Influence of the Manufacturing Technique on the Macro- and Microstructure of Reticulated Carbon-Bonded Alumina Foams

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Carbon-bonded alumina foams, prepared by means of the replica technique, are typically used as metal melt filters for the filtration of steel due to their low wettability and their good resistance towards thermal shock and corrosion. According to literature, there are different process routes for the preparation of carbon-bonded alumina foams, for example, dipping/rolling, spray- and dip- centrifugation coating. The influence of such process variations on macro- and microstructure and mechanical properties of carbon-bonded ceramic foams has not been analyzed fully yet. Herein, carbon-bonded alumina foams are manufactured by applying varying process routes regarding slurry preparation and coating steps. The macrostructure of the foams is analyzed by computer tomography, and for evaluating the microstructure, mercury intrusion porosimetry, optical microscopy, and scanning electron microscopy are applied. The determination of the cold-crushing strength of the carbon-bonded alumina foams allows the correlation of the structure and mechanical properties.

1. Introduction

Reticulated ceramic foams are applied as filter materials that are used for the filtration of metal melts or the removal of pollutant particles from gases, such as exhaust fumes.[1] Three different kinds of pores are found in reticulated ceramic foams. Functional pores, that are surrounded by struts, would be flown through by a metal melt or gas while the ceramic foam is in use as a filter. Strut cavities are formed by the thermal decomposition of the polyurethane (PU) template and possess a triangular, sharp-edged profile. The third kind of observed pores is material pores inside of the ceramic substrate.[2,3] For evaluating these various types of pores, different techniques are applied. Functional pores and the coating homogeneity can be analyzed by μCT imaging;[4] strut cavities and material pores are evaluated by means of mercury-intrusion porosimetry[5] as well as scanning electron microscopy (SEM); strut thicknesses can be measured by means of optical microscopy. In the last 5 years, the usage of carbon-bonded ceramic foams instead of oxidic ones has been the topic of extensive research in the field of metal-melt filtration.[5] Although the filtration of steel melts using carbon-bonded alumina filters has become state of the art,[6] these filters also showed promising reactions during immersion tests in an AZ91 magnesium alloy melt,[7] as well as in ongoing aluminum filtration experiments. Carbon-bonded ceramic foams have the advantage of a lower manufacturing temperature, as well as a higher resistance toward thermal shock and creep deformation and a lower wettability, which is advantageous for their application in filtering metal melts.[5,8] Ceramic foams made of carbon-bonded alumina are often produced following the replica technique developed by Schwartzwalder et al.[9] Following this technique, a PU foam template is coated with slurry, excess slurry is removed from the PU cells, and the foam is heat treated in a reducing atmosphere. During this thermal treatment, the PU template is burnt out, with the hollow ceramic foam strut structure remaining.[5] Typically, two coating steps are conducted to apply a sufficient quantity of slurry onto the foam template and to achieve a good filter surface quality.[9] There are different possibilities for applying a coating. Very often, a combined dipping and rolling process
is used, in which the PU template is squeezed into the slurry and the excess slurry is removed by passing a set of rollers.[10] A rolling gap adjusted to a distance equal to 20% of the foam thickness was determined to be optimal for the process.[10] Another possibility for the removal of excess slurry is a centrifugation step. According to Pu et al.[11] the centrifugation process commonly results in a more uniform distribution of the slurry on the template. The dipping/rolling process is suitable for the first coating step, whereas the dipping/centrifugation process is applicable for both the first and second coating steps. A further possibility for the application of slurry layers is spray-coating,[5] which is usable for both first and second coating layers. By applying the second coating, possible flaws in the first coating are closed, which may occur if rolling or a centrifugation process is used for the first coating step.[11] Flaws may be caused by the relaxation of the foam after rolling and inhomogeneities at the edges due to the non-uniform slurry distribution during the rolling process. The second layer should be applied as quickly as possible, to avoid damage to the dried first coating through the absorption of water from the applied second coating.[11] The slurry viscosity has a high significance for a successful manufacturing process, influencing strut thicknesses and pore diameters, as shown by Pu et al. in their investigation on the centrifugation coating of a PU foam template with a carbon-free, ball-milled, thixotropic silicon nitride slurry.[11] The dependency of the coating behavior of an alumina slurry on its viscosity adjusted by its thickener and solid content was furthermore shown by Voigt et al.[12] According to literature, the slurry should show a shear-thinning behavior, enabling it to easily fill and coat the foam, as well as a sufficient viscosity, allowing an adequate amount of slurry to remain on the static template after the respective coating step without dripping.[10–12] Newtonian fluids were determined to show insufficient coating behavior.[10] Voigt et al.[4] had investigated the properties of reticulated carbon-free alumina filters, having a second coating applied by spray coating or centrifugation. Their research showed that the coating procedure has a high impact on the homogeneity and compressive strength. The researchers emphasize the need to force the coating material into the middle of the foam using short spraying distances or a thorough dipping and pressing step prior to centrifugation to achieve high strength values.[4] By conducting computed tomography (CT) analysis of the foam’s microstructure, Voigt et al. showed the advantage of the usage of an alumina slurry with a low viscosity (solid content: 71.4 wt%) for a coating by centrifugation, whereas a slurry with a higher viscosity (solid content: 76.9 wt%) was identified to be the better choice for the manufacturing of a spray-coated foam.[4] To compare two alternative manufacturing routes for carbon-bonded ceramic foams, both based on the replica method, Luchini et al.[13] studied the cold crushing strength, surface properties, and μCT images of the benchmark rolled and spray-coated, as well as dip-coated and centrifuged carbon-bonded alumina foams. Furthermore, an in-between heat treatment at 300°C was carried out for 2 h on one of the centrifuged sample batches. Luchini et al. concluded, that centrifugation is the manufacturing technique that results in a more homogenized foam structure, reflecting in a smoother fracture behavior during the cold crushing test.[13] In this study, the influences of the mixing techniques applied for the slurry manufacturing and the coating routines on the macro- and microstructure of the carbon-bonded alumina foams are investigated. The determination of the cold crushing strength of the carbon-bonded foams allows the linking of the foam structure and the mechanical properties.

