

DEVELOPMENT OF A LOW-DENSITY PHENOLIC-IMPREGNATED FIBROUS ABLATOR

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ABSTRACT

ZURAM[®] is an ablative carbon-phenolic thermal protection material, developed by the German Aerospace Center (DLR) in cooperation with the Institute of Space Systems (IRS), University of Stuttgart. ZURAM[®] exhibits a performance comparable to similar low density thermal protection materials. It is based on a rigid, highly porous carbon fibre preform which is filled with a nano-porous matrix derived from a phenolic resin. In the context of the ongoing material development, possibilities to improve the material were investigated with the aim to lower the density at otherwise unchanged or improved performance. Preliminary results indicate that by substituting the carbon preform with a phenolic fibre preform, a significant reduction of the thermal conductivity can be achieved while recession rates are comparable to the ones of standard ZURAM[®]. The scope of the present work is the development of ZURAM[®]-K based on phenolic Kynol[®] fibres. Furthermore results from plasma wind tunnel tests at the DLR facility L2K and L3K, as well as data on the thermal conductivity and heat capacity will be presented.

KEYWORDS

Ablation, Recession, Thermal Protection Material (TPM), Thermal Protection System (TPS), Atmospheric Re-entry, Plasma wind tunnel, Transient Plane Source method, Thermal conductivity, Insulation

1. INTRODUCTION

During atmospheric entry, spacecraft are exposed to extreme thermal loads due to their high entry speed. For the entry manoeuvre, basically a distinction could be made between lifting and ballistic entries. Lifting entries are characterized by a comparatively long entry phase at moderate heat loads of e.g. $\dot{q} = 0.75 \text{ MW/m}^2$ in the case of the Space Shuttle. In contrast during ballistic entries these thermal loads could be exceeded by more than a magnitude, depending on the entry trajectory and the atmospheric conditions. In the case of the NASA experiment Stardust, an entry speed of 12.9 km/s associated with a heat load of 12 MW/m^2 was reached for example. In general ablative thermal protection systems are used to manage heat loads as they occur during ballistic entries. Depending on the entry conditions, thermal

protection materials differ in terms of material density and composition. ZURAM[®] belongs like PICA (NASA) and Asterm (Airbus Defence and Space) to the group of lightweight carbon-phenolic ablators. In the following section the manufacturing process of the non-commercial ZURAM[®] and the modified version ZURAM[®]-K will be described. ZURAM[®]-K is a further development of the standard version, whereby the objective was to lower the materials density respectively to improve the thermal isolation properties.

2. MATERIAL MANUFACTURING

The standard version of the ablative thermal protection material ZURAM[®] is based on a rigid carbon fibre preform with a porosity of $e' = 89\%$, which is infiltrated with diluted phenolic resin. By curing the resin in the diluted state according to the flow chart given in Figure 1, a phenolic matrix with an aerogel-like microstructure will be formed (Figure 2). The polymerization is done pressurized, to avoid boiling and evaporation of the solvent, which is added to the resin at a mass fraction of 50%. The degree of diluting makes it necessary to add a curing agent to supply the sufficient amount of formaldehyde, needed for the polymerization reaction. Because of the liquid solvent, the polycondensation is not fully completed during the pressurized curing. Therefore the resin matrix has to be cured completely in a subsequent tempering process after the removal of the solvent. The evaporation of the solvent is done in a laboratory oven at 90 °C until mass constancy. The vaporisation of the solvent goes hand in hand with a significant decrease of the thermal conductivity. As the tempering process is an exothermic cross-linking reaction, the risk of a destructive heat accumulation within the ablator increases with the growth of the component size. To avoid a ruining overheating, the ablator is infiltrated with water before tempering at 165 °C. Water is a reaction product of the cross linking of the phenolic resin, which means it doesn't influence the curing in a negative way. Besides the improved thermal conductivity, the infiltrated water is able to absorb the crosslinking energy released during the heat treatment, due to its heat capacity. The volumetric heat capacity of water exceeds with $c_{\text{vol,water}} = 4176,47 \text{ kJ/(m}^3 \cdot \text{K)}$ the one from air by a factor of 3450. A decisive advantage of the heat sink function of the water is independency versus scaling effects. When the curing is finished the resulting composite is dried at 90 °C to constant mass.

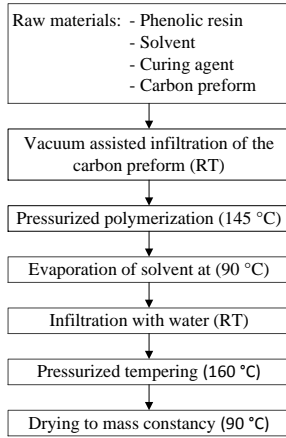


Figure 1: ZURAM[®] manufacturing process

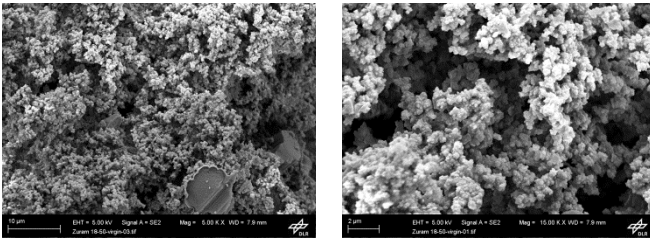


Figure 2: Aerogel-like microstructure of ZURAM[®] at 5.000x (left) and 15.000x (right)

