Production of carbon soot with a high content of C_{60} and C_{70} fullerenes by electric arc

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The effect of the parameters of the electric arc (helium pressure, current and voltage, clearance between electrodes) and of the peculiarities of the setup design (arrangement of electrodes, distance between the arc and the cooling surface, temperature of the soot condensation surface) on the yield of fullerenes has been studied. Conditions for producing soot with a C_{60} and C_{70} content up to 43 % (toluene extract) have been found.

Key words: carbon soot, fullerenes; cooling surface; electric arc, graphite electrodes; extract.

Study of the effect of various factors on the process of preparing fullerene-containing soot using an electric arc[1] is of importance for the optimization of the conditions for fullerene formation. The majority of the work devoted to the synthesis of fullerenes[2—4] present only specific data on a limited number of parameters for different setups (arc current, voltage, and heluim pressure) and on the content of C_{60} and C_{70} fullerenes obtained in the soot, which usually does not exceed 10 % after extraction with toluene.

The effect of helium pressure, current, and arc length on the yield of fullerenes in soot has been analyzed previously.[5] The optimization of only these parameters made it possible to increase the yield up to 11—14 %. The preparation of soot with a higher content of C_{60} and C_{70} fullerenes (~20 %) has been reported,[6] but the factors owing to which this has been achieved remain obscure. The present work is devoted to the study of the effect of various parameters of the electric arc and of the peculiarities of the setup design on the yield of C_{60} and C_{70} fullerenes, and is aimed at optimizing the conversion of graphite into fullerene-containing soot.

Experimental

Figure 1 represents the scheme of a multipurpose setup, which allows one to perform different experiments both in a simplified version for the optimization of helium pressure, current, and arc length, and in a more complex version to determine the temperature of the soot surface, study the effect of the distance from the arc to the surface on which the soot is deposited on the yield of fullerenes, and to "shield" the surface from irradiation by the arc. A stainless-steel vessel (*3*) (180 × 380 mm) with a water jacket is the base of the setup. The vessel is evacuated with a forevacuum pump down to ~10—20 Torr before the input of gaseous helium. Graphite

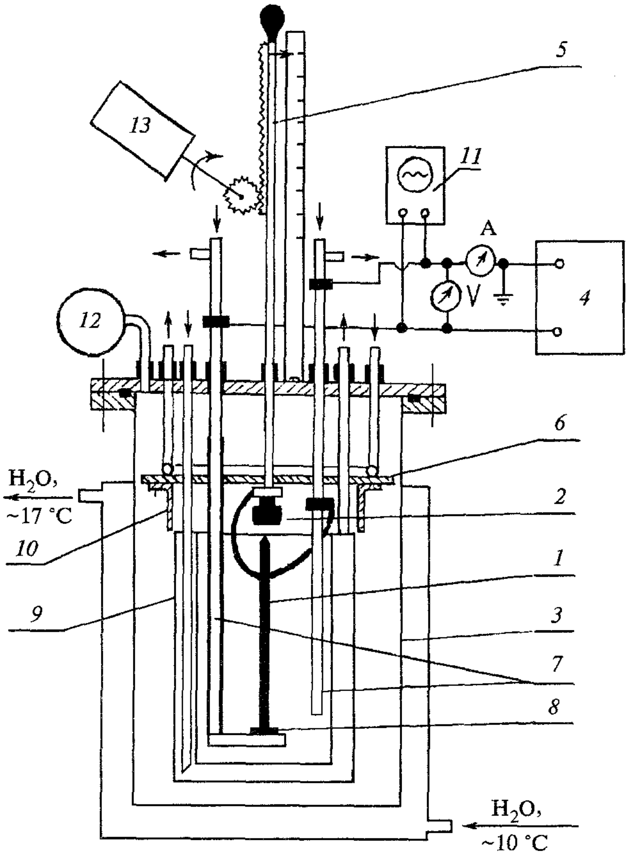

Fig. 1. Setup for the preparation of the fullerene-containing soot: *1,* graphite electrode to be volatilized; *2,* nonvolatilized electrode (cathode); *3,* main vessel; *4,* constant-current arc source; *5,* stainless-steel rod; *6,* cooled copper shield; *7,* current inputs; *8,* graphite ring; *9,* additional cooling vessel; *10,* additional copper shield; *11,* oscillograph; *12,* vacuumeter; *13,* a RD-09 driver.

