12th Ablation Workshop

Assessment of Density Grading for the Carbon-Phenolic Ablator ZURAM

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Outline

- Introduction
- Manufacturing of ZURAM
- Surface densification
- Characterization via arc heated wind tunnel
- Conclusion

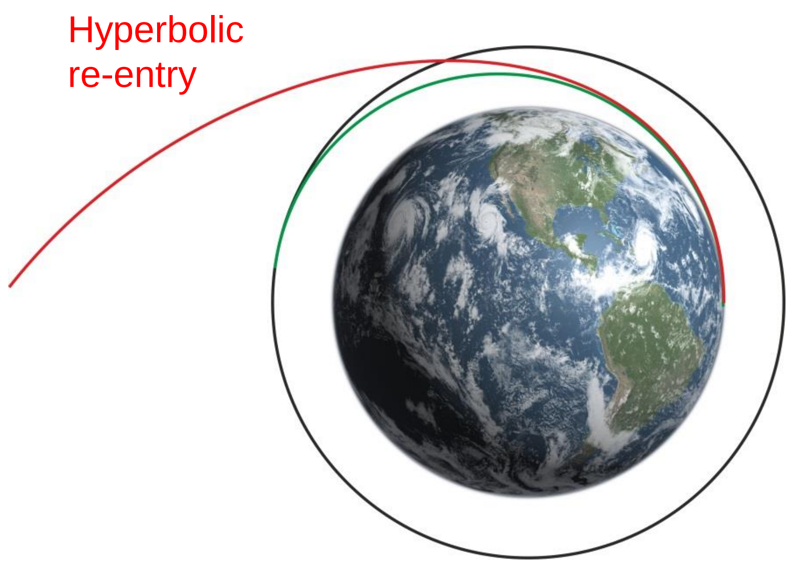
Atmospheric entry and ablative thermal protection materials

Depending on the entry trajectory during the atmospheric entry, spacecraft are exposed to extreme thermal loads due to their entry velocity. The Stardust capsule e.g. reached a re-entry speed of 12.9 km/s which resulted in a heat flux of 12.0 MW/m^2 in the stagnation point.

→ Need of ablative thermal protection materials

→ Due to their variable density and the effective energy dissipation, carbon-phenolic ablators are suitable as ablative thermal protection material for demanding return missions

→ To investigate this material class, the German Aerospace Center (DLR) developed the ablative carbon-phenolic thermal protection material ZURAM in cooperation with the Institute of Space Systems (IRS, University of Stuttgart)



ZURAM: Manufacturing process

Manufacturing process

Raw materials:
- Phenolic resin
- Solvent
- Curing agent
- Carbon preform

↓

Vacuum assisted infiltration of the carbon preform (room temperature)

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Pressurized polymerization (145 °C)

↓

Evaporation of solvent at (80 °C)

↓

Infiltration with water (room temperature)

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Pressurized tempering (160 °C)

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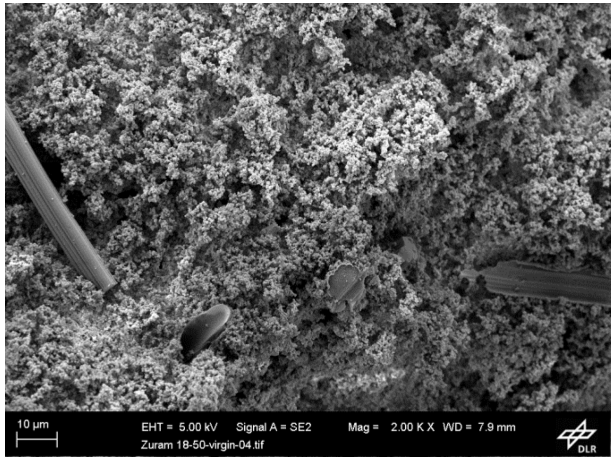
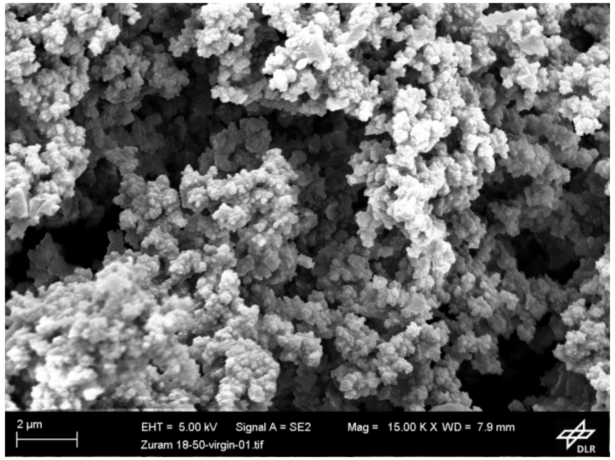
Drying to mass constancy (90 °C)

