Current State of the Development of Ceramic Fibers in the System Si-B-N-C

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Introduction

New, high-temperature resistant fibers are required for working temperatures up to 1300 °C. Commercially available fibers in the system Si-C show insufficient properties for this purpose. Thus, the development of new ceramic materials in the quarternary system Si-B-N-C, starting from single-source precursors, was taken on in the 1990´s [1].

On the eve of the new millennium, it was possible to develop ceramic fibers with the empirical composition $SiBN_3C$, showing an extraordinary resistance against crystallization (up to 1800 °C and more), a better oxidation stability in comparison with SiC fibers (due to the formation of an intrinsic double layer), a lower creep rate (BSR test), and a higher stability of their Young´s modulus at high temperatures [2]. However, a running technical process for the manufacture of fibers could not be established yet, primarily due to sensitive processing properties of the polyborosilazane derived from the precursor TADB (constant flow behavior of the polymer melt, etc.).

Precursor Chemistry

To overcome the difficulties in fiber spinning met in the past, an optimization of the rheological properties of the polyborosilazane melts, which would guarantee a stable fiber-spinning process under stationary conditions, was necessary. This was achieved by first using a modified single-source precursor, MADB, which contains a methyl group directly attached to silicon and thus blocking one crosslinking site in the molecule as compared to the formerly used TADB (Figure 1) [3, 4]. In a second step, the thermal conditions of crosslinking were adjusted, yielding polymers which show smooth flow characteristics in the molten state (Newtonian behavior at low shear rates, shear thinning at high shear rates, Figure 2).

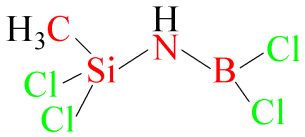

Figure 1. Molecular structure of MADB, showing the characteristic structural unit C-Si-N-B. The formerly used TADB contains one more chlorine atom instead of the methyl group

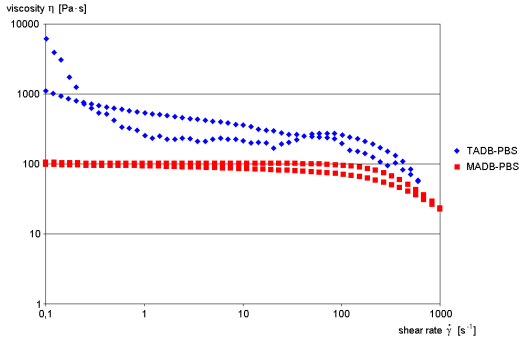

Figure 2. Flow characteristics of PBS polymer melts derived from TADB and MADB, respectively

Fiber Spinning, Curing and Pyrolysis (Laboratory Scale)

Due to the currently available amounts of polymer (~200 g/batch), fiber spinning, curing and pyrolyis are currently performed at a laboratory scale. At this scale, the experimental conditions for fiber spinning (temperature, diameter of the nozzles, draw ratios), curing (curing gas, concentration, time) and pyrolysis (temperature program) are under estimation. Even at this scale, fibers which show promising properties (diameters ranging from 8 to 13 µm, tensile strengths of ~1.3 GPa, Young´s moduli of ~130 GPa, and an oxygen content of < 1 mass-%) could be produced. Figure 3 shows the fracture surfaces of fibers having diameters smaller than10 µm. Considerable further improvements are to be expected when the fibers will be manufactured at a technical scale (see next column).

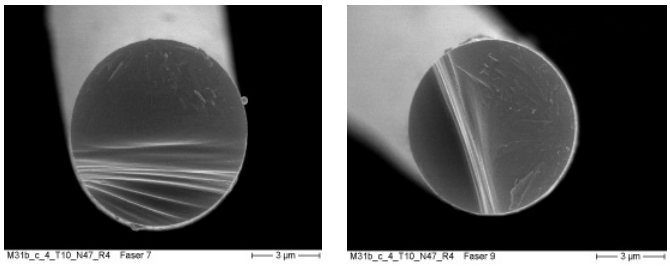

Figure 3. Fracture surfaces of fibers having diameters smaller than 10 µm

Upscaling of the Polymer Synthesis

For a further optimization of the fiber properties, well-defined polymer qualities at a scale of ~25 kg/batch must be available, then enabling a continuous multi-filament spinning process over several hours. Therefore, a pilot plant for the polymer synthesis is currently under construction. Figure 4 shows two of the reaction vessels already installed at Fraunhofer ISC. The installation of the plant is expected to be completed by December 2005, and as soon as early in 2006 it will be put into technical operation. The upscaling of the synthesis is being performed in cooperation with Degussa AG.Table 1 shows the fiber properties which are the goals of our efforts.

Figure 4. Reaction vessels already installed at Fraunhofer ISC

Table 1. Fiber properties aimed at in the current project

fiber diameter	8-13 µm
tensile strength	≥ 2 GPa
Young´s modulus	≥ 200 GPa
oxygen content	≤ 1 mass-%

Conclusions

The development of high-temperature stable fibers in the system Si-B-N-C is still in progress. Using a modified precursor, the processing properties of the polyborosilazane could be significantly improved, and the ceramic fibers obtained therefrom at a laboratory scale already show promising characteristics. A pilot plant for the polymer synthesis at a scale of ~25 kg/batch, which is necessary for a further optimization of the fiber properties, is currently under construction. Its technical operation is planned for 2006.

References

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Acknowledgement

The Bundesministerium für Bildung und Forschung BMBF (German Federal Ministry of Education and Research) is gratefully acknowledged for funding this work.

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degussa.