In the meantime ZURAM[®] was tested at a number of different heat fluxes up to 12.0 MW/m². These tests as well as tests during the early development phase of ZURAM[®] were carried out at the IRS plasma wind tunnel facilities PWK1 and PWK3 [1, 2]. Additional tests with the final ZURAM[®] version were done at the high enthalpy wind tunnel facilities of DLR's Supersonic and Hypersonic Technologies Department (AS-HYP) in Cologne. Here, ZURAM[®] was exposed to a maximum heat flux of 13.5 MW/m² at the arc heated facility L3K. During the tests ZURAM[®] has shown a performance comparable to current reference materials regarding the heat conduction and the recession rate. On the basis of these results, possibilities were investigated to improve the thermal insulation properties. As shown, ZURAM[®] is a composite consisting of a porous carbon preform and a phenolic resin matrix with an aerogel-like microstructure, of which the carbon fibre reinforcement is the main driver for the heat conduction. In consequence it was looked for a suitable replacement for the carbon preform. Besides low heat conductivity, the avoidance of a molten phase was a requirement for the preform material, as the melting of the fibre reinforcement is attended by an increased recession rate.

In this context Kynol[®] fibres were investigated. Kynol novoloid fibres are cured phenol-aldehyde fibres made by acid-catalysed cross-linking of melt-spun novolak resin to form a fully cross-linked, three-dimensional, amorphous polymer structure. Chemically, the fibres contain roughly 76% carbon, 18% oxygen and 6% hydrogen. Because of their chemical structure Kynol[®] fibres are infusible and

insoluble, the latter is of importance for the infiltration with the diluted resin during the ZURAM[®] manufacturing. Under heat exposure (e. g. atmospheric re-entry) the phenolic fibres are converted to amorphous carbon fibres with a low density and thermal conductivity in comparison to high-strength carbon fibres. Figure 3 shows the usually commercial carbon preform as well as the new Kynol[®] preform. The Kynol[®] fibre reinforcement on the right side consists of multiple stacked wet-laid nonwoven layers, which were sewed together to get a defined fibre volume content.

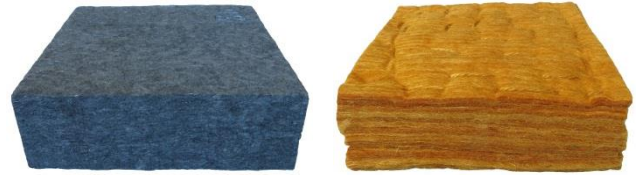


Figure 3: Rigid carbon preform (left): ZURAM[®]
Kynol[®] wet-laid preform (right): ZURAM[®]-K

The needed wet-laid plies were produced at the Faculty of Textile & Design, Reutlingen University, based on Kynol[®] short fibres with a fibre length of 6 and 10 mm, as well as ground ones with a mean fibre length of 0.3 mm and PVA fibres. The corresponding mass fractions are given in Table 1. The PVA fibres were admixed to the dispersed Kynol[®] fibres as a binder, which melts during the drying process of the wet-laid nonwoven and shrinks mainly on junctions of crossing Kynol[®] fibres. The area density of the resulting wet-laid was 533.3 g/m² for the 3.7 mm and 286.0 g/m² for the 2.0 mm thick material.

Table 1: Kynol wet-laid nonwoven composition

Fibre	Mass fraction [%]	Fibre length [mm]
KF-10BT (milled)	16	0.3
KF-0206	40	6
KF-1010	40	10
Polyvinyl alcohol (PVA)	4	-

The sewed Kynol[®] wet-laid plies were processed according to the manufacturing route, used for the making of standard ZURAM[®] (Figure 1). To point out the modified fibre reinforcement, the Kynol[®] fibre based ablator version, hereinafter will be called ZURAM[®]-K.

3. EXPERIMENTAL PROCEDURES

As indicated in the introduction, the improvement of the thermal insulation properties was one of the objectives of the modification on the TPM fibre reinforcement. To investigate the effect of the phenolic fibres on the heat conduction and recession rate of ZURAM[®]-K, samples were tested in plasma wind tunnel. By using Transient Plane Source measurements, thermal conductivity and heat capacity were determined.

3.1. Material response under thermal load: Arc heated facilities

DLR's arc heated facility consists of two test legs named L2K and L3K. The general setup is identical for both test legs, as illustrated by the sketch in Figure 4. The facilities use an arc-heater to energise the working gas to high enthalpy conditions. In L2K, a Huels-type heater is installed, which has a maximum electrical power of 1.4 MW. L3K is equipped with a segmented arc heater with a maximum power of 6 MW.

