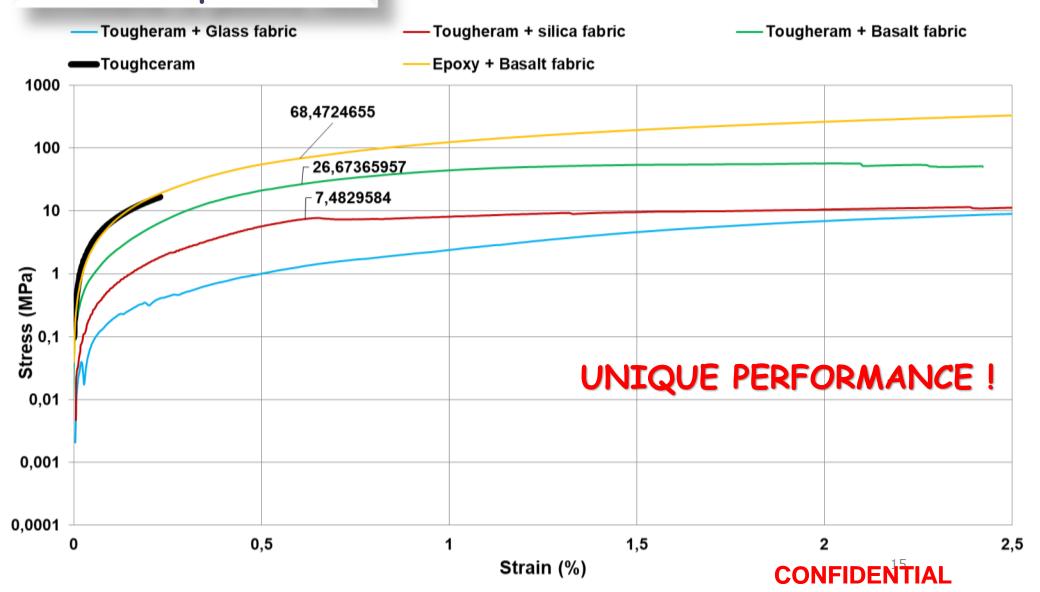
3 points bending test bed =>

Samples after test



Flexibilized TOUGHCERAM @ development campaign

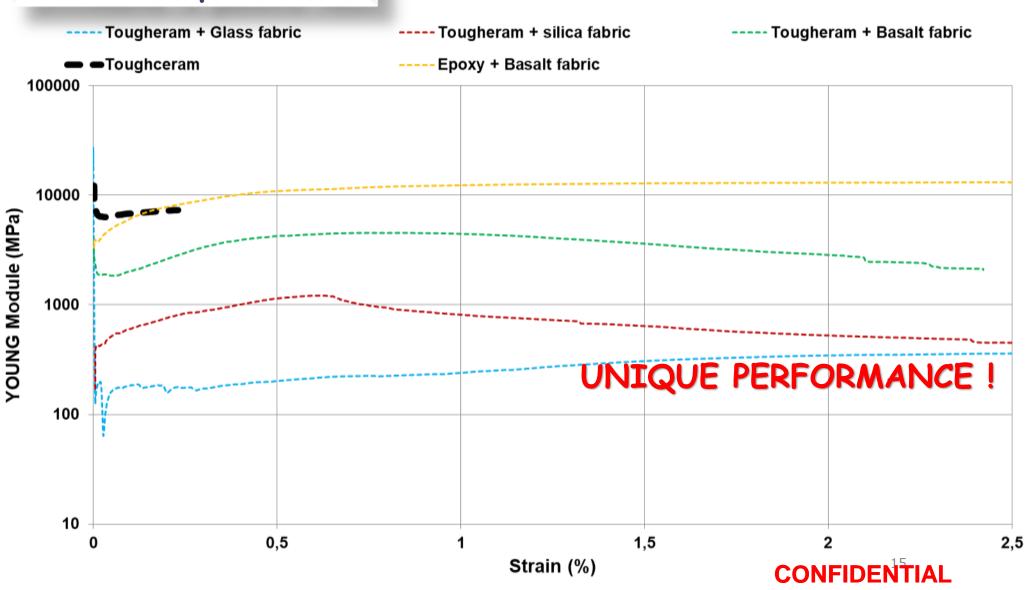
Ultimate 3 points test



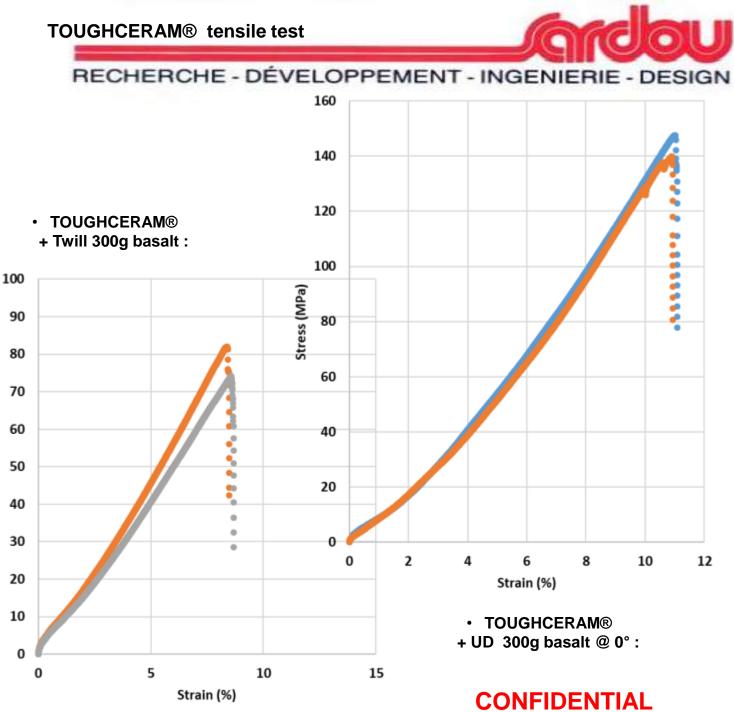
Flexibilized TOUGHCERAM @ development campaign

RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN

Ultimate 3 points test

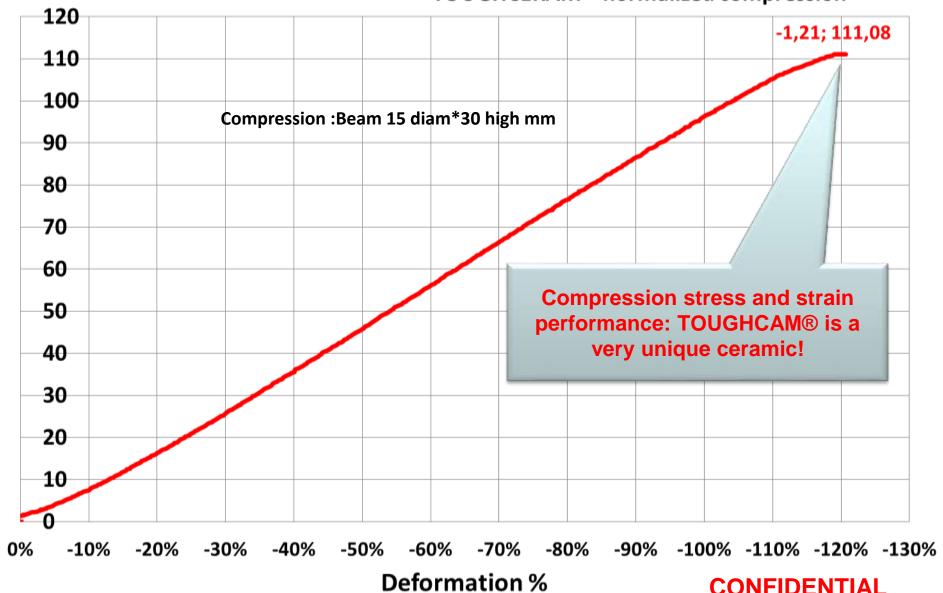








TOUGHCERAM ® normalized compression



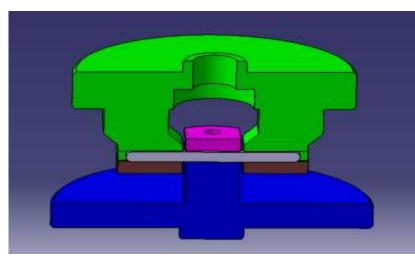
Flexibilised TOUGHCERAM @



RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN

SHEAR SET UP
Test sample dimensions = 4*2*50 mm
Shear gap = 0,9 mm
Test samples = 10 units minimum

