

## The role of Aluminium in the synthesis of Mesoporous 4H Silicon Carbide

Hvam, Jeanette; Skou, Eivind Morten; Warner, Terence Edwin; Morgen, Per; Wolff, Thomas

*Publication date:*  
2014

*Document version:*  
Submitted manuscript

*Citation for polished version (APA):*  
Hvam, J., Skou, E. M., Warner, T. E., Morgen, P., & Wolff, T. (2014). *The role of Aluminium in the synthesis of Mesoporous 4H Silicon Carbide*. Abstract from 10th European Conference on Silicon Carbide and Related Materials, Grenoble, France.

Go to publication entry in University of Southern Denmark's Research Portal

### Terms of use

This work is brought to you by the University of Southern Denmark.  
Unless otherwise specified it has been shared according to the terms for self-archiving.  
If no other license is stated, these terms apply:

- You may download this work for personal use only.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying this open access version

If you believe that this document breaches copyright please contact us providing details and we will investigate your claim.  
Please direct all enquiries to [puresupport@bib.sdu.dk](mailto:puresupport@bib.sdu.dk)

# The role of aluminium in the synthesis of mesoporous 4H silicon carbide

Jeanette Hvam<sup>1)</sup>, Terence E. Warner<sup>1)</sup>, Eivind M. Skou<sup>1)</sup>, Per Morgen<sup>2)</sup>, Thomas Wolff<sup>3)</sup>

<sup>1)</sup> University of Southern Denmark, Department of Chemistry-, Bio- and Environmental technology, Niels Bohrs Allé 1, 5230 Odense M, Denmark.

<sup>2)</sup> University of Southern Denmark, Department of Physics, Chemistry and Pharmacy, Campusvej 55, 5230 Odense M, Denmark.

<sup>3)</sup> Dinex A/S, Department of Research and Development, Fynsvej 39, 5500 Middelfart, Denmark.

E-mail: [jhva@kbm.sdu.dk](mailto:jhva@kbm.sdu.dk) (corresponding author)

Mesoporous SiC with a highly accessible porosity, i.e. pores in the micrometre diameter range, is the preferred material for hot gas filter units and may have a combined function as a catalyst support due to its high temperature stability and chemical inertness. Usually the porous structure is obtained by sintering the constituents at temperatures above 2000°C in an inert atmosphere [1-2]. In the present work SiC was produced from its elements, and small, added amounts of aluminium, by a stepwise temperature treatment under an inert atmosphere. The final result is a highly porous (65% accessible porosity) microstructure of hexagonal- interlocked crystals of highly crystalline 4H-SiC, suitable for multiple applications.

Samples were prepared by mixing equal atomic amounts of silicon and carbon with a varying amount of aluminium and adding a binder, an extrusion promoter, and water. The mixture was first pressed into plates and dried in air, and thereafter pyrolyzed under flowing nitrogen for 12h at 850°C. The pyrolyzed samples showed an increasing AlN matrix evolution with increasing aluminium content in the initial batch, see Fig. 1 a) and b). It is suggested that this matrix act as 3D template for the final SiC structure.

After sintering at 1450°C for 2h, the elemental silicon and carbon concentrations have reacted to form 3C-SiC. The AlN is at this point no longer apparent as a separate phase, but is now imbedded in a 3D SiC-AlN structure. The microstructure formed at this point has an overall glassy appearance, indicating that a solid-state reaction has occurred.

The high temperature treatment at 1950°C for 2h and subsequent cooling alters the sample significantly, in terms of both the crystal structure and the microstructure. For low aluminium contents, low final degrees of crystallinity and a polytypic mixture of SiC result. Whereas high aluminium contents result in a high degree of crystallinity of mainly the 4H-SiC polytype, Fig. 1 c). Aluminium thus does not only act as a diffusion agent under liquid phase sintering, but also as a structural promoter, that favours the recrystallization into 4H-SiC over other polytypes at these temperatures.

During sintering at 1950 °C, the microstructure of the 5 at% aluminium samples, evolves into individual interlocked hexagonal crystals with a narrow grain size distribution of 5-20µm. The final structure is stable and has large pores and 65% accessible porosity, Fig. 1 d). For lower aluminium contents, the grains are smaller and subhedral with a narrow grain size distribution and with very few and narrow bridges due to low diffusion through the Si-Al liquid alloy, whereas for higher aluminium contents the grains grow abnormally, with a broad grain size distribution and broken bridges. The crystals produced with high aluminium contents are polyhedrons, formed via 2D-nucleation on the flat (0001) silicon terminated- or (000-1) carbon-terminated-face of the crystal. The crystals seem to have a euhedral side and a subhedral side, thus growth is different on the two flat faces, i.e. the silicon-terminated and the carbon-terminated faces, of the crystal. The growth conditions are carbon-rich, as excess residual carbon is found in the structure as minor dark clusters on the crystal surfaces, Fig. 1 e). In summary, aluminium is believed to enhance the growth of SiC, not solely by surface diffusion, but also by being a structural promoter in the lattice for the bulk integration kinetics accompanying 2D-nucleation and the transition to 3D growth. The stability of these aluminium containing compounds is dependent on the aluminium vapour pressure which increases with increasing aluminium content in the initial batch, facilitating the growth of the SiC crystal. The recrystallization is therefore interpreted

to shift from surface diffusion- to bulk integration controlled and in this way responsible for the euhedral, and thus abnormal grain growth, with increasing aluminium content.

