

YOUNG'S MODULUS OF ELASTICITY OF CARBON-BONDED FOAM STRUCTURES AT ELEVATED TEMPERATURES

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ABSTRACT

The influence of temperature and porosity on the Young's modulus (E) of carbon bonded alumina as strut material for open cell foams and the foam structure itself, in a porosity range between 35 % and 61 %, was investigated. The foam structures extended that range up to ≈ 90 %. It was found out that $E(p)$ of the strut material and the foams followed two models described in the literature. Therefore, the elastic properties of carbon bonded foams could be modeled. E of the strut material was analyzed up to 1450 °C and varied in a range of ± 10 %. The measurement of $E(T)$ for the open cell structures was more complicated and revealed scattered results. However, an alumina containing coating on the basic filter structure increased the likelihood of a linear $E(T)$ behavior, known from the literature.

INTRODUCTION

Carbon-bonded cellular ceramics are common in metal melt filtration during steel casting. Their main task is to prevent impurities in the solidified steel. By doing so the mechanical properties of the steel is enhanced. During application, these materials are subjected to a severe thermal shock of 1400 – 1600 °C. Resisting that thermal variation is crucial for the filter integrity and, consequently, for the steel quality, as inclusions within the steel may lead to fatal failures during service.

According to the theories of Kingery and Hasselman the Young's modulus (E) of materials plays an important role for the thermal shock resistance. Hence, the knowledge of E of cellular foams is crucial to determine its thermal shock resistance.

The determination and description of the mechanical behavior of cellular foam structures was summarized by Gibson and Ashby¹. They also proposed the first theoretical model of the elastic behavior for open cell foams. According to them the elastic properties depend on the properties of the solid that the foam was made of and the bulk density of the foam (see Equation 1).

$$\frac{E}{E_s} = C_2 \left(\frac{\rho}{\rho_s} \right)^2 \quad (1)$$

Where E_s and ρ_s are the Young's modulus and density of the strut, respectively, and C_2 is a numerical constant depending on the cell shape of the foams. According to Rice², there are four general approaches to describe the porosity elasticity dependency. The Gibson - Ashby (GA) approach, a well known power law description, minimum solid area (MSA) models and computer models. The GA approach, the MSA as well as the computer models take the microstructure of the foams into account which qualifies these models especially for foams. However, Rice mentioned a lack in property measurements of ceramic foam structures.

Regarding the thermal shock behavior, not only the knowledge about the elasticity at room temperature but also at elevated temperature would be desirable. Already Kingery emphasized that his theory only holds in the case that E , α and ν "are taken as independent of temperature"³. Several researchers showed interesting dependencies for $E(T)$ for solid materials, besides the well known ones of alumina or magnesia. These results show in some cases that E at room temperature is completely different from what to expect at service temperature. Conferred to the foam structures, it is necessary to know the elastic behavior at elevated temperature to assess the thermal shock behavior of these components. Werner

et al. showed for carbon bonded alumina dense samples that there is a non linear dependency of $E(T)$ due to the composite feature of that material⁴. Furthermore, there is a study related to $E(T)$ of alumina gel cast structures by Ortega et al.⁵. They showed that the elasticity of foam structures in dependence on the temperature is comparable with that of solid structures. Thus, the models for porosity and temperature dependence could be merged to take both influences into account. Werner et al. also studied the influence of porosity on $E(T)$, however, for dense structures⁶. They found little influence of the porosity on $E(T)$.

Therefore, the purpose of this study was to investigate the variation of Young's modulus of carbon bonded alumina open cell foam structures with the temperature. Also the influence of different coating layers on the elasticity at room and elevated temperatures was investigated.

EXPERIMENTAL

According to the model of Gibson and Ashby¹ the strut material plays an important role regarding the elastic properties of foam structures. Therefore, the carbon bonded alumina used for the open cell foam preparation was shaped into bars to investigate its properties.

Raw materials used for the preparation of the composition were alumina (Martoxid MR 70, Martinswerk, Germany), modified coal tar pitch powder (Carbores[®]P, Rütgers, Germany), natural graphite (AF 96/97, Graphit Kropfmuehl, Germany) and a carbon black powder (Luvomaxx N-991, Lehmann & Voss & Co., Germany). The additives were lignosulfonate (T11B, Otto-Dille, Germany), Castament VP 95 L (BASF, Germany), and Contraspum K 1012 (Zschimmer & Schwarz, Germany).