The heated gas is accelerated to hypersonic velocities by a convergent-divergent nozzle. Similar nozzle geometries are used in L2K and L3K. In particular the geometry of the conical expansion part is identical, having a half angle of 12° . Different throat diameters from 14 mm to 29 mm are available and can be combined with nozzle exit diameters of 50 mm, 100 mm, and 200 mm. Due to its higher energy level, even an exit diameter of 300 mm can be applied in L3K. So, the facility setup can effectively be adapted to particular necessities of a certain test campaign.

At the nozzle exit, a free jet is formed in the test chamber. For testing, samples and models are moved into the jet. During facility start-up, when conditions are changing with time, samples can be parked in the background area of the test chamber. After reaching the desired test conditions, they are moved to the test location. A more detailed description of the LBK facility is given by Gülhan et al. [3, 4, 5].

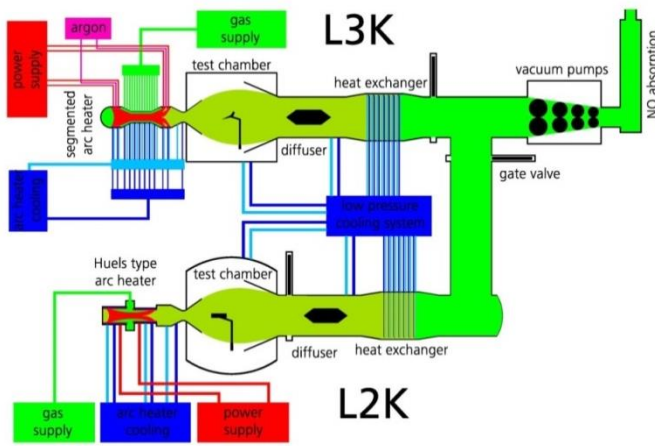


Figure 4: Setup of the LBK facility

The sample geometry used in L2K and L3K is given in Figure 5. While the front of the mushroom shaped sample is fully exposed to the free jet in the test chamber, the back area with the guide grooves for the thermocouples is covered by a C/C-SiC ceramic matrix composite (CMC) tube, which is heat-resistant and insensitive to thermal shock (Figure 9). The samples were equipped with four subminiature type K thermocouples (class 1) with a diameter of 0.5 mm. The thermocouples are positioned in a depth of 5, 10, 15 and 20 mm related to the sample front on the centre axis. As ZURAM[®] is a porous open-cell material the

thermocouples weren't embedded in adhesive within the boreholes. While the use of adhesive is basically useful because it supports the heat transfer between the sample and the thermocouple, the porous sample material would absorb the adhesive, which would locally change the material properties; however no form-fit embedding is achieved. To ensure the best possible heat transfer between the thermocouple and the sample, the thermocouple holes were made with a diameter of 0.6 mm. In this way it was possible to ensure a flat contact between the thermocouple tip and the borehole. The thermocouples were fixed in the guide grooves on the outer surface of the samples with thixotropic adhesive. At the end of the sample preparation the proper positioning of the thermocouple tip was checked by computed tomography.

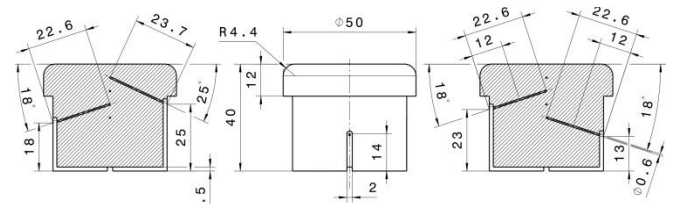


Figure 5: L2K & L3K sample geometry and position of the thermocouples

3.2. Measurement of thermal conductivity

Investigations of the density of ZURAM[®] have shown a variation over the thickness of the plates. The inhomogeneous density distribution is caused by the carbon fibre preform which shows a gradient from top to bottom. After resin infiltration a density distribution as shown in Figure 6 was measured. The lowest density was measured in the centre plane of the plates while there is a density increase towards the top and bottom of the plates.

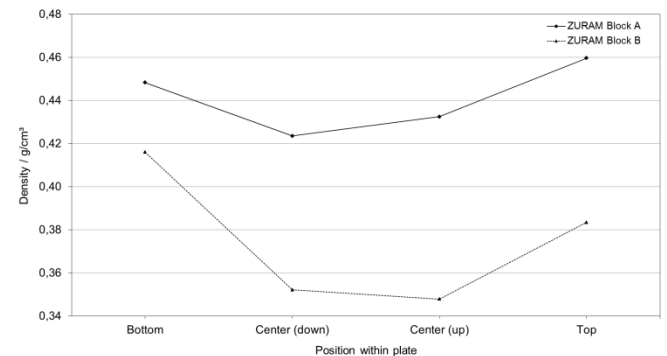


Figure 6: Density distribution over thickness from ZURAM[®] plate material

The overall density variation between different ZURAM[®] plates, as seen in Figure 6, is mainly the result of the variability of the density of the commercial carbon fibre preform. In Table 2 the density variation between the two plates ZURAM[®]-18/50-3 and ZURAM[®]-18/50-4 is given as well as density variation of the underlying fibre preforms.

It becomes obvious that the resin infiltration causes an identical density increase in both cases, which is an indicator for a reproducible infiltration process.

