UDK 621.762:621.039.524
Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 38(6)299(2004)

SYNTHESIS OF FULLERENES IN RF THERMAL PLASMA REACTOR

SINTEZA FULERENOV V RF TERMIČNEM PLAZEMSKEM REAKTORJU

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Prejem rokopisa – received: 2004-09-27; sprejem za objavo – accepted for publication: 2004-11-29

The process of fullerene formation in RF thermal plasma reactor has been studied in this work. Several graphite powders have been used as starting material. The influence of cohesive nature of graphite powders on fullerene synthesis in RF reactors has been considered. We have found that the cohesive nature of micrometer sized graphite powders impedes efficient evaporation and transformation into fullerenes.

Keywords: fullerene, RF plasma, SEM analysis

Raziskan je bil proces nastanka fulerenov v RF termičnem plazemskem reaktorju. Kot izhodni material so bili uporabljeni različni ogljikovi prahovi. Upoštevana je bila kohezijska narava grafitnih prahov pri sintezi fulerenov. Ugotovljeno je bilo, da kohezivna narava grafitnih prahov z velikostjo mikrometra zavira učinkovito izhlapevanje in pretvorbo v fulerene.

Ključne besede: fulereni, RF-plazma, SEM-analiza

1 INTRODUCTION

Since the fullerenes have been synthesized in macroscopic quantities in arc reactors, numerous methods of fullerene formation has been investigated[1]. In our experiments, we have tried to produce fullerenes by direct evaporation of several graphite powders injected into the radio frequency inductively coupled thermal plasma[2]. Only several reports have been written about fullerene formation in RF reactors[3]. The carbon arc is neither particularly efficient nor controllable with the conditions within the chamber varying dramatically between the discharge region and the outer walls. RF plasma is voluminous plasma and the residence time of species generated in hot plasma flame is much longer than in arc plasma under the same conditions. Residence times of species and particles in carbon arc and RF thermal plasma are typically estimated on 0.3 ms and 10 ms, respectively. Based on the above predictions, the synthesis of fullerenes in RF plasma torch has promising possibilities. Powders injected into thermal plasma undergo instant modifications in shape, surface morphology, chemical composition and crystal structure[4].

In this paper, special attention was devoted to the influence of cohesive nature of used graphite powders on efficiency of fullerene synthesis. Typically grains of powders below 100 μm are considered as fine powders and they are cohesive. Above 100 μm they are called grains, and they are non-cohesive[5]. The state of starting material determines efficiency of its evaporation and consequently fullerene yield. Also injection of electrically conducting graphite powder results in formation of dusty plasma. Unique quality of RF dusty plasma is to provide the large number of ions in the fullerene formation region which is not common situation for carbon arc plasma.

2 EXPERIMENTAL PROCEDURE

Several synthetic graphite powders (4827-Asbury Mills, graphite Aldrich) having a mean particle size of 3 μm and 6 μm were treated in a thermal plasma reactor, at atmospheric pressure, respectively. The RF power was produced by a generator operating at 3–5 MHz. Plate power of 30 kW was inductively coupled to a TEKNA PL-35 torch connected to the water cooled plasma reactor, cyclone and dust filter[2]. Helium was used as plasma gas (18 slpm) and carrier gas (12 slpm), respectively. The sheath gas was argon (45 slpm). The graphite powder was injected axially to the top of the plasma flame with feed rates of 16 g/h to 180 g/h. A TRIAX 550 spectrometer (Jobin-Yvon) connected to CCD 3000 detector monitored the optical emission of the plasma flame through a quartz glass window at a height of 10 cm below the tip of feeding nozzle.

3 RESULTS

Graphite powders used in our experiments are cohesive. Ratios of tapped and loose bulk density for Asburry and Aldrich powders are 4.7 and 3.2, respectively[6]. According to Hausner criterium, powders with ratio larger than 1.4 are cohesive. Cohesive character is caused by particle interaction forces. Main interaction force is van der Waals force that is proportional to the surface of interacting particles. Since graphite particles have disk like shape, contact area is relatively large.

