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The Effect of Electron Density on the Kinetics of Fullerene Formation in Carbon Plasma

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Abstract—The influence of the carbon cluster charge on their coagulation kinetics has been studied. The equations of kinetics have been solved and it is established that allowance for the cluster charging leads to an increase in the rate of fullerene formation under otherwise equal conditions. In connection with this, the role of minor impurities with a low ionization potential in carbon-containing plasma is discussed. © *2003 MAIK "Nauka/Interperiodica".*

There are many models of fullerene formation [1] which consider various precursor clusters and different transformation pathways. However, most of these models do not take into account that all effective methods of fullerene synthesis employ plasma technologies [2–4]. This implies that carbon clusters bear an electric charge that certainly influences the process of fullerene formation. The effect of cluster charging has been demonstrated experimentally [5] and described theoretically [6]. The signs and values of charges on carbon clusters depend on the plasma parameters, in particular, on the electron density and temperature. In this context, we have studied the effect of electron density on the efficiency of fullerene formation in carbon plasma.

The analysis is performed within the framework of a semiempirical kinetic model of the growth of carbon clusters. The main assumptions of this model are as follows. Every collision of two clusters, C_i and C_k, leads with a certain probability W_{ik} to the formation of a cluster C_{i+k}. The reverse process is ignored, since the rate of such fragmentation in the temperature range of cluster growth is small because the binding energy is sufficiently large [7]. The distribution of charges on clusters at a given temperature and electron density is determined by the Saha equations [6]. The electron density depends primarily on the presence of minor additives of readily ionized metals in the plasma. The rate of collisions between clusters is calculated according to the classical theory. The effect of cluster charging on the coagulation rate reduces to correcting the cross sections for the Coulomb interaction [6].

Equations describing the kinetics of cluster formation in a stationary flow are as follows:

$$\frac{dc_i}{dx} = \sum_{k=1}^{i/2} c_k c_{i-k} I_{k,i-k} - c_i \sum_k c_k I_{ik}, \quad \sum_i i c_i = 1. \quad (1)$$

Here $c_i = n_i/N_C(r)$ is the relative density of clusters of the ith type (C_i), x is the dimensionless spatial coordinate, and I_{ik} is the dimensionless coagulation rate. The latter quantity is given by the expression

$$I_{ik} = W_{ik}\sqrt{\frac{i+k}{ik}}\frac{(R_i+R_k)^2}{D_1^2} \times \sum_{q_i} P_i(q_i)\sum_{q_k} P_k(q_k)\left[1 - \frac{q_i q_k}{(R_i+R_k)3kT/2}\right], \quad (2)$$

where R_i is the effective size of clusters of the ith type, D_1 is the effective "diameter" of a monomer, q_i is the possible charge on the ith cluster, and $P_i(q_i)$ is the probability for the cluster to bear this charge. It is assumed that clusters can be either neutral or singly ionized, or can (in view of a large electron affinity) acquire a single or double negative charge.

The probabilities of various charged states of C_i clusters are given by the relations

$$\frac{P_i(q+1)c_e}{P_i(q)} = \frac{AT^{3/2}}{N_C(r)}\frac{Z_k^{q+1}}{Z_k^q}\exp\left(-\frac{E_i^q}{kT}\right), \quad (3)$$

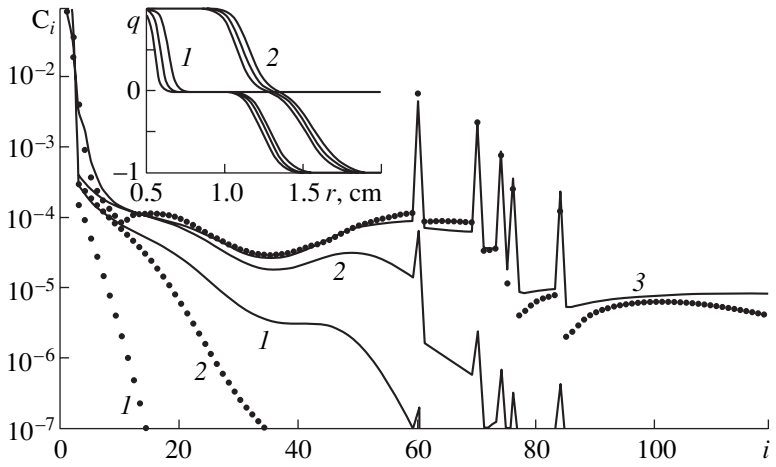

Fig. 1. Evolution of the cluster size distribution with increasing distance from the plasma source (see the text for explanations). The inset shows variation of the average charge profile for small (C_1–C_4, curves *1*) and large (C_{40}, C_{50}, and C_{60}, curves *2*) clusters.