Table 2: Density variation of ZURAM® plates

Plate	ρ_{Calcarb} [g/cm ³]	ρ_{ZURAM} [g/cm ³]	$\Delta\rho$ [g/cm ³]
ZURAM®-18/50-3	0,22	0,43	0,21
ZURAM®-18/50-4	0,16	0,37	0,21

As one method of the material characterisation Laser Flash Analysis (LFA) was used to determine the thermal diffusivity of the ablative material. Due to the dimensions of the LFA specimens ($\varnothing = 12\text{ mm}$, thickness = 4 mm), the measurement method is sensitive to the position of sample extraction. Even though ZURAM®-K is not based on the inhomogeneous carbon preform, the manually stacked Kynol® wet-laid nonwoven build-up goes along with macroscopic inhomogeneities, which makes a representative determination of the thermal conductivity via LFA also difficult. To get a more representative average value, the thermal conductivity was determined in the further course by Transient Plane Source method, which allows for the analysis of larger specimens.

The Transient Plane Source technique, also referred to as Hot Disk method described in the ISO standard 22007-2: 2008, allows for the transient dynamic determination of the thermal diffusivity α and in a separate measurement the specific heat capacity c_p . The thermal conductivity λ can be calculated in an additional step. For this purpose a film-like sensor, whose electrical resistance is known as a function of the temperature, is positioned between two specimens of the material to be examined (Figure 7). The sensor works both, as heating element and as temperature sensor. During the measurement a voltage is applied to the resistance element at constant current. Based on the temperature-dependent change in resistance of the sensor, the thermal diffusivity of the material to be investigated is calculated. The measurements were carried out with a Hot Disk TPS 3500 system. For the measurement of the thermal diffusivity and conductivity a Kapton®-insulated sensor type 5501 with a radius of 6.4 mm was used.

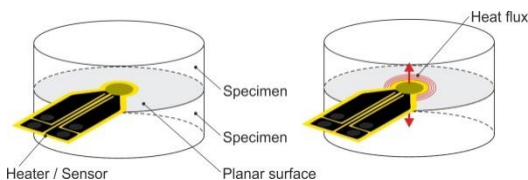


Figure 7: Transient Plane Source measuring method

The specific heat capacity was determined with a so called “gold cell” module shown in Figure 8, which allows for the measurement of solid or liquid samples. Therefore two measurements are needed. During the first measurement the empty gold container will be heated up a few Kelvin.

Subsequently the sample to be measured will be placed within the thermally insulated gold cell module. After the second run the difference between the two measurements gives the specific heat capacity.



Figure 8: Specific heat capacity module “gold cell”

4. RESULTS AND DISCUSSION

Hereinafter the thermal properties of ZURAM® and the Kynol® fibre based version ZURAM®-K determined via Transient Plane Source method will be presented. Furthermore the results from arc heated facility tests on both materials are compared.

4.1. Thermal insulation properties: Transient Plane Source method

The thermal isolation properties are a key characteristic of a thermal protection material. The measurements on ZURAM® and ZURAM®-K samples in virgin and heat-treated state were carried out at room temperature. The heat-treatment was done at 1650 °C in an inert gas atmosphere. Due to the sample size of about 65x55x23 mm³, the influence of locally limited material changes or inhomogeneities was reduced. LFA specimens require a preparation with graphite spray to ensure a defined emission coefficient, which implicates the risk to falsify the thermal properties by the penetration of graphite into the porous specimen. The Transient Plane Source method doesn't require a special sample preparation, it is sufficient if the sample surfaces facing the sensor are flat. In Table 3 and Table 4 the values determined for the thermal diffusivity and conductivity are given. As ZURAM® and ZURAM®-K are composites; their thermal properties are determined by the aerogel-like resin matrix and their respective fibre reinforcement. Due to the preferred orientation of the reinforcement fibres, both materials show different properties within or perpendicular to the plane of the fibre orientation. While virgin ZURAM® has a thermal conductivity of 0.256 W/(m·K) in thickness direction, the conductivity in-plane is 0.545 W/(m·K). The corresponding thermal conductivities for ZURAM®-K are 0.0423 W/(m·K) and 0.0747 W/(m·K). This means there is a factor of 6.1 between the thermal conductivities of ZURAM®-K and ZURAM® in thickness direction and a factor of 7.3 for the in-plane direction. The considerable discrepancy in thermal conductivity is caused by the different reinforcement fibres.

