

# ON THE SINTERING OF POWDER INJECTION MOLDED MESOPHASE CARBON

*Christian A. Rottmair, Michael Gruhl, Birgit Derfuss, Andreas Volek, Robert F. Singer  
Central Institute for Advanced Materials and Processing Technology, University of Erlangen, 90762 Fuerth, Germany*

## Introduction

Mesophase carbon powder is an excellent precursor material for the production of fine grained graphite parts with superior mechanical properties (Mochida, Gao). To provide a net-shape technique for complex as well as thick-walled carbon parts, a powder injection molding (PIM) process has been developed (Gruhl, Rottmair), by using a water-based binder system. Since water can be removed by mere drying, the critical overlap of binder removal and pyrolysis / sintering of mesocarbon is avoided. However specimens produced with the above mentioned process show significant lower densities and lower mechanical properties compared to uniaxially pressed parts. To overcome these disadvantages, the present study evaluates the sintering behavior of samples molded with mesocarbon microbead (MCMB) powder. In a theoretical approach we try to explain the sintering and densification mechanisms occurring during the change of the mesophase towards graphite material.

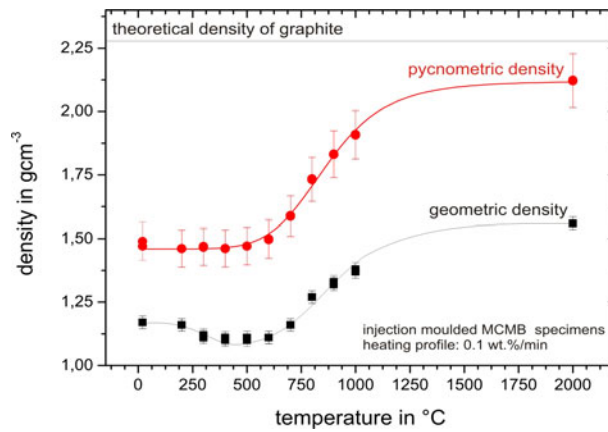
## Experimental

A compound of MCMB carbon mesophase powder (Osaka Gas), with a typical grain size of 6  $\mu\text{m}$ , water, agar as a binder and some additives was prepared by mixing and kneading the components. This mixture was then heated up for gelling, followed by extrusion for homogenization and granulation. With a conventional injection molding machine (Arburg Allrounder 320 C 600-250) equipped with a special screw for powder injection molding, the water-based feedstock was processed into bars with typical dimensions of 100 mm x 20 mm x 5 mm. After the demolding all specimens were dried in a climate controlled chamber. In a debinding furnace (MUT Jena) the samples were heat-treated up to a carbonization temperature of 1000 °C. With a step width of 100 °C samples were removed to determine changes in dimensions, weight and density. Further high temperature heat treatment for graphitization was conducted in a FCT high temperature furnace at 2000 °C for 1 hour. True densities of all samples were measured in a helium pycnometer. Porosity and average pore diameter of the injection molded specimens were measured with a mercury porosimeter (Pascal 140 / 440), assuming a cylindrical pore network without bottlenecks.

