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Optical diagnostics of fullerene synthesis in the RF thermal plasma process

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Abstract: In this work, the results of an optical emission study of fullerene synthesis in an inductively coupled radio frequency thermal plasma reactor are presented. The emission spectroscopy studies, based on the use of the Swan C_2 (0,1) and CN (0,0) vibrational emission spectra, were carried out to determine the plasma temperature. The evaporation process of graphite powder was observed by scanning electron microscopy.

Keywords: fullerene, otpical emission study, scanning electron microscopy.

INTRODUCTION

Fullerene molecules exhibit a wide range of novel phenomena, with a variety of exciting potential applications in various field. Until now, fullerenes have mostly been synthesized in an arc reactor in an inert gas atmosphere.[1] Only a few articles have been reported about the formation of fullerene in an RF thermal plasma reactor.[2,3] However, this method has certain advantages over the arc discharge method: the residence time of the species generated in the RF thermal plasma is much longer than in an arc plasma and more voluminous plasma flames are formed compared to arc plasma.[4]

Carbon vaporization was achieved through the evaporation of graphite powder introduced into an argon/helium plasma and the fullerene products were incorporated in the soot collected on the walls of the reactor. Optical emission measurements can give information about the parameters significant to fullerene synthesis: carbon concentration, plasma velocity and plasma temperature.

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The aim of this work was to determine the temperature of the species generated in an RF thermal plasma and to explain the evaporation process of the graphite powder injected into the plasma with the goal of determining their effect on the yield of fullerene. The C_2 radical plays an important role in the synthesis of new materials; therefore, the quantitative study of these radicals produced in an FR plasma is of great interest.

EXPERIMENTAL

Synthetic graphite powder (Aldrich) having mean particle size of 17 μm with size distribution in the range of 1 to 70 μm, and purity of 99.7 % was subjected to thermal plasma treatment at atmospheric pressure. Argon was used as the sheath gas (40 slpm). The plasma gas consisted of different mixtures of argon (> 99.95 %) and helium (>99.96 %) with a total flow rate of 15–21 slpm. The carrier gas (2–10 slpm) was helium. The RF power was produced by a generator operating at 3–5 MHz. The plate power of 27 kW was inductively coupled to a TEKNA PL-35 torch which was connected to a water cooled plasma reactor, cyclone and dust filter. The graphite powder was injected axially, onto the top of the plasma flame at a feed rate of 90 to 468 g h^{-1}. A scheme of the experimental set-up was presented previously.[4]

The emitted light was observed perpendicularly to the axis of plasma flame. The emission of the inert and carbon plasma was detected through a quartz glass window at a distance of 10 cm below the tip of the feeding nozzle. The wavelength was selected by a 55 cm focal length monochromator (medium resolution monochromator, TRIAX 550 Jobin-Yvon). A holographic grating with 1200 grooves/mm was used. The reciprocal dispersion was 1.55 nm/mm. Light was collected and transferred to the entrance slit (6 μm) by a multilegged fibre bundle. The exposure time varied in the range of 2 to 20 ms. Plasma emission was detected by an optical multichannel analyser (CCD-300, 1024 × 256 pixels). Operation of the spectrormeter arrangement and the processing of spectra was controlled by computer.

Changes in the morphology of the graphite powder due to plasma treatment were observed by SEM (JOEL JSN50A). SEM analysis was used to study the efficiency of graphite evaporation.

RESULTS AND DISCUSSION

Based on the kinetic model of fullerene formation developed previously,[5] it is possible determine the main parameters in fullerene synthesis: carbon concentration, velocity of gases from the inert heat bath, axis temperature and temperature gradient between the RF plasma and the chamber walls. According to the proposed kinetic model of fullerene formation, the fullerene yield Y has been described by the following equation:

$$Y = f(X) \tag{1}$$

where

$$X = k \frac{N_c \sqrt{T_0}}{V} r \tag{2}$$

In Eq. (2), N_c represents the carbon concentration in the plasma flame, V is the mean velocity of the plasma gases in the flame region, T_0 is the maximum plasma temperature, r represents the distance between the point of maximum temperature

and the observation point and *k* is a constant determined by the mass and radius of the carbon atom. During the synthesis of fullerene in the RF thermal plasma reactor, the effects of the carbon concentration, the mean velocity of the gases and the temperature in the plasma flame on the yield of fullerene were determined.