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rods (*1*) for spectral analysis (OSCh-7-3, 6 mm diameter, 200 mm length, ~9 g mass) were used as the electrodes to be volatilized. Nonvolatilized electrodes, cathodes (*2*) 12—16 mm diameter, were made of MPG-8 graphite. The graphite rods were preliminarily thermally treated for 2 h in a vacuum furnace at 800 °C and then stored in a vacuum-desiccator.

The setup can work with both direct and alternating current. An SG-300 arc-welding generator is used as the direct-current arc source (*4*). Its self-excitation winding is disconnected from the generator and fed from an independent constant-voltage source that provides more stable conditions of arc burning at 50—150 A. A TPO-10/20/40PK transformer serves as the alternating-current arc source. The voltage in its primary winding is regulated by an AOMN-40-220-75 UKhLCh autotransformer. The alternating-current arc is stabilized by connecting a throttle with inductivity of $0.6 \cdot 10^{-3}$ H and resistance of 0.019 Ohm in series into the circuit of the secondary winding of the transformer. The abruptly dropping voltaic characteristics both with alternating and direct current make it possible to stabilize the arc burning current so that it becomes independent of the arc length within a specified range.

The evaporation rate of the graphite rod and the arc length are controlled and maintained at a constant level by the voltage alteration in the winding of a RD-09 asynchronic driver (*13*). The nonvolatilized electrode (cathode) is moved by a rack gear through a thin stainless-steel polished rod (*5*) 4 mm diameter. A water-cooled copper shield (*6*), which increases the surface on which the soot is deposited and protects the rubber seals in the flange of vessel *3* from overheating, is arranged over the graphite electrodes. The current inputs (*7*) are made of copper pipes and also cooled with water. Thus, the whole surface on which the soot can be deposited is cooled. The copper holder of the rod to be volatilized near where the arc burns is protected from melting by a graphite ring (*8*). The setup can also work in the horizontal position with the use of an additional stand. In addition, its design allows one to change the mutual arrangement of the electrodes, which makes it possible to study the conditions of soot deposition and cooling at various positions of the electrodes and cooling surface.

For the experiments in a more complicated version, an additional water-cooled vessel (*9*) is placed inside vessel *3*, whose diameter (110 mm) is close to those of the cooling surfaces used in Refs. 2, 5, and 6, and seems to be optimum. The clearance between shield *6* and vessel *9* is closed with an additional copper shield (*10*). The temperature of this weakly cooled shield attached at several points to the water-cooled shield *6* is measured by a thermocouple. When shield *1* is removed, the soot can be deposited on the cooled surface of vessel *3* "shadowed" from arc irradiation.

Instead of vessel *9*, a water-cooled cylindrical screw helix with the same diameter of winding as the diameter of vessel *9* was used as the surface that would be simultaneously placed at the optimum distance from the arc and create a "shadow" on the surface of vessel *3*. The helix was wound from copper pipe 10 mm diameter and ~20 mm pitch.

The process was monitored both visually through a special glass window and by an ampmeter, a voltmeter, and an oscillograph (*11*). The stability of the direct-current arc burning was monitored by the voltage noise, and that of the alternating-current arc by the shape of the voltage curve on the display of the oscillograph.

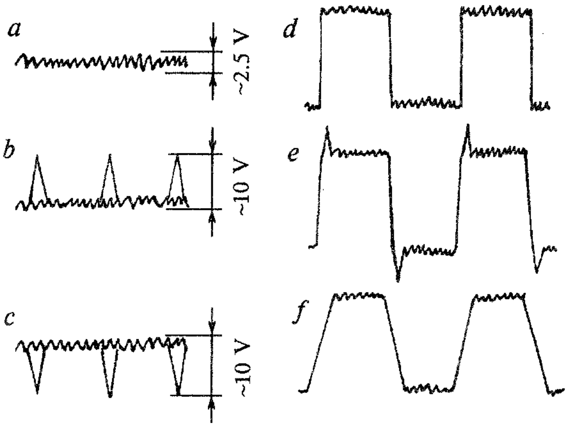

Fig. 2. Voltage oscillograms for direct- and alternating-current arcs. The explanations are in the text.