Fluid cooled tempering

Microstructure of aerogel-like phenolic matrix



2k magnification



15k magnification

- Since introducing the water-cooled tempering, ZURAM can be manufactured reliably and reproducibly
- The water cooling enables a safe dissipation of the crosslinking energy released during the tempering process
  → allows the scaling of the component size

ZURAM based on Calcarb or Kynol

Calcarb preform → ZURAM-18/50 & ZURAM-14/40

Kynol fiber preform → ZURAM-K

Calcarb preform:

- Commercially available insulation for high-temperature furnaces
- Rigid material with a density of 0.18 g/cm³ or 0.14 g/cm³ based on carbonised short rayon fibers
- Preform consists of pure carbon → no melting phase

Thermal conductivity ZURAM-18/50

	$\lambda_{\perp}$ /[W/(m·K)]	$\lambda_{\parallel}$ [W/(m·K)]
ZURAM® (virgin)	0.256	0.545
ZURAM® (pyrolyzed at 1650 °C)	0.468	0.741

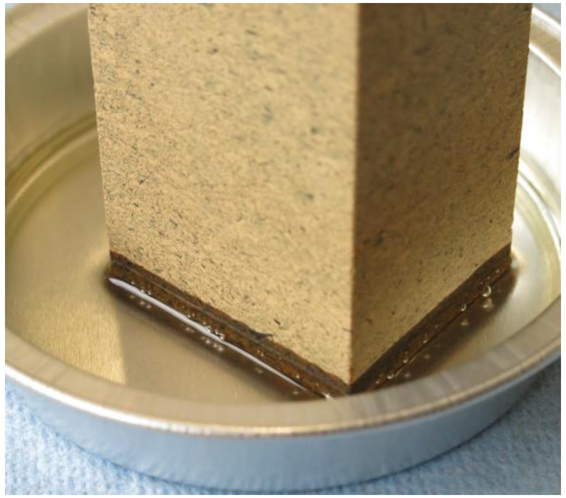
Kynol fiber preform:

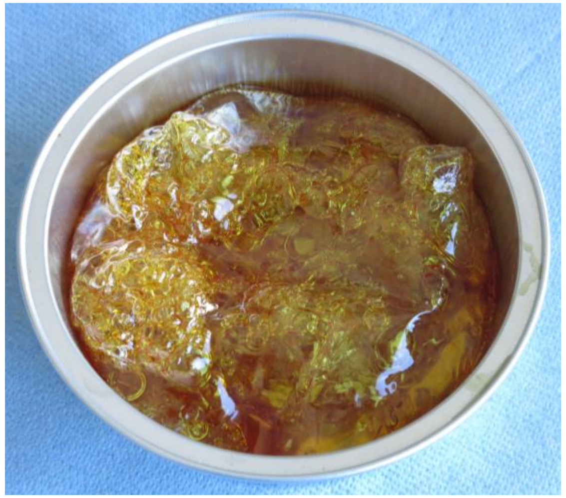
- Kynol fibers are cured phenol-aldehyde fibers
- No melting phase, fibers become carbon under thermal load
- Stacked nonwoven layers based on Kynol short fibers allows a variation of the fiber composition and the fiber volume content
- Compressible build-up with a density of 0.138 g/cm³

Thermal conductivity ZURAM-K

	$\lambda_{\perp}$ /[W/(m·K)]	$\lambda_{\parallel}$ [W/(m·K)]
ZURAM®-K (virgin)	0.0423	0.0747
ZURAM®-K (pyrolyzed at 1650 °C)	0.2089	0.5192

Surface densification process


Immersion infiltration


Foaming

Objective

- Reduction of the recession rate
- Mechanical stabilization of the ablator surface