The composition was prepared according to the spray slurry from Schmidt et al.⁷. Before shaping, the slurry was homogenized for a 24 h mixing in a ball mill. The samples were pressed at 150 MPa. Therefore, the slurry had to be dried prior to pressing at 110 °C. Afterwards, the samples were heat treated at 800 °C for 3 h in a pet coke filled retort according to Schmidt et al.⁷ samples of different porosity were produced to study the influence of the porosity on E .

E of these dense structures was investigated in a two step measurement up to 1000 °C and 1450 °C.

Carbon bonded open cell foam structures were produced ac-

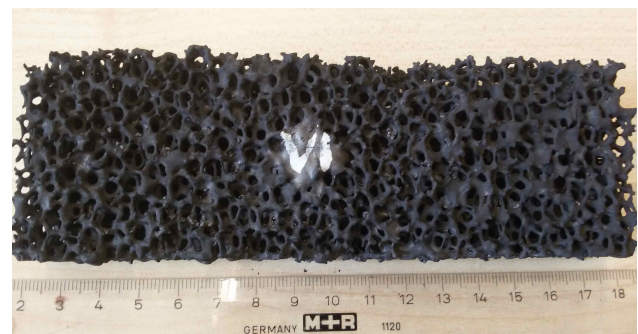


Fig. 1: Carbon bonded filter structure investigated within this study with a small drop of slurry in the middle of the sample acting as excitation area

ording to a procedure proposed by Schwartzwalder⁷ and edited by Schmidt et al.⁷ in a three step process. At first a polyurethane foam was impregnated with an Al₂O₃-C slurry, followed by the application of a second layer of the same slurry by spraying. Afterwards the filter foam structures were pyrolyzed up to 800 °C in a pet coke filled retort. Then so called coatings were applied by spraying onto these structures. Finally, a pyrolysis followed up to 1400 °C. Two different coatings were studied. An alumina (AC1_0) and an alumina modified coal tar pitch mixture (AC95_5). A third filter structure without coating was produced as reference (ref) also pyrolyzed twice as described above. Those different layers affect the filtration efficiency of steel melt filtration significantly. For the determination of E a special foam shape was produced apart from the common filter structure (50 × 50 × 20 mm³). The sample size was 150 × 50 × 20 mm³ (see Fig. 1).

The influence of these three coatings on E at room temperature and up to 1400 °C was investigated by the impulse excitation technique. This method is based on the resonance frequency of a structure for the calculation of the elastic properties. In this case the sample was excited with a small projectile resulting in an oscillation which was recorded with a microphone. Out of this audio signal one can obtain a frequency spectrum via fast Fourier transformation and from that spectrum the resonance frequencies can be found. This procedure followed ASTM E1876. The high temperature measurement was carried out using the same setup, however inside a furnace (HTVP 1600, IMCE, Belgium).

Nevertheless, there are several problems with this method in the case of the specific cell foams analyzed in this study. The equations for the calculation of the elastic properties are mainly valid for homogeneous and isotropic materials. The foam structures can not be regarded as isotropic nor as homogeneous. Furthermore, the pores within the foams can be regarded as continuous phase. In that case it is not clear if the structure even comprises the same modes as a dense structure of the same shape would do. Finally, there was a quite simple practical problem, namely how to excite the sample without destroying single struts. The first problems were taken into account by assuming that the foam material holds the requirements of the equations. The latter problem was solved by application of a small drop of slurry in the middle of the sample to offer an excitation area (see Fig. 1).

In order to analyze which factors affected the Young's modulus of the samples at room temperature, an analysis of variance (ANOVA) was carried out. Furthermore, the response values at the levels were compared by using the Tukey range test with a p -value of 0.05 (also known as Tukey's HSD [honest significant difference] test). It is a single step multiple comparison test. For the statistical analysis the software package "R" was used.

RESULTS AND DISCUSSION

Within this study the influence of the temperature on the Young's modulus (E) of carbon bonded foam filter structures was investigated. According to the approach by Gibson et al., the so called strut material (bulk material) was firstly investigated regarding its elastic behavior first. Afterwards, foams of the same compositions were analyzed and the results will be compared with findings from the literature.

The influence of the apparent porosity of the pyrolyzed material with 20 wt % Carbores[®] was also correlated with those models describing $E(T)$ from the literature^{6;8;1}. The Carbores[®] content was chosen according to the content of the foam structures. The results are shown in Fig. 2. By changing either the forming technology (pressing or slip casting) or adding a pore forming agent, a porosity range from 35 to 61 % for the bulk material was achieved. Furthermore, results from carbon bonded foams were added to extend this range (macroscopic porosity of 85 to 91 %).