The voltage oscillograms for direct-current (*a, b, c*) and alternating-current arcs (*d, e, f*) in various operating regimes (stable and unstable) are shown in Fig. 2. Noise is minimum when burning of the direct-current arc is stable (see Fig. 2, *a*). Bright luminescence of the arc with intense evaporation of graphite as a white vapor is observed. The increase in the arc length results in the appearance of noisy voltage splashes up to ~10 V (see Fig. 2, *b*) on the background of the minimum noise, and the arc luminescence decreases. A similar pattern can also be observed in the decrease in the arc length (see Fig. 2, *c*) but the voltage splashes are of another polarity and the white vapor turns brown. Another pattern is observed with the alternating-current arc. Its burning is stable with maximum brightness of the luminescence when the change in the voltage polarity results in the abrupt decrease in the transition (see Fig. 2, *d*). Increasing the arc length results in the appearance of ignition peaks on the voltage curve (see Fig. 2, *e*), and the transition becomes more shallow (see Fig. 2, *f*) as the length decreases.

The appearance of noises of different polarity in the direct-current arc or changes in the shape of the voltage curve in the alternating-current arc allow one to correct the velocity of electrode feeding and stabilize the evaporation of the rod by maintaining the arc length between the electrodes at the optimum level of ~4 mm. (The arc length was determined with a measuring ruler when the current source was disconnected, dropping the mobile electrode until contact with the other electrode.)

The yield of fullerenes was determined by the following procedure: ~4 g of the soot was placed into a Soxhlet apparatus and extracted with 1.3 L of toluene; the number of cycles was usually 7—8. Then the solvent was removed on a rotary evaporator, the extract was washed with diethyl ether, dried *in vacuo* for ~1 h at 80 °C, and weighed. Toluene mainly extracted lower fullerenes, C_{60} and C_{70}. The concentrations of C_{60} and C_{70} in the extract were determined by HPLC (a Milichrom-2 chromatograph, UV detector, λ = 330 nm, column 2x80 mm, Silosorb-Diol, hexane as the eluent) and spectrophotometrically by the Firordt method at λ_1 = 330 nm ($\varepsilon_{C_{60}} = 5.13 \cdot 10^4$, $\varepsilon_{C_{70}} = 2.4 \cdot 10^4$) and λ_2 = 400 nm ($\varepsilon_{C_{60}}$ = 400, $\varepsilon_{C_{70}} = 1.44 \cdot 10^4$). The results obtained with both methods were similar.

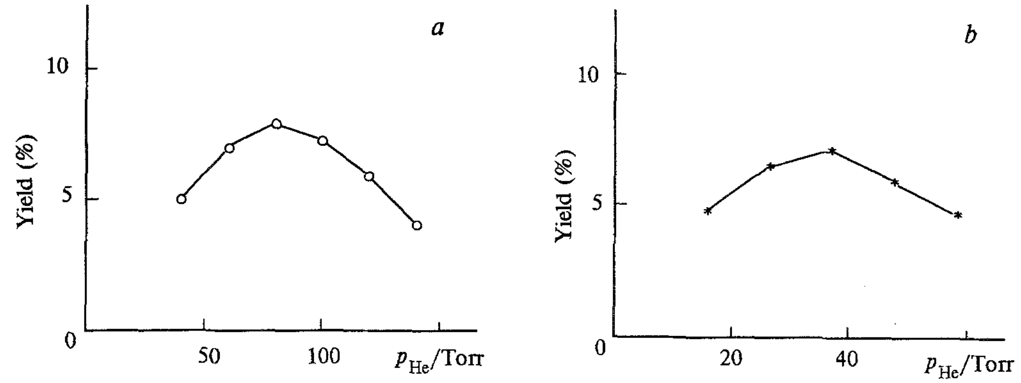

Fig. 3. Dependence of the yield of fullerenes on the helium pressure: *a*, direct current; *b*, alternating current.