Table 3: Thermal diffusivity of ZURAM[®] / ZURAM[®]-K

	α_{\perp} [mm ² /s]	α_{\parallel} [mm ² /s]
ZURAM [®] (virgin)	0.752	1.601
ZURAM [®] -K (virgin)	0.0961	0.1696
ZURAM [®] (1650 °C)	2.406	3.812
ZURAM [®] -K (1650 °C)	0.4741	1.1783

Table 4: Thermal conductivity of ZURAM[®] / ZURAM[®]-K

	λ_{\perp} [W/(m·K)]	λ_{\parallel} [W/(m·K)]
ZURAM [®] (virgin)	0.256	0.545
ZURAM [®] -K (virgin)	0.0423	0.0747
ZURAM [®] (1650 °C)	0.468	0.741
ZURAM [®] -K (1650 °C)	0.2089	0.5192

To get material properties comparable to the char layer of the ablative TPM, specimens were heat-treated at a temperature of 1650 °C. At this temperature the phenolic aerogel-like matrix and in the case of ZURAM[®]-K also the phenolic resin fibres are entirely converted into carbon. The conversion of the resin matrix causes in the case of ZURAM[®] an increase of the thermal conductivity in thickness direction to 0.468 W/(m·K) and in-plane direction to 0.741 W/(m·K). Due to the additive conversion of the Kynol[®] fibres, the increase of the thermal conductivity between the virgin and the heat treated state is higher for ZURAM[®]-K compared to the standard material. The thermal conductivity in thickness direction is 0.2089 W/(m·K), in-plane direction it has a value of 0.5192 W/(m·K).

The heat capacity of ZURAM[®] and ZURAM[®]-K at room temperature are given in Table 8, in the virgin and heat treated state. As the aerogel-like matrix has a higher specific heat capacity in the polymer than in the pyrolysed carbon state, the heat capacity of the ZURAM[®] composite decreases in consequence of the heat treatment from 873.46 J/(kg·K) to 600.16 J/(kg·K). For ZURAM[®]-K the specific heat capacity is 1097.82 J/(kg·K) in the virgin and 791.0 J/(kg·K) in the heat treated state. In the virgin state, the heat capacity of ZURAM[®]-K is 25.7 % higher compared to the carbon fibre based version. The higher heat capacity in the virgin state is explained by the fact that ZURAM[®]-K is completely based on phenolic resin.

Table 5: Heat capacity of ZURAM[®] / ZURAM[®]-K at room temperature

	Heat capacity c_p [J/(kg·K)]
ZURAM [®] (virgin)	873.46
ZURAM [®] (1650 °C)	600.16
ZURAM [®] -K (virgin)	1097.82
ZURAM [®] -K (1650 °C)	791.0

4.2. Material response under thermal load

Plasma wind tunnel facilities offer the most realistical ground based method of simulating atmospheric entry manoeuvres. ZURAM[®]-K samples were tested in the arc heated facilities L2K and L3K under varied test conditions as given in Table 6.

Table 6: Test conditions for ZURAM[®] and ZURAM[®]-K samples

Sample	Preform	Facility	Atmosphere	Time [s]
ZURAM [®] -K V2 #4	Kynol [®]	L2K	Air	62.0
ZURAM [®] P5-7	Carbon	L2K	Air	60.2
ZURAM [®] -K V1 #7	Kynol [®]	L3K	Air	29.3
ZURAM [®] 18/50 #3	Carbon	L3K	Air	29.1
ZURAM [®] -K V1 #8	Kynol [®]	L3K	Air	13.4
ZURAM [®] 18/50 #4	Carbon	L3K	Air	13.0

Sample	Heat flux [MW/m ²]	Stagnation point pressure [hPa]	Mass flow [g/s]
ZURAM [®] -K V2 #4	0.91	38	50
ZURAM [®] P5-7	0.91	38	50
ZURAM [®] -K V1 #7	6.1	210	101
ZURAM [®] 18/50 #3	6.1	210	101
ZURAM [®] -K V1 #8	13.5	675	101
ZURAM [®] 18/50 #4	13.5	675	101

Figure 9 shows the ZURAM[®]-K sample V2 #4 before and after the test in the arc heated facility L2K at a heat flux of 0.91 MW/m². In contrast to the previously tested carbon based specimens, the samples with Kynol[®] fibre reinforcement show a distinct radial shrinkage. The diameter of the charred ablator material above the CMC sleeve amounts to 48.3 mm after the test. The radial shrinkage of 3.4 % is, in addition to the pyrolytic conversion of the microporous resin matrix and the oxidative material removal, caused by the length reduction of the phenolic resin fibres. Due to their geometric in-plane alignment, the Kynol[®] fibres determine the radial shrinkage when they heat up.



Figure 9: ZURAM[®]-K sample V2 #4 before (left) and after test (right) in L2K facility (heat flux: 0.91 MW/m², test duration: 62 s)

The recession of ZURAM[®] is primarily caused by oxidation of the carbonaceous char layer, respectively by sublimation, if the surface temperature is sufficiently high. Figure 10 shows aceros oxidated carbon fibres at the surface of the char layer from the sample ZURAM[®]-18/50 #5 after 30 s test time at 12 MW/m² in PWK1 at IRS.