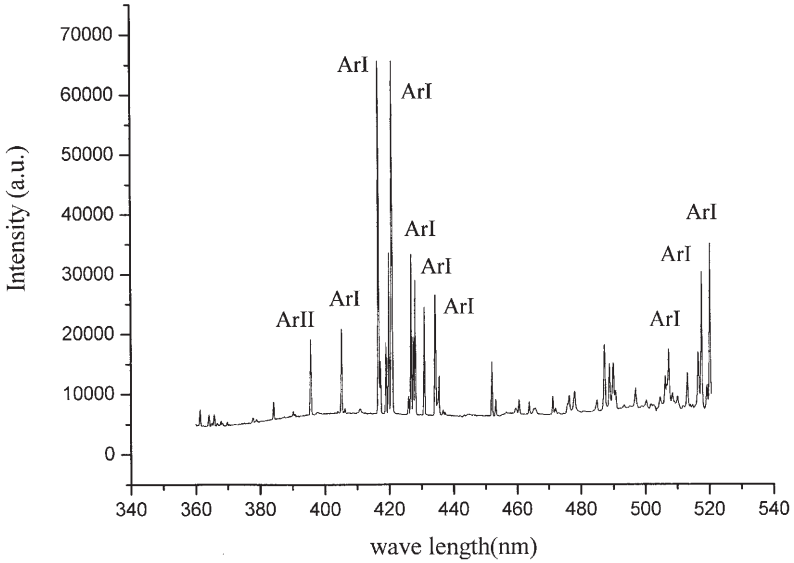

Fig. 1. Optical emission spectrum of the species generated in the plasma before introducing graphite powder into the RF plasma reactor.

The emission spectrum of the argon plasma before introducing the graphite powder into the RF thermal plasma reactor is presented in Fig. 1. Only atom and ion lines of argon (Ar I and Ar II) can be detected in the spectrum before the introduction of graphite powder. After the graphite powder had been injected into the reactor, the molecular bands of C_2 and CN radicals can be observed in the spectrum: two vibrational sequences with bandheads at 388.3 nm ($\Delta\upsilon = 0$) and 421.6 nm ($\Delta\upsilon = -1$) belonging to the Violet system ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) of CN and three vibrational sequences with bandheads at 516.6 nm (($\Delta\upsilon = 0$), 473.7 nm (($\Delta\upsilon = 1$), and 438.2 nm ($\Delta\upsilon = 2$) corresponding to the Swan bands of C_2 (Fig. 2).

The presence of CN molecular bands in the recoded spectrum can be explained by the impurity of the argon sheath gas. Although the argon purity was better than 99.95 %, the formation of CN radicals was possible because of the high flow rate of the sheath gas. The intensity of the selected CN molecular band was higher than the selected C_2 molecular bands. When the fullerene yield was the greatest (4.1 %), the intensity of C_2 radicals was higher than the intensity of CN radicals.

The vibrational temperatures of C_2 and CN radicals were determined using the Boltzmann plot method. On varying the feed rate (90 – 468 g h^{-1}), the vibrational temperature of the C_2 radicals was nearly constant (4800 – 5000 K). The vibra-

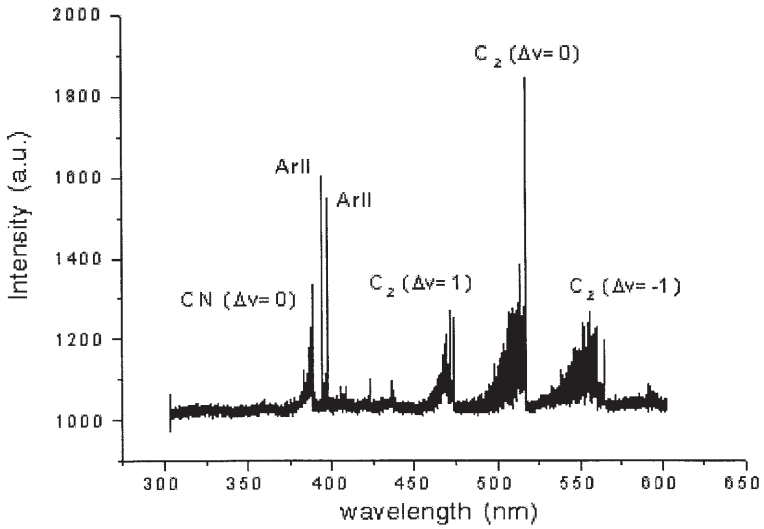

Fig. 2. Optical emission spectrum of the species generated in the RF plasma after introducing graphite powder into the RF plasma reactor.

tional temperature of the CN radicals was in the range of 5100 –7200 K. The temperature of the CN radicals was always higher than the temperature of the C_2 radicals. Thus, there was no thermal equilibrium in the plasma. The radio of the intensities of the C_2 and CN emission bands positioned at 473.7 nm and 388.3 nm, respctively, is represented as $I(C_2)/I(CN)$. The value of $I(C_2)/I(CN)$ generally increased with increasing concentration of helium in the argon plasma gas due to the higher heat conductivity of helium. Consequently, the graphite powder is heated and evaporated much faster in helium than in argon.[6] It is known that C_2 is the basic building block of fullerenes. Increased concentrations of C_2 produces more favourable experimental conditions for fullerene synthesis.