Contact forces between graphite grain depend on surface hardness as well. Graphite is one of the softest material in nature that results with large contact force. The value of hardness by Moh's is 0.5[7].

In **Figure 1a**, SEM micrograph of Aldrich graphite powder is presented. Particle size distribution of corresponding powders is presented in **Figure 1b**. It was obtained using computer code Diameter Distribution Analyser[8]. It is obtained from these figures that mean particle diameter is 6 μm. Graphite particles have typical disk plate shape. Particle size distribution is very wide. **Figure 2a** shows SEM micrograph of fullerene soot obtained by processing of Aldrich powder in RF thermal plasma reactor. Besides disk plate particles, round shape particles with diameter smaller than 1 μm can be easily detected. Disk plate particles partially evaporated depending on particle size. Furthermore, carbon vapor and fullerenes produced by evaporation of small graphite particles deposit on large graphite particles. Round shape particles have amorphous structure. They consist of products of synthesis of various carbon clusters. The particle size distribution of fullerene soot has shown the presence of particles with reduced diameter compared to starting powder (**Figure 2b**).

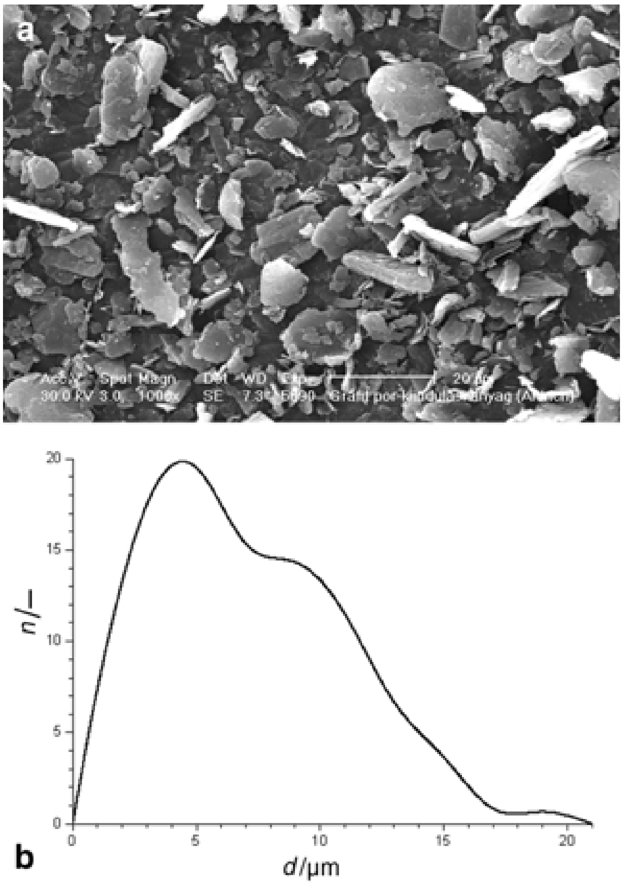

Figure 1: (a) SEM micrograph and (b) particle size distribution *n* of Aldrich graphite powder before plasma treatment
Slika 1: (a) SEM-posnetek in (b) velikostna porazdelitev *n* zrn grafitnega prahu Aldrich pred obdelavo v plazmi