$E(p)$ followed the assumed exponential like relationship. The measured Young's modulus values were in the range of 0.5 to

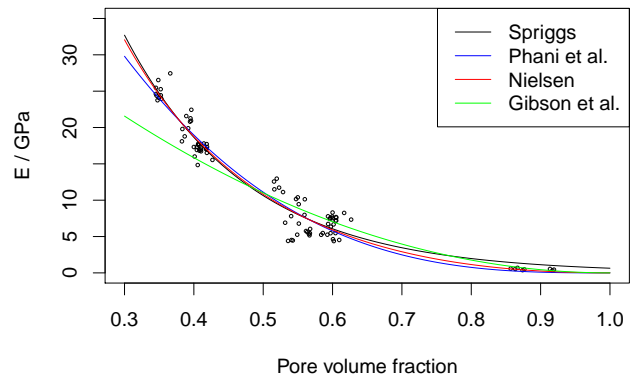


Fig. 2: Young's modulus of the bulk and foam material (20 wt % Carbores[®] content) as a function of the porosity. Models found in the literature were fitted versus the experimental data to analyze their applicability for this composite material

Table 1: Theoretical models compared with the experimental data for $E(P)$ for the carbon-bonded bulk and foam material (20 wt % Carbores[®] content). $p < 0.05$ indicates significance of the estimates

Model	E_0 / GPa	p
Spriggs et al. ⁶	176.32	$< 2 \times 10^{-16}$
Nielsen ⁸	283.91	0.0519
Phani et al. ⁶	84.84	$< 2 \times 10^{-16}$
Gibson et al. ¹	73.51	$< 2 \times 10^{-16}$

29 GPa. Within that broad porosity range all the models fit the experimental data quite well. However, it was evident that Spriggs' model did not fit well for the highest porosity. This model does not fulfill the boarder condition $p = 0 \rightarrow E = 0$ which may be the reason for this behavior. On the other hand Gibson's model did not fit the lower porosity data well, which was not surprising as it was proposed for cellular materials.

Furthermore, model fittings (see Tab. 1) were quite different. The Nielsen's and Spriggs' model resulted in very high E_0 values whereas the Gibson Ashby and Phani's one were significant lower. The significance of these fittings was below 0.05 for all models except for Nielsen's.

Therefore, the Spriggs' and Nielsen's models might not be suitable for a prediction of E within the investigated porosity range. The models by Gibson et al. and Phani et al. fitted the data quite well. Furthermore, the estimation of E_0 , the Young's modulus of the pore free material, was quite in the same range (73 and 84 GPa). Thus, these two models might be appropriate for E prediction within the investigated porosity range of this material. Besides that, the power factor n of the Gibson et al. model was computed and found to be approximately 3. This parameter describes the cell structure of the foam and was found to be 2 for open cell foams. The constant C_1 was assumed to be 1 according to Gibson et al.

In Fig. 3 the $E(T)$ of the strut material is presented. The change of E of the bulk material is quite comparable to the evolution of E for coarse grained carbon bonded alumina⁴. There was a slight decrease of E up to 500 °C. Above it E increased till the samples former pyrolysis temperature, which was in this case 800 °C. Over 800 °C a small decrease was registered which was superimposed by an increase of E during the holding time. After holding at 1000 °C E remained almost constant (5 % above the initial value).

Reheating up to 1000 °C resulted in a constant decrease of E . Increasing the temperature above resulted in a strong decrease of E (-10 %) up to 1450 °C. During the holding time at 1450 °C E

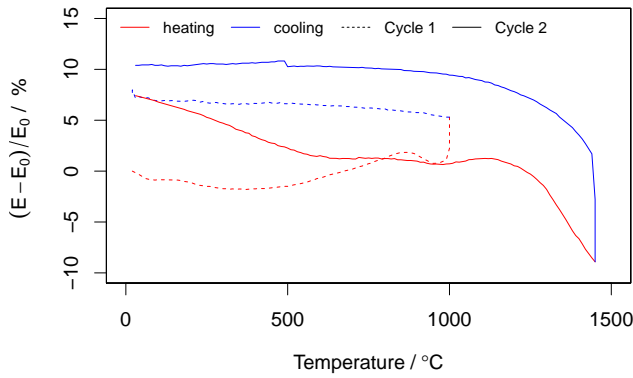


Fig. 3: Young's modulus normalized to its initial value versus the temperature of the strut material

Table 2: E values of the investigated open cell foam filter structures and the p -values of the pairwise comparison ($p < 0.05$ means significant)

Composition	AC1_0	AC95_5	E / MPa
Ref	3.60×10^{-5}	2.08×10^{-4}	175
AC1_0	-	0.782	657
AC95_5	-	-	587

values of the carbon bonded alumina increased significantly. After the holding time there was an increase of E up to approximately 1000 °C during cooling. Below E remained constant at around 10 % of the initial value.