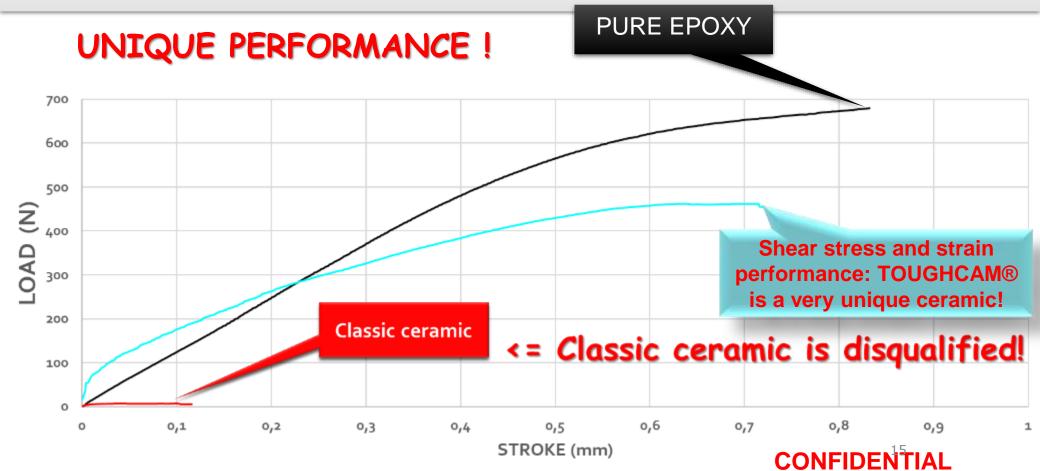




Flexibilized TOUGHCERAM @ development campaign

Shear comparison with organic epoxy; TOUGHCERAM @+basalt fibers has:

86% of ultimate stroke 67% of ultimate load



TOUGHCERAM ®

processing example # 1

TOUGHCERAM® LDN



TOUGHCERAM® is a compound of ultra low cost, easy to use mineral epoxy and silica reinforcing. Silica has a high specific surface area. During the polymerization, interlocked dendritic silica reinforce the matrix

TOUGHCERAM® is an excellent "green" & low cost thermal structure (see annex for more)

0,1 µm

Nozzle preform

TOUGHCERAM®

polymerization @ 120°C











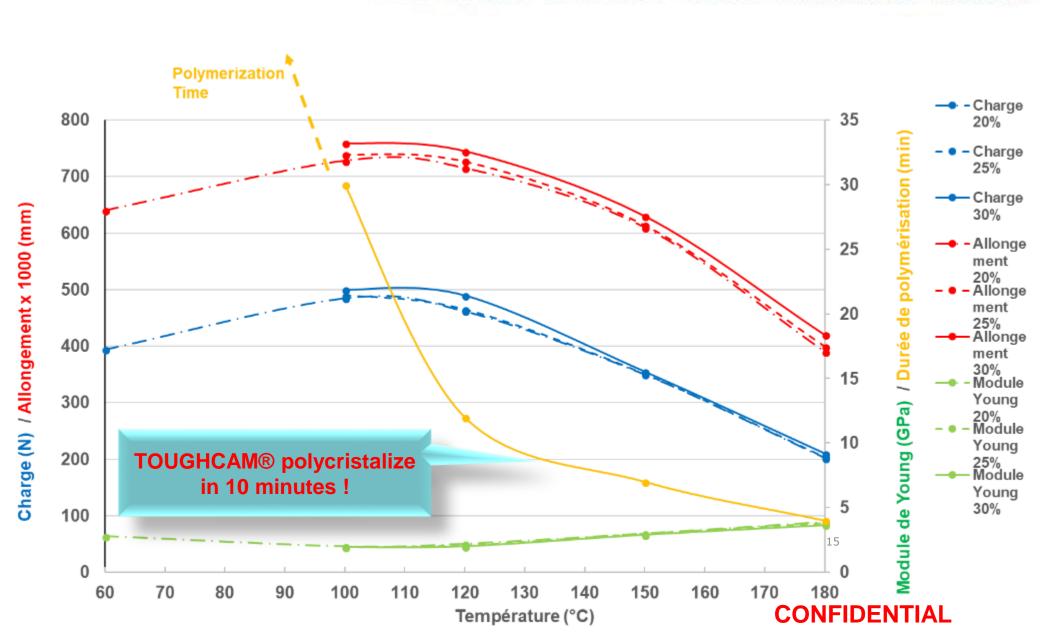




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RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN





Testing in plenum NORMALISED MARINE TEST

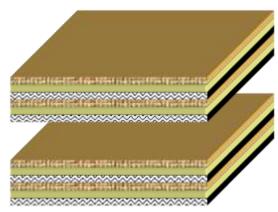
TOUGHCERAM® "anti fire panel" kerosene flame test done at 1000°C for 1 hour by southwest research institute





Thermal conductivity measurement by Hot-Disc method

- Caractéristiques de échantillons de composite fournis par Sardou SA le 02/02/2017 : 2 échantillons parallélépipédiques :
 - 1) Échantillon 1 : environ 47x36x11mm³
 - 2) Échantillon 2 : environ 47x39x11mm³



- Mesure moyenne : le volume de matière inspecté correspond à une pseudosphère de 13.4mm de diamètre autour de la sonde de 3mm de diamètre
- <u>résultats</u> (3 essais) : $\lambda_{\text{essai n}^{\circ}1} = 0.764 \text{ W.m}^{-1}.\text{K}^{-1}$

: $\lambda_{\text{essai n}^{\circ}3} = 0.738 \text{ W.m}^{-1}.\text{K}^{-1}$

: $\lambda_{\text{essai n}^{\circ}3} = 0.752 \text{ W.m}^{-1}.\text{K}^{-1}$

 $\lambda_{Mean} = 0.75 \pm 0.013 \text{ W.m}^{-1}.\text{K}^{-1}$

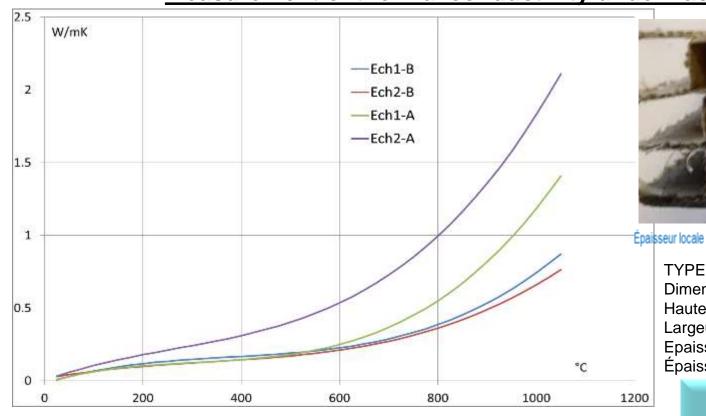
Massive TOUGHCAM® mean conductivity value







Measurement of thermal conductivity under vacuum



1.2 1.6 1.6

TYPE A

Dimension des cellules :

