CHEMISTRY LETTERS, pp. 551-554, 1976. Published by the Chemical Society of Japan

SIMPLE SYNTHESIS OF THE CONTINUOUS SiC FIBER WITH HIGH TENSILE STRENGTH

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A polycarbosilane, the starting material of β-SiC fibers, was prepared without autoclave. The new method is simple and more economical than the previous one. Furthermore, a great number of bundles of SiC fibers were obtained by way of oxidative reactions of polycarbosilane fibers.

A continuous SiC fiber with high tensile strength was already prepared from an organosilicon polymer.$^{1,2)}$ The synthetic method was as follows. Metallic lithium is allowed to react with dimethyldichlorosilane as the starting material, to dechlorinate the dimethyldichlorosilane and hence to produce dodecamethylcyclohexasilane. The dodecamethylcyclohexasilane is purified by means of recrystallization and sublimation. It is heated at 400°C for 48 hr in an autoclave; the product is polycarbosilane. Its low-molecular-weight portion is removed by acetone fractionation, resulting in the average molecular weight of about 1000∿2000. Polycarbosilane is dissolved in benzene or xylene to have the viscous substance. It is spun into fibers by dry spinning. The fiber is heated up to 1300°C or 1500°C in vacuum at the rate of 100°C/hr to remove the organic groups. The heat-treated product is a continuous SiC fiber with high tensile strength.

The above method, however, was revealed to be technically difficult, expensive and time-consuming in chemical reaction, because of the following criteria; i.e., usage of lithium metal, autoclave, acetone fractionation, and dry spinning. To remove these difficulties, a simple procedure as follows was contrived. A three-necked flask was equipped with a reflux condenser, a dropping funnel, a stirring rod and an argon-gas inlet. Xylene and metallic sodium were introduced into the flask, and the liquid surface was covered with an argon gas. Dimethyldichlorosilane was placed in the stopping funnel. And, the flask was heated, while being refluxed. The metallic sodium thus melts, staying at bottom of the flask. Stirring the liquid in the flask, dimethyldichlorosilane was dropped from the funnel. It was dechlorinated by the molten sodium, resulting in the precipitate of polydimethylsilanes of a chain with about 55 Si atoms.$^{3)}$ After completion of the reaction, the polysilane was removed by filtration. The sodium attaching to the polydimethylsilane was removed by means of the reaction with methyl alcohol. It was washed with water and dried; the product was pure polysilane. The polysilane (100g) was then placed in a two-necked silica tube as the reaction vessel, which was equipped with a reflux condenser and the inlet of an argon gas. After replacing the air with argon, the polydimethylsilane was heated to 320°C in an electric furnace and converted to a liquid state. The liquid was refluxed for 5 hr and then heated up to 470°C, to remove volatile materials. Upon cooling to room temperature, highly viscous products were taken out from the silica tube as a n-hexane solution. The solution was filtered and concentrated at reduced pressure, and then heated in vacuum above 200°C for 2 hr to remove the low molecular weight components. The substance thus obtained was polycarbosilane (35g), as indicated by its infrared absorption spectrum (B) and that of a polycarbosilane sample obtained by the previous method (A) in Fig.1. The molecular weight distribution of polycarbosilane measured by a fractional solution method is shown in Fig.2; the average molecular weight was about 948.

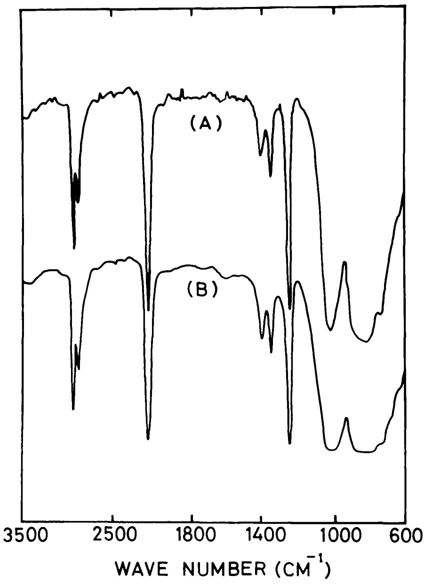


Fig.1 IR spectra of polycarbosilane

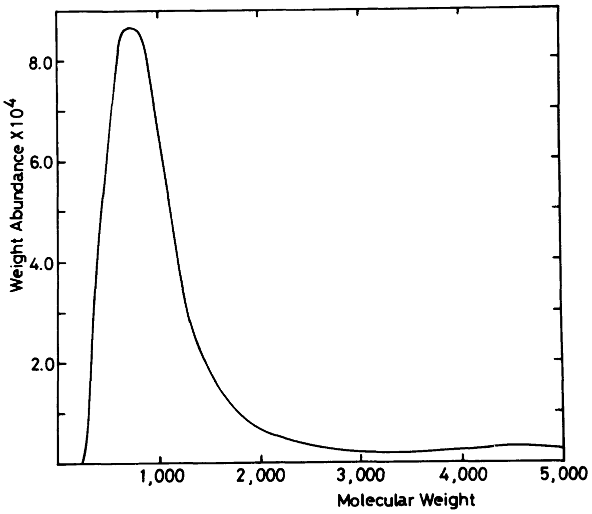


Fig.2 Molecular weight distribution curve of polycarbosilane

This synthetic method of polycarbosilane is very simple and economical. Polycarbosilane as the melt was spun into the fiber, unlike the previous case of dry spinning.[1)] A bundle of the fibers was heated up to about 200°C in the air to produce a thin silicate film over surface of the fiber; 20° to 150°C for 2.5 hr, 150° to 180°C for 30 minutes, 180°C for 30 minutes. This is conducted to protect the fibers from melting in a latter process. The bundle was then heated up to 1300°C in a vacuum at the rate of 100°C/hr and held at 1300°C for 1 hr, in order to remove the organic groups; the product was the continuous SiC fibers.