## Results

### *Density*

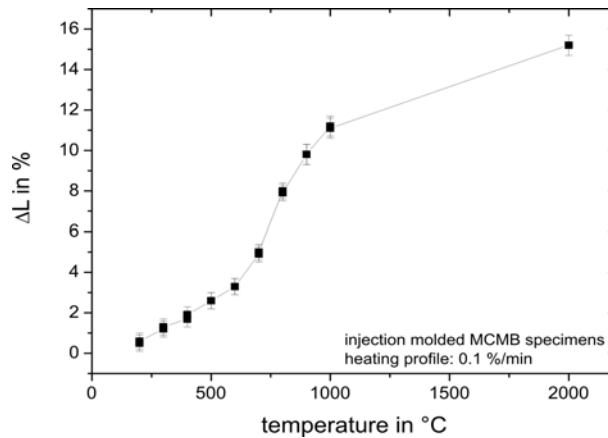
Up to 600 °C there are no significant changes in true density. Starting at 600 °C there is a sharp increase in density from 1.47  $\text{g}/\text{cm}^3$  to 1.9  $\text{g}/\text{cm}^3$  at 1000 °C. In the temperature range from 1000 °C to 2000 °C there is only a minor increase to 2.12  $\text{g}/\text{cm}^3$  (filled circles in **Figure 1**). Geometric density is stable at 1.17  $\text{g}/\text{cm}^3$  up to 200 °C. Between 200 °C and 500 °C a drop down to 1.1  $\text{g}/\text{cm}^3$  occurs. Along with true density, the geometric density shows a sharp increase in the temperature range from 600 °C to 1000 °C (1.38  $\text{g}/\text{cm}^3$ ), increasing slightly further after 1000 °C and reaching 1.58  $\text{g}/\text{cm}^3$  at 2000 °C.



**Figure 1.** Dependency of the true density and the geometric density of injection molded mesophase specimens on heat treatment temperature up to 2000 °C.

**Shrinkage**

In the drying step, a linear shrinkage of ~8 % in dimensions is measured. At the end of the subsequent thermal treatment for sintering and graphitization (2000 °C, 1 h) shrinkage reaches 15 %. A more thorough examination in steps of 100 °C reveals a linear shrinkage rate from the dried state up to 600 °C. Between 600 °C and 1000 °C a steep increase in shrinkage is noticed, which slows down again in the high temperature region from 1000 °C to 2000 °C (**Figure 2.**)



**Figure 2.** The shrinkage of mesophase specimens as change in length during the heat treatment.

**Porosity**

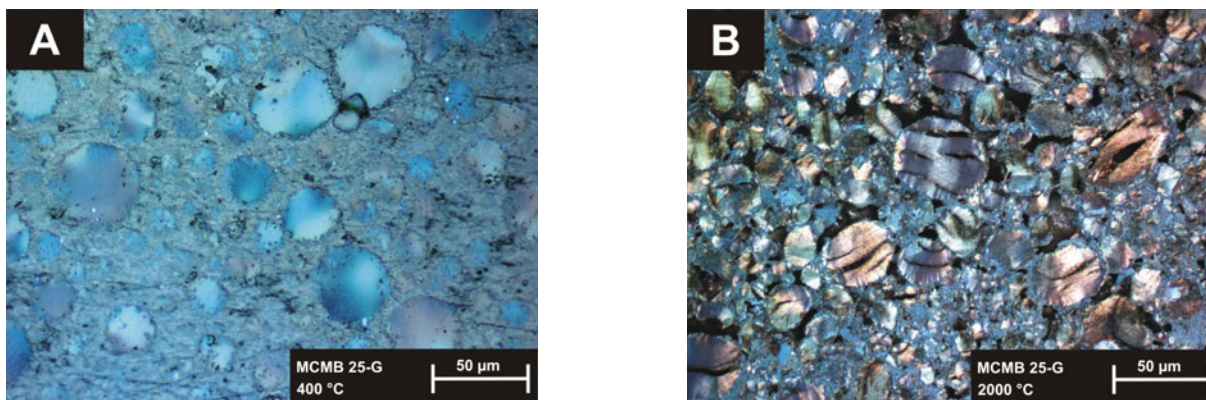
Injection molded specimens in the dried state exhibit a porosity of 17.4 vol.% with an average pore diameter of 0.05 μm. During the heat treatment up to 2000 °C porosity and average pore diameter are not changing significantly and level off at around 21 vol.% porosity and a diameter of 0.3/0.4 μm (**Table 1.**)

Table 1. Porosity and average pore diameter of the injection molded mesophase specimens at different stages of thermal treatment.

		dried	500 °C	600 °C	800 °C	1000 °C	2000 °C
open porosity	Vol. %	17.4	21.3	21.5	20.5	20.5	22.2
average pore diameter	μm	0.05	0.4	0.4	0.3	0.3	0.4