Hauteur: 9mm Largeur: 20mm

Epaisseur totale: 31 mm Épaisseur pli = 0.4mm

> **Hollow TOUGHCAM®** conductivity value

 λ_0 @ 200 °C = 0.12±0.013 W.m⁻¹.K⁻¹

 λ_0 @ 400 °C = 0.148±0.013 W.m⁻¹.K⁻¹

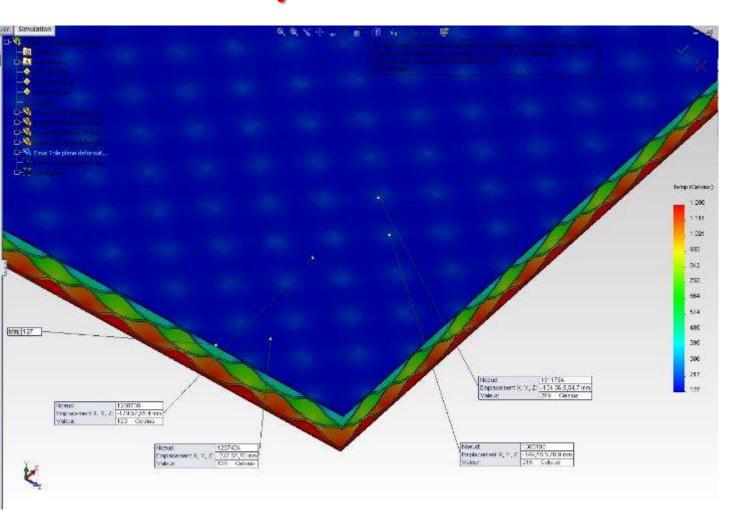
 λ_0 @ 600 °C = 0.15±0.013 W.m⁻¹.K⁻¹

 λ_0 @ 800 °C = 0.3±0.013 W.m⁻¹.K⁻¹

 λ_0 @ 1000 °C = 0.71±0.013 W.m⁻¹.K⁻¹



"anti fire panel structure"





SOUTHWEST RESEARCH INSTITUTE®

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FIRE TECHNOLOGY DEPARTMENT
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FIRE PERFORMANCE EVALUATION OF A MATERIAL IN ACCORDANCE WITH PART 1 OF ANNEX 1 OF IMO RESOLUTION MSC.307(88), INTERNATIONAL CODE FOR APPLICATION OF FIRE TEST PROCEDURES 2010

MATERIAL ID: TOUGHCERAM LDN

FINAL REPORT

5.0 TEST RESULTS

Testing was conducted in accordance with IMO Part 1, on April 7, 2014, beginning at approximately 10:55 a.m. by Abraham Mata, Senior Technician. No flaming was observed on any of the five runs. As required by the standard, average moisture and organic content data are presented in Table 2. Tabular test data and graphs of the measured temperatures, plotted with respect to time, are presented in Appendix A.

Table 2. Moisture Content.

Material ID	~ Moisture Content by Weight*	~ Organic Content by Weight*
Toughceram LDN	3.2 %	5.8 % (6.1%)*

^{*} Calculated/Measured by SwRI Personnel

6.0 CONCLUSIONS

The material, Toughceram LDN, tested in this program meets the test criteria for non-combustibility, as outlined in Part 1 of Annex 1 to the IMO FTP Code "Non-Combustibility Test", using the end-of-test criteria specified in Annex 3 to IMO FP 44/18

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ILLUSTRATION OF THE GOOD THERMAL BEHAVIOUR OF TOUGHCERAM®

Pictures of the test rig of a TOUGHCERAM® "anti fire panel" test in a kerosene flame test done @ 1000°C for 1 hour: IMO FTP 44/18

