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ScienceDirect
Journal of Nuclear Materials 363–365 (2007) 1190–1194
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Modelling of carbon dust formation by cluster growth in argon plasmas

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Abstract

In tokamaks with carbon plasma-facing components, one can observe the presence of nano-sized dust particles. Understanding such dust particle formation is a prerequisite to any attempt to limit or avoid this dust that may be responsible for tritium retention and pollution of the plasma. We report on coupled modeling of carbon chemistry and dust particle nucleation, growth, and transport in a plasma discharge. The chemical model used for carbon cluster dust growth is described in detail. The results are consistent with measurements made at LPIIM from low-pressure argon DC discharges in a stainless steel reactor with a graphite cathode [C. Arnas, C. Dominique, P. Roubin et al., J. Nucl. Mater. 337–339 (2005) 69], serving as a proxy for the tokamak plasma edge. The time evolution of the 'large' dust particles consists of a nucleation phase followed by an accretion phase. These reach a dust grain size of 40 nm on a timescale comparable to the experimental observations (minutes to hours).

PACS: 82.40.Ra; 52.25.Tx; 52.40.Hf; 52.65.−y

Keywords: Carbon impurities; Dust; Erosion and deposition; Sputtering

1. Introduction

The aim of this paper is to investigate the coupled phenomena of carbon dust particle nucleation, growth, and transport, in the low-pressure DC argon discharges developed at the LPIIM in Marseille [1]. These take place inside a stainless steel reactor, where the only possible source for carbon is the graphite cathode used to initiate and maintain the discharge. Carbon dust (tens of milligrams) is found to collect on the anode for discharges lasting more than a few minutes. The discharge ions travel through the collisional sheath and impact the cathode with an average energy of order 20 eV, enough to cause sputtering. Energetic charge exchange neutrals may also impact the cathode. Carbon is then sputtered from the cathode by the incident argon flux, and then transported inside the discharge, where it experiences collisions with electrons, ions, resulting in charge transfer, electron attachment/detachment, ionisation, etc. Collisions also take place between carbon species, which leads to the formation of carbon clusters up to a critical size at

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0022-3115/$ - see front matter
doi:10.1016/j.jnucmat.2007.01.161

which nanoparticle nucleation takes place. The so-formed particle population undergoes subsequent growth, through processes of coagulation (meaning two spherical clusters form a larger sphere) and aggregation (meaning two clusters merge but do not significantly alter their shape).

The experimentally observed particle population is the net result of this complex chemistry, transport and aerosol dynamics mechanism. Modeling the formation of the carbon particles in the LPIIM vessel requires describing the different phenomena listed above and answering the following questions:

- What is the homogenous chemistry that governs these species and the chemical model, in term of species and reactions, which can accurately describe the plasma resulting from sputtering at the cathode?
- What kind of model can we use to describe the nucleation phase and the whole aerosol dynamics?
- A major issue at this point is related to the particle charging. This will affect their transport and residence time in the discharge.

2. Model description

For simplicity, we take advantage of some assumptions that can be easily made for the discharge conditions in [1] and focus on a few points involved in the dust-particle formation process. The sputtering of argon onto carbon is computed from a convolution of the incident argon energy and angle distribution function and deduced from the TRIM [2] database. Small amounts of C_2 and C_3 may be also obtained as reported in [3]. Analytical models [4] exist that enable one to estimate the dimensions and electric field variations in the different discharge regions for set-ups such as the DC argon plasma produced at LPIIM for dust generation. The information needed with respect to the discharge characteristics is derived from the simultaneous use of those analytical models and experimental measurements. We assume that the discharge behaviour is not affected by the dust particles, which is true only if the dust-particle density and associated charge density remains small enough. This is the case here as the dust density is only of order 10^{-6} of the Argon gas density.