### Microstructure

The microstructures presented in **Figure 3**, were taken of samples prepared by MCMB powders with equal chemical composition but larger grain size ( $\sim 25 \mu\text{m}$ ), in order to better visualize crack formation and changes in shape. **Figure 3. A** shows the microstructure of a sample heat-treated up to  $400 \text{ }^\circ\text{C}$  and **Figure 3. B** shows a sample graphitized up to  $2000 \text{ }^\circ\text{C}$ . In picture B the formation of distinctive cracks within the mesocarbon microbeads is visible. The black areas indicate pores. The determination of the sphere diameters shows an average shrinkage of around 13 %, which correlates with the changes of dimension ( $\sim 14.5 \%$ ) between  $400 \text{ }^\circ\text{C}$  and  $2000 \text{ }^\circ\text{C}$ . Despite these changes in dimension, the shape of the MCMB spheres is stable during the heat treatment. Furthermore intensive analysis of the microstructures in all states between room temperature and  $2000 \text{ }^\circ\text{C}$  reveals no distinctive sintering neck formation.



**Figure 3.** Microstructure of MCMB specimens heat-treated at  $400 \text{ }^\circ\text{C}$  and  $2000 \text{ }^\circ\text{C}$ .

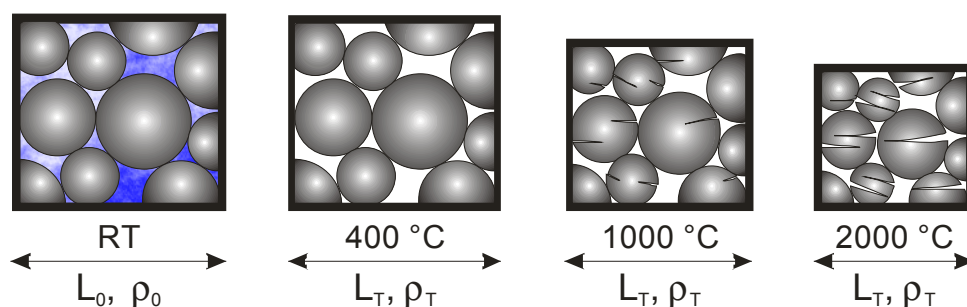
### Discussion

As shown in our results, the heat-treatment of the injection molded specimens from organic mesophase and binder towards graphite is characterized by distinctive changes in geometry and density. That is a well described (German) phenomenon during sintering processes and mostly explained by the removal of porosity.

Additionally, true density of the mesophase material is changing during the heat treatment, mainly in the temperature region between  $600$  and  $1000 \text{ }^\circ\text{C}$ . Here, mesophase differs from observations made in sintering metallic or ceramic powders. The decrease in geometric density in the temperature region between  $200$  and  $600 \text{ }^\circ\text{C}$  from  $1.17$  to  $1.1 \text{ g/cm}^3$  ( $6 \text{ wt.}\%$ ) can be attributed to the burn off of binder ( $\sim 7 \text{ wt.}\%$ ) within the injection molded specimens.

Uncommon for sintering processes, shrinkage cannot be correlated with a reduction of porosity. Shrinkage in the temperature range up to  $600 \text{ }^\circ\text{C}$  could mainly be explained by a rearrangement of the spheres, or subsiding processes due to binder removal. Still the binder removal and the subsiding processes seem to equal out each other, so that there is no major change in porosity up to  $600 \text{ }^\circ\text{C}$ . In fact it is much more interesting, that between  $600$  and  $2000 \text{ }^\circ\text{C}$  porosity and mean pore diameter are not changing at all. These results are opposite to all proposed sintering theories so far.