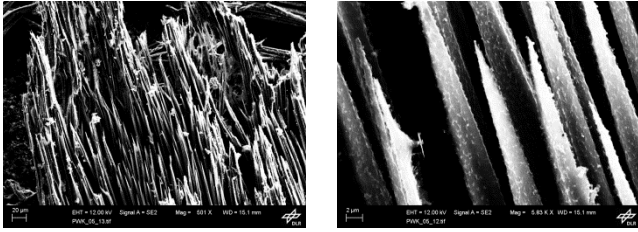


Figure 10: Aceros oxidation of carbon fibres within char layer (ZURAM®-18/50 #5, 30 s at 12 MW/m² in PWK1 at IRS)

On ZURAM®-K these effects are superimposed by shrinkage processes due to the pyrolytic decomposition of the phenolic resin matrix and the compressible Kynol® nonwoven reinforcement. In contrast to the fibre-dominated radial shrinkage, the thermal decomposition of the resin matrix determines the shrinkage in thickness direction. Sample evaluation showed a mass loss rate of 0.0716 g/s for the carbon based sample material and a mass loss rate of 0.0723 g/s for the Kynol® fibre reinforced samples (see Table 7). In addition to the shrinkage effects, the 34.2% higher recession rate of the ZURAM®-K sample can be explained at least partly by its 8.8% lower density and the at the same time comparable mass reduction rate of the two samples.

Table 7: Test in arc heated facility L2K (AS-HYP) at 0.91 MW/m²

Sample	Density [g/cm ³]	Test duration [s]	Mass loss rate [g/s]	Recession rate [mm/s]
ZURAM®-K V2 #4	0.41	62.0	0.0716	0.051
ZURAM® P5-7	0.45	60.2	0.0723	0.038

Figure 11 shows the temperature profiles within the samples ZURAM®-K V2 #4 and ZURAM® P5-7, recorded during the test in the arc heated facility at a heat flux of 0.91 MW/m². While the black temperature graphs represent the temperatures recorded within the ZURAM®-K sample, the red graphs show the temperatures within the ZURAM® samples.

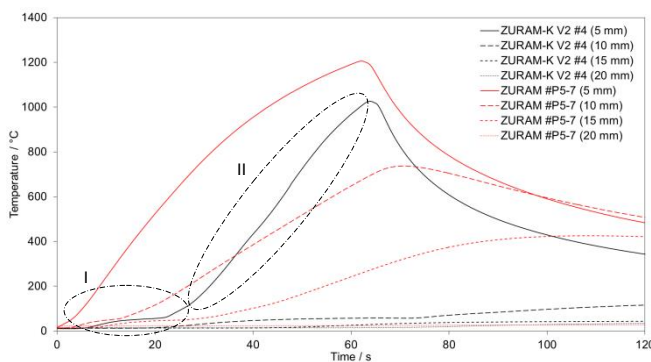


Figure 11: Test in arc heated facility L2K at 0.91 MW/m²
Test duration ZURAM®: 60.2 s
Test duration ZURAM®-K: 62.0 s

The graph shows that the temperature increase within the ZURAM®-K samples can be divided into two phases. While the temperature initially rise slowly compared to the carbon fibre reinforced ZURAM®, it increases in the second phase with a noticeably higher temperature gradient. Figure 12 shows the temperature profile within the samples ZURAM®-KV1 #7 and ZURAM® 18/50 #3. The samples were tested in the L3K facility at a heat flux of $\dot{q} = 6.1 \text{ MW/m}^2$ during a test period of 29.3 s, respectively 29.1 s. Type-K thermocouples are basically suitable for temperature measurements up to 1200 °C. The abrupt end of the marked temperature graphs indicates the failure of the thermocouples in a sample depth of 5 mm.

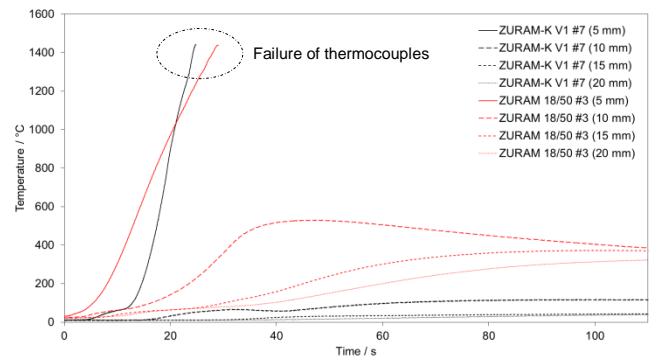


Figure 12: Test in arc heated facility L3K at 6.1 MW/m²
Test duration ZURAM®: 29.1 s
Test duration ZURAM®-K: 29.3 s

The Kynol® fibre reinforced material, used for sample ZURAM®-K V1 #7 had an 8.1% higher density compared to the standard ZURAM® material. The post-test measuring showed a 22.7% higher mass loss rate and a 19.4% higher recession rate for sample ZURAM®-K V1 #7 in comparison to sample ZURAM® 18/50 #3 (see Table 8).

Table 8: Test in arc heated facility L2K (AS-HYP) at 6.1 MW/m²

Sample	Density [g/cm ³]	Test duration [s]	Mass loss rate [g/s]	Recession rate [mm/s]
ZURAM®-K V1 #7	0.40	29.3	0.227	0.172
ZURAM® 18/50 #3	0.37	29.1	0.185	0.144

Figure 13 shows the temperature graphs within the samples ZURAM®-K V1 #8 and ZURAM® 18/50 #4, recorded during 13.4 s, respectively 13.0 s test time in the arc heated facility L3K. The samples were subjected to a heat flux of $\dot{q} = 13.5 \text{ MW/m}^2$. As at the 6.1 MW/m² test condition, the thermocouples in a sample depth of 5 mm failed during the test (see marking).