for 1 hour: IMO <u>FTP 44/18</u>

panel after a test done in a kerosene flame =>

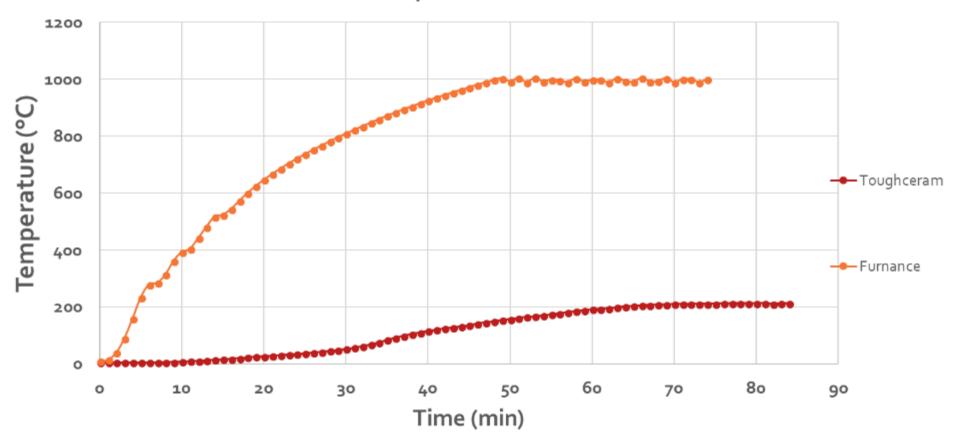






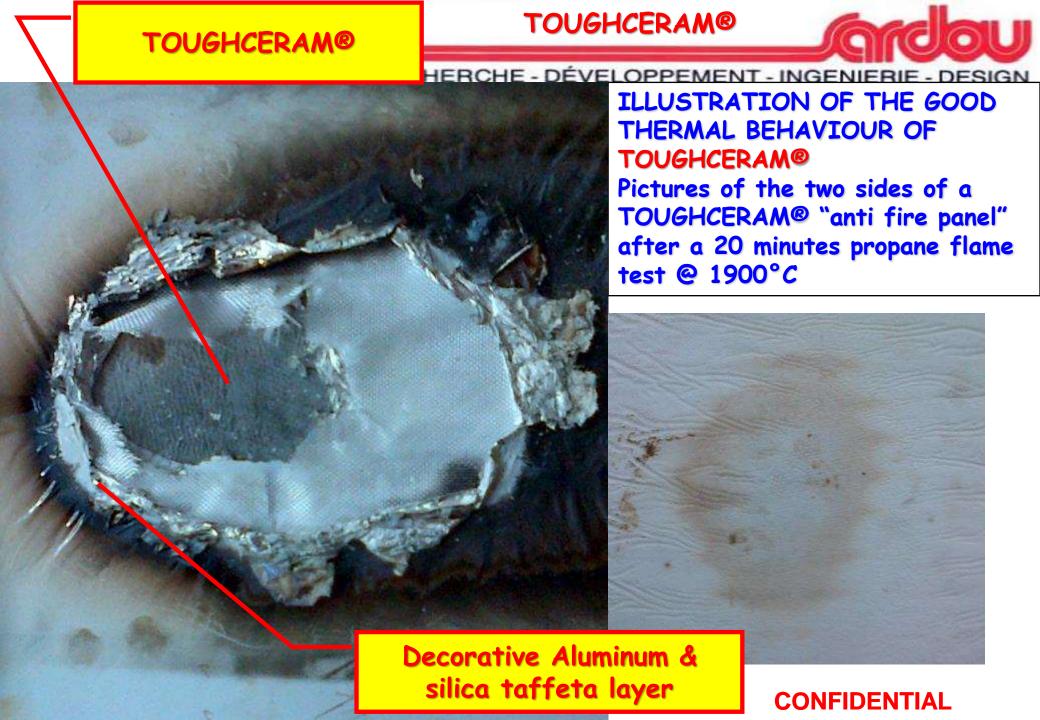
TOUGHCERAM ®

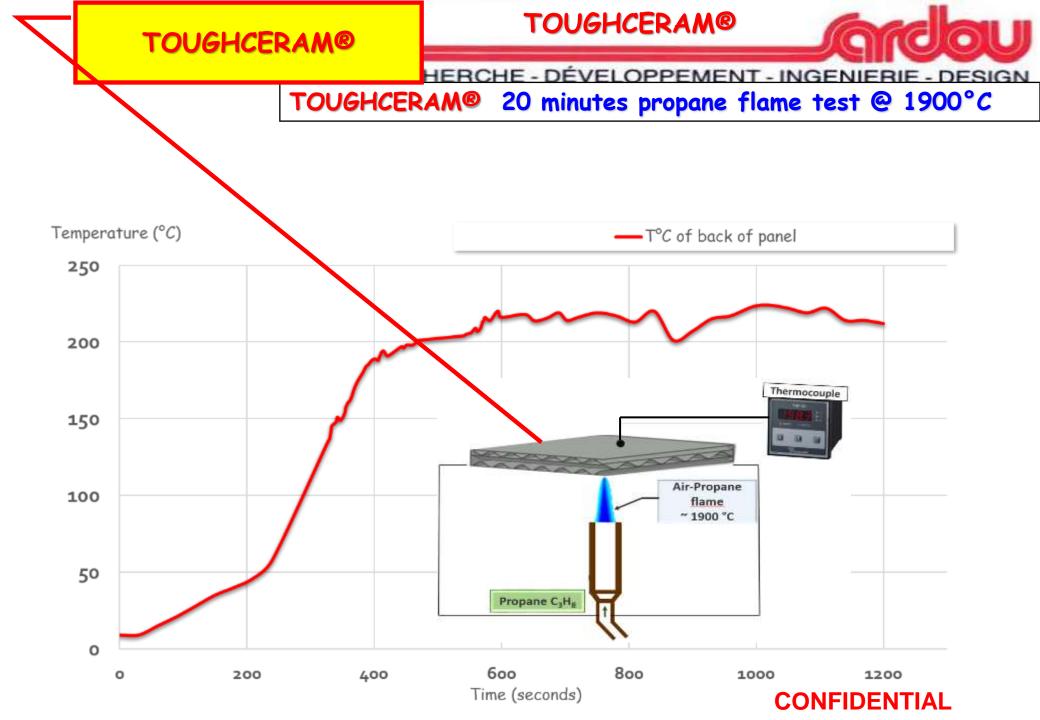
R&D Sardou panels - Furnace test results



TOUGHCERAM ®

Testing panel in open air @ 1900°C For 20 minutes!







TOUGHCERAM @ new generation panel

Plenum simulation Testing panel @ 1900°C For 90 minutes!



Plenum is used in order to simulate confined gap between TPS and aluminum structure of the IXV

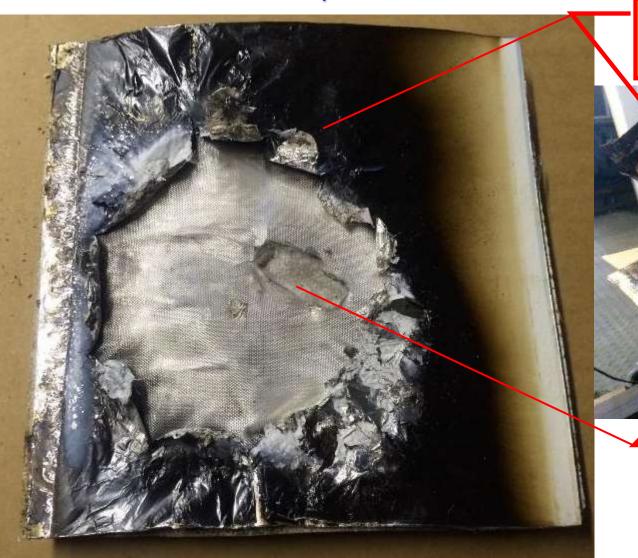


TOUGHCERAM® 90 minutes propane flame test @ 1900°C



Pictures of the front side after test sides of a TOUGHCERAM® panel

TOUGHCERAM® is in perfect condition

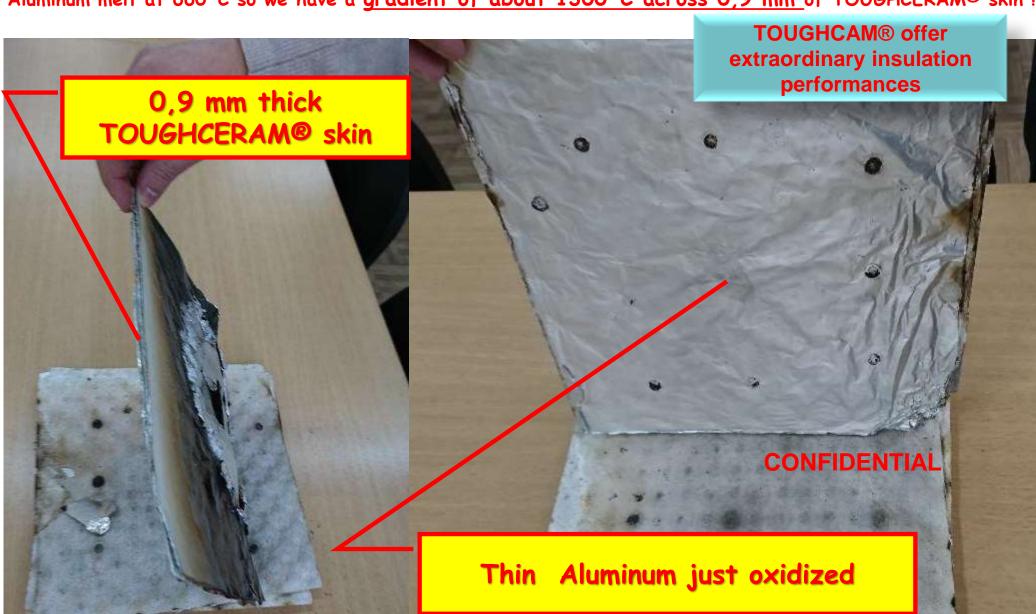


Decorative Aluminum & silica taffeta layer

TOUGHCERAM®

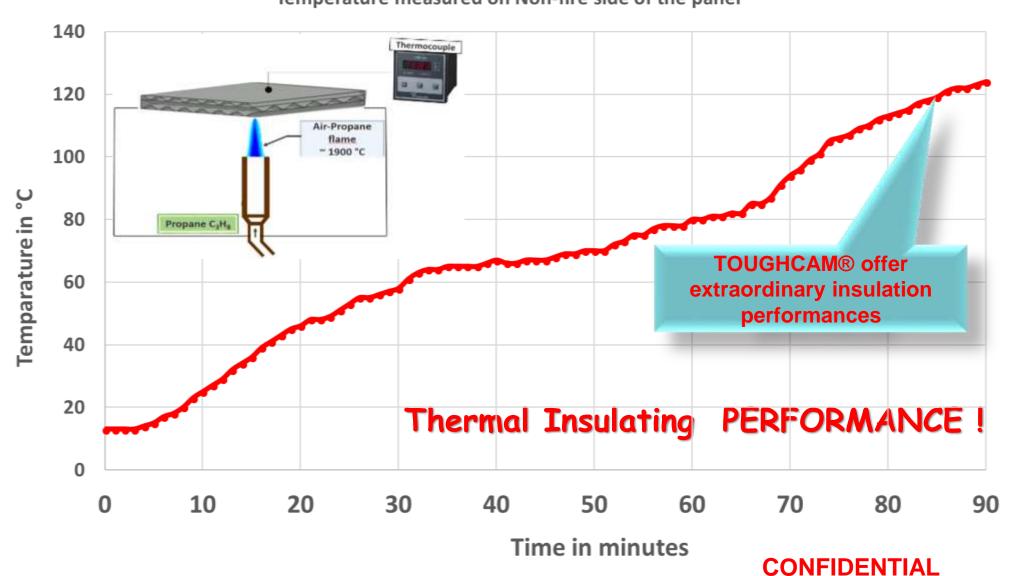
Rear view of the first TOUGHCERAM® skin

RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN Aluminum melt at 660°C so we have a gradient of about 1300°C across 0,9 mm of TOUGHCERAM® skin!





