

THE PRODUCTION OF SILICON INCLUDED VAPOR GROWN CARBON FIBERS USING THE LIQUID PULSE INJECTION TECHNIQUE

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Introduction

Vapor grown carbon fibers (abbreviated to VGCFs) grow through a combined process of catalysis and thermal chemical vapor deposition (CVD). First, thin primary fibers grow through the catalysis of ultra-fine metal particles (*e.g.* iron). These fibers thicken as pyrolytic carbon layers deposit on the outer surfaces of them. Previously we reported that benzene is the dominant hydrocarbon which contributes to the elongation process [1]. On the other hand, various hydrocarbons, as well as other chemical substances are expected to contribute to the CVD thickening process. Therefore, there is a high possibility to easily include hetero atoms into the structure of VGCFs using a gaseous mixture of benzene and another compound which includes a hetero atom.

In this work, we attempted to include silicon into the structure of VGCFs by simply growing them from a mixture of benzene and a silicon compound using the liquid pulse injection technique, a new method developed by the authors [1-4]. This technique not only allows the rapid elongation of VGCFs, but also a high thickening rate. Fibers as long as 50 mm with diameters over 10 μm can be obtained from benzene within 30 s by employing this new technique. Silicon included fibers are expected to possess high oxidation resistivities. They may also have a high lithium ion capacity when used as the anode material of lithium ion secondary batteries [5].

Experimental

Silicon included fibers were produced using the same apparatus and experimental procedures reported in our previous reports [2-5]. Mixtures of benzene and phenyl silane were used as the fiber source. The concentration of phenyl silane was varied in the range from 5 to 20 wt%. The flow rate of the fiber source was fixed at 0.05 $\text{cm}^3 \text{min}^{-1}$. A 10 wt% benzene solution of ferrocene was used as the catalyst source. The amount of catalyst source injection was 0.02 cm^3 . The temperatures of the

gases in the preheating and reaction zones were 800 °C and 1100 °C, respectively. The flow rate of the carrier gas (hydrogen) was 60 $\text{cm}^3\text{-NTP min}^{-1}$. Experiments were conducted for 3 min. The obtained fibers were characterized by measuring their oxidation resistivities, tensile strengths and electrical resistivities.

Results and Discussion

Fibers were successfully obtained when the concentration of phenyl silane in the fiber source was 5 wt%. However, at higher concentrations, fibers were hardly obtained. It is clear that silicon reduces the catalytic activity of ultra-fine iron particles. In fact, the maximum length of fibers obtained at a phenyl silane concentration of 5 wt% was 20 mm, which is quite short when compared with the maximum length of 50 mm obtained when pure benzene was used as the fiber source. The carbon yield of the obtained fibers, which was calculated by dividing the amount of carbon in the obtained fibers by the amount of carbon included in the fiber source, was 0.23. Typical yields obtained when pure benzene was used as the fiber source were in the range 0.2 to 0.3, indicating that the mixing of silicon compounds in the fiber source does not decrease the productivity of the fibers.

Figure 1 shows the transient change of the weight loss of the fibers due to gasification in an air atmosphere, where W/W_0 is the relative weight of the fibers, and T temperature. That of fibers obtained from benzene is also shown for comparison. The rates of temperature increment in both experimental runs were 5 °C min^{-1} . The oxidation resistivity of the fibers increased approximately 100 °C by including silicon in the fibers. From the weight loss of the fibers, the Si/C ratio of the obtained fibers was calculated as 0.027, assuming that the fiber residue was silica. Such a small amount of silicon drastically improves the oxidation resistivities of the fibers. This value is higher than that of the fiber source, which is 0.014.

