

Physical Processes of Cluster Formation in Gas Aggregation and Fast Atom Bombardment

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An understanding of the physical processes underlying cluster formation has been one of the fundamental issues in the field of cluster physics. It has not reached at a level of enough understanding yet. Recently, we have analyzed the experimental data coming from both a magnetron-sputter-type gas aggregation source and a fast atom bombardment(FAB) source. We have obtained a new insight on the physical processes underlying cluster formation in these two cases. In the case of gas aggregation source, our observation was quite different from the expectation of classical nucleation theory. We have assumed a simple but nontrivial picture, i.e., a coexistence of a flux of postthermalized atoms and a steady flow of prethermalized atoms at an earlier stage of gas aggregation. The calculation based on this picture has reproduced the experimental observation quite well. In the case of FAB source, we have observed cluster abundance spectra for the 3d transition metals. Motivated by an apparently recognized power-law nature of the spectrum for Cu, we have applied a scaling *Ansatz* for those spectra. Surprisingly, all the spectra coincide with each other. Guided by the observation of this remarkable regularity, a bond percolation model assuming a mechanical break-up of the sputtered surface has been examined. The calculation based on this model has reproduced all the observed spectra remarkably well. In conclusion, simple but nontrivial pictures seem to work sufficiently well to describe the physical processes underlying cluster formation.

Key words: Metal Cluster, Formation Mechanism, Gas Aggregation, Sputtering

1. INTRODUCTION

An understanding of physical processes underlying cluster formation has been one of the fundamental issues in the field of cluster physics. It has not reached at a level of enough understanding yet [1].

Actually, clusters can be formed in many ways, e.g., a supersonic nozzle jet, a gas aggregation process and a sputtering process, each of which involves a considerable degree of complication. At first glance, it may be seen very difficult to understand the physical processes underlying cluster formation.

Recently, we have reexamined such a commonly accepted viewpoint through an analysis of the experimental data coming from both a magnetron-sputter-type gas aggregation source and a fast atom bombardment(FAB) source.

We have observed a cluster growth from a monomer atom to a cluster of several thousands atoms in the case of gas aggregation source. On the contrary, we have observed clusters possibly coming from the fragmentation of bulk surface in the case of FAB source.

With use of simple but nontrivial physical pictures based on kinetics and mechanics, we have obtained a new insight on the physical processes underlying cluster formation in these two cases.

2. EXPERIMENT WITH GAS AGGREGATION SOURCE

We have observed a cluster growth from a monomer to a cluster of several thousands atoms for the metals Al, Ti, Zn, Zr, Ta and W. The measurements of cluster cations have been carried out with use of a metal cluster source controlled with a magnetron sputtering and a gas aggregation in conjunction with a reflectron TOF mass analyzer.

Metal clusters were formed inside an aggregation cell filled with a flowing undercooled inert gas, i.e., a mixture of He and Ar, while a magnetron sputtering provided a sufficient vapor pressure. The cluster size could be varied by changing an aggregation length L , i.e., the distance between the magnetron target and the exit slit, under a given combination of a gas pressure, a gas temperature and a sputtering rate in the aggregation cell.

As for the abundance spectra for Ti(see Figure 1-(a)), monomer atoms dominate at $L = 7$ cm. With the increase of L , larger clusters grow gradually. Furthermore, we can find an apparent two bands structure with a dip around a cluster size of 15 in the spectra with a larger L . The position of the dip was almost independent on both the temperature of aggregation cell and the sputtering rate. The similar tendencies are also observed

for the cluster growth of other materials(see Figure 1-(b)).

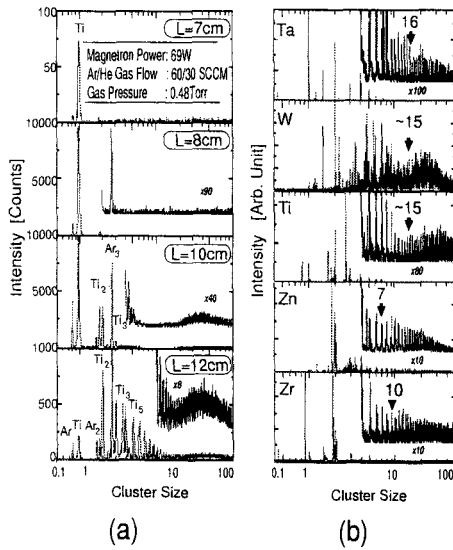


Figure 1. Cluster abundance spectra (a)for Ti with various L 's and (b)for Ta, W, Ti, Zn and Zr.