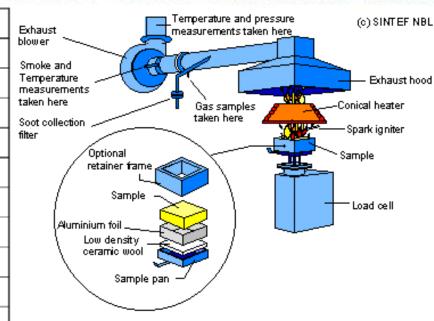
Temperature measured on Non-fire side of the panel



TOUGHCERAM®

RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN

testing mode						
	75 KW/m^2					
extraction rate of	0,024 m^3/s					
test samples						
square samples	100*100mm					
exposed surface	0,084 m ²					
laminates	sample 1	sample 2				
thoughceram®	0,5 mm	3,6 mm				
epoxy carbon	2,5 mm					



laminates	sample 1	sample 2	2/1	ratio	
thickness (mm)	3	3,6			
initial mass (g)	37,4	57,3			TOUGHCAM®
final mass (g)	23	· · · · · · · · · · · · · · · · · · ·		does	not burn nor smoke
ratio (init/end)	61%	92%			
average mass loss(g/(m^2*s))	2,12	0,09		4,2%	
total heat release MJ/m^2	27,2	0,8		2,9%	
maximum heat release value Kw/m^2	374	22,9		6,1%	
time to sustain flaming (s)	23	104			
extinguishing time (s)	118	114			
test duration (s)	744	742			CONFIDENTIAL

Following are examples of potential applications

We are searching for

- OEM
- ESA
- HORIZON 2020
- etc
 interested in the following fields



Our following suggestion is made in humility and with the deepest respect of previous solutions and works

TOUGHCERAM © TPS SLIPPER concept...

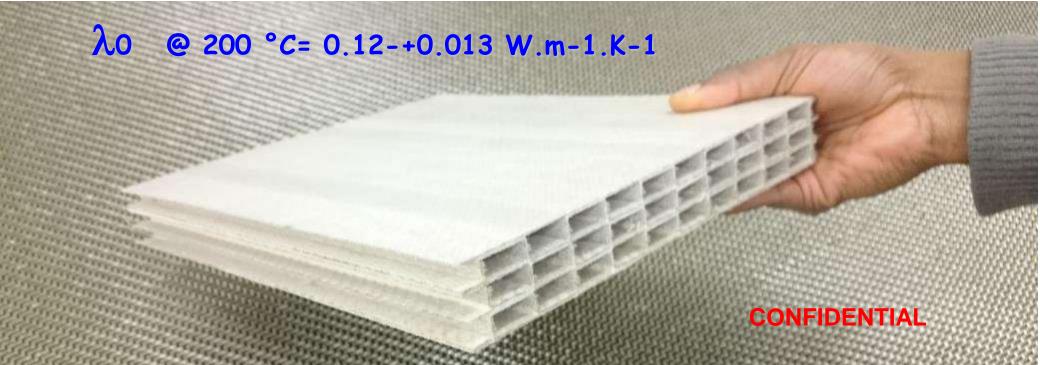




State of the art solution: 30 CERAMIC TILES + NOSE CONE



TOUGHCERAM Structural solution

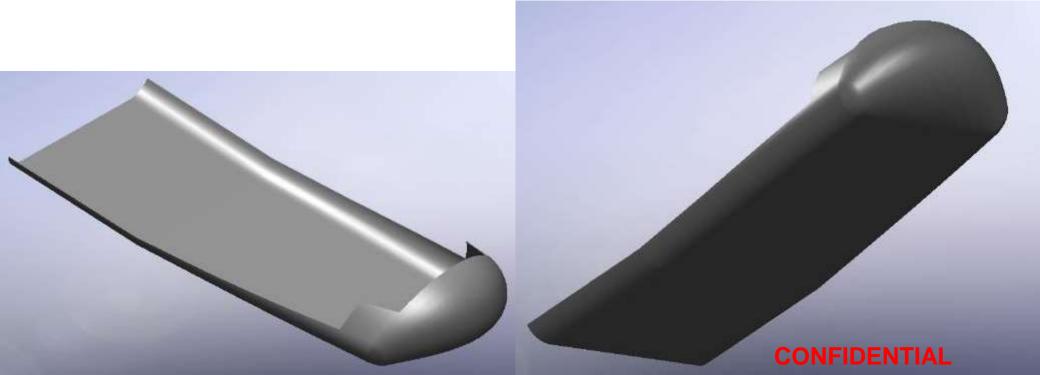


Poly-crystallization of one piece structural panel in complex "ventilated" shape as big than an hypersonic air craft fuselage at only 60°C (no glue, no additional insulation needed!)



One piece disposable low cost structural TPS skin produce with a low cost mold in one week

Polycristalization at only 60°C in 40 MINUTES



TOUGHCERAM @



One piece disposable low cost structural TPS skin integrated on IXV & SpaceRider as easy to fix as a SLIPPER....

We are perfectly conscious that there is a lot of tests to pass in order to validate this kind of technology!

I repeat
WE ARE SEARCHING FOR OEM
WILLING TO IMPLEMENT OUR
TECHNOLOGY FOR THEIR
APPLICATIONS



Computed need for IXV is 16 minutes 1800°C

Measured temperature for IXV is 16 minutes 1400°C

TOUGHCERAM ® has been demonstrated 90 minutes at 1900°C



TOUGHCERAM® Used as Satelite shield

- * It is possible to pproduce panels with dyneema, or aramid fibers with the below structure in one co polymerization, such panels can destroy micro debris and protect satellite.
- * Such panel with ceramic fibers could be used in sloar probe in order to be an efficient heat shield





TOUGHCERAM® Used as DEPLOYABLE heat shield

TOUGHCERAM ® flexibilized can be used for thermal insulation fire protection and

reentry heat shield











RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN

Tough & flexible low cost ceramic







RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN





GIANT structural components

CHERCHE - DÉVELOPPEMENT - ING

A two component dispenser with its static mixing unit =>

Rolled up thin tube containing :UD & braided carbon fibers =>

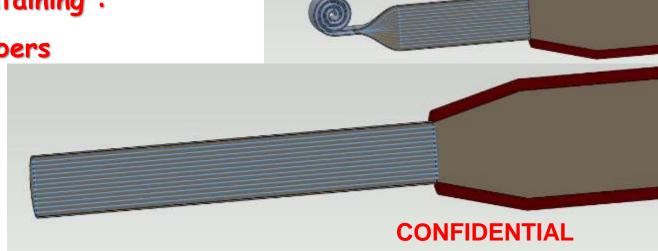
In <u>SPACE DEPLOYMENT</u> and <u>SUN CURING</u> of TOUGHCERAM®

Thin tube fully deployed containing:

- * UD plus braided carbon fibers
- * TOUGHCERAM ®

& ready for

solar polymerization =→



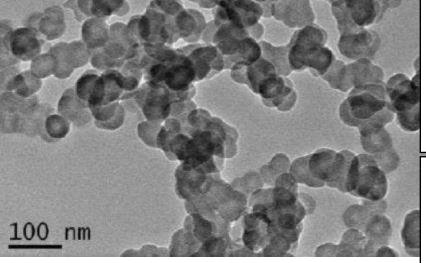


TOUGHCERAM © ceramized For NOZZEL application processing example # 2

TOUGHCERAM @ C



RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN



TOUGHCERAM® C is a compound of ultra low cost, easy to use alumina & metakaolin. Alumina has a high specific surface area. During the sintering, interlocked dendritic alumina reinforce the matrix

Sintering @ 1410°C under vacuum. During sintering aluminum, and silicon turn to a dense and POROUS MULLITE needles interlocked NETWORK .20% POROUS NETWORK is an excellent thermal insulating & tough structure