Figure 2 shows the tensile strengths (σ) of the silicon

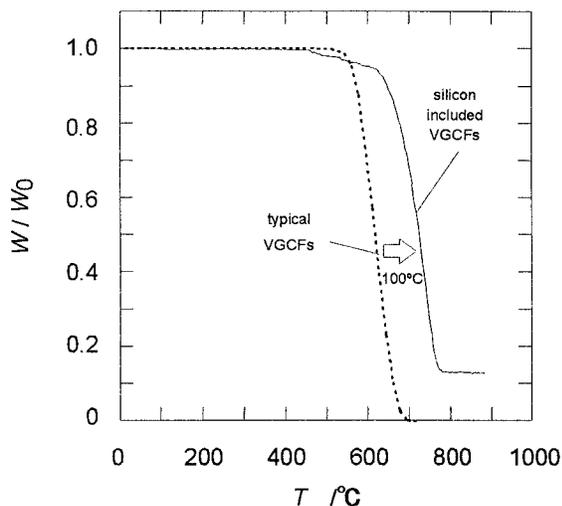


Fig. 1 Oxidation Resistivities of the Obtained Fibers

included fibers plotted against their diameters (d). Those of fibers obtained from pure benzene are also shown for comparison. No significant difference between the fibers obtained from different sources can be observed, indicating that the inclusion of silicon does not alter the mechanical properties of the fibers.

Figure 3 shows the electrical resistivities of the silicon included fibers and those of fibers obtained from pure benzene, where ρ is the electrical resistivity of the fibers, and d diameter. As silicon and silicon carbide are semiconductors, it was expected that the electrical resistivities of the fibers would increase due to silicon inclusion. However, against this expectation, the electrical resistivities of the fibers decreased.

The above results show that it is possible to improve the oxidation resistivities and electrical conductivities of VGCFs without altering its mechanical properties, by including a small amount of silicon in them.

Conclusion

The oxidation resistivities and the electrical conductivities of VGCFs were improved by including a small amount of silicon in them. This inclusion can be easily achieved using the newly developed liquid pulse injection technique, by simply mixing phenyl silane into the carbon source (benzene) of the fibers.

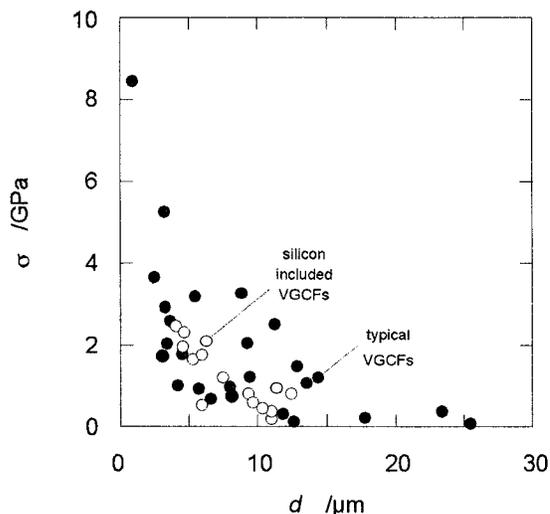


Fig. 2 Tensile Strengths of the Obtained Fibers

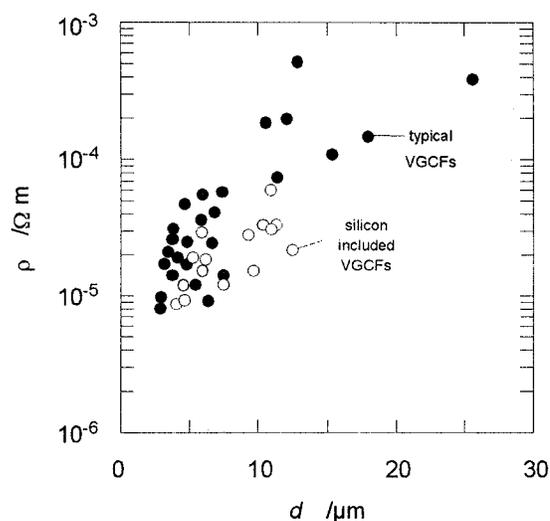


Fig. 3 Electrical Resistivities of the Obtained Fibers

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