Solution approach

- Near-surface re-infiltration with phenolic resin
- Immersion infiltration with the matrix resin proved to be a suitable method to produce small samples in a reproducible way

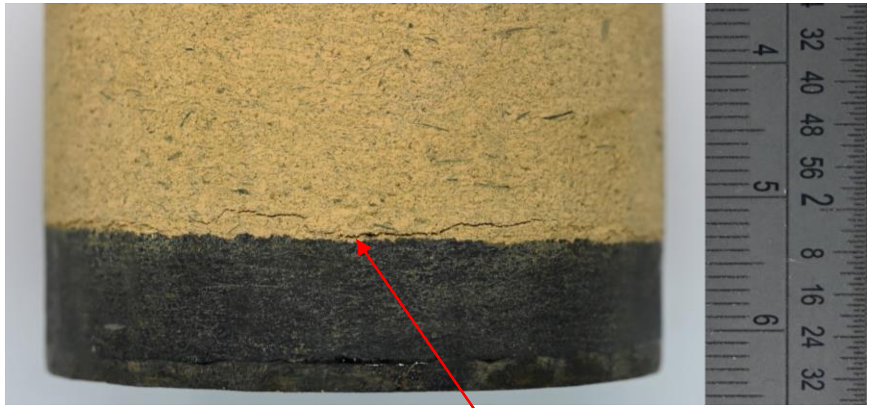
Challenge

- Curing at atmospheric pressure, which is requested for the process, leads to foaming of the resin

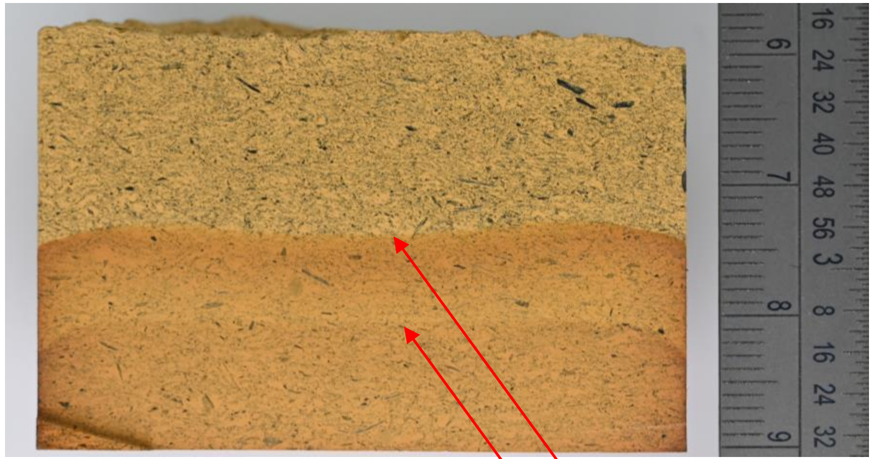
Solution

- Adjustment of curing process
  1. Evaporation of the solvent at 90°C
  2. Curing of resin in subsequently step at 145°C

Surface densification process



Cracks occurred after curing



I. Infiltration front

II. Infiltration front

Challenge

- After curing at 145°C cracks occurred along the infiltration front

Solution approach

- Dilution of the Resin with 2-propanol to create a smoother transition to the original material
- A two-stage infiltration enables a further increase in material density

Density increase

Material	Treatment	Density [g/cm^3]
ZURAM-18/50	unmodified	0.37
	1 infiltration, undiluted resin	1.07
	1 infiltration, diluted resin	0.62
	2 infiltrations, diluted resin	0.77
ZURAM-14/40	unmodified	0.31
	1 infiltration, undiluted resin	0.76
	1 infiltration, diluted resin	0.43
	2 infiltrations, diluted resin	0.58