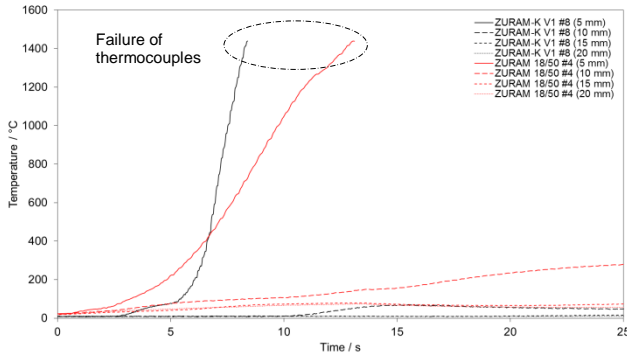


Figure 13: Test in arc heated facility L3K at 13.5 MW/m²
 Test duration ZURAM[®]: 13.0 s
 Test duration ZURAM[®]-K: 13.4 s

Analogous to the previous experiments with lower heat fluxes, the Kynol[®] fibre based sample has a higher mass and volume loss than the standard material. The mass loss rate of the ZURAM[®]-K V1 #8 sample was 31.6% and the recession rate 70.5% higher than that of the comparative sample ZURAM[®] 18/50 #4. Table 9 lists the post-test values for recession and mass loss rate.

Table 9: Test in arc heated facility L2K (AS-HYP) at 13.5 MW/m²

Sample	Density [g/cm ³]	Test duration [s]	Mass loss rate [g/s]	Recession rate [mm/s]
ZURAM [®] -K V1 #8	0.39	13.4	0.425	0.525
ZURAM [®] 18/50 #4	0.37	13.0	0.323	0.308

The arc heated facility tests with varied heat fluxes have shown that the temperature increase within the ZURAM[®]-K samples can be divided into two phases. While the temperature initially rise slowly compared to the carbon fibre reinforced ZURAM[®], it increases in the second phase with a distinctly higher temperature gradient. The delayed temperature increase is mainly the result of the improved thermal insulation properties of ZURAM[®]-K in the virgin state, which is due to the lower thermal conductivity of the Kynol[®] fibres. Furthermore the increased heat capacity (see section 4.1) and the additional energy absorption by the endothermic decomposition of the phenolic resin fibres helps to keep the temperature low during the first phase, compared to the carbon fibre based material.

In general, pyrolysis gases from the thermally decomposed Kynol[®] fibres are released in addition to the pyrolysis gases from the phenolic aerogel-like matrix. The process gases cause in addition to a thickening of the boundary layer, an increased convective heat dissipation from the TPM. Moreover, carbon molecules contained in the pyrolysis gas lead to a shielding of the thermal radiation in the boundary layer and thus contribute to a reduction of the radiative energy input.

The mass loss of the thermally loaded ZURAM[®] samples consists of the mass loss due to the pyrolytic decomposition

of the matrix resin and the oxidative material removal from the char layer. In the case of ZURAM[®]-K, the mass loss due to the pyrolytic decomposition of the Kynol[®] fibres is added. Kynol[®] wet-laid specimens showed a mass loss of 47.4% after a heat treatment at 1650 °C, at which the thermal decomposition of phenolic resin is virtually entirely completed. The heat treatment was done under a protective gas atmosphere to avoid any oxidation of the resulting carbon fibres. The pyrolytic decomposition of the phenolic resin fibres causes a microstructure with increased porosity, compared to the standard material. The increased porosity allows for more penetration of hot gases into the char layer, which has two effects. As oxidation is mainly responsible for the recession of the ablators char layer, the increased penetration of the oxygen-containing hot gases goes along with an enhanced recession rate as seen in the experiments. In addition to the influence on the recession rate, the increased penetration of the hot gases causes an accelerated temperature increase. The rapid temperature increase within the char layer during the second phase otherwise couldn't be explained by the thermal conductivity, as the thermal conductivity of ZURAM[®]-K is $\lambda_{\perp} = 0.2089 \text{ W}/(\text{m}\cdot\text{K})$ in the charred state, which is lower than the thermal conductivity of charred ZURAM[®] with $\lambda_{\perp} = 0.468 \text{ W}/(\text{m}\cdot\text{K})$ (see Table 4).

5. CONCLUSIONS

Besides the reduction of the material density, the improvement of the thermal insulation is an objective of the continuing work on ZURAM[®]. To achieve this, the carbon fibre based preform was replaced by Kynol[®] fibres. Therefore a wet-laid nonwoven out of ground and chopped Kynol[®] fibres was produced. Due to the manufacturing process the fibres are predominantly aligned within the wet-laid plane, which facilitates a homogenous in-plane heat distribution and helps to prevent an excessive heat flow in thickness direction. The fibre preform is built up out of stacked wet-laid nonwoven sheets which are sewn together. By varying the number of sheets the fibre volume content and hereby the density of the later TPM composite can be controlled. During the tempering process of the ZURAM[®]-K sample plates, a destructive heat build-up occurred, which wasn't known from the carbon fibre based ZURAM[®] versions before. The problems during final curing were solved by developing the fluid cooled tempering. For the fluid cooled tempering the plate material will be infiltrated with water, which acts as a heatsink that is able to absorb the released crosslinking energy.