Figure 3 shows schematically the present method of synthesizing the SiC fiber and the previous one.[1,2] X-ray diffraction patterns of the SiC fiber resulting from its heat treatment up to 1300°C by the modified method approached to that of β-SiC, as in the case of the previous method.[2] Figure 4 is the relation between tensile strength and Young's modulus, on one hand, and the diameter, on the other, for a SiC fiber.

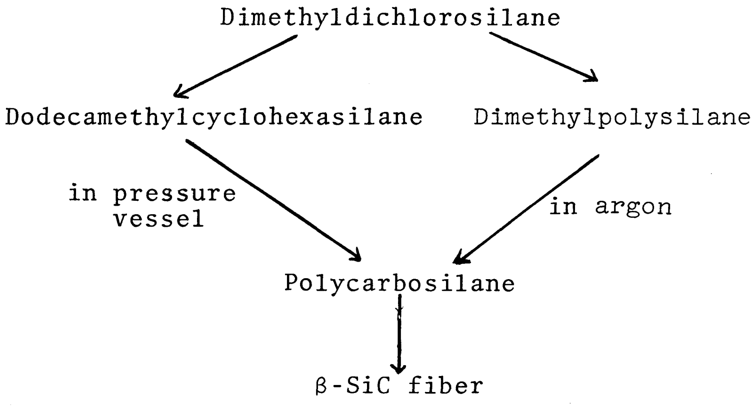


Fig.3 The synthetic method of β-SiC fiber

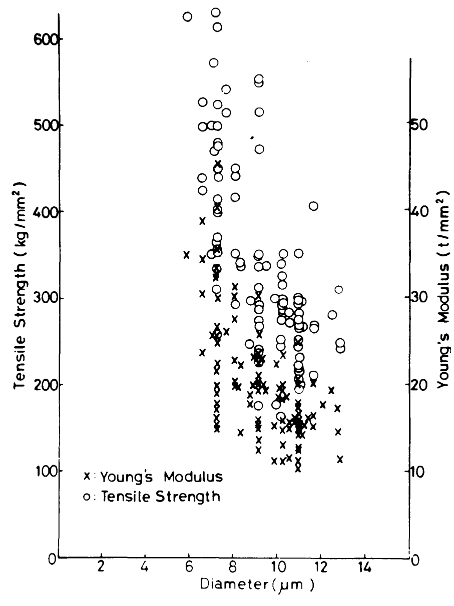
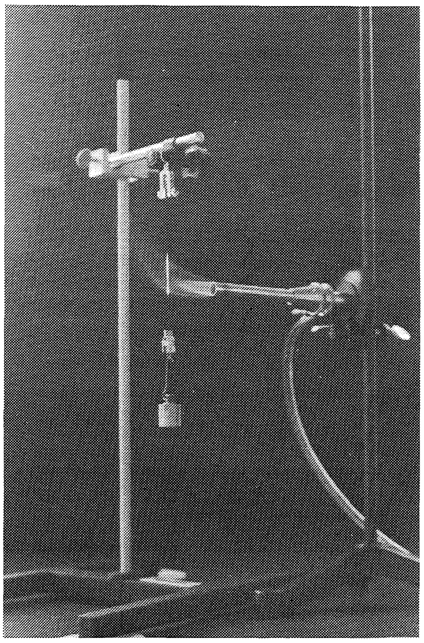


Fig.4 Tensile strength and Young's modulus of SiC fiber



Fing.5 Thermostability of SiC fiber

The fiber produced was extremely heat resistant. As shown in Fig. 5, subjected to tensile stress about 200 kg/mm^2 at about 1250°C of the burner flame, the SiC fiber did not break off for three days. The SiC fiber newly developed can be incorporated with a variety of metals, giving the promising fiber reinforced metals.

It is possible to produce the continuous SiC fiber in industry. Figure 6 illustrates this possibility. Polycarbosilane fibers are rolled continuously on reels. These are then cut to appropriate length later, and then heated up to 1300°C. Figure 7 shows the β-SiC fibers produced in quantity in this manner.

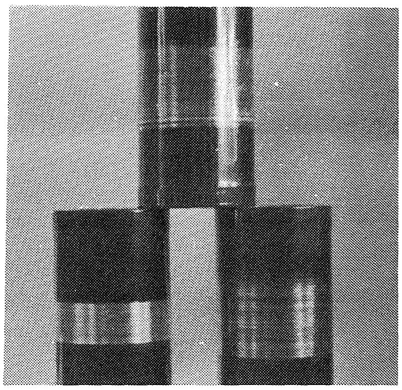


Fig.6 Polycarbosilane fibers spun industrially

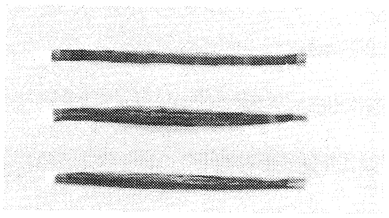


Fig.7 Continuous SiC fiber obtained by the heat-treatment of polycarbosilane fiber

References

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(Received March 22, 1976)