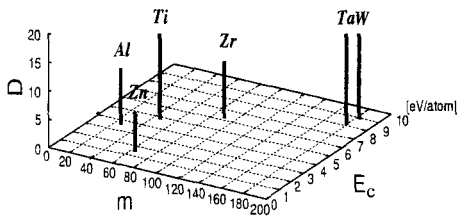


Figure 2. Dip position D as a function of the mass m and the cohesive energy E_c .

Previously, a classical nucleation theory was successfully applied to an experiment of a cluster growth for CO_2 within a supersonic nozzle jet source [2]. In the experiment, a uniform exponential decrease in cluster abundance spectrum was observed for a lower concentration of monomers while a log-normal distribution was observed for a higher concentration. The theoretical expectations were consistent with these observations [3] [4].

Our observation was quite different from such expectation of classical nucleation theory. Furthermore, the observed dip positions D 's seem to show a certain regularity as a function of the mass m of monomer atom and the cohesive energy E_c of bulk material, i.e., a function such as an elliptic paraboloid $D = (m - 200)^2/25000 + E_c^2/10$ (see Figure 2).

In order to understand a possible mechanism making such specific features, we have carried out a model calculation based on a simple kinematical picture under the following assumptions; (1)No evaporation, i.e., supersaturation, (2)Dominance

of condensation at a sticking rate of 100 % with a geometrical cross section, and (3)Cluster coalescence in addition to a monomer absorption.

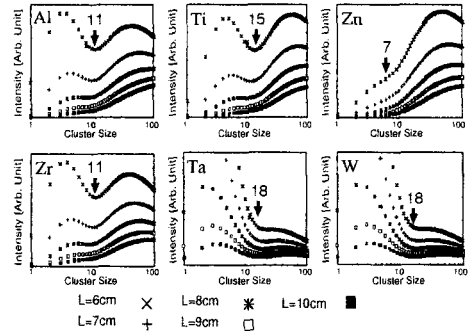


Figure 3. Results of the model calculations.

Then, the corresponding rate equations are written as;

$$\begin{aligned} \frac{dn_k}{dt} &= F(t) - \sum_i C_{ik} n_i n_k \text{ (if } k = 1) \\ &= \sum_{i+j=k, i \leq j} C_{ij} n_i n_j - \sum_i C_{ik} n_i n_k \text{ (otherwise),} \end{aligned} \quad (1)$$

where $n_k(0) = 1$ (if $k = 1$) or 0 (otherwise), $F(t) = F_0$ (if $0 \leq t \leq \frac{W}{v_D}$) or 0 (otherwise), and F_0 , W and v_D are a flux of postthermalized atoms, a width of postthermalization region and a velocity of gas flow. C_{ij} is an aggregation coefficient for a cluster of size i and a cluster of size j [5].

It should be noted that we have assumed a simple but nontrivial picture in the equations (1), i.e., a coexistence of a flux of postthermalized atoms and a steady flow of prethermalized atoms at an earlier stage of gas aggregation.

Figure 3 shows the results of our calculation for abundance spectra. Here, the flux F_0 and the width W are estimated with use of a molecular dynamics simulation assuming the initial energy distribution of monomer atoms for each material determined by its cohesive energy [6]. It is found that our calculation successfully reproduces the observed spectra and their dip positions.

As for the dip position, the model suggests the following qualitative understanding. The dip position is determined by the competition between two processes of cluster formation, i.e., a monomer absorption and a cluster coalescence. The more dominant the monomer absorption, the larger the dip position. The contribution of monomer absorption becomes dominant as the coefficient C_{11} increases with a decrease of the mass m . It also remains dominant for a longer time with an increase of the cohesive energy E_c because a shift of initial energy distribution to higher energy side due to the increase of E_c effectively results in an increase of the width W .

