POSTER

PREPARATION OF VAPOR GROWN CARBON FIBRES BY FLOATING CATALYST METHOD

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Introduction

Vapor grown carbon fibres (VGCFs), prepared by chemical vapor deposition of hydrocarbons in the presence of transition metal catalyst, have unique structure and excellent performance, and can be used in many fields, especially as the composite reinforcing agent for metal, plastics and ceramics etc .

Two methods for forming VGCFs have been developed: seeding catalysts on a substrate[1] and floating catalysts in a reaction space[2]. Although VGCFs formed by the floating catalysts method usually had a much smaller diameter and shorter length, it is possible to significantly reduce the production cost of "discontinuous" carbon fibres, and it thought to be promising for an industrial process of forming VGCFs. Matsubara et al [3] reported the effects of operation conditions by floating catalysts method in Linz-Donawitz converter gas. Some studies on the formation, properties and application of VGCFs have been reviewed[4]. In this paper, VGCFs were manufactured by floating catalysts method using benzene as the carbon source. Some preparation conditions for fibre growth were investigated, the morphologies of VGCFs were studied by SEM, TEM and XRD, and the influences of preparation conditions on the properties of VGCFs were also discussed.

Experimental

The experimental apparatus for preparing VGCFs is shown in Fig.1. A quartz tube (inner diameter 50mm, length 1500mm) was used as a reactor, which was installed in a vertical electric furnace (1000mm in height) and used a vessel tank as a collector for the formed VGCFs. After heating the reactor up to 800 ℃, argon was replaced with hydrogen. When the reaction temperature was raised to 1050-1250 ℃, a benzene solution with dissolved ferrocene and thiophene was introduced into a region of about 680 ℃at a constant rate and the reaction was started, then carried out for 30 minutes.

The VGCFs formed were recovered from the collector and then treated with supersonic cleaner in a certain solvent where fibres can be separated from soot. The carbon fibre yield was calculated from the mass of VGCFs dividing by that of carbon in the benzene solution.

Results and Discussion

1. Influences of experimental conditions

1.1. Ferrocene concentration

Fig.2 shows a plot of VGCFs yield against the ferrocene concentration. From Fig.2, the VGCFs yield increased with the increase of ferrocene content in the range of 0-0.05 g/ml. Further addition (>0.06g/ml) of ferrocene resulted in a decrease of the yield with the highest yield about 49% at the ratio of 0.05g/ml. If the catalyst concentration is much too high, the particles formed by ferrocene decomposition will coagulate into large agglomerates and lose the catalytic activity. However, if much too low, carbon fibres are not formed because the particles could not aggregate the minimum size (5nm) required for formingVGCFs.

1.2. Thiophene concentration

Fig.3 illustrated the effect of the atomic ratios of sulfur in thiophene to iron in catalyst on the yield of VGCFs. Without sulfur in the feedstock, a few fibres were mixed with much soot, while adding small quantities of sulfur to the feedstock, the yield of VGCFs was rapidly increased. The highest yield of VGCFs amounted to 42%. With continual increase of the sulfur ratio, the yield of VGCFs was basically at a constant. However, the SEM showed that continual increase in sulfur, the fibres exhibit a larger diameter and a shorter length, implying the decrease of quality of VGCFs. It is because small amounts of sulfur in iron liquefies the particles, enhancing the ratio of filament nucleation and enabling Vapor-Liquid-Solid process. But, excess sulfur in the catalyst particles would result in the saturation of the iron coating and the increase of sulfur concentration in the particles, producing lower-quality fibres.

1.3. Feedstock flow rate

Fig.4 indicated the effect of the flow rate of benzene-ferrocene-thiophene on VGCFs yield. The optimum flow rate is about 0.05ml/min. with the highest yield of about 46%. If the feedstock flows so slowly that the vapor partial pressure of benzene solution is below its saturation, it will quickly evaporate and the ferrocene deposite on the wall of reactor, so the VGCFs are formed on the wall in seeding substrate method. When the flow rate is so high that the concentration of its vapor in the gas phase would be above saturation, the nozzle for the injection of benzene solution rapidly cools and causes soot formation, which may block up the reactor.

2. Properties of VGCFs

In this study, fibres of length of 50-500 μm, and diameter of 0.01-0.1μm were produced by the floating method under proper conditions. The SEM photographs show that the texture of VGCFs are various, besides the straight type, the meandering, branched and beady type fibres were also obtained depending on the different conditions. Fig.5 shows the typical micrograph of the VGCFs. TEM indicate that there are iron particles at the tip of VGCFs. By graphitization at 2800 ℃, the VGCFs change to a single crystal-like graphite by the observation of XRD, exhibiting its high graphitizability.