2. Experimental Section

2.1. Preparation and Evaluation of the Slurries

Table 1 shows the composition of the slurries used for the experiments. Martoxid MR70 (Martinswerk, Germany, 99.8% Al₂O₃, d₉₀ < 3.0 µm) was chosen as the alumina source. Carbores P (Rütgers, Germany, d₉₀ < 0.2 mm), graphite (Graphit Kropfmühl, Germany, d₉₀ < 30 µm), and carbon black (Lehmann & Voss, Germany, primary particle size: 200–500 nm) formed the carbon sources. Comparing the particle sizes, it was visible that Carbores P was the component with the coarsest particles, therefore presumed to have a high influence on the rheological properties of the slurry, depending on its grinding degree, due to the applied mixing technique. As additives, ammonium lignin sulfonate (Otto-Dille, Germany), Castament VP95L (BASF, Germany), and Contraspum K1012 (Zschimmer & Schwarz, Germany) were used. The chemical composition of the slurries for the first and second coating step was the same.

Table 1. Composition of the used ceramic slurries.

| Component | wt% | Function | Particle size[9] | Manufacturer |
|-----------|-----|----------|------------------|--------------|
| Martoxid MR70 | 66 | Al₂O₃ source | d₉₀ ≤ 3.0 µm | Martinswerk GmbH, Germany |
| Carbores P | 20 | Binder, carbon source | d₉₀ ≤ 0.2 mm | Rütgers, Germany |
| Carbon black MT N991 | 6.3 | Carbon source | 200–500 nm | Lehmann & Voss & Co., Germany |
| Graphite AF | 7.7 | Carbon source | 99.8 wt% <40 µm | Graphit Kropfmühl GmbH, Germany |
| Additives (relative to the sum of raw materials) | | | | |
| Ammonium lignine sulfonate | 1.5 | Wetting agent, temporary binder | | Otto-Dille, Germany (Baeck GmbH & Co. KG) |
| Castament VP95L | 0.3 | Dispersing agent | | BASF, Germany |
| Contraspum K1012 | 0.1 | Antifoam agent | | Zschimmer & Schwarz, Germany |
| Solid content (wt%, relative to total slurry weight, composition of solid content remains unchanged) | | | | |
| Slurry for coating 1 | 82.2 | – | – | – |
| Slurry for coating 2 | 70 | – | – | – |
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Before the measuring operations were started, the slurries were
mixed with the help of a stirrer and placed inside a sealed plastic drum along with
alumina grinding balls. Grinding balls (2.6 and 0.75 kg) with a
diameter of 30 and 0.65 mm, respectively, were used for a slurry
weight of 1.5 kg. The ball milling was carried out on a roller bed
at 80 rpm for 24 h.

