Journal of Aerosol Science 91 (2016) 33–42

Contents lists available at ScienceDirect

Journal of Aerosol Science

journal homepage: www.elsevier.com/locate/jaerosci

Changing of the shape and structure of Cu nanoclusters generated from a gas phase: MD simulations

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ARTICLE INFO

Article history:
Received 11 June 2015
Received in revised form
19 September 2015
Accepted 21 September 2015
Available online 24 October 2015

Keywords:
Gas-phase condensation
Computer simulations
Tight-binding potential
Copper
Nanoclusters
Diffusion

ABSTRACT

The gas-phase condensation of 85,000 Cu atoms is examined by molecular dynamics simulation with a tight-binding potential. A detailed study of the evolution of the system cooled at a constant rate from 1000 K to 77 K is presented. The results are used to identify four distinct stages of the evolution from a hot atomic gas to a few synthesized particles. The effect of the subsequent thermal treatment on the shape and structure of synthesized particles was studied by simulating their gradual heating in a range of 100–1200 K. It is concluded that short-term heating leads to significant ordering of the internal structure in 70% of agglomerated nanoparticles with the predominant formation of spherical shapes. In order to explain this result, the main mechanisms of cluster formation from the gas phase have been analyzed and it is found that the agglomeration temperature plays the main role in the formation of clusters with unified shape and structure.

1. Introduction

Studying individual nanoparticles and the nanostructured state is currently one of the most intensively developing fields of research in physics, chemistry, and engineering. Great scientific and practical interest in such research results from the unique properties of nanoparticles that are already or will be widely used in the immediate future for the fabrication of miniature electronic devices, and production of new materials.

Copper clusters hold a most unique position among the whole range of currently used metal nanoparticles. These particles have many unique properties and are relatively inexpensive for manufacturing. Relating to conducting properties copper nanosized particles may compete with silver. Also the range of their usage is wide in the form of catalysts (Dubey et al., 2012). However the formation of nanoparticles of copper with implementation of application area dependent properties specifies very strict requirements to their producing and processing. One of the promising techniques of nanodispersed particles synthesis process is metals evaporation and condensation in the inert gas atmosphere. Theoretically, this technique makes it possible to synthesize nanoparticles with controlled chemical composition (Starsich et al., 2014), defect density, structure, and size distribution. Moreover, it is relatively easy to control the parameters of gas-phase synthesis under experimental conditions (Kauffeldt & Kauffeldt, 2006; Weber et al., 2006; Seipenbusch et al., 2007).

However one of the main characteristics of vapor phase synthesis method is the substantial inner structure and external shape discontinuity of resulting nanoparticles. Therefore, depending on process parameters up to 90% of particles non-spherical shape and different inner structure may be formed. Production of nanoparticles of desired shape, and structure

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http://dx.doi.org/10.1016/j.jaerosci.2015.09.004
0021-8502/

can be another important step toward their more versatile use. However, the preparation of clusters of certain morphology is a formidable technical task. To solve this problem the method of heat treatment of obtainable metallic particles can be used as a final stage of synthesis from gaseous phase.

It is necessary to have precise information on morphological changes in particles under study throughout the heating process to create the most effective process of thermal action. For this purpose two methods of particles heat treatment studying are experimentally used—*differential electrical mobility analyzers* (DMA) and *transmission electron microscopy* (TEM) (Tsyganov et al., 2007).

These methods are appropriate for particles concentration, diameter and morphology determination before and after heat treatment, but they fail to provide total information on the processes which occur during materials heating and phenomena which affect structuring and shaping of the treated particles. Only computer modeling can provide such information to the full extent. Therefore, the paper provides the results of the modeling of heat treatment of nanosized copper particles synthesized from gaseous phase in order to produce particles of proper shape and internal structure.

One of the first theoretical attempts of the detailed description of the process of sintering of nanoparticles was realized by Koch and Friedlander (1990). Koch and Friedlander developed a self-preserving model for the sintering by assuming the minimization of the agglomerate surface as the essential driving force for the sintering process. Based upon these studies, models for the mutual interplay between interparticles coalescence and coagulation of agglomerates were developed (Kruis et al., 1993; Seto et al., 1995).