After the tests in the arc heated facilities a radial shrinkage of 3.4% was measured on the ZURAM[®]-K specimens, which is the result of the longitudinal shrinking of the fibres. Although this shrinking is limited to the comparatively thin pyrolysis zone and the char layer in the front area of the ablator, the influence on the sealing in-between adjacent

tiles of a potential heat shield has to be checked. During the tests in the L2K und L3K facilities at varied heat fluxes, the temperature rise within the ZURAM[®]-K specimens could be separated into two phases. While the temperature initially rises slowly, it increases in the second phase with a higher gradient compared to the carbon based material. Reasons for the slow initial temperature rise are beside the improved thermal insulation properties and the increased heat capacity of ZURAM[®]-K in virgin state, the additional energy absorption by the endothermic decomposition of the phenolic resin fibres. The second phase begins with the convergency of the char layer to the respective thermocouple. Under thermal load the Kynol[®] fibres show a mass loss of 47.4%, which causes extra porosity. The thus more porous structure facilitates the penetration of hot gases into the char layer, which has basically two effects. First, the hot gases cause an accelerated temperature increase in the char layer. Second, the increased penetration of the oxygen-containing hot gases goes along with an enhanced recession due to oxidation. During the tests in the jet heated facilities, ZURAM[®]-K has shown an increased recession and mass loss rate, especially at higher heat fluxes. After a test time of 13s at heat flux of 13.5 MW/m², a recession rate of 0.525 mm/s and a mass loss rate of 0.425 g/s was determined. The mass loss rate was thus 31.6% and the recession rate 70.5% higher compared to the standard material on base of carbon. One cause of the increased mass loss rate is the weight reduction due to the pyrolytic decomposition of the Kynol[®] fibres under thermal load.

In parallel to the tests in the arc heated facilities, the thermal conductivity and the heat capacity were measured by Transient Plane Source technique. ZURAM[®]-K shows in virgin state a thermal conductivity of 0.0423 W/(m·K) in thickness direction, for ZURAM[®] a value of 0.256 W/(m·K) was measured in comparison. For ZURAM[®]-K a specific heat capacity of 1097.82 J/(kg·K) was measured, while the heat capacity of ZURAM[®] is 873.46 J/(kg·K) in the virgin state.

Overall the first results seem to be promising. The arcjet tests have shown, there is a reduction of the heat input in the depth direction of the material due to the reduced thermal conductivity and the increased heat capacity of the virgin ZURAM[®]-K material. Beside this, the structure of the Kynol[®] based fibre reinforcement can be modified in a wide range. In addition to a variation of the fibre volume content, there is e.g. the possibility to added fibres during the wet-laid manufacturing, which do not shrink under thermal load and thus act as a shrinkage inhibitor in the final TPM composite.

During the development phase of the carbon based ZURAM[®], systematic investigations on material versions with a varied density were done at IRS [2]. In addition to the ongoing material characterization of ZURAM[®]-K, it would be of interest to investigate samples with varied fibre

volume content and thus a modified density to get the influence of these variations on the recession rate. In contrast to the carbon based ZURAM[®], whose options for variations are limited, the wet-laid nonwoven preform used for ZURAM[®]-K enables a more extensive modifications of the material properties.

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REFERENCES

- [1] Ch. Zuber, G. Herdrich, H. Hald, "Screening-Tests zur Entwicklung ablativer Thermalschutzmaterialien für hochenthalpe Wiedereintrittsmmissionen". 62. Deutscher Luft- und Raumfahrtkongress, 10.-12.9.2013, Stuttgart, Germany
- [2] Pagan, Ch. Zuber, B. Massuti-Ballester, G. Herdrich, H. Hald, S. Fasoulas, "The Ablation Performance and Dynamics of the Heat Shield Material ZURAM[®]", June 2017, 31st International Symposium on Space Technology and Science, At Matsuyama, Japan
- [3] A. Gülhan, B. Esser, *Arc-Heated Facilities as a Tool to Study Aerothermodynamic Problems of Reentry Vehicles*, in: Lu, F.K.; Marren, D.E. (Eds.): *Advanced Hypersonic Test Facilities*, Progress in Astronautics and Aeronautics, Vol. 198, p. 375-403, AIAA, 2002.
- [4] A. Gülhan, B. Esser, U. Koch, K. Hannemann, *Mars Entry Simulation in the Arc Heated Facility L2K*, 4th European Symposium on Aerothermodynamics of Space Vehicles, October 2001, Capua, Italy, ESA SP-487, 2002.
- [5] A. Gülhan, B. Esser, *A Study on Heat Flux Measurements in High Enthalpy Flows*, 35th AIAA Thermophysics Conference, Paper AIAA 2001-3011, Anaheim, CA, USA, June 11-14, 2001.