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THE CONDITIONS FOR EFFECTIVE CLUSTERING IN A PLASMA-DISCHARGE SOURCE IDENTIFIED VIA MONTE-CARLO SIMULATIONS

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Abstract – *The assumption that the ionization and coagulation of metal particles in a plasma-generating cluster source can be described by the orbital limited motion theory, examined by Monte Carlo calculations, was found inadequate. That assumption cannot firstly predict the modes of cluster ionization observed experimentally. Secondly, the effectiveness of coagulation was found to depend on the initial size of the condensing particles. Specifically, the coagulation of dust particles proceeds in a satisfactory degree. The coagulation of single atoms in a cluster source, however, saturates at about 140 atoms per cluster, in serious underestimation of relevant experimental data. ©1999 Acta Metallurgica Inc.*

INTRODUCTION

Certain of the most important cluster sources (such as the laser-ablation, the magnetron and the hollow-cathode source) generate plasma during particle coagulation. Nevertheless, clustering under plasma conditions is very poorly studied and understood. On the experimental front, it has been observed that negatively as well as positively ionised clusters coexist during coagulation (1), suggesting that electromagnetic interactions may be responsible for clustering. On the theoretical front, the coagulation of 10 Å-radius dust particles in a steady-state plasma was successfully described in terms of electrostatic and dipole interactions (2). The untested use of this model to describe clustering in a gas-aggregation source, however, is not safe because in the source the coagulation conditions are significantly less favourable than those previously assumed (2). The purpose of the present study is to examine whether or under what conditions the model of Ref. (2) is applicable to a plasma-discharge cluster source. The relevant realistic conditions tested in the present Monte Carlo calculation is that clustering starts from atoms and that the interaction time is about 1 msec (1).

SIMULATION ALGORITHM

A sample volume, 10^{-15} m^3, of the experimental apparatus has been considered with periodic boundary conditions. Monte Carlo calculations take into account the interaction of metal particle with each other and with the plasma components, i.e. electrons and ions. A constant electron density is assumed and the overall neutrality is obtained by adjusting the ion density. All plasma components and metal particles are considered in thermodynamic equilibrium. The scattering rate of a particle with a specific type of scattering center is calculated using the formulae

$$f_i = \int_0^\infty N(\varepsilon) * v(\varepsilon) * \sigma_i(\varepsilon) * d\varepsilon, \qquad [1]$$

where N is the density of scattering centers, v the relative velocity of the particle and the scattering center and σ the cross section which is calculated in the center of mass reference system. Both coagulation and ionization cross sections are calculated taking into account electrostatic forces. In particular, a neutral particle interacts with a charged particle via a dipole moment induced by the latter to the former. Finally, the temperature of clusters is considered to be size independent, while the density of all plasma components follows a Maxwell-Boltzmann distribution over energy. More details may be found in Ref.(2). The calculations were performed for two kinds of particles, differentiated by their initial size. A radius of 1.5 Å represents Cu atoms, while a radius of 10 Å represents the metal dust particles used in the previous calculation (2).

SIMULATION RESULTS AND DISCUSSION

It may be instructive first to describe qualitatively the evolution of events taking place when Cu atoms (or dust particles) and plasma are mixed. As soon as the interaction is turned on, all the present (initially neutral) Cu atoms are negatively ionized. This happens because the number of collisions with electrons is overwhelming compared to those with Ar^+ ions. As a consequence, a short-lived outburst of clustering observed at the very outset, caused by Cu^0-Cu^- dipole interaction, stops because, as already mentioned, all the particles become negatively charged and repulse each other. Nevertheless, a few dimmers manage to be formed in the mean time. As the particle-plasma interaction continues, some of the negatively charged metal particles will turn to neutral when they collide with Ar^+. These fresh neutrals are very short lived. They almost instantly interact with either other negatively charged Cu particles leading to larger negative clusters, or with electrons reverting to negatively ionized clusters of the same mass. This clustering process, however, soon fades out because the density of scattering centers is reduced due to clustering. Nevertheless, because in the mean time the dimensions of the clusters have increased, a second coagulation stage, supported by multiple ionization, becomes possible. During that stage, the mean negative charge per cluster increases significantly causing a commensurate increase in the strength of the dipole interaction, giving a fresh outburst of clustering events.

In more quantitative terms, Figure 1a shows the evolution in time of the mean number of atoms per cluster and Figure 1b of the mean charge per cluster, for two kinds of particles with initial radius 1.5 Å and 10 Å. The results of Figure 1a clearly demonstrate that the efficiency of coagulation depends significantly on the initial dimensions of the particles involved. In fact, while the 10 Å particles, in agreement with Ref. (2), coagulate efficiently, the coagulation initiated by single atoms stops relatively soon, reaching a plateau at about 140 atoms per clusters. This is a serious size underestimation since the experimental sizes range between 1,000 and 300,0000 atoms per cluster (1).