Characterization: Arc heated wind tunnel

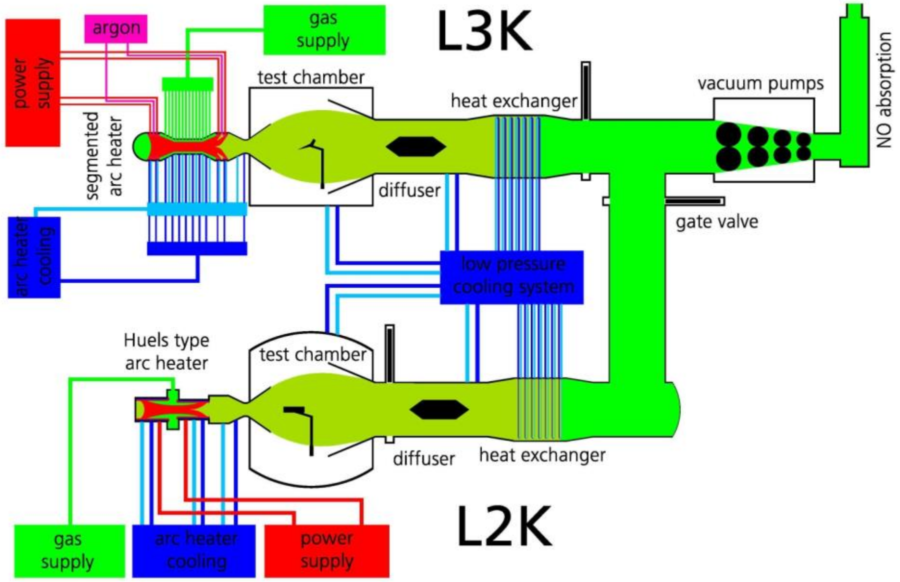
Material characterization within the arc heated wind tunnel L2K at DLR, Cologne

Test conditions in the arc heated wind tunnel L2K:

Heat flux:	6.1 MW/m²
Stagnation point pressure:	210 hPa
Test gas:	Air
Test duration:	30 s
Thermocouples:	Type-K, diameter = 0.5 mm TC tips are not embedded in resin 5 mm (TC1) 10 mm (TC2) 15 mm (TC3) 20 mm (TC4)

Test sample:

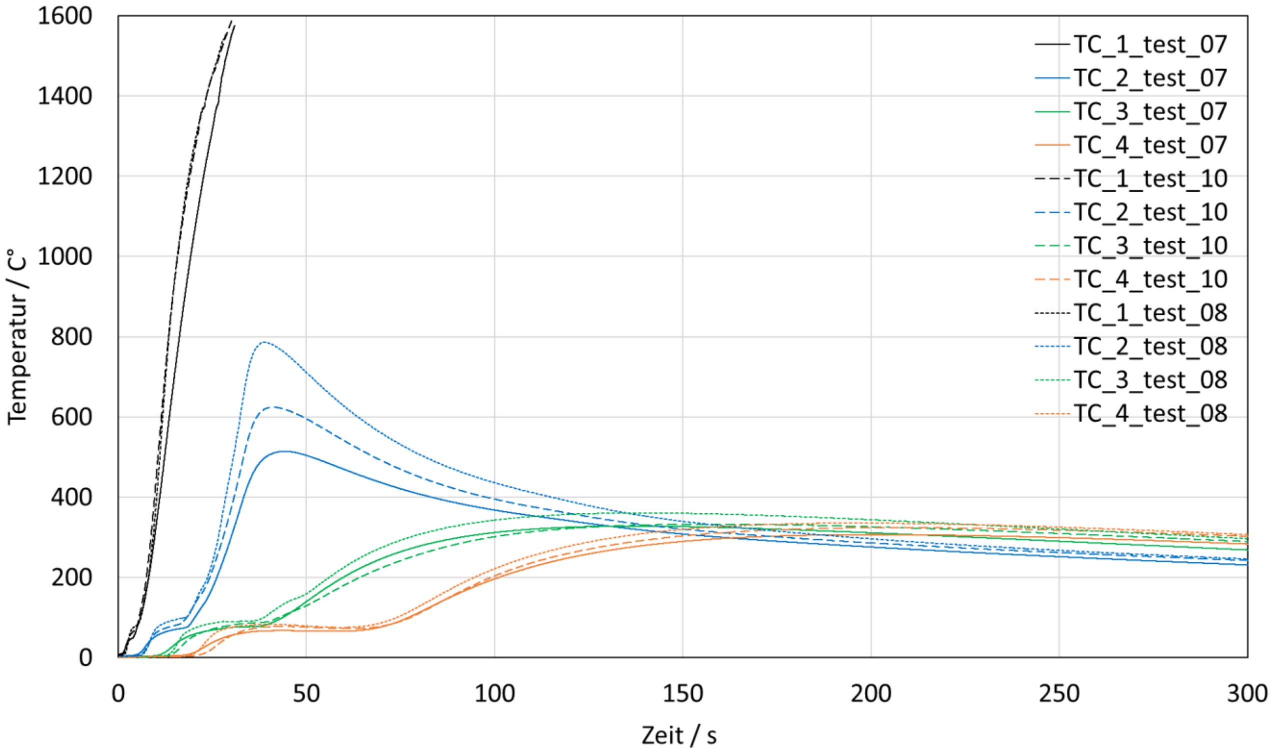
Diameter:	50 mm
Edge radius:	4.4 mm
TC bore diameter:	0.6 mm