Results and Discussion

The effect of helium pressure on the yield of C_{60} and C_{70} fullerenes was studied on the setup (see Fig. 1) without vessel *9* and shield *10* at constant arc current. The helium pressure increases by 10—15 % two to three minutes after the beginning of the arc burning and then does not change. Maintenance of the stable volatilization of the rod by monitoring the arc length was a necessary condition of the experiments. Monitoring was performed by the voltage oscillograms and visually. The highest yield of fullerenes in the soot (8 %) in the direct-current arc is achieved at the helium pressure 80 Torr (Fig. 3, *a*); and in the alternating current the yield of fullerenes is 2 % lower, and the maximum is observed at p_{He} = 35 Torr (Fig. 3, *b*). The effect of the arc current (I_a) on the yield of fullerene was studied under the optimum helium pressure found (Fig. 4, *a*, *b*). The optimization of the arc current allowed us to increase the yield up to 12 % for the direct current (see Fig. 4, *a*; I_a = 60 A) and up to 10 % for the alternating current (see Fig. 4, *b*; I_a = 120 A). It should be mentioned that increasing the helium pressure results in bright luminescence of the arc at lower current, but the time of the volatilization of the rod increases. In the majority of the experiments, the C_{60} : C_{70} ratio in the extract was ~85 : 15. It shifted to higher C_{70} content as the arc current increased.

The volatilization of one rod (9 g) results in the formation of ~4 g of soot. A portion of the volatilized graphite (up to ~40 % of the rod mass) is deposited on the cathode as a caking 6—8 mm in diameter and 5—7 cm in length for direct current and up to ~12 mm in diameter and 3—3.5 cm in length for alternating current. The amount of caking decreases as the arc current increases, but the yield of fullerene decreases. The voltage measured at the current input changes during arc burning. For direct current, it increases, because the increase in the caking results in a faster voltage drop on it than that on the rod to be volatilized. By contrast, the voltage at the current input decreases for alternating current.

The effect of the temperature of the surface on which the soot is deposited on the yield of fullerenes has not yet been studied. We used liquid nitrogen instead of water to cool vessel *3*. This allowed us to increase the yield of fullerenes ~1.4-fold; the arc parameters remained the same as those for water cooling. However, we gave up the use of nitrogen due to its large consumption and experimental inconveniences. Nevertheless, the result obtained showed that a further increase in the yield of fullerenes can also be achieved by decreasing the

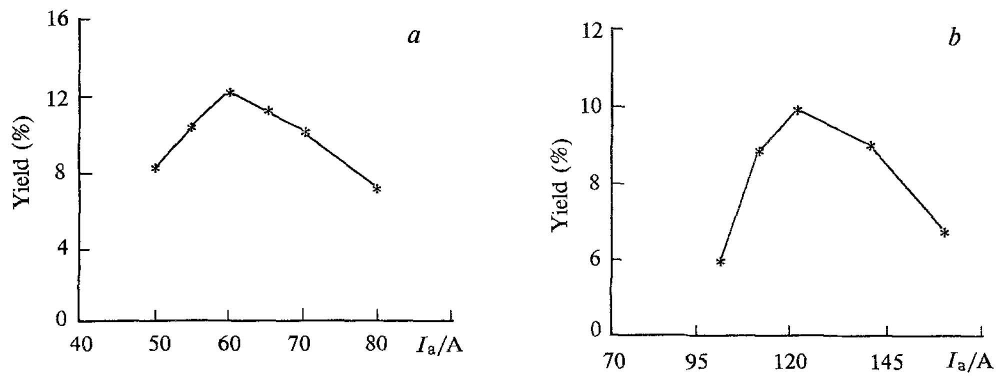

Fig. 4. Dependence of the yield of fullerenes on the arc current: *a*, direct current; *b*, alternating current.

temperature of the upper layers of the soot, which undergo heating from the arc irradiation the most. The temperature of the soot surface seems to depend on the temperature of the cooling support, heat conductivity of the soot, thickness of the layer, and the amount of heat that the surface receives due to the arc irradiation. It is known that this amount of heat is proportional to the cosine of the angle between the beam direction and a line perpendicular to the surface, and is inversely proportional to the square of the distance from the irradiation source to the surface.