Nozzle preform

TOUGHCERAM® C HP RTM

Drying @ 300°C

SINTERING
under vacuum@ between
1270°C & 1410°C









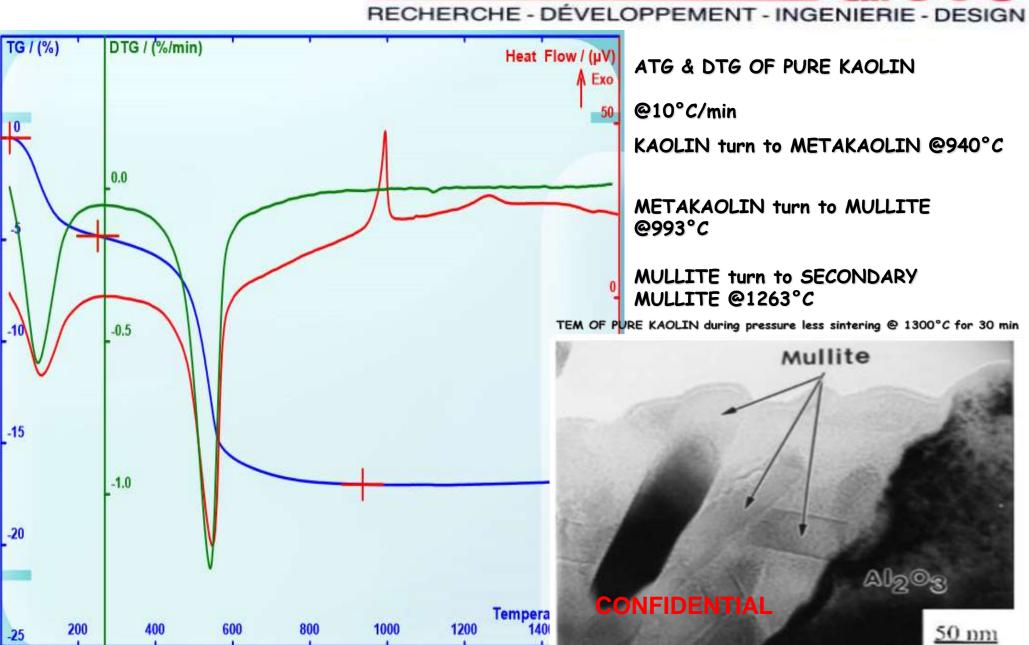




TOUGHCERAM @ M

-25



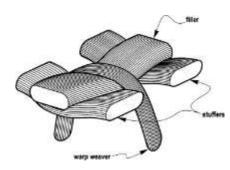




ÉVELOPPEMENT - INGENIERIE - DESIGN

NOZZEL application

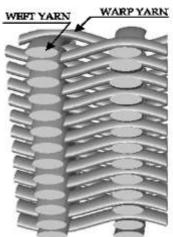
<= Nozzle preform is produced by interlocked braiding on a mandrel</p>

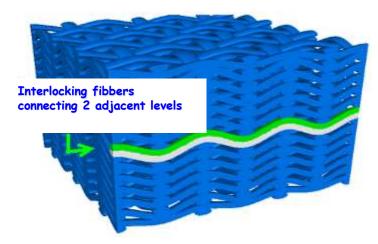


interlocked braiding detail

<=Cross section of a 3 D
Multi layers interlocked
braiding
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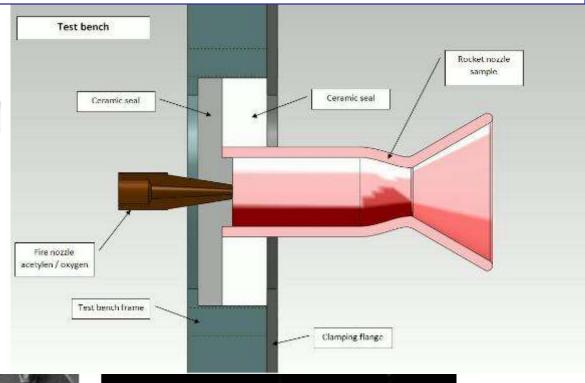
Welding blowtorch create $3000^{\circ}C$, produce gas flow and are inexpensive! We plan to use such device in order to build up a mini test bench. Nozzle can be just a 2 mm diameter, easy to produce and to test!

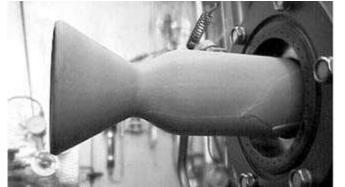
Principle of a

SMALL TEST BENCH

For

NOZZEL application







Small NOZZE RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN

demonstrator



Nozzle impregnated with TOUGHCERAM ceramized @ 1100°C





3 D interlocked Braided carbon fiber structure

and its mold



TOUGHCERAM ® mold and nozzle insert for hybrid rocket motor test bench (massive shape is in order to replace graphite insert)



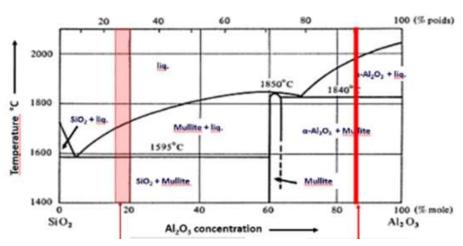
Polycrystallization done at 60°C



Detail of the collar after machining
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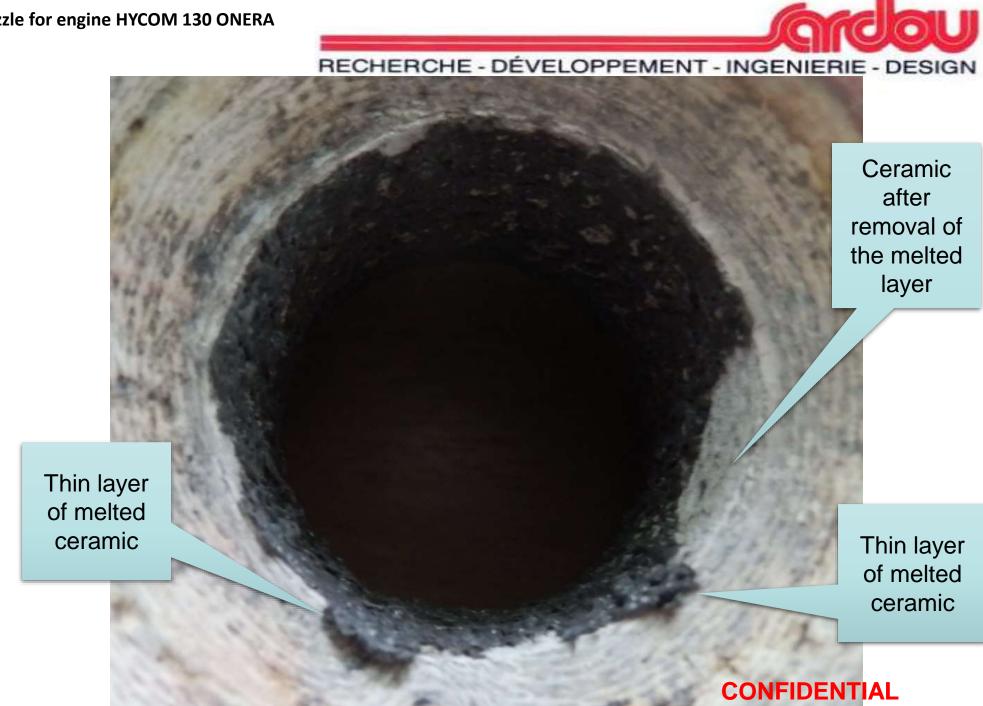
Nozzle for engine HYCOM 130 ONERA



Perspective view of the engine. The nozzle area is circled in red. Atmosphere:

CO2 @ 35%
Water vapor @ 60%
Oxidizing medium
Flame 2700 ° k (2426 ° C)
6.3 output ratio

Basalt fibers resist a temperature of -260 $^{\circ}$ C to 815 $^{\circ}$ C. The vitrification temperature is 1050 $^{\circ}$ C . The melting temperature of 1450 $^{\circ}$ C.







"CARBON FREE GREEN MINERAL POLYMER"

TOUGHCERAM ® Other application field





"foamed" TOUGHCERAM®

Interface between "foamed" & massive TOUGHCERAM® =>

TOUGHCERAM ® can be used for thermal insulation fire protection and reentry heat shield in ablative mode.