The coating behavior of a slurry during the replica process was
directly influenced by its rheological properties. Therefore, the
influence of the applied slurry-manufacturing route on the rhe-
ological properties of the respective slurries was to be studied.
The rheological properties of the slurries at room temperature
were measured using the rheometer Haake MARS 60
(Thermo Fisher Scientific, USA). The rheometer was pro-
grammed using the software RheoWin Job Manager (Haake,
Germany). For processing the acquired rheological data, the pro-
gram RheoWin Data Manager (Haake, Germany) was used.
Before the measuring operations were started, the slurries were
stirred for 15 min at 350 rpm to avoid any settling of the solid
content. To determine the flow curves, linearity limits and yield
points, the cylindrical, coaxial measuring system CC38/Ti/SE
01170079 with a profiled surface was used; this system allowed
measurements with good reproducibility. Measurements using a
parallel plate—plate geometry (P35/Ti/SE-02150597) or an
unprofiled cylindrical system with an approximately 5 times
smaller gap size (CC10 DIN/Ti-02150015) did not yield useful
reproducible results for the investigated slurries due to their
quick drying behavior. For the measurement of the flow curve,
the shear rate range was chosen to be 0.1–1000 s⁻¹, for the coating
slurry with a solid content of 70%, since 1000 s⁻¹ was a shear rate
that was determined to be a value commonly reached in the
spray-coating process. The slurry with a higher solid content of
82.2% was measured at shear rates up to 100 s⁻¹, due to torque
overload of the measuring device at shear rates exceeding this
value. Considering the low reproducibility of the other measur-
ingsystems, the usage of a system that would, in theory, be able
to measure higher viscosities, was not possible. The acceleration
from 0.1 s⁻¹ to the maximum shear rate was done stepwise in
20 steps, each step having a holding time of 10 s at the respective
speed. After a holding time of 90 s at the highest respective value,
the shear rate was reduced back to 0.1 s⁻¹ in the same stepwise
way to determine the thixotropy, which was marked by the hys-
teresis loop between the ascending and descending measured
values of the shear stress depending on the shear rate. The vis-
cosity was calculated from the measured shear stress. The flow
curves yielded information about the viscosity and thixotropy of
the respective slurry. The linearity limits and yield points of the
slurries were determined by conducting an amplitude test with a
frequency of 1 Hz, in which the slurries were subjected to a shear
stress ranging from 0.01 Pa up to 350 Pa. In the following, the
linearity limit describes the shear stress, at which the storage
modulus (G’) of the slurry deviates from its linear behavior, indi-
cating the beginning of the nonlinear yield zone, which leads to
the yield point. The deviation boundary was defined as 10%.[15]
The intersection of the graphs of the G’ and the loss modulus
(G’”) marks the transition from solid to liquid behavior and
therefore complies as the yield point.[15] The G’ describes the
elastic portion of the viscoelastic behavior, corresponding to
the solid-state behavior, whereas the G’” represents the viscous
portion of the viscoelastic behavior, correlated to the liquid-state
behavior.[15] The yield point is defined to indicate the critical
shear-stress limit, below which the slurry sample behaves like a
solid, and above which the rheological behavior of the slurry
equals that of a liquid. Furthermore, uncoated slurry flake sam-
plexes, which were dried at room temperature, were analyzed using the
SEM (ESEM FEG XL30, FEI Eindhoven, Netherlands), as well as
energy-dispersive X-ray spectroscopy (EDX), a device manu-
factured by EDAX-Ametek, USA, to evaluate the structure and
prevalent sizes of the grains.

2.2. Manufacturing of the Ceramic Foam Samples

The carbon-bonded alumina foam samples were manufactured
by means of the replica technique. PU foams (polyester, 50 × 50 × 20 mm³, 20 ppi, made by Eurofoam, Germany) were
used as templates, as described by Emmel et al.[5]

In Table 2, ten different sample types with their equivalent
abbreviations are summarized regarding their mixing and coating
procedure. The first and third letters of the abbreviation
describe the variation of slurry manufacturing used for the
respective coating. B indicates ball-milled slurry, M marks a
slurry prepared in the high shear mixer. The second and fourth
letters indicate the application method of the respective slurry.
For the first coating, R marks foam samples that were rolled
using a hand-operated rolling device with two counter-rotating
rolls to remove excess slurry after submerging the sample into
the slurry entirely and hand pressing it. The gap between the rolls
was set to 4 mm, which corresponds to 20% of the foam sample
thickness. Such a rolling pass was reported by Zhu et al. and
Jiang et al. to be the optimum for removing excess slurry from
the open foam cells.[10,16] Another technique used for applying
first as well as second coating layers was centrifugation (C).
The centrifugation coating steps were done for 10 s at 800 and
700 rpm for the first and second coating step, respectively, using
centrifugation cages attached to a stirrer (Hei-Torque Value 400,
Heidolph, Germany) at a radius of 5 cm. For the first coating, the
foam template was submerged into the slurry with the higher
viscosity (solid content: 82.2%) and hand pressed before the cen-
trifugation step. A slurry with a lower viscosity (solid content:
Table 2. Applied manufacturing technique combinations.