The model is designed to follow the time evolution of the spatially resolved densities of carbon clusters C_n as a function of plasma parameters and nucleation and growth mechanisms. Above a certain critical size, n_{crit}, individual clusters are no longer followed, but rather a 'large dust particle' population is considered, whose mass density (hence average size and diameter) is followed. Each cluster species has a given diffusion coefficient and a mobility (according to Ref. [5]), which govern their spatial distribution. It is assumed that clusters are absorbed at the device walls and at the anode. Thus, after long times, each cluster population is at equilibrium between its creation rate (directly *via* sputtering or indirectly *via* chemistry) and its destruction rate (*via* further chemistry or diffusion to the walls). The problem is treated as 1-D in space, in the direction from cathode to anode.

For all the reactions types above, there exist very little detailed data in the literature. Many values are only rough order-of-magnitude estimates of the real rate constants (see e.g. [6]). We have chosen to follow an approach described by Bernholc and Phillips [7], based on formation enthalpies, which allows one to take into account, to some extent, certain experimental characteristics, like the preponderance of even-numbered neutral clusters, for example. The different reaction types between carbon clusters can be categorized as an aggregation:

$$C_n + C_x^q \rightarrow C_{n+x}^q \quad \text{and} \quad C_n^q + C_x \rightarrow C_{n+x}^q, \tag{1}$$

where q can be either $+1$, 0, or -1; and charge transfer:

$$C_n^q + C_x \leftrightarrow C_n + C_x^q. \tag{2}$$

In models such as [6], the value of x is limited to the size of the initially sputtered carbon species, hence $x = 1$–3. But extensions of the model as per [7] relax this constraint and both n and x can go up to n_{crit}, provided the relevant enthalpies are known.

As an intermediate step in the modelling, we have chosen to consider only neutral and negatively charged clusters in the chemical model. We neglect positively charged particles as they are expected to have very short residency times in the plasma and to be rapidly expelled, thus have little chance of interacting with other clusters and build up large dust agglomerates. This yields an upper bound to the cluster density, as the neglected positively-charging processes (such as charge-exchange with Ar^+ ions or electron-impact ionisation) would otherwise act as sinks.

The amount of negative ions produced by sputtering is function of the material work function

and the electron affinity of the emitted carbon species (1.26 eV for C, 3.30 eV for C_2 and 1.95 eV for C_3) [8]. This dependence may be expressed through the equation [9]:

$$P^- = \exp\left(-\frac{\Phi - A}{\varepsilon_0}\right), \tag{3}$$

where P^- is the ionisation probability, i.e., the probability that a particle is emitted as a negatively charged species, Φ is the target work function, A is the electron affinity of the emitted particle, ε_0 is a characteristic parameter that depends on the Fermi level of the target material, the electron affinity of the emitted particle and a characteristic decay length of the material and the emitted particle. This parameter is in the range 0.2–0.4 eV.

Using the work function of pure graphite, ≈5 eV, one can estimate the ratio of negatively charged ions to their corresponding neutrals for C, C_2 and C_3 species. Eq. (3) gives the following ranges for neutral to negatively charged species population ratios (from the limit values of ε_0):

$$10^{-8} < \frac{C^-}{C} < 10^{-4}, \quad 10^{-4} < \frac{C_2^-}{C_2} < 10^{-2}$$
$$\text{and} \quad 10^{-7} < \frac{C_3^-}{C_3} < 10^{-4}. \tag{4}$$

It appears therefore that a significant amount of negatively charged C_2^- ion may be produced at the graphite cathode, while negative ion emission can be neglected for C and C_3.