The high temperature Young's modulus of the strut material of the filter, was found to be in accordance to the model shown by Werner et al.⁴. A small decrease of E up to 500 °C was followed by an increase up to the former pyrolysis temperature. However, compared to the E increase of the coarse grain compositions from the former mentioned study (70 to 150 %), the change of E of the bulk material was very small (2 %). Still it seems like some preexisting gaps or pores were closed up to the former pyrolysis temperature. A big difference between the results from the literature and the recent studied material was the maximum alumina particle size of $\approx 3 \mu\text{m}$ compared to 0.5 mm in the literature. It was shown by Solarek et al.⁹ that there is a more viscous-plastic behavior of this material above 1300 °C, which might have contributed to the decrease of E above 1250 °C. The results shown here are in very good accordance to those shown by Solarek et al.⁹.

In Tab. 2 the E values of the different foam structures at room temperatures are shown. An ANOVA revealed a significant influence on the E values for the different coatings. A further insight is gained by the pairwise comparison of the different coatings. It can be seen that there was a significant difference between the alumina containing coatings compared to the original one. The two alumina rich coatings AC1_0 and AC95_5 do not differ significantly from each other. The reason for the increase of E by the application of an alumina rich coating onto the Al_2O_3 filter substrate can be found in a stiffening of the structure due to a stronger sintering of these coatings. Hence, the substrate is subjected to compression stress leading to an increase in E .

The high temperature measurement of E of the filter samples is shown in Fig. 4. All measurements were conducted on one sample. AC1_0 and AC95_5 were measured twice. Firstly, a big difference between the two AC95_5 measurements can be seen. It is not clear what is the reason for that, however comparing the increasing AC95_5 curve with the other results, there is strong evidence that not the filter structure itself was the source of the audio signal, but something else. Furthermore, the maximum measurement

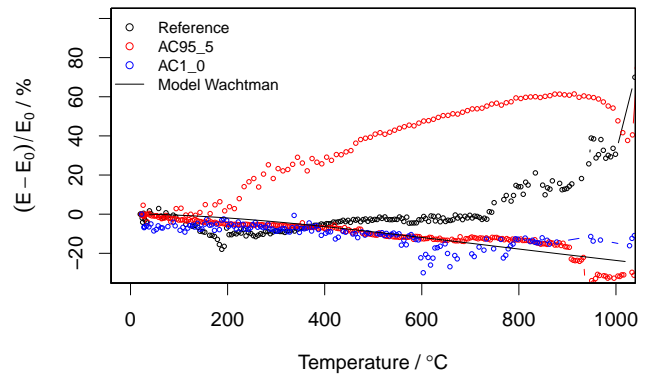


Fig. 4: Young's modulus normalized to its initial value in dependence on the temperature of the filter structures and the dependence of dense alumina on E according to Wachtman et al.¹⁰

temperature was limited to 1000 °C due to further microstructural changes above this temperature which would disturb the analysis of the measurement.

The reference sample showed a more non linear behavior compared to the samples with the coatings. These samples followed in very good accordance a relationship shown by Wachtman¹⁰ for dense oxide materials and confirm the results obtained by Ortega et al.⁵. So it could be assumed that these structures are more likely to behave as an oxide material in terms of $E(T)$ than as a carbon bonded alumina material. The curve of the reference sample however can be seen in accordance with the results of the strut material described above. However, these structures were pyrolyzed up to 800 °C, whereas the filter was fired at 1400 °C. This means $E(T)$ of the filter structures would be assumed to be like the second cycle of the strut experiment, slightly decreasing up to 1000 °C.

Due to the uncertainties with the measurement method a further investigation regarding the appropriate measurement technique and equipment will be carried out.

CONCLUSIONS

Carbon bonded alumina bulk samples with a carbon content of 30 wt. % and open cell foam structures of the same material and additionally coated were investigated in this study. Two different alumina containing coatings were compared.

It was shown that $E(p)$ of this material can be described by two models found in the literature in a porosity range of 35 to 91 %. Furthermore, was shown that the application of an alumina containing coating on a carbon bonded alumina open cell foam led to an increase in the stiffness.

The influence of the temperature on E of the strut material was comparable to earlier investigations with bigger alumina grain sizes. However, the overall change of E during a measurement was relatively small with ± 10 %. $E(T)$ of the foam structure was found to be comparable to the well known behavior of oxide materials. However, there were several problems with the measurement of the foam structures resulting in a great scattering of the results. Therefore, further research regarding an appropriate measurement method and equipment has to be carried out.

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