| Abbreviation | Manufacturing of the slurry (first coating, 82.2% solid content) | Application technique for the first coating | Manufacturing of the slurry (second coating, 70% solid content) | Application technique for the second coating |
|--------------|---------------------------------------------------------------|-----------------------------------------|---------------------------------------------------------------|-----------------------------------------|
| MRBC         | High shear mixer                                             | Rolling                                 | Ball mill                                                     | Centrifugation                          |
| MRBS         | High shear mixer                                             | Rolling                                 | Ball mill                                                     | Spray coating                           |
| MCBC         | High shear mixer                                             | Centrifugation                          | Ball mill                                                     | Centrifugation                          |
| MCBS         | High shear mixer                                             | Centrifugation                          | Ball mill                                                     | Spray coating                           |
| MCBC-T-BC    | Application of mixer slurry in the first step and ball mill slurry in the second step through centrifugation (900 rpm), thermal treatment (800 °C, 3 h; end mass ≈15 g), application of second layer of ball mill slurry through centrifugation, and final thermal treatment (800 °C, 3 h) |
| BS           | Only spray coating (slurry made in Ball mill, 70% solid content), 3 layers |
| BC           | Only centrifugation (slurry made in Ball mill, 70% solid content), 3–4 layers |

70%) was used for the second coating and the sample was only submerged into the slurry before centrifugation. No squeezing step was performed during the application of the second coating, because this would damage the already dried first coating layer. Another technique for applying second coating layers onto the foam samples is spray coating (S), which was conducted in a spray chamber by means of a spray gun with a nozzle diameter of 2 mm (Krautzberger HS-25HVPL, Germany) at an air pressure of 3 bar. The distance between the nozzle and foam sample was kept at approximately 10 cm. After the application of each coating layer, the foam samples were dried at room temperature for at least 24 h. The coated and dried samples were thermally treated under reducing atmosphere for 3 h at 800 °C in a petcoke-filled steel retort, following the temperature regime described by Emmel et al. The sample batch marked with MCBC-T-BC received three coatings in total and an additional heat treatment for 3 h at 800 °C, marked by T in the abbreviation, to access the influence of an in-between coking heat treatment on the formation and closure of cracks in the ceramic layer.

All of the ceramic foam samples were manufactured to target an end weight of approximately 25 g after the final heat treatment. Samples made for the conduction of mercury porosimetry were smaller in size (17 × 17 × 17 mm³) and had a target weight of approximately 2.3 g.

2.3. Investigation of Foam and Pore Structure

The material porosity and the strut cavities of the samples were characterized by means of the mercury-intrusion porosimeter Autopore 5 (Micromeritics, USA). Penetrometers with 15 cm³ cup volume (15 bulb) were used, allowing the measurement of the prepared samples (sized 17 × 17 × 17 mm³). The stem volume of the penetrometers (volume of the capillary) was 1.13 cm³. The samples were evacuated to a vacuum of <50 μm Hg before the penetrometer was filled with mercury. The equilibrium time was 5 s. The mercury-intrusion measurements consisted of one intrusion step with at least 290 measuring points. At least two foams per sample type were measured. The pressure (p) was converted into the corresponding pore size (r) with the help of the Washburn Equation (1),

\[ p = \frac{-2\gamma \cos \theta}{r} \]

whereas a surface tension (\(\gamma\)) of 0.485 Nm⁻¹ and a contact angle (\(\theta\)) of 150° (see Voigt et al.) were used. The measurements were corrected with the associated blank measurements (measurements without a sample). The negative intruded volume, which was caused by expansion and contraction of the mercury while heating and cooling, was displayed. To determine the functional open-foam porosity and homogeneity of the coating distribution, one ceramic foam sample of each sample type was analyzed by means of X-ray CT using the software MAVI (Modular Algorithms for Volume Images, Fraunhofer, Germany). The negative intruded volume, which was caused by expansion and contraction of the mercury while heating and cooling, was displayed. To determine the functional open-foam porosity and homogeneity of the coating distribution, one ceramic foam sample of each sample type was analyzed by means of X-ray CT using the software MAVI (Modular Algorithms for Volume Images, Fraunhofer, Germany).

Figure 1 shows exemplary images from the performed processing steps of the recorded CT data using the software MAVI (developed by Fraunhofer, Germany). After cropping the raw CT images (Figure 1a), a binarization step using Otsu’s threshold was performed. The resulting image (Figure 1b) shows the voxels belonging to the ceramic material in white, and the background, corresponding to the area of pores, in black. Being known as a suitable method for determining macroporosities of ceramic foams, X-ray CT was used to evaluate and quantify these functional open pores. Other kinds of pores, such as strut cavities and micropores were not investigated by CT analysis due to its limited resolution and were therefore eliminated by applying image post-processing steps as shown in Figure 1 and described in the following. For the removal of the strut cavities and material pores from the images, the following procedure was applied on the foreground (ceramic material) and background. A “Closure” step (cubic size parameter 5) was performed, followed by a “Labelling” operation (neighborhood 6/4), an “Object features” analysis step, and the application of an
It was not possible to remove all of the closed PU pores by means of the “Closure” operation with the cubic size parameter 5, since this technique tends to change the outline of the struts, when on a higher setting. Thus, the application of the “Object filter” was needed for both the fore- and background (cf. Figure 1c). The readily processed image of the foam can be seen in Figure 1d after the final binarization step. These images were then used for the following calculations. By applying the operation “Field Features”, the porosity of the ceramic foam sample image was determined, evaluating the ratio between the number of white voxels and the total number of voxels of the 3D image. To calculate the mean pore diameter of the sample, a complex morphology cell reconstruction operation was applied. The “DynamicH”-parameter, that is related to local contrast extrema and the cell diameter, was set to 5. Additionally, the strut thicknesses of the foam samples were measured using a digital optical microscope (Keyence VHX2000, Japan; with a VHZ20R objective). Per filter sample, 40 struts were evaluated and respective mean values and standard deviations were determined. To evaluate the microstructural properties and the morphology of the strut cross-section, samples were cut from the ceramic foams, embedded in epoxy resin, polished and sputtered with carbon. SEM was performed on the samples using the microscope ESEM FEG XL30 (FEI Eindhoven, Netherlands).