AS-HYP, DLR Cologne

Material response under thermal load

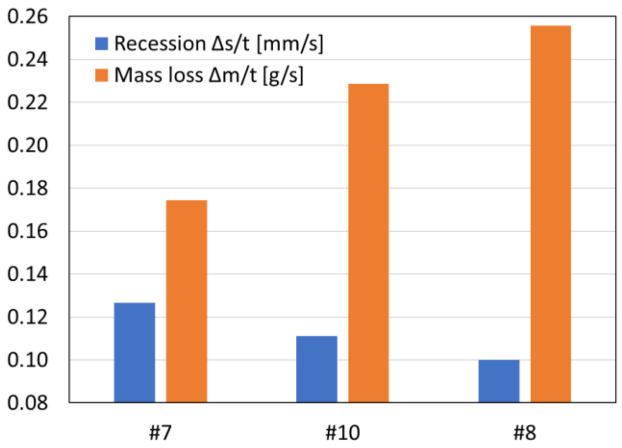
ZURAM-18/50 density graded



Test 07: ZURAM-18/50, ρ = 0.37 g/cm³

Test 10: ZURAM-18/50, 1-level graded (ρ ≈ 0.62 g/cm³)

Test 08: ZURAM-18/50, 2-level graded (ρ ≈ 0.77 g/cm³)

