Computational prediction of niobium-silicide nanopowder growth in thermal plasma synthesis

[共同研究成果]

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A growth process of niobium-silicide nanopowder from the precursory binary vapors of niobium and silicon in a thermal plasma environment has been computed using a unique mathematical model as a recent application of supercomputing. The collective and simultaneous growth behavior through nucleation, co-condensation and coagulation has been clarified. Because of the time lag of binary co-condensation between niobium and silicon, the synthesized nanopowder has wide ranges of the size and the silicon content.

1. Introduction

Efficient production of nanopowder which is composed of nanoparticles is intensively expected for numerous applications in industrial, biomedical, and environmental purification processes because nanoparticles exhibit unique electronic, optical, and catalytic properties which are different from those of larger particles of micrometer size or bulk materials. However, the synthesis of functional nanoparticles of ceramics and alloys seems to be practically arduous by conventional methods since their raw materials have too high melting points to be decomposed. Even combustion processes cannot generate a sufficiently high temperature to vaporize the raw materials; furthermore, combustion requires an oxidation atmosphere, which is undesirable for synthesis of nanoparticles and which produces contamination from combustion products (CO_2, H_2O, etc.).

To overcome such a problem, thermal plasmas have been anticipated as a promising tool for efficient fabrication of nanoparticles [1] because thermal plasmas offer a distinctive thermofluid field involving a higher temperature, high chemical reactivity and variable properties. Moreover, thermal plasmas are controllable by external electromagnetic fields [2-4]. By virtue of such a field, a large amount of raw materials, even that with high melting/boiling points, are vaporized completely. The vapors of the raw materials are transported downstream with the plasma flow to the plasma's tail region where the temperature decreases rapidly; and consequently the vapors become highly supersaturated. Because the supersaturated state is unstable, the vapors change their phases quickly to very small particles through the collective and simultaneous formation through nucleation, condensation and coagulation among the particles themselves. In consequence, nanoparticles are mass-produced at a high rate.

However, it is still difficult to investigate the formation mechanism of functional nanoparticles of ceramics and alloys generated in/around a plasma because the process involves remarkably severe and intricate heat/mass transfer associated with phase conversions in a few tens of milliseconds in a complex thermofluid field. Experimental approaches using a direct measurement or observation are currently impossible owing to technological limitations, whereas numerical studies have struggled with the mathematical formulation to express the intricate multi-scale physics and the shortage of computational resources to obtain practically meaningful solutions. Meanwhile, the recent progress of supercomputing systems is noticeable, which has made it possible to simulate multi-scale and complicated phenomena with sufficient accuracy: even for numerical investigations of the nano-material processing by thermal plasma. This paper presents a computational clarification of a binary growth process of a functional ceramic nanopowder under a thermal plasma condition.

2. Model description

The vapor phase syntheses of a binary functional nanopowder can be computed using a unique mathematical model that was recently developed by the author [5, 6]. The model describes a collective and simultaneous growth process of two-component nanoparticles in a binary vapor system with the following assumptions:

(i) nanoparticles are spherical;

(ii) inertia of nanoparticle is negligible;

(iii) the temperature of nanoparticles is identical to that of the bulk gas surrounding them;

(iv) heat generated by condensation and the electric charge of nanoparticles are neglected; and

(vi) the material vapors are regarded as an ideal gas.

To treat the particle size and composition during the growth, the model introduces the particle size-composition distribution (PSCD) on the basis of two-directional nodal discretization [7]. Using the PSCD, the net production rate of nanoparticles having the volume v_k and the content of the second material x_n is written by the increment of the number density N during the infinitesimal time Δt as:

$$
\begin{aligned}
\frac{\Delta N_{k,n}}{\Delta t} = {} & J_{binary}\xi_k^{(nucl)}\psi_n^{(nucl)} \\
& + \sum_i \sum_l \frac{\left(\xi_{i,l,k}^{(cond)}\psi_{i,l,n}^{(cond)} - \delta_{i,k}\delta_{l,n}\right)N_{i.k}}{\Delta t} \\
& + \frac{1}{2}\sum_i \sum_j \sum_l \sum_m \xi_{i,j,k}^{(coag)}\psi_{i,j,l,m,n}^{(coag)}\beta_{i,j,l,m}N_{i.l}N_{j,m} - N_{k,n}\sum_i \sum_l \beta_{i,k,l,n}N_{i.l}
\end{aligned}
\tag{1}
$$