3. Results and Discussions
3.1. Rheological Analysis of the Slurries

For the rheological characterization of the slurries that contained grains with sizes up to 200 μm (see Table 1) and a tendency to dry up quickly, the cylindrical measuring system CC38/Ti/SE 01170079 with a profiled surface and the capacity to hold 40 mL of slurry allowed measurements with good reproducibility. This measuring system was able to measure the high viscosity slurries with a solid content of 82.2%, prepared in the high shear mixer (ball mill) up to a shear rate of only 100 s⁻¹ (80 s⁻¹) due to torque overload of the measuring device at higher shear rates.

The viscosity diagram (Figure 2) showed differences between slurries with different solid contents, as well as significant differences between slurries with an equally solid content (82.2%), but a varied mixing step. This was attributed to the observation of different grain sizes present in the slurries, caused by different mixing routines. The scanning electron micrographs of the thermally untreated samples showed the formation of significantly different microstructures of the ball-milled or mixed slurries. The ball-milled slurry had a significantly finer grain size than the slurry prepared in the high shear mixer, as well as a dispersed
and homogenous structure (see scanning electron micrograph in Figure 3a), due to the crushing of the large and relatively soft Carbores P grains in the ball mill. The material prepared in the high shear mixer showed large, dark grains (Figure 3b), which were identified as carbon-rich by means of EDX analysis. According to the grain size distribution of the raw materials, these large grains could be identified as Carbores P grains.

The finer grained, ball-milled material absorbed water more effectively than the one with coarser grains, therefore showing a higher viscosity (see Figure 2). Comparing the viscosity curves of the coating slurries (solid content: 70%, see Figure 2), it could be seen, that the mixed and the ball-milled slurries did not show a significant difference. It is also worth noting, that the ball-milled slurry with a solid content of 82.2% exhibited a higher thixotropy than the remaining three slurries. This was determined by a larger hysteresis area in the viscosity curve (see Figure 2). The shapes of the viscosity functions (see Figure 2) lead to the conclusion, that the carbon-bonded alumina slurries displayed a shear-thinning behavior.[15] For every slurry type, seven oscillation measurements for the determination of the mean linearity limits and yield points were done. Figure 4 shows typical graphs of measured values for each slurry type, with the linearity limits and yield points marked accordingly. The linearity limit was determined according to the method presented by Mezger,[15] through visual evaluation of the respective $G'(\tau)$-graphs. This value describes the end of the linear-viscoelastic region and the beginning of the nonlinear deformation behavior of the slurry, which is also known as the yield zone. To determine the approximate linearity limit, the mean value of the linear region of the $G'(\tau)$-graph at small shear stresses was calculated for every slurry, and a tolerance value of 10% was chosen. Therefore, the linearity limit was regarded to be the shear stress that corresponded to a $G'$ value reaching 90% of the mean value of its linear region. The following mean linearity limits were determined for the slurries and marked in Figure 4: 4.43 ± 2.59 Pa (high shear mixer, solid content: 82.2%), 1.02 ± 0.15 Pa (ball mill, solid content: 82.2%), 0.36 ± 0.16 Pa...
(high shear mixer, solid content: 70%), and 0.18 ± 0.02 Pa (ball mill, solid content: 70%). The high standard deviations of the linearity limits are explained by the quick-drying behavior of the carbon-bonded alumina slurry, that made measurements at low shear rates difficult, despite the comparatively high reproducibility of the measured curves. For the yield point evaluation of each slurry, the respective shear stress was determined, at which the G' and the G'' had the same value.\(^{(4)}\)

The calculated mean yield points were 193 ± 24 Pa (high shear mixer, solid content: 82.2%), 86 ± 11 Pa (ball mill, solid content: 82.2%), 12 ± 4 Pa (high shear mixer, solid content: 70%), and 11 ± 0.3 Pa (ball mill, solid content: 70%). These measurements revealed higher yield points, as well as linearity limits, for higher solid contents as well as larger grain sizes (see scanning electron micrographs, Figure 3). The larger grains of the slurry with the high solid content tended to “wedge” into each other, and therefore a network of secondary forces having a cohesive effect on the edges and areas of the grains was present. Consequently, it took a larger force to “tear” these grains apart when the slurry was sheared.\(^{(15)}\) For the coating slurries with a solid content of 70%, the linearity limits as well as flow limits did not show significant differences (see Figure 4). This showed the influence of the higher water content in these slurries, lowering the impact of the friction forces between the slurry grains.