where $c_e = n_e/N_C(r)$, Z_i^q is the electron partition function for clusters with the charge q, and E_i^q is the ionization energy of such clusters. In writing Eq. (3), it is assumed that the ratio of vibrational and rotational partition functions for clusters of the same type possessing various charges is unity. The parameters of energy structure, ionization energies, and electron affinities of clusters necessary for the calculations were calculated using a VASP program package [8].

It should be also noted that, in a quasi-one-dimensional approximation, the dimensionless coordinate x is related to the distance r from the arc source as $dx = N_C(r)v_C(r)\sigma_{11}dr/U(r)$, where v_C is the thermal velocity of carbon atoms, σ_{11} is the gaskinetic cross section for the collision of monomers, and $U(r)$ is the mass flow rate. Assuming the motion of a gas–plasma mixture to be nearly adiabatic ($T \sim \rho^{\gamma-1}$) and representing a change in the carbon concentration and flow velocity as $N_C(r) = N_{C0}(r_0/r)^\delta$ and $U(r) = U_0(r_0/r)^\beta$, respectively (N_{C0} and U_0 being the carbon concentration and jet velocity at the exit from the discharge zone, respectively, and r_0 the electrode radius), we can write the relation between r and x as

$$r = r_0 \times \begin{cases} (1 + \alpha Lx/r_0)^{1/\alpha}, & \alpha \neq 0, \\ \exp(Lx/r_0), & \alpha = 0. \end{cases} \quad (4)$$

Here, $L = U_0/(N_{C0}v_{C0}\sigma_{11})$ is the particle pathlength between two monomer collisions in the mass flow for the initial plasma parameters and $\alpha = \beta + 1 - \delta(\gamma + 1)/2$. For $\beta = \delta = 1$ and $\gamma = 2$, the distribution of gasdynamic characteristics corresponds to that of a flat turbulent jet [7, 9]. In this case, $\alpha = 1/2$ and the quantities N_C, U, and T decrease in inverse proportion to the distance: $(N_C, U, T) = (N_{C0}, U_0, T_0)(r_0/r)$.

The relative densities of electrons (c_e), impurity atoms (c_M), and impurity ions (c_M^+) are described by relations

$$\frac{dc_e}{dx} = \frac{N_C V_R}{v_C \sigma_{11}} c_e \left[c_M \frac{AT^{3/2}}{N_C} \frac{Z_M^+}{Z_M} \exp\left(-\frac{J_M}{kT}\right) - c_M^+ c_e \right], \quad (5)$$

$$\frac{dc_M}{dx} = -\frac{dc_e}{dx} = -\frac{dc_M^+}{dx},$$

where V_R is the impurity recombination rate [10]. It should be noted that the balance for electrons does not take into account cluster charging. Use of the equilibrium approximation is related to the absence of reliable information concerning the rates of ionization and recombination processes in the system studied. Nevertheless, even this (not quite self-consistent) formulation allows the effect of electric charge on the cluster coagulation dynamics to be evaluated.

In numerically solving the equations of kinetics, the dependence of R_i on the number of carbon atoms was empirically set taking into account experimental data on the cluster dimensions. This distribution function is nonmonotonic, reflecting an increase in R_i in the region of existence of chains and both flat and double rings ($10 \le i \le 40$). The probability of coagulation was calculated according to the model [9], whereby $W_{ik} \sim N_{He}a^3$ for small ($i, k \le 2$) clusters ($a = 1.4$ Å is the bond length and N_{He} is the buffer gas (helium) concentration) and $W_{ik} \approx \exp(-5800/kT)$ for the large ones. Following [7], we reduced the probability of coagulation for selected fullerenes ($i = 60$, 70, 74, etc.) and some other species so as to reflect their stability.