To conclude the above discussed results, MCMB spheres seem to shrink homogeneously without any material transport phenomena leading to pore reduction or annihilation. Our observations and experiments state that porosity is not changing significantly during heat treatment, which support a shrinkage model developed by Norfolk. In his model he proposes that shrinkage is caused only by changes in density and size of the mesophase spheres. Taking the crack formation of the mesospheres into account, which can be observed in **Figure 3. B**, even the slight increase in porosity at  $2000 \text{ }^\circ\text{C}$  can be explained. All theories discussed above are summarized in the following model (**Figure 4**): At room temperature (RT) a volume element of an injection molded sample consists mainly of mesophase spheres held together by microporous binder. At temperatures around  $400 \text{ }^\circ\text{C}$  there is only a slight shrinkage due to some rearrangement of the spheres caused by the binder burn off. Looking at a volume element of a carbonized sample exhibits the same percental amount of porosity since only the size and the density of the single spheres has changed. At  $2000 \text{ }^\circ\text{C}$  further increase in density and shrinkage can be seen, and the formation of cracks within the spheres causes a  $1 \%$  additional porosity.



**Figure 4** Changes during the temperature treatment in length and density without

Starting at 600 °C, mechanical properties such as bending strength increase as well which suggests that in this temperature range chemical reactions take place at the touching points in between the spheres. These reactions are gluing the spheres together and are responsible for the resulting mechanical properties of the specimens.

## Conclusion

As our experiments reveal, there are no signs of liquid sintering mechanisms such as a reduction of porosity during the heat treatment or a formation of sintering necks as stated by Hoffmann. The shrinkage of the specimens can be explained by mere shrinkage of the mesophase spheres according to a model first proposed by Norfolk. Carbonaceous mesophase is a rather complex material, the properties are strongly dependent on the manufacturing process and the raw materials used (synthetic pitch, coal tar pitch or petroleum pitch). Therefore our results present properties for the MCMB powders used in these experiments. The use of a more sinter-active powder with lower viscosity and higher reactivity could significantly reduce porosity and enhance mechanical properties. Experiments with such powders are currently conducted; results will be presented at CARBON 2007.

## Acknowledgements

A financial grant of the Bavarian State Ministry of Sciences, Research and the Arts and the Objective 2 Funding of the European Union is gratefully acknowledged.

## References

- Gao, Y., H. Song, et al. (2003). "Self-sinterability of mesocarbon microbeads (MCMB) for preparation of high-density isotropic carbon." *Journal of Materials Science* 38(10): 2209-2213.
- German, R. M. (1996). *Sintering Theory and Practice*. New York, John Wiley & Sons, Inc.
- Gruhl, M., B. Derfuss, et al. (2006). "Powder Injection Moulding (PIM) of Mesophase Carbon with Water-based Binders." *Advances in Science and Technology* 45: 711-713.
- Hoffmann, W. R. and K. J. Huttinger (1993). "Demonstration of spontaneous liquid-phase sintering of mesophase powders." *Carbon* 31(2): 259-262.
- Hoffmann, W. R. and K. J. Huttinger (1993). "Modeling of the apparent viscosity of pitches and mesophases at linear temperature increase up to 500 °C." *Carbon* 31(2): 263-268.
- Hoffmann, W. R. and K. J. Huttinger (1994). "Sintering of powders of polyaromatic mesophase to high-strength isotropic carbons--I. Influence of the raw material and sintering conditions on the properties of the carbon materials." *Carbon* 32(6): 1087-1103.
- Mochida, I., R. Fujiura, et al. (1995). "Carbon disc of high density and strength prepared from heat-treated mesophase pitch grains." *Carbon* 33(3): 265-274.
- Norfolk, C., A. Mukasyan, et al. (2004). "Processing of mesocarbon microbeads to high-performance materials: Part I. Studies towards the sintering mechanism." *Carbon* 42(1): 11-19.
- Rottmair, C. A., J. Bauer, et al. (2006). "Influence of pressure and heating rate on the mechanical properties of mesophase based sintered parts." *Advances in Science and Technology* 45: 584-589.