3.2. Investigation of the Foam and Pore Structure

For the characterization of ceramic foam samples, different analysis methods had to be used due to the different kinds of pores (functional pores, strut cavities, and material pores, see Section 1) and therefore different pore scales and structures of the foams. First, the carbon-bonded alumina foams were examined with the unaided eye. All sample types showed a suitable foam structure, exceptions being the BC, BS, and the MCBC-T-BC samples. The BC samples, which were manufactured exclusively through the centrifugation of coating slurry with a solid content of 70%, showed occasional clogging of the pores, due to the slurry quickly drying on the sample surface, while the centrifugation was still in progress. An adjusted slurry with a higher water content should, therefore, be considered for this purpose in future experiments. The samples that were manufactured through spray coating only (BS) displayed occasional drop-like coating accumulations on the side they were dried on, signaling that the liquid coating was flowing down, increasing the inhomogeneity of the foam. The lowering of this flow down can be minimized by using a slurry with a higher viscosity in future experiments, as proposed by Voigt et al. previously.\(^{(4)}\) It should be noted that the MCBC-T-BC samples showed an extremely fragile behavior after their first thermal treatment; erosion of the edges and surface could be observed on some samples during the third coating step. This is due to the thinner struts, resulting from the lower weight of the first two coatings that was chosen to reach a final sample weight target of approximately 25 g after the final coking step, to ensure comparability with the rest of the sample types. Therefore, it can be concluded, that in-between heat treatment is technologically, as well as economically, not feasible and thus not recommended for the production of carbon bonded alumina foams of this size and strut thickness. For a quantitative characterization of the foam structure, X-ray computer tomography and optical microscopic analysis were used. In Table 3, the properties of the ceramic foam samples are presented. It can be seen, that all manufacturing techniques succeeded to produce ceramic foams of a comparably similar mean porosity, mean pore diameter, and mean strut diameter; an exception being the strut diameter of the BS samples (only spray-coated). This could be explained with the higher inhomogeneity of the sample caused by the nature of the spraying technique, with a lower quantity of slurry reaching the inner parts of the sample, causing thinner struts inside; an effect that has been addressed in literature.\(^{(4)}\) Another reason was the observed flow off during the drying of the sprayed-on slurry with lower viscosity, furthering material loss in the inner region of the foam. Another exception was seen in the high strut diameter of the MCMC samples, caused by the inhomogeneous, coarse mixer slurry used for their coatings.

In the next step, every sample type was virtually cut into five layers along the height of the sample. The total porosity of each layer was determined to verify the homogeneity of the sample in dependence of the position in the foam. Each layer was cropped to a thickness of about 100 voxels each, however, the restriction

| Table 3. Results of measurements conducted by means of µCT and optical microscopy. |
|-------------------------------|----------------|------------------------|--------------------------|--------------------------|--------------------------|
| Sample types        | Mass [g] | Mean total macroporosity determined by µCT analysis [%] | Mean strut diameter, determined by optical microscopy [mm] | Mean macropore diameter, determined by µCT analysis [mm] | Maximal difference of macroporosity between layers determined by µCT analysis [%] (absolute value) |
|--------------------|----------|------------------------------------------------------|-----------------------------------------------------------|-----------------------------------------------------------|-----------------------------------------------------------------|
| MRBC               | 25.4     | 69                                                   | 0.57 ± 0.09                                                | 3.5 ± 0.6                                                   | 4.46                                                             |
| MRBS               | 25.1     | 68                                                   | 0.66 ± 0.21                                                | 3.5 ± 0.6                                                   | 6.02                                                             |
| MCBW               | 24.9     | 68                                                   | 0.57 ± 0.10                                                | 3.6 ± 0.5                                                   | 4.10                                                             |
| MCB               | 25.2     | 69                                                   | 0.59 ± 0.15                                                | 3.6 ± 0.7                                                   | 3.43                                                             |
| MCM               | 24.9     | 67                                                   | 0.72 ± 0.17                                                | 3.6 ± 0.5                                                   | 12.07                                                            |
| MCM               | 24.9     | 69                                                   | 0.56 ± 0.11                                                | 3.7 ± 0.5                                                   | 14.87                                                            |
| BC                 | 25.0     | 65                                                   | 0.60 ± 0.10                                                | 3.6 ± 0.7                                                   | 3.76                                                             |
of limited resolution through the respective voxel sizes and numbers is to be taken into account. Furthermore, it is to be noted that the spatial resolution of the μCT images is limited by the focal spot of the X-ray tube, the active diode area of the detector, the sample size, as well as the reconstruction process of the volume image and the post-processing, most notably, the binarization steps.