Here, we present the results of solving Eqs. (1)–(5) for the following values of flow parameters in a flat turbulent jet: $N_{C0} = 10^{16}$ cm^{-3}; $U_0 = 10^4$ cm/s; $T_0 = 5000$ K; $r_0 = 0.5$ cm. The initial system was composed of carbon

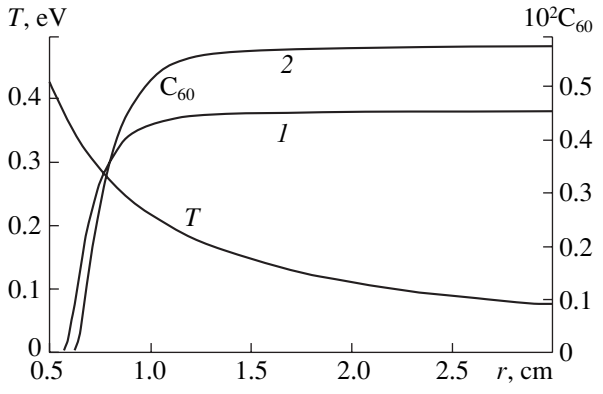

Fig. 2. Profiles of the jet temperature T and the fullerene C_{60} yield calculated (*1*) without and (*2*) with allowance for cluster charging.

monomers and approximately corresponds to an equilibrium composition at the given initial temperature. Note that, for $r \geq 3$ cm, the flow parameters are considered constant, their values decreasing to 1/6 of the initial values. The impurity metal was scandium, known to possess a low ionization potential. Scandium additives provided for the electron density N_e in the range from 10^8 to 10^{15} cm^{-3}, depending on the molar fraction and temperature.

Figure 1 shows evolution of the cluster size distribution for $x = 8.9$ (*1*), 14.1 (*2*), and 891 (*3*), corresponding to the distances $r = 0.54$, 0.57, and 9.2 cm, respectively. Solid curves represent the distributions calculated with neglect of the charges on clusters, while dotted curves are constructed with allowance for the effect of cluster charging. In the initial stage, the rate of coagulation is markedly higher for uncharged clusters, but eventually the trend changes to the opposite. This behavior is related to the dynamics of cluster charging. As can be seen from the inset in Fig. 1, small clusters predominantly bear a positive charge (due to ionization). In the course of jet expansion, the small clusters exhibit recharging to acquire a negative charge at $r > 0.75$ cm. The greater the cluster size, the later the moment of the charge sign reversal. For this reason, the growth rate of charged clusters exhibits a sharp increase within the interval of $r \approx 0.8$–1.25 cm.

Figure 2 illustrates the dynamics of variation of the concentration of fullerene C_{60} in the two cases under consideration and shows the jet temperature profile. This analysis confirms the previous conclusion [6] that there exists an optimum density of free electrons that provides for the maximum yield of fullerenes (in this example, ~10^9 cm^{-3}). At the same time, these results only outline general trends in the processes studied, detailed description requiring a knowledge of cluster charging kinetics. In conclusion, it should also be noted that the absolute values of fullerene yield strongly depend on the reactivity of clusters (W_{ik}) and the profiles of hydrodynamic parameters of the gas–plasma flow.

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REFERENCES

1. Yu. E. Lozovik and A. M. Popov, Usp. Fiz. Nauk **167**, 751 (1997) [Phys. Usp. **40**, 717 (1997)].
2. W. Kratschmer, K. Fostiropoulos, and D. R. Huffman, Chem. Phys. Lett. **170**, 167 (1990).
3. H. W. Kroto, J. R. Heath, S. C. O'Brien, *et al.*, Nature **318**, 162 (1985).
4. G. N. Churilov, Prib. Tekh. Éksp., No. 1, 1 (2000).
5. D. V. Afanas'ev, G. A. Dyuzhev, and V. I. Karataev, Pis'ma Zh. Tekh. Fiz. **25** (5), 35 (1999) [Tech. Phys. Lett. **25**, 182 (1999)].
6. G. N. Churilov, A. S. Fedorov, and P. V. Novikov, Carbon **41**, 173 (2003).
7. O. A. Nerushev and G. I. Sukhinin, Zh. Tekh. Fiz. **67** (2), 41 (1997) [Tech. Phys. **42**, 160 (1997)].
8. G. Kresse and J. Furthmuller, Comput. Mater. Sci. **6**, 15 (1996).
9. N. I. Alekseev and G. A. Dyuzhev, Zh. Tekh. Fiz. **72** (5), 121 (2002) [Tech. Phys. **47**, 634 (2002)].
10. G. S. Romanov, K. L. Stepanov, and L. K. Stanchits, Zh. Prikl. Spektrosk. **62**, 181 (1995).

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