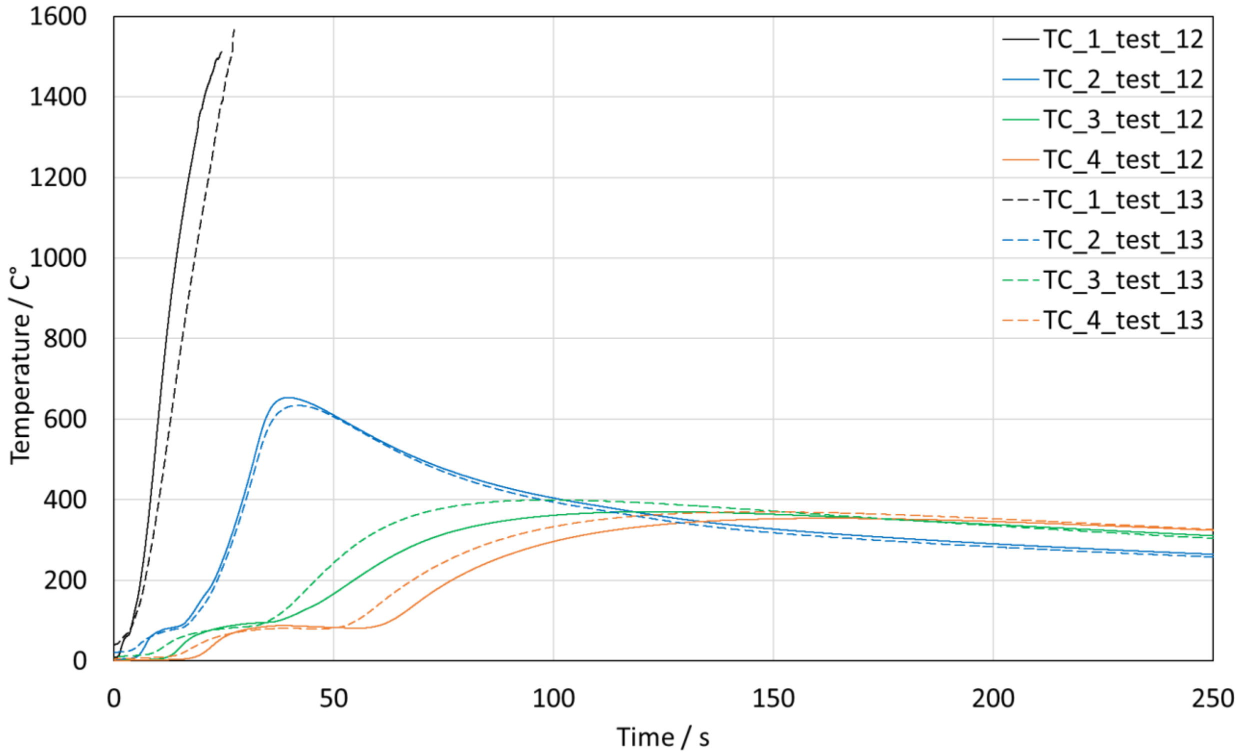


The increased material density …

- leads to an increased thermal conductivity and thus to an accelerated temperature rise in the depth direction of the sample (TC1 &TC2)
- causes a reduction of the recession rate
- leads to an increased mass loss due to the pyrolysis of the additive re-infiltration resin → this mass loss doesn’t instantly correlate with the recession of the charred material