Here, ξ_i and ψ_i denote the splitting operators for the size and composition, respectively. δ is the Kronecker's delta. The first term on the right-hand side represents the contributions of binary homogeneous nucleation. The second term means the production rate caused by vapor condensation on the particles having v_i and x_l. The third and fourth terms express the gain and loss by coagulation among nanoparticles. β is the collision frequency function for nanoparticles resulting from Brownian motion [8]. Subscripts i and j denote the node numbers for size, whereas subscripts l and m signify those for composition. To obtain the homogeneous nucleation rate J_{binary} for a binary system, the theoretical formula derived by Wyslouzil and Wilemski [9] is used.

When the growth rate of nanoparticles by heterogeneous condensation of the vapor of material M, the following formula considering the rarefied gas effect correction is used to calculate the volume increment $v_{(M)i,l}$ during the infinitesimal time increment Δt:

$$
\begin{aligned}
\frac{\Delta v_{(M)i,l}}{\Delta t} = {} & 2\pi d_i D_{vap(M)}v_{vap(M)}\left(N_{vap(M)} - N_{S(M)i,l}\right) \\
& \times \left[\frac{0.75\alpha_{(M)}(1+\mathrm{Kn}_i)}{0.75\alpha_{(M)} + 0.283\alpha_{(M)}\mathrm{Kn}_i + \mathrm{Kn}_i + \mathrm{Kn}_i^2}\right]
\end{aligned}
\tag{2}
$$

where, d is the diameter, D is the diffusion coefficient, and Kn is the Knudsen number. The subscript *vap* denotes vapor. α represents the accommodation coefficient which has a value of 0.1 here. N_S means the saturated vapor concentration considering the effects of material mixture and surface curvature [10]. Note that the nanoparticles are allowed to grow by condensation only when the free energy gradients for particle formation, W, in a binary system is negative or zero:

$$\frac{\partial W}{\partial n_{(M)}} \leq 0 \qquad\qquad (3)$$

where, $n_{(M)}$ represents the number of monomers of material M in a nanoparticle. W is composed of the chemical potentials and the surface energy. The population balance equations of the material vapors are also computed simultaneously because the number densities of the material vapors crucially affect the growth process:

$$\frac{\Delta N_{vap(M)}}{\Delta t} = -\sum_{k} J_{binary}\xi_k^{(nucl)}n_{(M)}^* - \sum_i \sum_l \frac{N_{i,l}\Delta v_{(M)i,l}}{v_{vap(M)}\Delta t} \qquad\qquad (4)$$

where $n_{(M)}^*$ represents the number of monomers of material M composing a stable nucleus. In the computation, the melting point depressions due to nano-scale size and the mixture effect are considered [11]. It is assumed that the nanoparticles with the temperature lower than their melting point cannot grow by coagulation.

3. Computational conditions

The synthesis of niobium silicide nanopowder is selected as a target process. Those nanoparticles have attracted a plenty of interests of physicists and chemists as well as engineers because their collective and simultaneous growth from the vapor phases is a complicatedly interacting process and the fabrication of them with well-controlled sizes and compositions is still very difficult. Those problems are fundamentally attributed to the large difference of the saturation vapor pressures of niobium and silicon. Currently, only the model described in the previous section seems to be able to analyze the detailed mechanism of the collective and simultaneous growth of niobium silicide nanopowder. The computation is demonstrated under a typical condition of the synthesis using a thermal plasma as follows. Coarse precursory powders of niobium and silicon are injected in the ratio of Nb:Si = 1:1 into the thermal plasma. The vapor ratio of the precursors to Ar is set to be 0.5 %. They are vaporized immediately in the high-enthalpy plasma and the vapors are transported downstream with the decrease in their temperature. The computation begins from this situation in which the vapors are about to be supersaturated. The temperature decreases monotonically at the cooling rate of 10^5 K/s. The mathematical model embeds the discrete nodes in the size-composition space. Here, 101 x 101 nodes were placed in the size and composition directions, respectively. The material properties of niobium and silicon were obtained from Ref. [12].