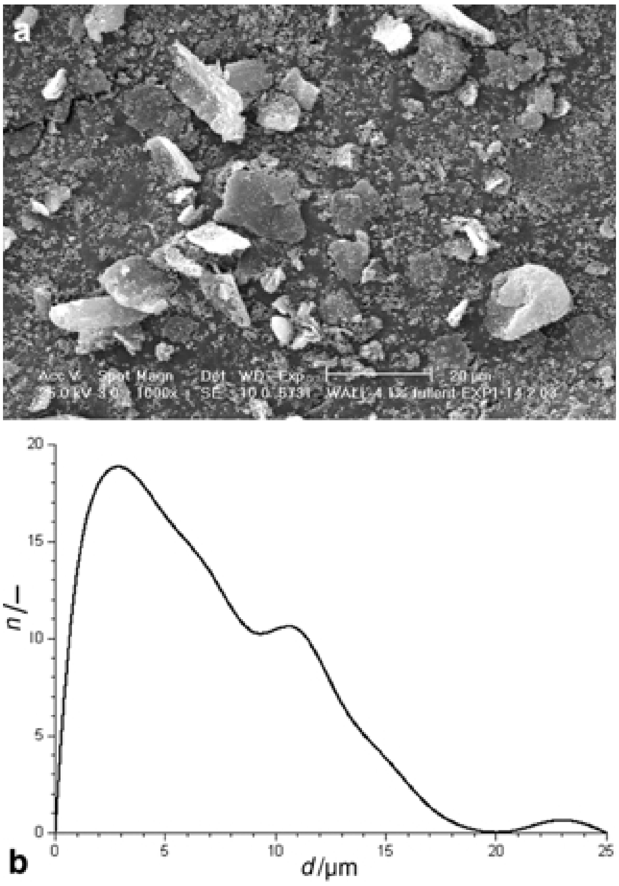

Figure 2: (a) SEM micrograph and (b) particle size distribution *n* of Aldrich graphite powder after plasma treatment. Feed rate was 156 g/h
Slika 2: (a) SEM-posnetek in (b) velikostna porazdelitev *n* zrn grafitnega prahu Aldrich po obdelavi v plazmi. Hitrost dodajanja 156 g/h

In **Figure 3a**, SEM micrograph of graphite powder 4827 (Asburry Mills) is presented. **Figure 3b** depicts the particle size distribution of mentioned powder. Compared to first powder, 4827 powder have smaller mean particle diameter 2.73 μm and narrower particle size distribution. Majority of particles has the diameter between 0.5 μm and 1.5 μm.

After the injection of this powder in hot plasma flame, the evaporation of powder is not complete even at very small feed rate (**Figure 4a**). **Figure 4b** shows the particle size distribution of processed 4827 powder. In

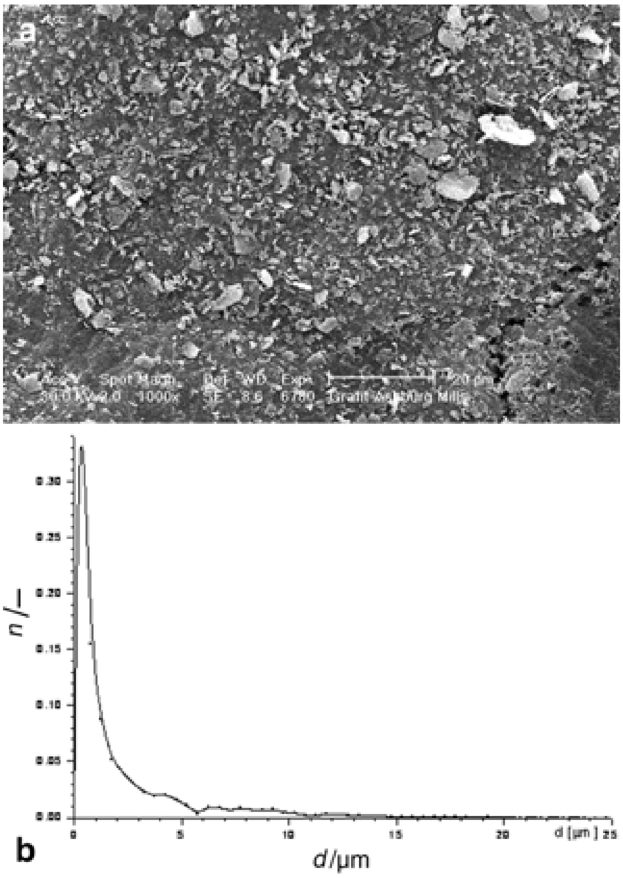

Figure 3: (a) SEM micrograph and (b) particle size distribution *n* of graphite powder of Asbury Mills-4827 before plasma treatment