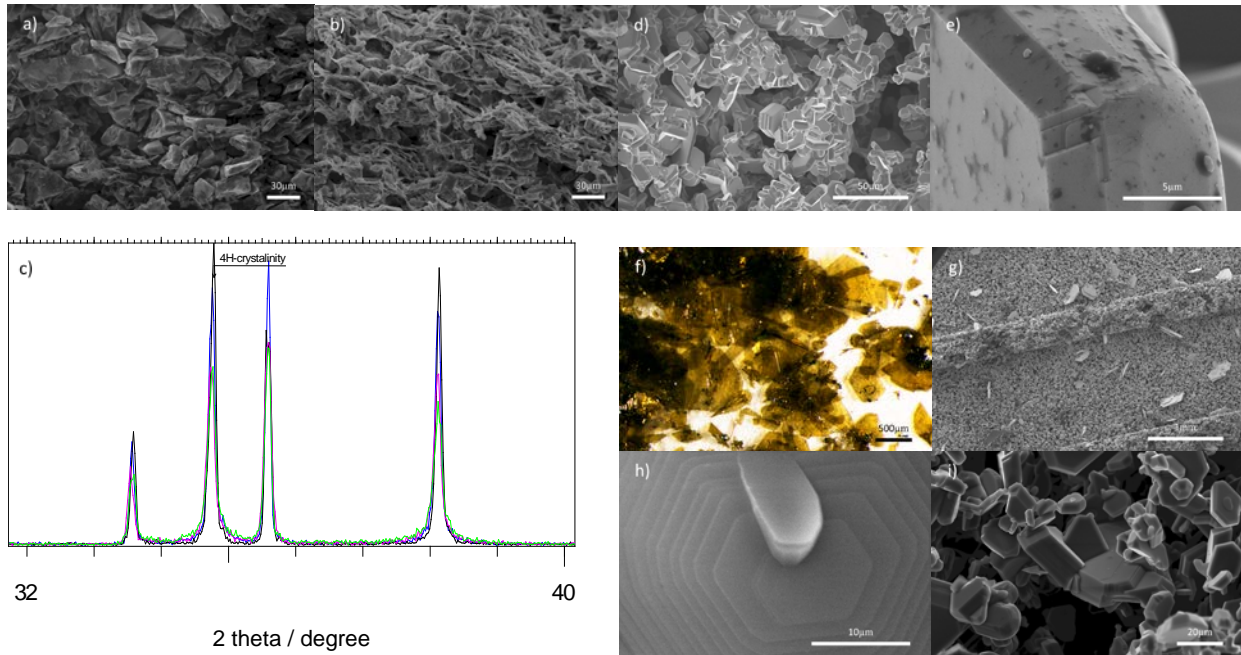


Fig. 1 a) Pyrolyzed samples with 0 at% aluminium. b) Pyrolyzed sample with 20 at% aluminium. c) XRD of sintered samples with varying amounts of aluminium; 20 at% (black) 5 at% (blue) 0.5 at% (pink) no aluminium (green). d) Sintered sample with 5 at% aluminium. e) Close-up of a SiC-crystal from Fig. 1 d). f) Translucent ternary carbide crystals. g) Ternary carbides protruding the sample surface, intergrown with SiC. h) Spiral growth of ternary carbide crystals. i) Sintered sample with ternary carbide crystals as additive corresponding to 5 at% aluminium.

In addition to the pure SiC structure, large hexagonal yellow translucent crystals are also produced at some point during this process. They are found on the surface of the SiC samples, or on the walls of the furnace. Some of these are intergrown with SiC crystals protruding from the sample-surface, Fig. 1 f) and g). The amount and size of the crystals is proportional to the aluminium content in the initial batch. They exhibit clear spiral and pyramidal features in some areas, Fig. h), confirming that integration in the bulk through the surface is responsible for the growth of these crystals. These compounds are identified as solid-solutions of isostructural, aluminium containing ternary carbides; mainly  $\text{Al}_4\text{SiC}_4$  and/or  $\text{Al}_5\text{C}_3\text{N}$  and minor amounts of  $\text{Al}_4\text{Si}_2\text{C}_5$  and/or  $\text{Al}_6\text{C}_3\text{N}_2$ , consisting of  $\text{Al}_4\text{C}_3$  and SiC layers and  $\text{Al}_4\text{C}_3$  and AlN layers respectively. All the aluminium in the initial batch has gone into these crystals. This implicitly confirms the presence of  $\text{Al}_4\text{C}_3$  and AlN at some point during sintering. The increasing amounts of ternary carbide crystals for increasing aluminium content in the initial batch is facilitated by differences in the aluminium and silicon vapour pressure over these ternary carbides and SiC [3]. Experiments with lower gas-exchange rates in the furnace produced a higher ratio of  $\text{Al}_4\text{Si}_2\text{C}_5$  to  $\text{Al}_4\text{SiC}_4$ , from decomposition of  $\text{Al}_4\text{SiC}_4$  with resulting higher aluminium vapour pressure [4].

As a final verification, an experiment with adding ternary carbide crystals to the initial batch, corresponding to a net aluminium content of 5 at%, yet leaving out the elemental aluminium, showed that the ternary carbides, or the compounds comprising them, are the actual structural promoters in the 4H-SiC recrystallization process. The sample consists of euhedral grains showing abnormal grain growth, Fig. 1 i). From this it is interpreted that integration kinetics is at least as dominant as for 20 at% aluminium content in the initial batch. The enhanced growth is therefore decisively attributed to aluminium containing compounds acting as structural promoters.

- [1] S. Yifeng, W. Ying and Z. Dongyuan, Chem. Soc. Rev. 40, 3854 (2011)
- [2] T. Wolff and H. Friederich, EP 2,597,075 (29 May 2013)
- [3] A. Yamaguchi and S. Zhang, J. Ceram. Soc. Jap. 103, 20 (1995)
- [4] J. Lee, S. Lee T. Nishimura, N. Hirotsaki and H. Tanaka, J. Euro. Ceram. Soc. 29, 3419 (2009)