4. Results and discussion

Figure 1 shows the evolution of the PSCD in the Nb-Si binary system, which expresses the collective and simultaneous growth of niobium silicide nanopowder. As the temperature decreases, niobium vapor becomes supersaturated at a higher temperature than silicon vapor. The supersaturated niobium vapor starts to generate stable nuclei which are the embryos of nanoparticles; and the neclei grow up to niobium-rich nanoparticles (Figs.1(a) and 1(b)). After silicon vapor becomes supersaturated, the vapors of niobium and silicon co-condense on the existing nanoparticles (Figs.1(c) and 1(d)), because the saturation pressure of niobium is much lower than that of silicon. Following the consumption of niobium vapor, silicon vapor is consumed and consequently the silicon content of the nanopowder becomes larger (Figs.1(e) and 1(f)). During this process, coagulation among the nanoparticles also takes place simultaneously. As a result of this growth behavior, the Nb-Si system produces a nanopowder having wide ranges of the size and the silicon content because of the time lag of co-condensation between niobium and silicon. Figure 1 also tells that the majority of the nanoparticles have the diameters around 10 nm and the silicon content of 50 at.%. It is noteworthy that the other smaller nanoparticles have smaller contents of silicon. These features are
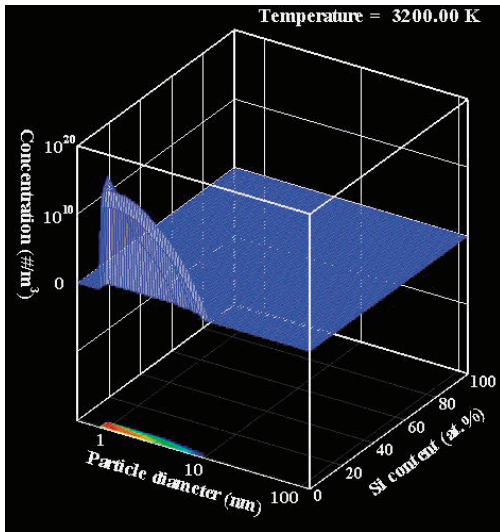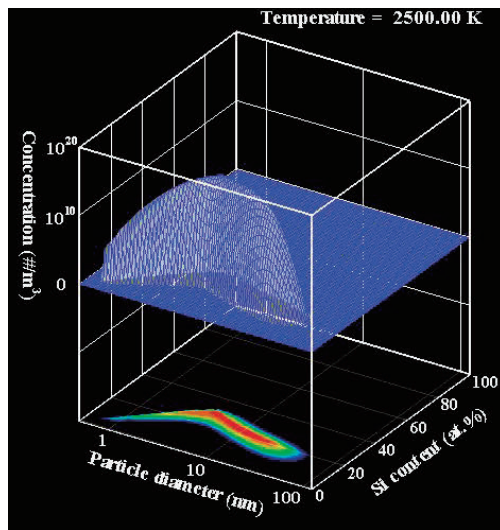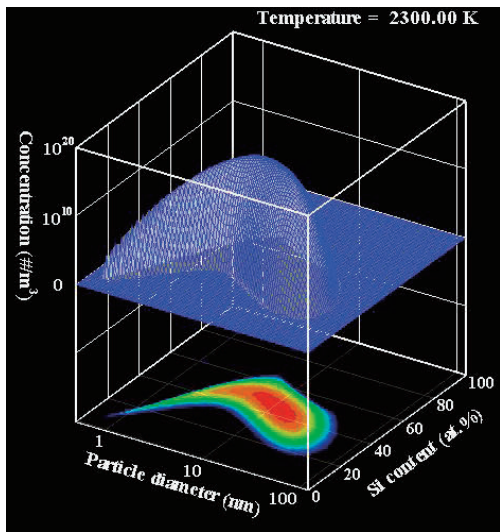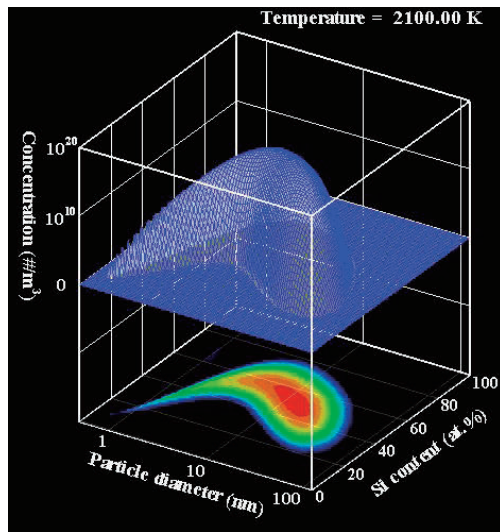
(a) 3200 K
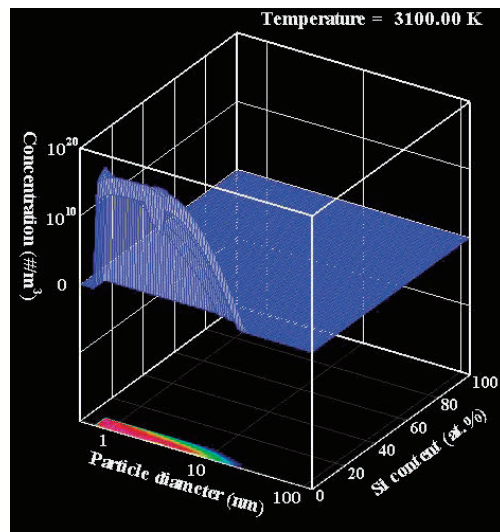
(b) 3100 K
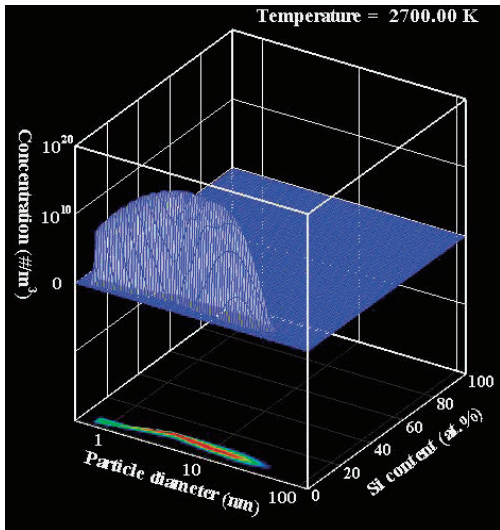
(c) 2700 K

(d) 2500 K

(e) 2300 K

(f) 2100 K

Fig. 1　Growth process of Nb-Si nanopowder

determined by the balance of the particle size and the condensation rate which is a function of the particle size as described in Eq. (2).

5. Summary

The high performance of supercomputing systems has made it feasible to clarify multi-scale physics. As a recent application of supercomputing, a growth process of niobium-silicide nanopowder from the precursory binary vapors of niobium and silicon in a thermal plasma environment has been computed using a unique mathematical model. The collective and simultaneous growth behavior through nucleation, co-condensation and coagulation has been clarified. Because of the time lag of binary co-condensation between niobium and silicon, the synthesized nanopowder has wide ranges of the size and the silicon content. The nanopowder also has some nanoparticles deviated from the mean size and the mean silicon content.

Acknowledgements

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