It is possible:

* to get a combination of FOAMED AND STRUCTURAL TPS * to impregnate the foam with phenolic resin





can be used in Solid-fuel rocket as:

Internal Thermal protection (foamed)

CASSING Structural component (fiber reinforced)

NOZZEL Structural component (fiber reinforced)



IS FIRE & SMOKE PROOF

"foamed" TOUGHCERAM® ==>

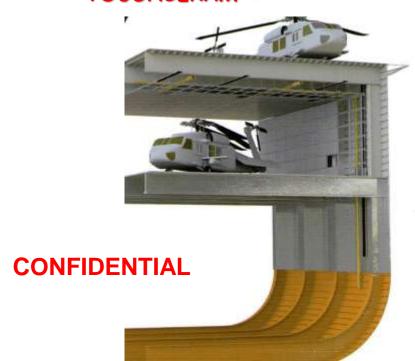


engine thermal insulation & fire protection compartment with TOUGHCERAM ®



MARINE examples acoustic thermal insulation & fire protection compartment In an air craft carrier deck

TOUGHCERAM ®

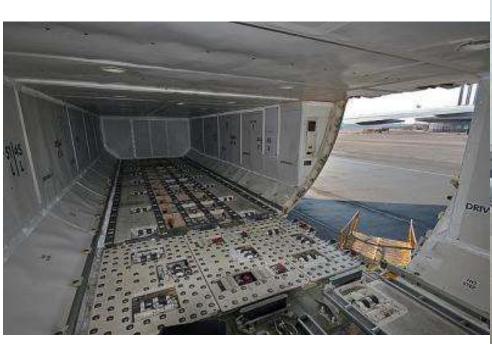




Where to use TOUGHCERAM® and save a lot of WEIGHT & get MECHANICAL PROPERTIES ACOUSTIC, THERMAL INSULATION & FIRE PROTECTION



habillage intérieur d'avion, container à bagages de soutes et soutes structurales anti incendie aircraft : interior, cargo compartment and unit load device (fire and explosion proof container ULD).







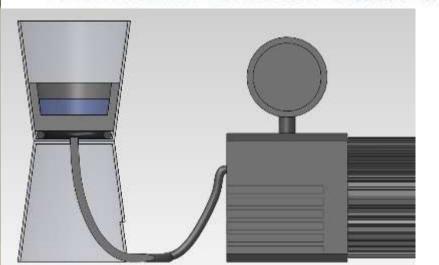


IE - DÉVELOPPEMENT - INGENIERIE - DESIGN

Nous proposons de remplacer le béton dans les Conteneur destiné au stockage des déchets MAVL (déchets de moyenne activité à vie longue) Par du **TOUGHCERAM®**



RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN



8:1

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Vacuum permeation tests, We have compared:

- TOUGHCERAM®
- geopolymer
- Cement

Drain 150 ml in 5 minutes with Geopolymer and cement

Drain only 25 ml in 3 days with TOUGHCERAM®



"CARBON FREE GREEN MINERAL POLYMER"

TOUGHCERAM ®

DAMAGE TOLERANT high performance "heat shields" & "thermal encapsulation" applications examples for thermic cars



"heat shields" & "thermal encapsulation"

=> perfect applications for TOUGHCERAM @





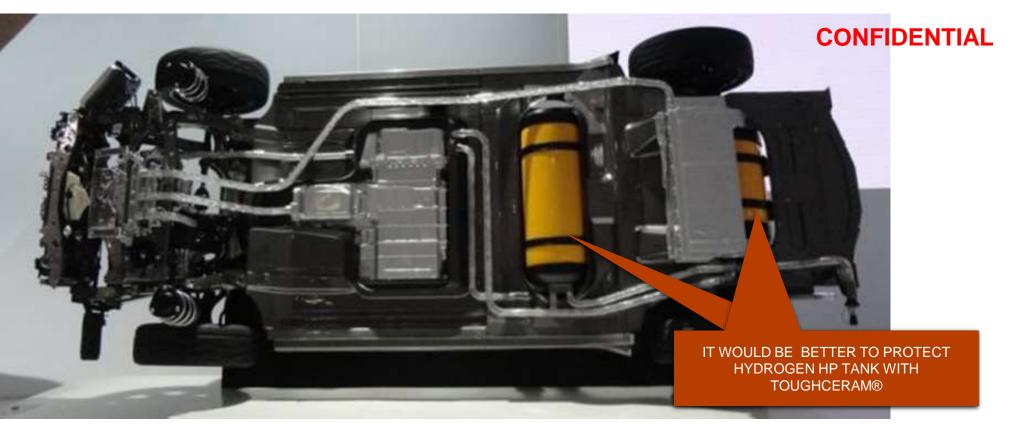


"CARBON FREE GREEN MINERAL POLYMER"

TOUGHCERAM ® DAMAGE TOLERANT SHIELD & ANTI FIRE SOLUTION FOR HYDROGEN TANKS



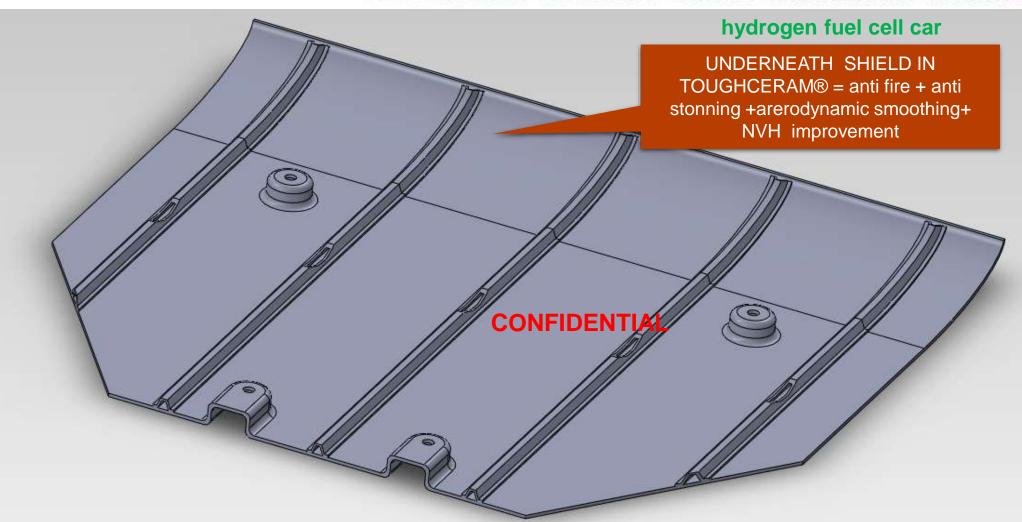
Mirai, Toyota :hydrogen fuel cell car



Where to use TOUGHCERAM® and save a lot of WEIGHT & get MECHANICAL PROPERTIES ACOUSTIC, THERMAL INSULATION & FIRE PROTECTION with a shield under the car or a wrapping around the HP Hydrogen tank



RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN

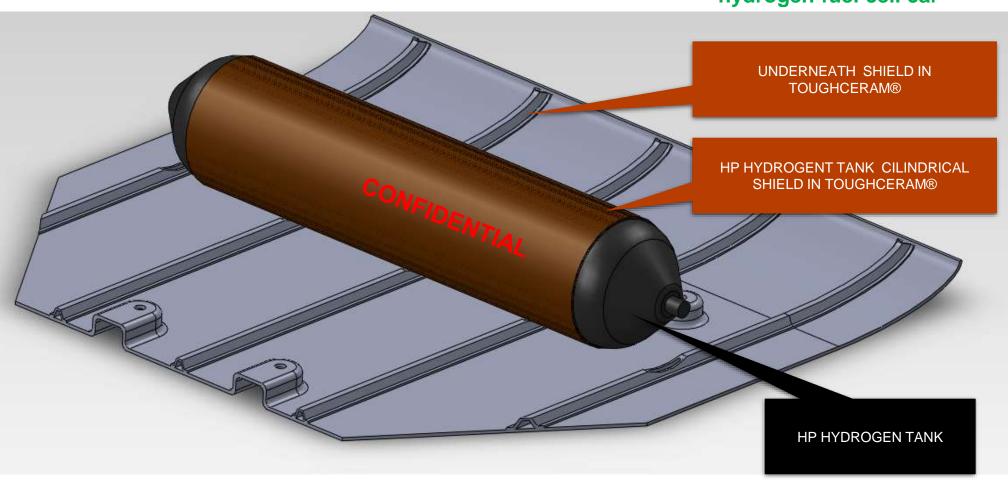


Where to use TOUGHCERAM® and save a lot of WEIGHT & get MECHANICAL PROPERTIES ACOUSTIC, THERMAL INSULATION & FIRE PROTECTION of HP Hydrogen tank with a shield under the car



RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN

hydrogen fuel cell car



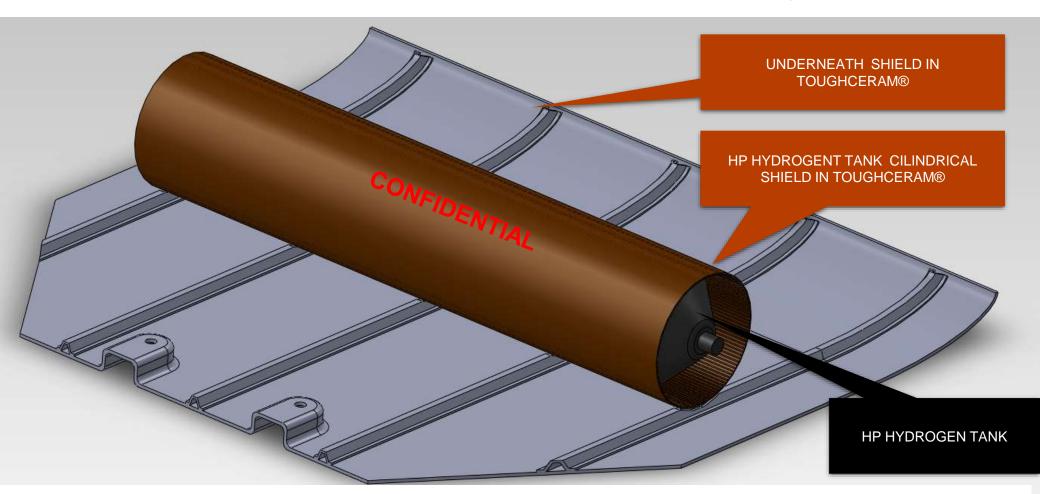
Where to use TOUGHCERAM® and save a lot of WEIGHT & get MECHANICAL PROPERTIES ACOUSTIC, THERMAL INSULATION & FIRE PROTECTION of HP Hydrogen tank with a shield under the car

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RECHERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN

hydrogen fuel cell car



Where to use TOUGHCERAM® and save a lot of WEIGHT & get MECHANICAL PROPERTIES ACOUSTIC, THERMAL INSULATION & FIRE PROTECTION of HP Hydrogen tank with a shield under the car



TOUGHCERAMINIERCHE - DÉVELOPPEMENT - INGENIERIE - DESIGN

Hyundai ix35 hydrogen fuel cell car





THIS COULD BE IN TOUGHCERAM®

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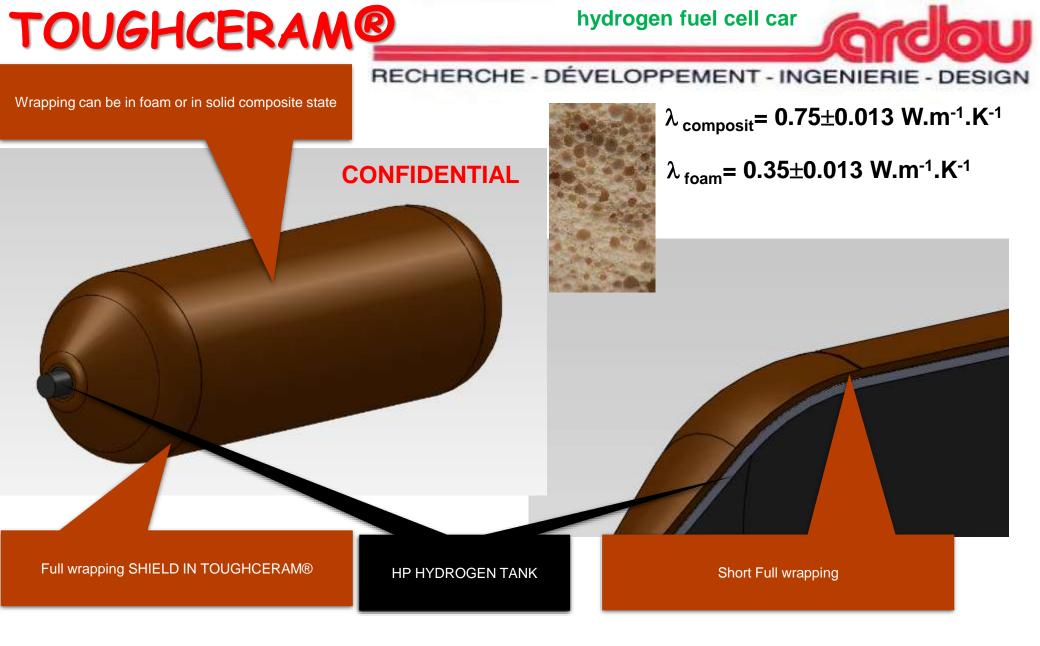
Where to use TOUGHCERAM® and save a lot of WEIGHT & get MECHANICAL PROPERTIES ACOUSTIC, THERMAL INSULATION & FIRE PROTECTION with a shield under the car or a wrapping around the HP Hydrogen tank

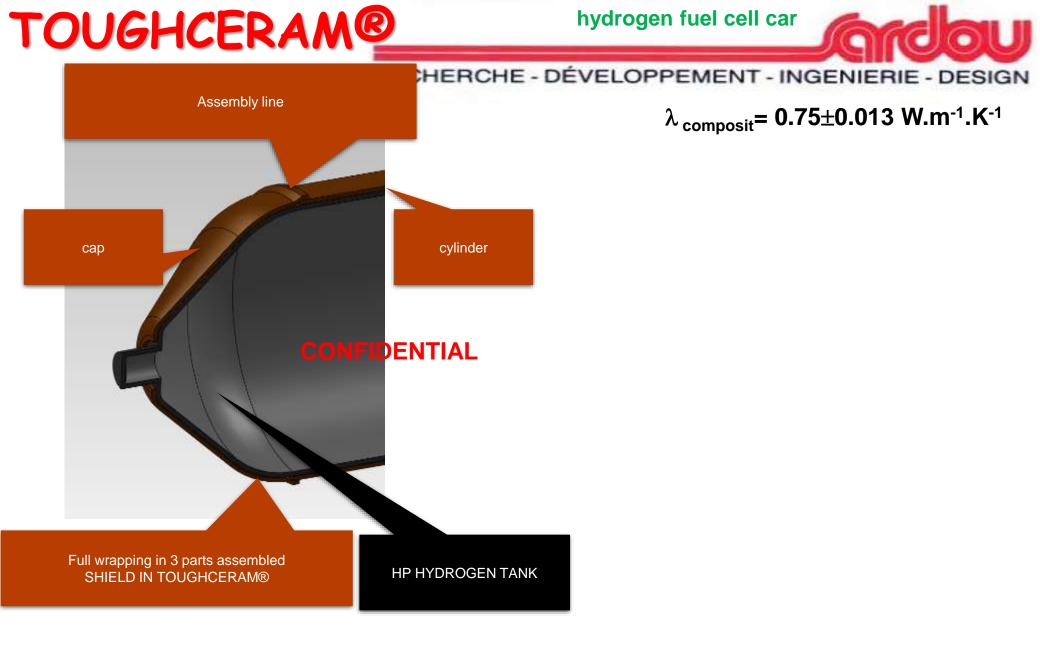


Where to use TOUGHCERAM® and save a lot of WEIGHT wrapping around the HP Hydrogen tank air gap improve cooling











"CARBON FREE GREEN MINERAL POLYMER"

TOUGHCERAM ®

DAMAGE TOLERANT SHIELD & ANTI FIRE UNIQUE SOLUTION FOR BATTERIES HYBRID VEHICLE

This feature is as much important in the car than during batteries cargo transportation and in workshop storage!

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ENVELOP OF THIS BATERY COULD BE IN TOUGHCERAM @





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THANK YOU FOR YOUR ATTENTION