3. EXPERIMENT WITH FAB SOURCE

We have observed cluster abundance spectra for the 3d transition metals Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn by bombarding a target material with a 6keV Xe atom coming from a FAB source (see Figure 4). The cluster cations accelerated by an extraction potential of 10 kV were guided to a high resolution mass analyzer (JEOL JMS - HX110) with a mass resolution of $\frac{m}{\Delta m} \sim 5000$ and a mass range up to 5000 amu.

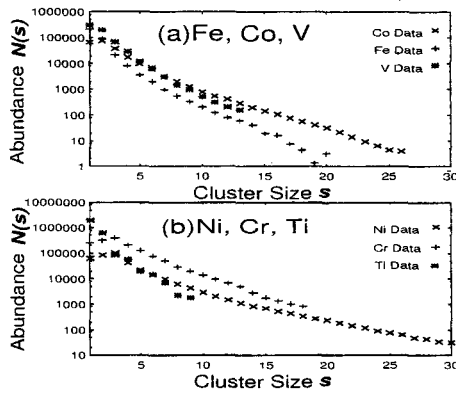


Figure 4. Cluster abundance spectra for some materials.

Motivated by an apparently recognized power-law nature of the spectrum for Cu, we have applied a scaling Ansatz [7] for those spectra. The abundance spectrum $N(s)$ for the cluster size s should be given by a scaling form

$$N(s) = N_0 s^{-\tau} f(s/S), \quad (2)$$

where N_0 is a normalization factor, τ is a critical exponent, $f(s/S)$ is a cutoff function and S is a mean cluster size, i.e., only one characteristic size, defined by

$$S = \frac{\sum_{s=1}^{\infty} s^2 N(s)}{\sum_{s=1}^{\infty} s N(s)}. \quad (3)$$

In the equation (2), the term $s^{-\tau}$ describes a scale-independent part while the term $f(s/S)$ describes a scale-dependent one, i.e., a finite-size effect.

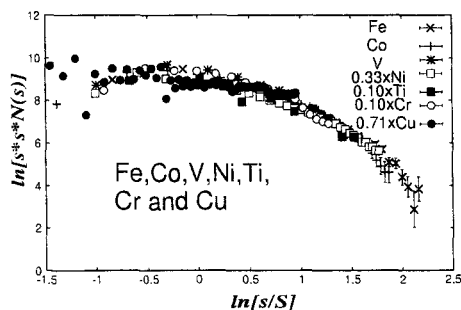


Figure 5. Scaling plots for some materials.

We have made scaling plots for the measured cluster abundance spectra $N(s)$ with a value of 2, i.e., a *superuniversal value*, for τ (see Figure 5). Surprisingly, it is found that all the spectra overlap each other by adjusting their normalization factors except for Mn and Zn cases. As a result, we have found a remarkable regularity among the measured cluster abundance spectra.

As for Mn and Zn, the situation is quite different, but the cluster abundance spectra $N(s)$ are reproduced very well by an exponentially decreasing function with exponents of 3.3 and 3.7 for Mn and Zn, respectively. Since they don't follow the observed scaling function for other materials at all, the cluster formation mechanism for them seems to belong to a different universality class.

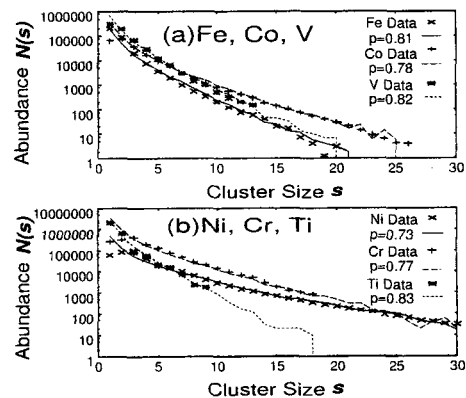


Figure 6. Results of model calculations.

To understand further, we have carried out a calculation based on a percolation theory [8] [9]. To keep the situation as simple as possible, it is assumed that the metal surface consists of the atoms arranged in 2-dimension and connected with each other by a bond and that a cluster is formed when all of its circumferential bonds are broken. Here, the concentration p of broken bonds was an only parameter to fit the experimental data.

