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Silicon Nitride Carbide Fiber from Spinnable Polymethylsilazanes

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Silicon nitride carbide fiber was prepared from polymethylsilazanes comprizing binary components. The gelatinous polymethylsilazanes obtained from the binary system consisting of commercially available methyltrichlorosilane and dimethyldichlorosilane were remarkably suitable precursors to make the amorphous ceramic fibers.

The purpose of this paper is to describe the preparation and some properties of silicon nitride carbide fibers.

Conventionally, polyorganosilazanes have been prepared by ammonolysis of many kinds of organochloro- or organochlorohydrosilanes in a single component system.1-3)

In this work, the spinnable polymethylsilazanes were prepared according to the previous paper4) describing the preparative procedures in detail. At first, the methylsilazanes were prepared by co-ammonolysis of a commercially available $MeSiCl_3/Me_2SiCl_2$ mixture with molar ratios of 2.0 - 3.0 in diethylether-liq. ammonia solution.

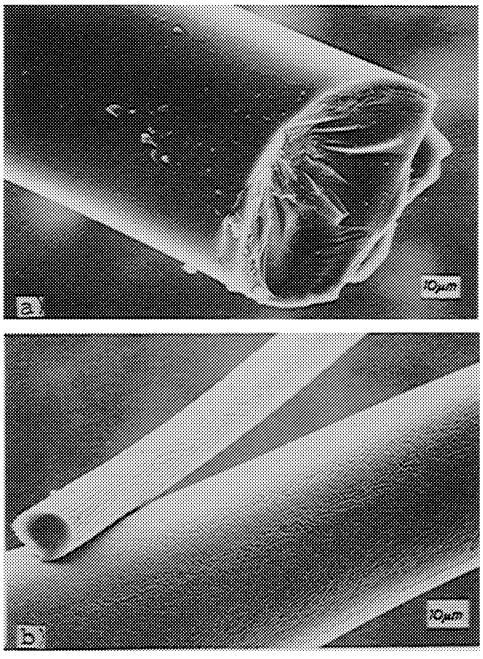

Fig.1. Electron Micrography of Silicon Nitride Carbide Fibers Heat-treated at 800 °C(a) and 1000 °C(b).

Molecular weight of the methylsilazanes increased merely upon standing at room temperature without use of any catalysts, owing to their self-condensation character, and further increased by heating to about 50 - 100 °C for 40 to 50 h. In this way, the methylsilazanes were moderately convertible into the gelatinous polymethylsilazanes.

Under dried atmosphere, the gelatinous polymethylsilazanes could be easily spun into fiber by pulling up the glass rod inserted into them. The diameter of the obtained fibrous gel was in 30 - 100 µm. The fibrous gel was then after-cured to make them infusible by standing at room temperature for 20 to 100 h in a nitrogen atmosphere. The resulted fibrous gel was elastic and translucent. The after-cured fibrous gel was converted into the ceramic fibers merely on heating (heating rate being 2 °C/min) to 800 or 1000 °C and keeping at the temperature for 2 h in nitrogen. As shown in Fig.1, the surface of the fibers was nearly smooth but showed somewhat wrinkling caused by shrinkage.

During the heating process up to 800 °C, the fibrous gel lost its weight. In the case of the gelatinous polysilazanes of molecular weight of 800 which were after-cured for 20 h, 38% loss was observed, while 31% loss was noticed for polysilazanes of molecular weight of 1300 which were after-cured for 100 h. The weight loss of the after-cured fibrous gel proceeded stepwise but was hardly observed over 800 °C. From the results of the weight loss and gaschromatography, it was confirmed that large amounts of weight loss below 400 °C are mainly due to the evolution of ammonia and the loss at 600 to 700 °C are of methane as well as ammonia.

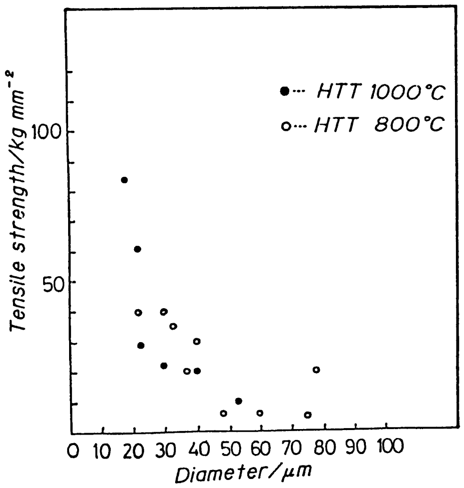

Fig.2. Tensile Strength of the Fibers to the Diameter (heat-treated to 800 °C and 1000 °C).

The tensile strength was measured on the fibers prepared at 800 and 1000 °C. The relation of the tensile strength to the diameter of the fibers was shown in Fig.2. Now, the values of the tensile strength are widespread, and show a tendency to increase with decreasing of the fiber diameters. The maximum value is 100 kg/mm^2, and it is fully expected to prepare a stronger fiber by improvement of a spinning technique.

The values of the density of the fibers prepared by heat-treatment at 800 and 1000 °C gave 2.1(g/cm^3) in both cases.

Elemental analysis of the fibers prepared at 800 °C showed silicon(51.6%), nitrogen (14.8%) and carbon (8.9%), and the fibers at 1000 °C, 51.1%, 17.1%, and 10.6% respectively.

One of the most characteristic features of these fibers is that the fibers are amorphous and show thermal stability. Even in the fibers prepared at 1400 °C, a crystalline state did not appear in their XRD profiles.

The following conclusions are drawn from the present results:
1) The combination of methyltrichlorosilane and dimethyldichlorosilane is favorable as the precursors to ceramic fiber. 2) The Si-N and Si-C bondings originally existed in the precursor materials were still inherited in the ceramic fibers.
3) The amorphous structure of the ceramic fibers were kept at least up to 1400 °C.
4) The use of commercial methylchlorosilanes as the starting materials seems more advantageous than that of organochlorohydrosilanes by their moderate availability together with commercially reasonable cost.

References

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