The rate constants for aggregation reactions (1) are determined assuming that the activation barrier of the aggregation processes corresponds to the energy required to grow each of the aggregating clusters by one carbon atom. This assumes that the aggregation process starts by the interaction between one of the clusters and one given carbon atom of the other cluster [5]. This simple and approximate model leads to the following straightforward expression for the aggregation rate constants:

$$k_{ij} = \alpha R_{ij}^3 e^{-\gamma \frac{\left(\Delta G_i' + \Delta G_j'\right)}{kT}}, \tag{5}$$

where k_{ij} is the rate constant for the aggregation between C_i and C_j. R_{ij} is the collision radius for C_i and C_j. This may be approximated by $\frac{R_i + R_j}{2}$ [10], and γ and α are adjustable parameters. $\Delta G_i'$, respectively $\Delta G_j'$, is the difference between the formation free enthalpy per atom for cluster C_{i+1} and C_i:

$$\Delta G_i' = n(\Delta G_{i+1} - \Delta G_i)$$
$$= n(\Delta H_{i+1} - \Delta H_i) - nT(\Delta S_{i+1} - \Delta S_i), \tag{6}$$

where ΔH_i and ΔS_i are the enthalpy and the entropy of formation for the cluster C_n and T is the temperature.

An interesting feature of the Bernholc model is that the reaction rate constants only depend on the thermodynamic and geometrical characteristics of the cluster. One has indeed to estimate the collision diameter of the different clusters as well as their formation enthalpies and entropies, which can be extrapolated from the cross-sections in [11]. The formation entropy is assumed to be constant for chain clusters $C_{n<10}$. The entropy difference between chain and ring ($C_{n>9}$) clusters was estimated at 20 cal/mol/K [7] per cycle. This is an illustrative first step to the effect of cyclization in the carbon cluster growth process. A more complex model (in preparation) will allow for multiple ring cycles and various isomers for each cluster size starting at $n = 6$.

In general, electron detachment energy is very close to the electron affinity [12]. This is fairly well known for most of the clusters and may therefore be used to estimate the detachment rate constants. Charge transfer between clusters may be well estimated using the approach of Bernholc with an equation similar to (6) where the enthalpies are replaced by the electron affinities. This leads to:

$$T_{i^-j} = \alpha R_{ij}^3 e^{-\xi^- \frac{\Delta A_j + \Delta H_j}{kT}}. \tag{7}$$

For certain values of cluster size, specific data on electron attachment and detachment can be found in [13]. For larger sizes that those given by Bernholc, we extrapolate the enthalpy data, using rules for periodicity of 'magic numbers' as given in [12].

3. Results and discussion

As per the LPIIM experiment, the plasma pressure is assumed to be 0.5 mbar, the DC voltage applied at the cathode $V_{DC} = -550$ V, the inter-electrode distance 5 cm, the electrode diameter 8 cm, with ambient Ar gas temperature (300 K), and a drawn current $I = 0.07$ A. This yields an incident Ar^+ incident flux of order 10^{16} particles/cm^2, roughly doubled when accounting for the energetic charge-exchange neutrals, and an ionisation degree of order 10^{-6}. The sputtering rate has been computed using a Monte-Carlo method, inspired from [14], to deduce the angular and energy distribution

of incident Ar^+ ions onto the cathode, which yielded an average sputtering coefficient for these conditions of 1.17×10^{-4}.

Fig. 1 shows the density of carbon clusters halfway between the two electrodes as a function of carbon cluster size, in steady state (after 1200 s of discharge time). The fine structure of the enthalpy periodicities is washed out, except for the dip between sizes 9 and 10, which is due to the presence of the cyclization entropy in Eq. (6) as we assume that clusters with $n \geqslant 10$ form rings. At this point in the model, though, only the first cyclization is considered, and multi-rings isomers are neglected. Extensions are planned which will include multiple isomers for large n [6,11,15]. It is interesting to note that earlier results from our model following a simpler cluster chemistry based on the work of Creasy [6] and including only neutral clusters yielded much smaller densities of large n clusters for the same conditions. It is expected that the presence of (possibly trapped) negatively charged clusters and dust particles in the discharge contributes to the build-up of these clusters. This will be further investigated by prescribing an electric potential with a maximum inside the discharge, thus creating a double sheath. Fig. 2 shows the time evolution of the density (bottom panel) and average size (top) of the 'large' dust particles with $n > n_{crit}$. Here, n_{crit} was chosen to be 60, i.e. the dust particle seed can be a C_{60} fullerene. One can clearly distinguish two phases. Early on, there is a fast nucleation phase during which the large dust particles are being aggregated from smaller clusters, according to reaction (1), then there is a long accretion phase during which the dust particles