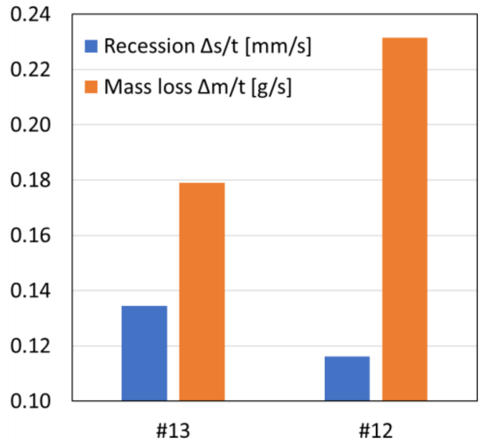
Material response under thermal load

ZURAM-14/50 density graded



Test 13: ZURAM-14/50, ρ = 0.35 g/cm^3

Test 12: ZURAM-14/50, 1-level graded

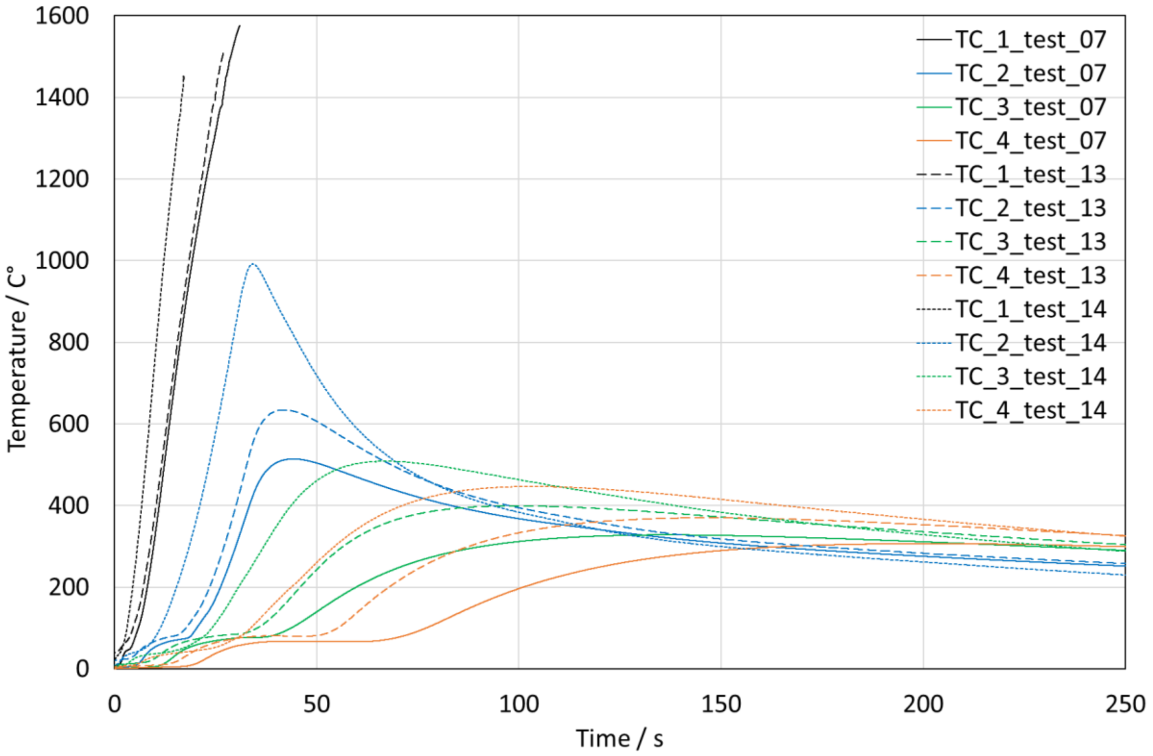


The increased material density…

- has no clear influence on the temperature rise in the front area, TC3 and TC4 show a accelerated temperature rise for the graded material
- causes a reduction of the recession rate
- leads to an increased mass loss due to the pyrolysis of the additive re-infiltration resin → this mass loss doesn't instantly correlate with the recession of the charred material

Material response under thermal load

Density reduced ZURAM



Test 07: ZURAM-18/50, ρ = 0.37 g/cm^3
Test 13: ZURAM-14/50, ρ = 0.35 g/cm^3
Test 14: ZURAM-14/40, ρ = 0.30 g/cm^3

The reduced material density...

- leads to an accelerated temperature rise over the whole sample depth, the maximum temperatures also increase
- causes an increased recession rate
- has no significant influence on the mass loss

Conclusion

- With ZURAM-18/50 an ablative low-density carbon-phenolic thermal protection material is available

- The material density close to the ablator surface can be increased by a re-infiltration with resin

  → The re-infiltration leads to a increased mechanical stability which makes the handling easier

- A method was found to cure the resin at atmospheric pressure without foaming

- Cracks along the infiltration front can be avoided by diluting the infiltration resin

  → The material density can be further increased by a repeated infiltration with the diluted resin

- Samples were tested in the arc heated wind tunnel

  Temperature

  → The increased material density in the re-infiltrated area leads to an accelerated temperature rise and increased

  → The reduced ablator density also leads to an accelerated temperature rise and higher maximum temperatures

  Possible explanation: Hot gases can penetrate the ablator material more easily due to the increased porosity

  Recession rate

  → The increased material density causes a reduced recession rate

  → Conversely, a material density decreased by the lighter preform CBCF 14VF-2000 and/or a reduced resin mass fraction leads to an increased recession rate

Thank You

For Your Attention

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Gradation of ZURAM-K
Reduction of recession rate

Backup

ZURAM-K:

- The layered structure of wet fleece layers with varied fiber volume content enables density grading in the direction of thickness
- The pyrolytic decomposition of the phenolic fibers is accompanied by longitudinal shrinkage of the fibers and leads to radial shrinkage of the material

  → The addition of carbon fibers effectively reduces radial shrinkage in the front area