In several articles (Zhu & Averback, 1996; Hendy et al., 2003; Arcidiacono, Bieri, Poulikakos, & Grigoropoulos, 2004) the sintering process of single-crystal spherical nanoparticles of metals (Cu and Au) of different sizes in an inert-gas atmosphere and vacuum were simulated with the help of molecular-dynamics method. In other studies (Alarifi et al., 2013; Buesser & Pratsinis, 2015) sintering of composite Au nanoparticles, composed of two, three and four primary spherical clusters was studied. It was found, that the sintering process is realized in two stages-surface diffusion and plastic deformation nearer to the melting point.

However, in all the works presented above, the sintering processes were studied for nanoparticles, which consisted of single-crystal spherical clusters cut out from the perfect lattice arranged at short intervals from one another. In our work, while studying the processes of thermal effect, Cu nanoparticles synthesized from the gas phase and therefore having different sizes, shape and degree of agglomeration will be used for the first time.

2. Simulation technique

This section gives a description of the basic principles of the MD procedure used in this study. Any simulation method must first choose some potential of interaction between atoms in the system under consideration. The interatomic potentials used in computer simulations range from *ab-initio* to simple Lennard-Jones type empirical ones.

The choice of a particular potential depends on the problem formulation, the properties to be examined, the available computing resources, and the desired accuracy of results. Upon analysis of various representations of the potential energy of interatomic interaction, we decided to simulate the formation of Cu nanoclusters from the high-temperature gas phase in terms of the well-established modified tight-binding TB-SMA potentials as introduced by Cleri and Rosato (Cleri & Rosato, 1993). According to this model, the potential energy of the atomic system is calculated using the following expression:

$$E=\sum_i\left[-\left(\sum_{i\neq j}\xi_{\alpha\beta}^2 e^{-2q_{\alpha\beta}\left(r_{ij}/r_{\alpha\beta}^0-1\right)}\right)^{1/2}+\frac{1}{2}\sum_{i\neq j}A_{\alpha\beta}e^{-p_{\alpha\beta}\left(r_{ij}/r_{\alpha\beta}^0-1\right)}\right], \tag{1}$$

where r_{ij} is the distance between ith and jth atoms and subscripts α and β indicate various types of atoms. The quantities $\xi_{\alpha\beta}$, $p_{\alpha\beta}$, $A_{\alpha\beta}$, $q_{\alpha\beta}$, and $r_{\alpha\beta}^0$, which determine the parameters of system elements are as defined in (Cleri & Rosato, 1993). We believe that this potential of interaction ensures quite adequate description of the process of metal cluster formation on time scales characteristic of its nucleation, coagulation, and subsequent growth and takes into account the main features of interatomic interaction in copper particles.

A simple and efficient computer program is employed in this study to simulate the evolution of several thousands of atoms over a time interval of several nanoseconds. This is impossible to achieve with more realistic models, such as *ab-initio* methods, even on high-performance computers.

The starting point of the condensation process was a spatial configuration consisting of 85,000 Cu atoms, which were uniformly distributed in a region of space with a volume of $V=42{,}600\ \mathrm{nm}^3$ and periodic boundary conditions. The atomic velocities were set according to the Maxwell–Boltzmann distribution at an initial temperature of $T_i=1000$ K, which is quite typical of the gas phase synthesis processes (Backman, Jokiniemi, Auvinen, & Lehtinen, 2002). In the inert-gas–metal–vapor mixture used to produce Cu nanoclusters by gas-phase condensation, the inert gas is mainly required to cool the metal vapor and control its temperature. In our approach, external influences are reduced to heat removal from the simulated system. At the start of the simulation, a supersaturated metal vapor fills the condensation region.

The main idea of the proposed gas-phase condensation model is to minimize the rate of formation of primary nuclei from a supersaturated metal vapor. Otherwise, single atoms or small clusters will be captured on the collection surface. This