Slika 3: (a) SEM-posnetek in (b) velikostna porazdelitev *n* zrn grafitnega prahu Asburry Mills-4827 pred obdelavo v plazmi

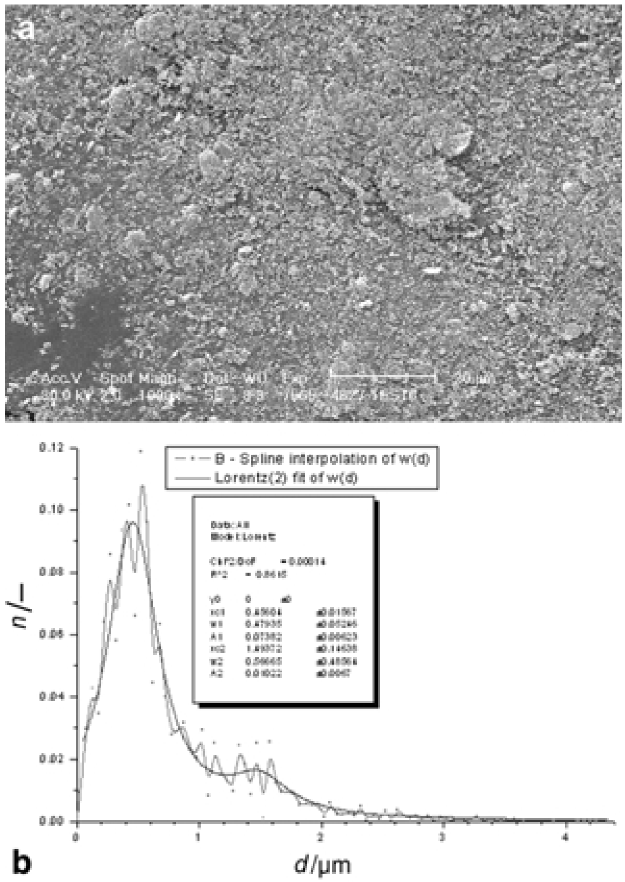

Figure 4: (a) SEM micrograph and (b) particle size distribution *n* of graphite powder of Asbury Mills-4827 after plasma treatment. Feed rate was 16.2 g/h

Slika 4: (a) SEM-posnetek in (b) velikostna porazdelitev *n* zrn grafitnega prahu Asburry Mills-4827 po obdelavi v plazmi Hitrost dodajanja 16,2 g/h

fullerene soot, there are two dominant groups of particles:ones have diameters about 0.5 µm and the others having diameter about 1.5 µm. In order to prove this fact, double Lorentzian fit has been done[8]. The possibility of the presence of particles having diameter larger than 3 µm is very small.

4 DISCUSSION

One of the major reasons of incomplete evaporation of graphite is cohesive nature of used powder. Powder is injected into RF plasma in the form of agglomerate. In Aldrich powder, small particles are attached to one large particle that represents core of agglomerate. Surface layer of agglomerate is heated and evaporate. After that, inner surface layer of agglomerate can be heated and transformed in carbon vapor. In the course of flight of agglomerate through plasma flame, hot inert gas manages to evaporate several layers of agglomerate. The largest fullerene yield after processing of Aldrich graphite was 4.1 %.

Larger value of Hausner ratio indicates us that particles of 4827 powder form larger agglomerates than Aldrich graphite. Agglomerate have form of multiple necklaces bonded together. Hot inert gas in the plasma flame manages to evaporate necklaces located at the outer boundaries of agglomerate. Necklaces of graphite particles located in the core of agglomerate remain intact. Deposits of small amorphous carbon aggregates ($d < 0.5$ µm) on large unevaporated crystalline graphite ($d > 1.5$ µm) are clearly seen on SEM micrograph of processed powder. Maximum fullerene yield after processing of 4827 powder was 3.2 %.

5 CONCLUSION

On the basis of the experiment, we have found that cohesive nature of micron sized graphite powders impedes efficient evaporation and transformation into fullerenes.

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