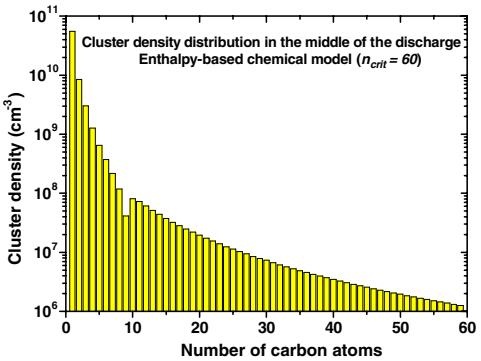

Fig. 1. Density distribution of carbon clusters, for $n_{crit} = 60$, halfway between the two electrodes, in steady-state. One can notice the impact of the entropy of cyclization, here only included between C_9 and C_{10} for illustrative purposes. See text for model description.

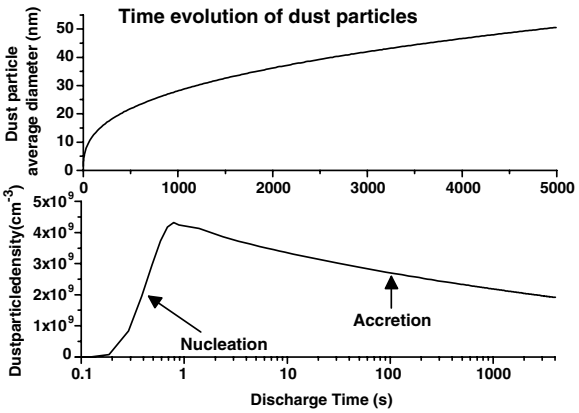

Fig. 2. Time evolution of 'dust' particles (with size $n > n_{crit}$) density (bottom) and average diameter (top). Same conditions as in Fig. 1. One clearly distinguishes a fast early transient nucleation phase, followed by a long steady accretion phase during which the dust particles grow in size to several tens of nanometres.

grow in size as they stick together, while simultaneously still aggregating middle-size and small clusters, as can be seen in the top panel, where their average diameter (assuming a spherical shape) is shown to increase steadily in time. This latter process is limited by the collision frequencies between 'large' dust particles. Although the timescale to reach a dust grain size of 40 nm is only a factor of two lower than the observed experimental time inside the LPIIM device, the lack of a saturation mechanism at very long times and the sensitivity of these results to the value of n_{crit} (for $n_{crit} = 30$, a much larger quantity of 'dust' particles and faster growth is observed) and the strong impact of cyclization energy lead us to believe that the model is in need of further refinements. Some of the discrepancy can also be explained by the fact that the LPIIM dust is observed to be highly porous, and thus the assumption of solid spheres dust particles used to compute their average diameter is an underestimate of their true average size.

4. Conclusions

A numerical model of carbon dust formation by cluster nucleation, growth and aggregation has been developed. Initial results are consistent with experimental observations, but are quite sensitive to model parameters. The latter are for a large part obtained from scaling principles, as very little exists in terms of measured or calculated rate coefficients

for carbon cluster chemistry reactions. Isomerization effects are found to be important for determining individual cluster populations and need to be further addressed in more detail. The possibility also exists of an electric potential maximum inside the plasma column, trapping negatively charged clusters and dust particles for very long times, hence enhancing their potential as dust particle growth sites, and studies of dust production in such a configuration and with a more detailed model will be the topic of a later paper.

Acknowledgement

This work has been supported in part by CEA Technofusion Contract #V3464.001.

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