First, we made an attempt to improve the cooling of the soot surface by distributing the soot more uniformly in order to obtain a thinner layer. It was observed in the visual monitoring that the soot was nonuniformly distributed[7] on the walls of the cooling vessel: if the volatilization of the rod occurs at the same site relative to the cooling vessel, the soot is deposited more extensively on the walls near the arc than on the parts further removed. Such a situation is realized for the vertical arrangement of the electrodes, when the thin rod to be volatilized serves as the mobile electrode (Fig. 5, *a*). When the cathode becomes the mobile electrode (Fig. 5, *b*), the soot is distributed more uniformely on the walls of the vessel.

A different pattern of soot deposition is realized in the horizontal arrangement of the electrodes. The majority of the soot (up to 90 %) is deposited above the arc due to convective flows (Fig. 5, *c* and *d*). As in the case of the vertical arrangement (see Fig. 5, *b*), a more uniform soot layer above the arc is formed when the cathode is moved (Fig. 5, *d*). It turns out that the fullerene content in the soot uniformly distributed over the surface (see Fig. 5, *b*) is 3—4 % higher than that in nonuniformly distributed soot. Apparently, the increase in the yield of fullerenes in this case is associated with the formation of a thinner soot layer, which is better cooled.

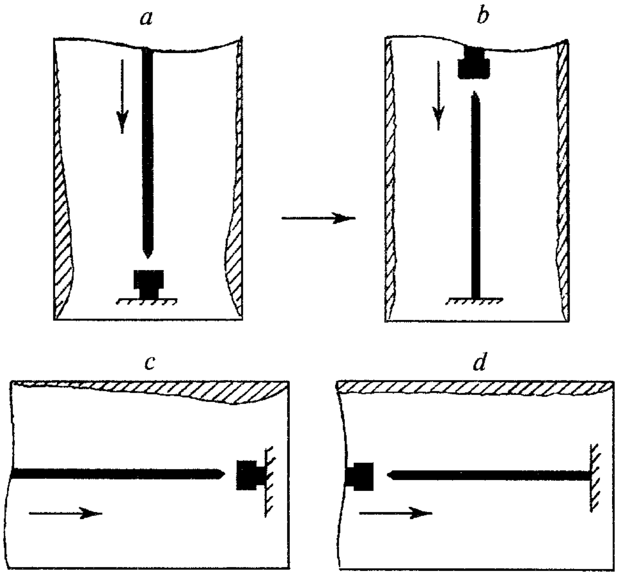

Fig. 5. Soot distribution for different arrangements of the electrodes in the vertical and horizontal arrangement of the setup. The explanations are in the text.

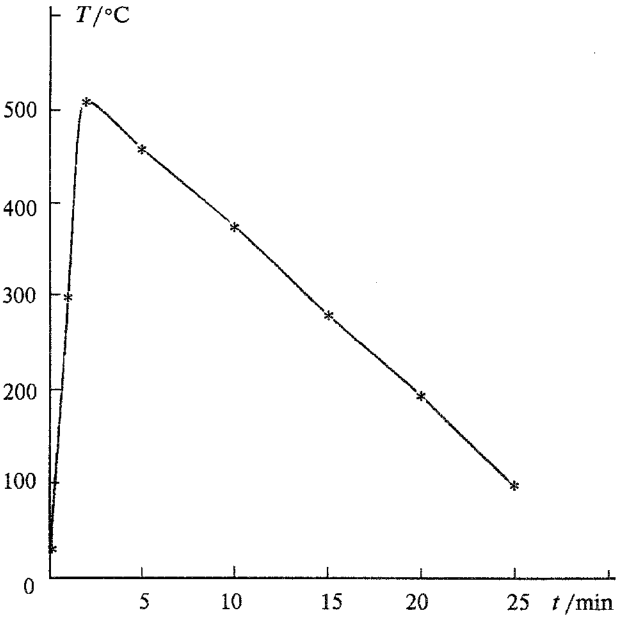

Fig. 6. Dependence of the change in temperature of the copper shield *10* on the duration of the rod volatilization.