The evaluated porosities per layer are plotted in Figure 5, with the maximum porosity difference listed in Table 3. Centrifuged carbon-bonded alumina foams showed a slight tendency to a higher porosity on one side of the sample (see Figure 5a), which was an observation that has been made in alumina foams before.[4] This could be attributed to the process of the centrifugation technique, in which one side of the foam was in contact with the centrifugation cage, causing a slight gradient in the slurry distribution, and therefore a porosity gradient, along the height of the ceramic foam. The spray-coated ceramic foam samples did not show such a tendency; the spray-coating technique being more dependent on the operator, and in this case, showing the tendency to form a more homogenous distribution of the ceramic material in the foam (Figure 5b); an exception was seen in the MCMS sample, which showed a significantly higher porosity in its center. The evaluation of the maximum porosity differences between the five layers showed values between 3.4% and 14.9%. The two sample types with the largest porosity difference between the layers (MCMC and MCMS) exhibited differences larger than 10%; the cause for this large inhomogeneity seeming to be the usage of the high shear mixer for the preparation of the second-coating slurry. It is conceivable that the slurry with a larger yield point (see Section 3.1) was less suitable for the application of a homogenous coating onto the foam. Considering the sample types with maximum porosity differences <5%, no similarities struck—the samples were prepared by rolling, centrifugation, and spraying. The only exception is the usage of ball-milled slurry for the second coating step, which showed good results. Being fine-grained and more homogenous, ball-milled slurry showed to be more advantageous for manufacturing the finishing coating of the samples in regards of a more homogenous final foam structure.

For the microstructural analysis of the struts, the samples were embedded, polished, and investigated by SEM. The area of the first and second coating could be distinguished for most of the sample types, see Figure 6 and 7. It was noticeable that the first coating possessed some round pores which are not detectable in the second coating. The cause was a more difficult removal of air from a slurry with a high viscosity. The sample types showed clear differences with regard to porosity and homogeneity of the microstructure. The most obvious difference was the microstructure of ball-milled versus high shear mixer slurry. The coatings applied using a ball-milled slurry possessed a homogenous microstructure with small pores. The long mixing time of approximately 24 h, along with the effect of ceramic grinding balls, enabled the crushing of Carbores P grains, which in turn caused small pore sizes and a fine structure in the finished coating. In contrast, coatings applied using slurry mixed in a high shear mixer showed large (up to 140 μm) angular pores which are not distributed homogeneously. These angular pores were caused by the Carbores P grains which soften, melt, and flow into the surrounding structure, leaving large pores behind during the coking step at 800 °C. The second coating, consisting of slurry prepared in the high shear mixer, exhibited round and light areas (approximate diameter: 40 μm) which were probably agglomerated alumina particles (see Figure 6 and 7). Notable was the micrograph of the MCBC-T-BC sample, which had received an additional coking step at 800 °C (Figure 7e), followed by a third centrifuged coating layer. Large cracks can be seen going through the final coating that was applied after the in-between coking step. The cracks stopped at the boundary to the second coating layer and could also be seen going along the boundary between the coatings. Furthermore, it was noticeable that the BC sample (only centrifugation using ball-milled slurry—Figure 7f) showed a chain of elongated pores along the boundary of the first coating layer. Such an effect was observed in previous, unpublished studies but could not be explained so far.
In the next step, the pore structure of the sample types was investigated by mercury-intrusion porosimetry, which allowed a quantitative characterization of the pore structure by the volume of intruded mercury into the accessible pores. It has to be kept in mind that only open pores are measurable by means of mercury-intrusion porosimetry. Furthermore, in mercury-intrusion porosimetry, pores in the interior of the specimen can only be reached by mercury through a chain of intermediate pores with different sizes and shapes. The large pores in the center of the specimen are not intruded by mercury until sufficient pressures are reached to penetrate narrower entryways. That way, the mercury-intrusion porosimeter measures the largest entrance of a pore and not the pore cavities themselves. The mercury-intrusion porosimetry measurements possessed a used stem volume between 48% and 63%. The stem volume is the volume of the capillary of the penetrometer, while the used stem volume gives information about the utilization of the measurement range. According to literature, the used stem volume can be between 10% and 90%, but ideally should be between 70% and 80%. The intruded mercury volumes of the different foam types were between 0.23 and 0.25 mL g\(^{-1}\) and the porosities between 37.7% and 39.1%, excepting the BC (0.27 mL g\(^{-1}\) and 42%), MCMC (0.28 mL g\(^{-1}\) and 42.5%), and the MCBC-T-BC (0.28 mL g\(^{-1}\) and 42.8%) samples which possessed slightly higher values. Such small differences in the amount of porosity between the different sample types were surprising due to the large differences in pore size and amount according to the scanning electron micrographs presented before. On the condition of the existence of mostly open pores, these small differences showed that the influence of mixing and coating routines on the absolute porosity value in the sample was small. The two measurements, which were performed for every sample type were in good agreement. The cumulative mercury volume in dependence on the pore diameter showed a comparable curve progression for large pore sizes (from 320 to approximately 75 μm); the sharp rise was caused by the filling of the strut cavities. For smaller pore sizes (<75 μm), there were visible differences, which could be matched with the process route, by considering the incremental pore volume, see Figure 8 and 9. The measurements of samples with a centrifuged second coating showed a strong peak in the incremental mercury volume at around 150 nm, whereas samples with a sprayed second coating possessed double peaks in the incremental pore volume at around 200 and 500 nm. Further relationships between the preparation routine and the pore structure, measured by mercury-intrusion porosimetry, were not detected. This showed the discrepancies between the pore structure observed by SEM and mercury-intrusion porosimetry. The large angular pores that were left by the melting of the Carbores P grains were not detectable by the mercury-intrusion porosimetry due to the measurement of pore entrances by this measuring technique, as mentioned earlier.