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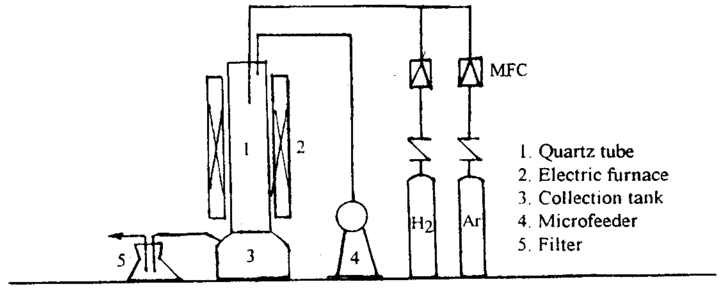

Fig. 1 Schematic diagram of the apparatus for preparing VGCFs

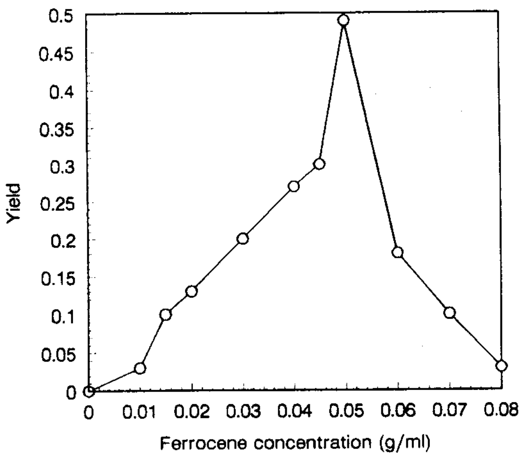

Fig.2 A plot of VGCFs yield against the Ferrocene concentration

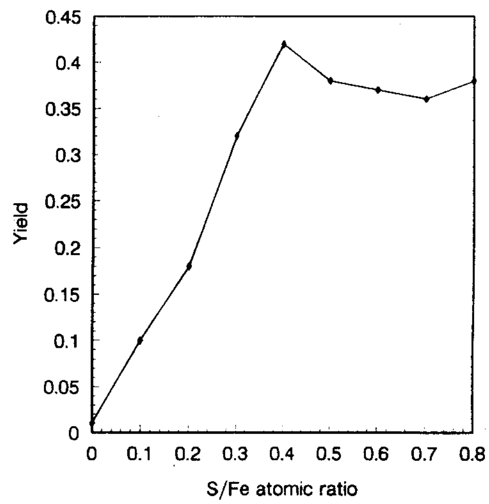

Fig.3 The effect of concentration of sulfur on VGCFs yield at 1150°C

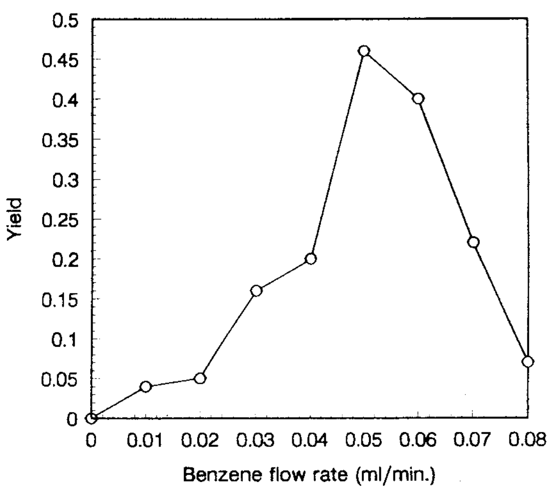

Fig.4 The effect of flow rate of benzene on the yield of VGCFs at 1200°C

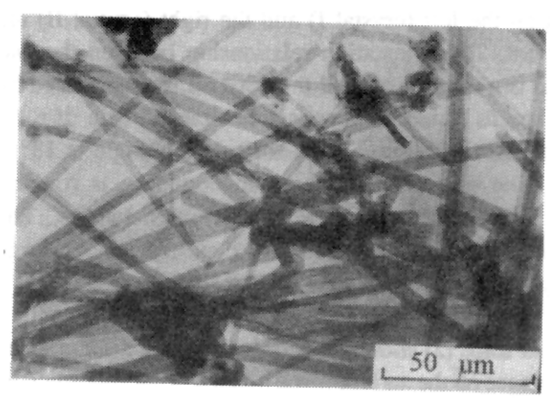

Fig.5 The micrograph of VGCFs