In order to study further the effect of the surface temperature of the fullerene-containing soot on the yield of fullerenes, we changed the design of the setup. An additional vessel *9* and shield *10* were placed inside vessel *3* (see Fig. 1), and the temperature of the shield was monitored by a thermocouple. The arc parameters remained the same as in the experiments without the additional vessel (p_{He} = 80 Torr, I_a = 60 A). The temperature of shield *10* reached 510 °C during the first two minutes of the rod volatilization and then decreased almost linearly to 100 °C as the arc was removed from the shield (Fig. 6). Since only 0.3 g of soot condenses on shield *10* (Table 1), and the soot is distributed as a thin layer, one may consider that the temperatures of the shield and the soot are the same. The fullerene content in this soot reaches ~43 % (toluene extract).

Table 1. Amount of soot and the yield of fullerenes taken from surfaces at different temperatures

Surface from which soot was taken	T/°C	Mass of soot/g	Yield of fullerenes (%)
Vessel *9*	10—17	2.26	16.8
Shield *10*	10—510—100	0.30	43.6
Current inputs	10—17	0.82	23.0

It is likely that under ordinary conditions, when the thickness of the soot layer is ~1—2 mm and it is irradiated intensely by the arc, the temperature of the soot surface may exceed 510 °C and reach values at which C_{60} is sublimed[8] or is not formed at all due to the high temperature. This may account for the low yield of fullerenes in soot obtained by the usual method.[2—5] The soot at the bottom surface of vessel *9*, near the place where the arc burning ends, is black. The same is observed at the parts of the current inputs turned toward the arc. The color of the soot both at the surface of vessel *9* and at the current inputs changes smoothly from black to light-brown as it becomes more remote from the place where the arc burning ends. Black soot can be seen under the light-brown soot layer (if the latter is carefully removed). This is probably deposited when the arc passes near these surfaces. Both the inner and outer layers of the soot are of the same light-brown color at the "shadowed" sides, opposite to the arc, of the current inputs. The black soot contains almost no fullerenes (<3 %), while their concentration in the light-brown soot reaches 17 %. The low content of fullerenes in the black soot is likely associated with its heating above the decomposition temperature. Nevertheless, the overall yield of fullerenes in the soot taken from the water-cooled surface of vessel *9* is 17 %, which exceeds the yield of fullerenes formed on the surface of vessel *3* in the experiments without the additional vessel *9*.

In further experiments shield *10* was removed (see Fig. 1), and the soot was taken from the surface of vessel *9* and the surface of vessel *3* "shadowed" from arc irradiation. It can be seen from the data of Table 2 that the yield of fullerenes in the soot from the "shadowed" surface of vessel *3* is almost 1.5-fold higher than that from the surface irradiated by the arc (24.3 and 16.8 %, respectively) and is almost 1.6-fold greater than the yield of fullerenes from the same surface of vessel *3* in the experiments without the additional vessel *9* (15 %).

Thus, in these experiments we designed and tested a modified setup in which the additional vessel *9* (see Fig. 1) is replaced by a cylindrical screw helix. The part of the helix surface located above or below the arc is "shadowed". In addition, the helix itself provides partial "shadowing" of the surface of vessel *3*. Hence, the modified setup made it possible to realize conditions in which the major part of the surface on which the soot is deposited, is in the "shadow" of the arc. The overall yield of C_{60} and C_{70} fullerenes in the setup with the helix reaches 25 %.

Table 2. Amount of soot and the yield of fullerenes from surfaces at different distances from the arc

Surface from which soot was taken	Distance from the arc /mm	Mass of soot/g	Yield of fullerenes (%)
Vessel *9*	55	1.47	16.8
Vessel *3*	90	0.37	24.3
Current inputs	40	0.70	23.0

Thus, the effect of various parameters on the formation of fullerene-containing soot has been studied, and a setup allowing one to obtain C_{60} and C_{70} fullerenes in 25 % yield has been designed. The possibility of increasing the yield to 43 % has been demonstrated.

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