$\varnothing_{\text{virgin}} = 49{,}54\,\text{mm}$

$\varnothing_{\text{virgin}} = 49{,}89\,\text{mm}$

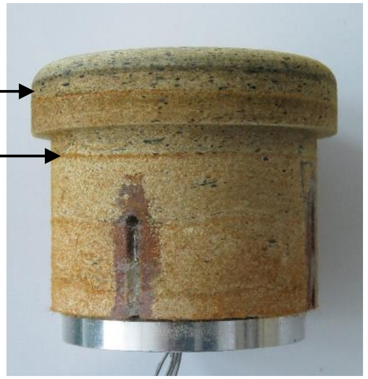
Pyrolysis
1650 °C
Argon

$\varnothing_{1650\,°\text{C}} = 40{,}35\,\text{mm}$

$\varnothing_{1650\,°\text{C}} = 48{,}55\,\text{mm}$

Addded C-fibres

Binder layer between wet fleece layers

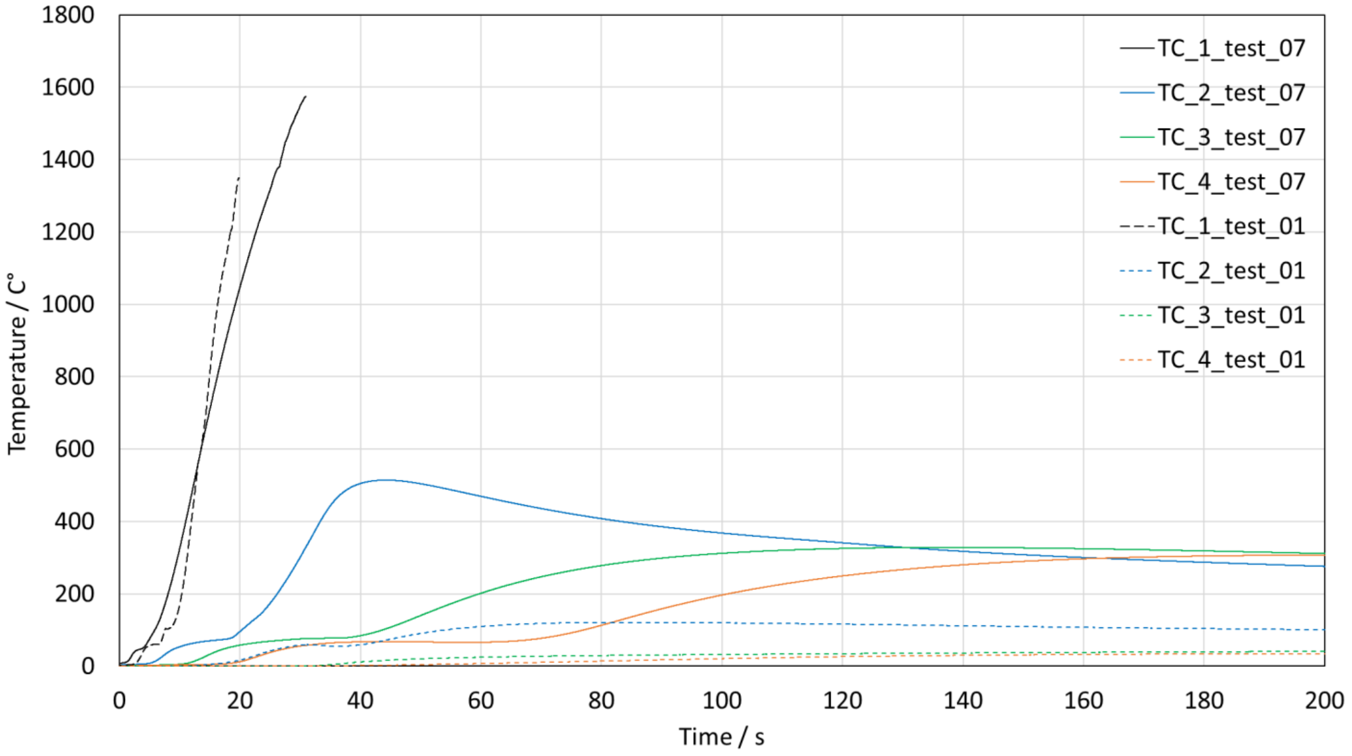


ZURAM-K sample for LBK L2K

Gradation of ZURAM-K

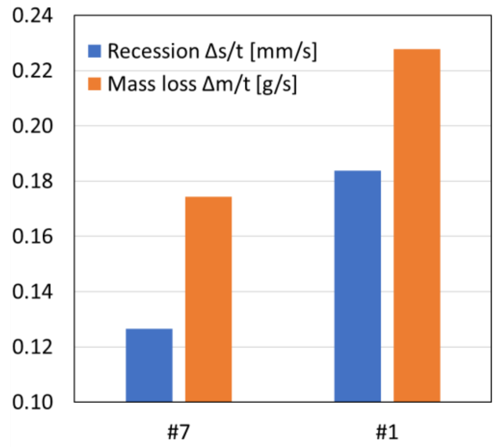
Reduction of recession rate

Backup



Test 07: ZURAM-18/50, ρ = 0.37 g/cm^3

Test 01: ZURAM-K, graded density in depth direction, additive carbon short fibers in the front area



- Despite the increase in material density in the front area, the recession rate is still above that of ZURAM-18/50
- Heat conduction is reduced by phenolic fiber preform
- Added carbon fibers in the front area reduce the radial shrinkage