### 3.3. Results of the Cold Crushing Strength Tests

For every manufacturing route of the ceramic foams, the cold crushing strength of 20 samples was measured, as described in Section 2.4. Due to small differences between the cold crushing strengths, the complex stress states inside of the irregular foam structures during the cold crushing tests and the high standard deviations (see Figure 10), it is only possible to evaluate tendencies of the dependency of the cold crushing strength on the manufacturing process. The tendency to the highest cold crushing strengths were shown by the ceramic foam samples that had received a second...
Figure 7. Scanning electron micrographs of the ceramic foam samples, which received their final coating through centrifugation: a) MRBC, b) MCBC, c) MCMC, d) BCBC, e) MCBC-T-BC, and f) BC.

Figure 8. Cumulative pore volume in dependence on the pore diameter of different sample types.

Figure 9. Incremental pore volume in dependence on the pore diameter of different sample types.
coating consisting of centrifuged, ball-milled slurry, whereas the first coating seemed to be of minor importance (MCBC, BC, BCBC, MRBC). The high strength seemed to be caused by the fine and homogeneously distributed pores of the second coating, see Figure 6 and 7. Notable was a relatively high porosity difference between the five layers of the BC sample of 7.87% (see Table 3), which showed a minor effect on the crushing strength. The lowest crushing strength was measured for the BS sample, which was probably caused by the lowest mean strut diameter (0.51 mm). Previous tests showed that the spraying process tends to form thick nodes, but low strut thicknesses, while centrifugation, is prone to a more uniform slurry distribution, due to the higher automatization of the process and the lower dependency on the operator. The low crushing strength of the MCBC-T-BC sample, which had been coked twice, was likely caused by the shrinkage cracks (see Figure 7e) in the final coating and was connected with manufacturing problems described in Section 3.2, which leads to the conclusion that this manufacturing technique is not recommended for the production of carbon-bonded alumina foams of this size.

4. Conclusions

In this study, carbon-bonded alumina foams were prepared by applying varying process routes regarding mixing and coating steps. The macrostructure of the foams was analyzed by CT and optical microscopy, and for evaluating the microstructure, mercury-intrusion porosimetry and SEM were applied. In the last step, the crushing strength of the different sample types was measured. The CT analysis showed comparable mean macroporosity values for all ten different sample types. Considering the SEM analysis, the mixing step showed the largest influence by grinding (ball mill) and not grinding (high shear mixer) the Carbores P grains, which resulted in a fine and homogenous (ball mill) or an inhomogenous, coarse foam structure (high shear mixer). The coatings made using slurries prepared in the high shear mixer possessed angular and large pores (up to 150 μm). Regarding the mercury-intrusion porosimetry, the application step showed an influence on the measurement results. The samples with a centrifuged second coating showed a peak in the incremental mercury volume at around 150 nm, whereas samples with a sprayed second coating possessed double peaks in the incremental pore volume at around 200 and 500 nm. The large angular pores that were left by the melting of the Carbores P grains were not detectable by mercury-intrusion porosimetry due to the measurement of pore entrances by this technique. The tendency to the highest cold crushing strengths was shown by the ceramic foam samples that had centrifuged second coatings made of ball-milled slurry, whereas the first coating seemed to have minor importance regarding the mechanical strength. The lowest cold crushing strength was measured for the samples, that received sprayed coatings exclusively (BS), which was correlated to the lowest mean strut diameter measured in these samples.

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Conflict of Interest

The authors declare no conflict of interest.

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