The gas temperature in the plasma observation region corresponds to the rotational temperature of the CN radicals, since only 10 collisions are required to achieve translational-rotational equilibrium. In order to achieve thermal equilibrium among the vibrational and translational population of the CN radicals, at least 1000 collisions with inert atoms must occur.[7] These conditions are easily achieved in an RF plasma at atmospheric pressure, because only a few μs are required for the thermalization of the CN radicals and inert atoms. The rotational temperature of the CN radicals was obtained by comapring the experimental and simulated spectra of CN radicals. The vibrational sequences with $\Delta\upsilon = 0$ ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) for the violet band were selected to simulate the emission spectra. Comparision of the experimental and simulated spectra of CN molecules has performed by the LIFBASE program.[8] The best agreement between the mentioned spectra of the CN radicals could be obtained when the rotational temperature was equal to the vibrational one (thermal population).

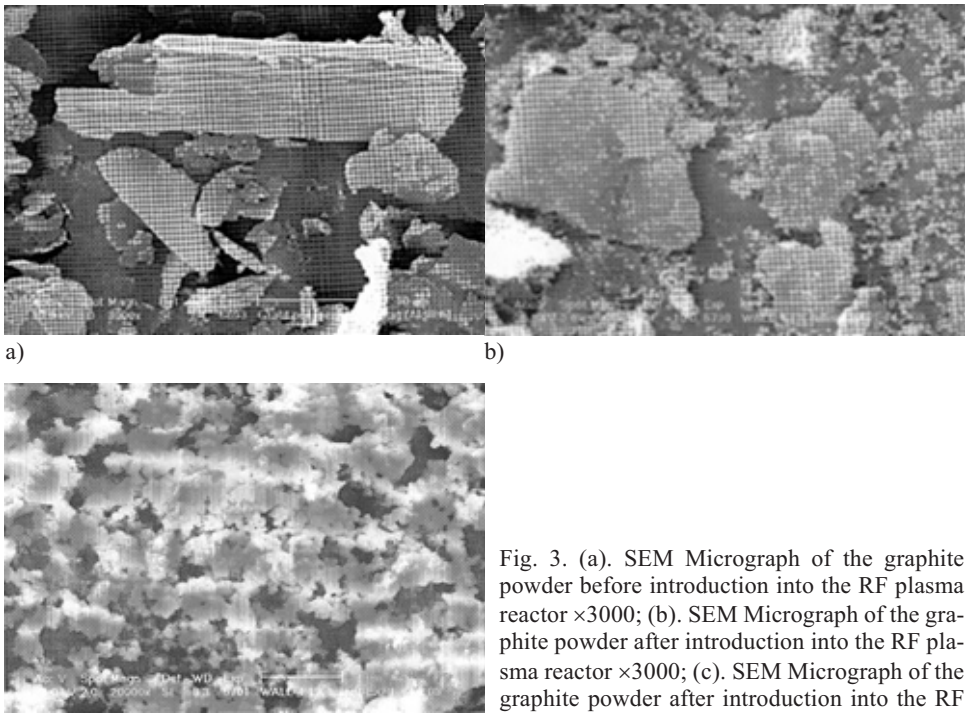

Fig. 3. (a). SEM Micrograph of the graphite powder before introduction into the RF plasma reactor ×3000; (b). SEM Micrograph of the graphite powder after introduction into the RF plasma reactor ×3000; (c). SEM Micrograph of the graphite powder after introduction into the RF plasma reactor ×20000.