The measured cluster abundance spectra for the metals Ti, V, Cr, Fe, Co and Ni are reproduced very well with a suitable value of p (see Figure 6). We assume that the bonds are broken by a thermal excitation so that the value of p for each target material should depend on both the effective bond energy and local temperature of bombarded surface, which are considered closely related to the cohesive energy E_c and thermal conductance k of a bulk material, respectively. Among the target materials, their k 's [10] are very much different from each other while their E_c 's [11] are almost similar to each other. Then, we have examined a possible correlation between the p and k for each material as shown in Figure 7. It is found that the p is strongly anti-correlated with the k at 1000K [12].

The observed anti-correlation between the concentration p and the conductivity k may be inter-

preted as follows. When k is small, the energy deposited by an energetic atom can not be delocalized so much before sputtering and the temperature around the local area remains high resulting in a large p because of the thermal excitation. By the same token, a small p is resulted when k is large.

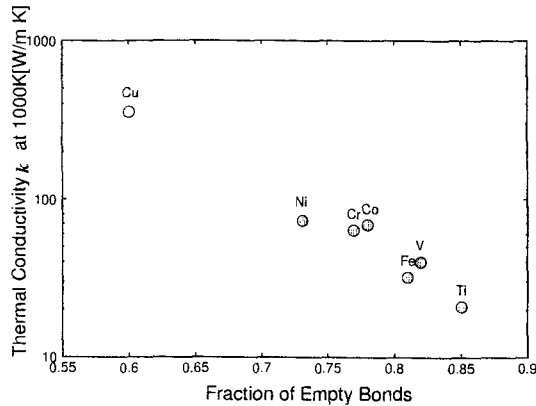


Figure 7. Anti-correlation between p and k .

In the case of Mn, the energy delocalization becomes extremely small because of its small k , i.e. $7.7W/m \cdot K$. Therefore, an evaporation of monomer atoms will dominate. In the case of Zn, an evaporation will also dominate because of its considerably low boiling temperature, i.e., $1176K$. Thus, a different mechanism such as an instantaneous explosion may be working. The exponential decreases of cluster abundance spectra for them are well understood because an agglomeration rate after the explosion is expected to be small [13].

4.SUMMARY

In summary, we have analyzed the experimental data coming from both a magnetron-sputter-type gas aggregation source and a FAB source. We have obtained a new insight on the physical processes underlying cluster formation in these two cases.

In the case of gas aggregation source, we have observed an earlier stage of cluster growth from a monomer to a cluster of several thousands atoms for the metals Al, Ti, Zn, Zr, Ta and W. Our observation was quite different from the expectation of classical nucleation theory. To understand further, we have assumed a simple but nontrivial picture, i.e., a coexistence of a flux of postthermalized atoms and a steady flow of prethermalized atoms at an earlier stage of gas aggregation. The calculation based on this picture has reproduced the experimental observation quite well.

In the case of FAB source, we have observed cluster abundance spectra for the 3d transition metals Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn. Motivated by an apparently recognized power-law nature of Cu spectrum, we have applied a scaling

Ansatz for those spectra. Surprisingly, all the spectra coincide with each other except for Mn and Zn cases. Guided by the observation of this remarkable regularity, a bond percolation model assuming a mechanical break-up of the sputtered surface has been examined. The calculation based on this model has reproduced all the observed spectra remarkably well except for Mn and Zn cases. As for Mn and Zn, a different mechanism such as an instantaneous explosion may be working.

In conclusion, simple but nontrivial pictures seem to work sufficiently well to describe the physical processes underlying cluster formation.

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$$C_{ij} = 2\sigma_{ij} \left(\frac{2k_B T}{\pi} \right)^{1/2} \left(\frac{m_i + m_j}{m_i m_j} \right)^{1/2} \quad (4)$$

$$= C_{11} \frac{(i^{1/3} + j^{1/3})^2}{4\sqrt{2}} \left(\frac{i+j}{ij} \right)^{1/2}, \quad (5)$$

where $C_{11} = \frac{PS_1}{\sqrt{2\pi m k_B T}}$, σ_{ij} is a geometrical cross section. m_i and m_j are the masses, P and T are a vapor pressure and a temperature, respectively and S_1 is a surface area of monomer atom.

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