It should be pointed out that several contradictory effects are competing with each other, and depending on the particular circumstances the one or the other may assume ascendancy. Such a case is, for instance, in the very early stages of clustering, when as Figure 1a reveals single atoms coagulate faster than dust particles. To understand this feature which

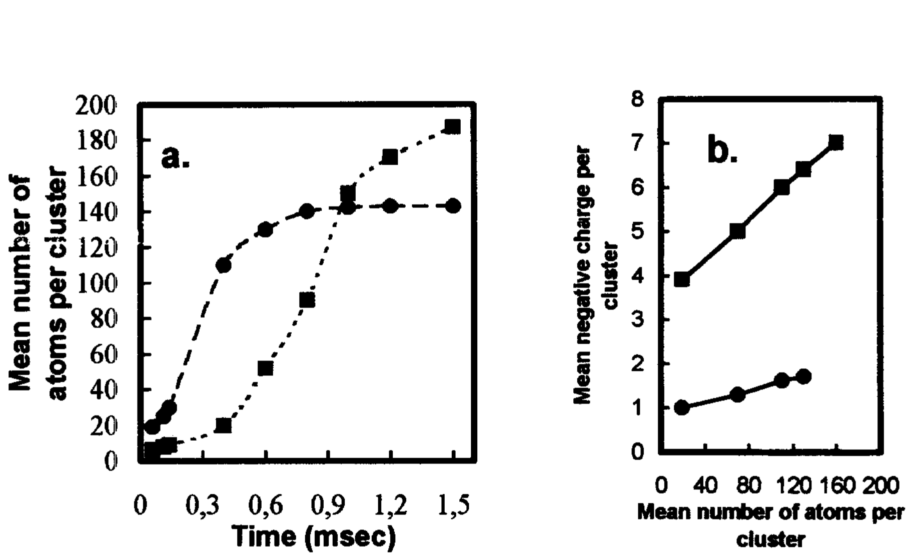

Figure 1. The dependence of mean number of particles per cluster on (a) time and (b) on mean negative charge per cluster for two different atomic radius:(circles 1.5 Å and squares 10 Å).

seems inconsistent with the final outcome, it must be taken into account that, as Figure 1b shows, the small clusters built by atoms sustain smaller negative charge than the clusters composed of dust particles. Consequently, the probability for the former clusters to get neutralized via collisions with Ar^+, and as a consequence to coagulate, is larger than that for the later. This coagulation, however, reduces the number of the atoms and of the atom-composed clusters, leading to the plateau observed in fig. 1a. On the other hand, the charge on the dust-composed clusters, as Figure 1b shows, increases faster with size than on the atom-composed clusters. Apparently, this faster increase is sufficient to compensate for the decreasing number of the dust-composed clusters (see Equation 1), ensuring the unhindered coagulation of these particles.

Let us conclude with a brief demonstration of the effect of various cluster-source conditions on the size of the clusters produced under these conditions. Figure 2 shows the size distribution of dust-composed clusters produced after coagulation of 0.1 msec. Different values of electron temperature, initial particle concentration and electron density are tested. The straight lines obtained indicate that in all cases the calculated cluster-size distribution is in perfect agreement with a lognormal-distribution behavior, previously identified to be associated with neutral particle clustering (3). The present results, however, clearly indicate that particle neutrality is not at all a prerequisite for log-normal clustering behavior. Figure 2 shows, furthermore, that particle coagulation stops when the number of metal particles becomes comparable to the number of electrons. It is interesting to notice that the same effect is produced either by changing the number of metal particles or the number of electrons. Therefore, a very important parameter in plasma clustering is the ratio of the initial number of particles over the number of electrons. Finally, the energy of electrons is also a factor of consequence. Specifically, low energy electrons, being more efficient negative particle ionizers, cause enhanced coagulation.

CONCLUSIONS

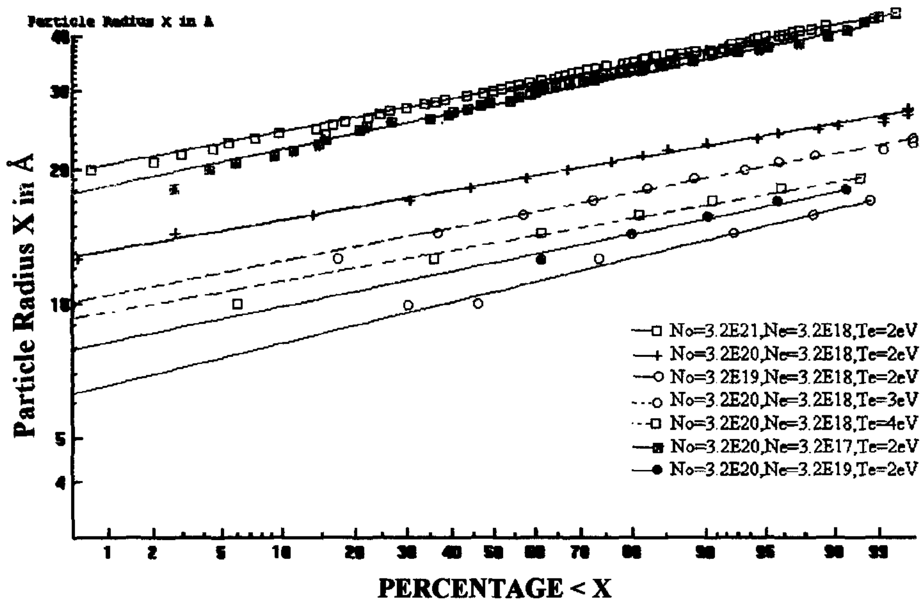

Figure 2. The particle distribution as a function of initial number of particles (No), electron density (Ne) and electron temperature (Te)

A model for particle coagulation in plasma (2) was tested under conditions associated with a plasma-generating, gas-aggregation cluster source. The theoretical calculations reproduced neither the ionization nor the size of the clusters observed experimentally. With respect to the former, while the calculations predict the presence of only negatively charged clusters (and a few virtual neutrals) from the very beginning, the experimental data indicate that negative, positive and neutral clusters coexist during at least the first msec of interaction. In fact, the theoretical underestimation of cluster size, is most probably the consequence of the extremely restricted mode of ionization predicted by the model. Obviously, if positive, negative and neutral particles coexist, their coagulation, via various electrostatic interactions, will be much more efficient and faster than the predictions of the presently tested model (2). It seems, therefore, that the future effort should be directed towards a more realistic description of particle ionization in a plasma-discharge cluster source.

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