SEM analysis enabled the observation of the graphite evaporation process. In Figs. 3 (a, b and c), the graphite powder before and after plasma treatment can be seen. The graphite particles having a mean diameter above 10 μm did not evaporate even under the optimum experimental conditions (feed rate 156 g h^{-1}, He/Ar = 33.67 %), as can be seen in Fig. 3b. In the case of the fullerene soot (Fig. 3c), the structure are quite different and look "amorphous" and the aggregates have a characteristic "round" shape. The observed structures in this case were very similar to those obtained using the arc process, as described in the literature.[9]

The influence of the carbon concentration, rotational temperature of the CN radicals and the velocity, υ, of the plasma flame ($N_c T_{rot}^{0.5}/\upsilon$) on the yeld of fullerene is presented in Fig. 4. As can be seen, the fullerene yield is a linear function of the product of the carbon concentration, the rotational temperature of the CN radicals and the velocity of the plasma flame. This result is in agreement with the proposed kinetic model of fullerene formation mentioned previously. The evaluation of the carbon concentration was based on the feed rate of the graphite powder and the degree of evaporation of the graphite powder. The degree of evaporation of the graphite powder was evaluated by analysis of the SEM micrographs. The area under tho non-evaporated particles was compared with the total area of all particles by software especially developed for the analysis of SEM micrographs.[10] The

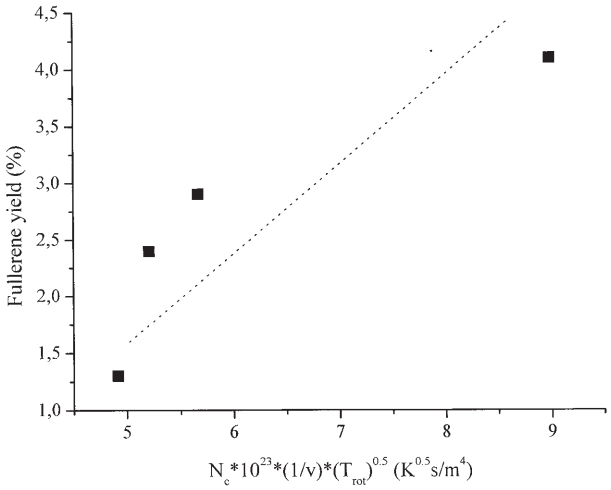

Fig. 4. Fullerene yield as a function of the product of $N_c(1/\upsilon)\ (T_{rot})^{0.5}\ 10^{23}$.

fullerene yield has a maximum value (4.1 %) when the mean velocity of the gases in the plasma flame was $\upsilon = 12.736$ m s^{-1} with a carbon concentration N_c of 1.348×10^{23} m^{-3}. The temperature of the CN radicals in this case was 7200 K. The gas velocity increased when the feed rate of graphite was increased. In this experiment, the fullerene yield had a maximum value when the graphite feed rate was 156 g h^{-1}. At this moment, the graphite evaporation is the largest but not complete as can be seen in the SEM micrograph – Fig. 3b. For higher feed rate (468 g h^{-1}), there were no C_2 molecular bands in the recorded spectra. Thus, the evaporation of the graphite was quite small and the content of fullerene in the soot was very small (0.05 %).

CONCLUSION

The standard arc process being applied for the production of fullerene allows the production of a soot with a high fullerene yield. Unfortunately, this process is not adaptable for the bulk production of fullerenes on an industrial scale; the main limitations are: high jet velocity from the interelectrode space and a low residence time of the generated species in the inert heat bath with dimensions determined by the temperature gradient.

To overcome these limitations, a new original plasma process for fullerene production is under development. The process consists of treating graphite powders using thermal plasma flow.

The obtained results show that the jet velocity of plasma flame and the carbon concentration have a significant influence on the yield of fullerene. The emissions of C_2 and CN radicals were used to determine the vibrational and rotational temperature. It was found that the system was not in a state of thermodynamic equilibrium. SEM analysis showed that even for the optimum fullerene yield (156 g h^{-1}), the evaporation of the used graphite powder was not quite complete. Based on the

obtained fullerene production (6.4 g h^{-1}) it can be concluded that this method for fullerene synthesis has good perspectives.

ИЗВОД

ПРОУЧАВАЊЕ ПРОЦЕСА СИНТЕЗЕ ФУЛЕРЕНА У РАДИОФРЕКВЕНТНОМ РЕКАТОРУ МЕТОДОМ ОПТИЧКЕ СПЕКТРОСКОПИЈЕ

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У раду су приказани резултати проучавања процеса синтезе фулерена у радиофреквентном плазма реактору методом оптичке спектроскопије. Помоћу снимљених вибрационих спектара C_2 и CN радикала одређена је температура плазме. Сканирајућа електронска микроскопија је коришћена за проучавање процеса испаравања коришћеног графитног праха. На основу анализе резултата, утврђене су вредности концентрације угљеничне паре, брзине и средње температуре плазме које одређују ефикасност синтезе фулерена.

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