Kinetics and mechanisms of nanoparticle formation and growth in vapor phase condensation process

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Abstract

Design of nanoparticle synthesis by inert-gas condensation process was studied according to the mechanisms and kinetics of nucleation and growth in the vapor phase. The effect of process parameters, e.g., source temperature, evaporation rate, and the inert-gas pressure, on the particle size and particle shape was examined at the example for silver and copper–tin alloy. The synthesized nanopowders had near spherical shape with particle size range from 10 to 60 nm dependent on the processing condition. Scanning and transmission electron microscopy (SEM and TEM) analyses showed that the crystallites are subunits of larger agglomerate particles, and relatively large particles display crystal habit. Based on the experimental results and theoretical principles, nucleation, growth, coagulation and coalescence of the particles were analyzed. Accordingly, the kinetics and mechanisms of nanoparticle synthesis in low-pressure gas phase was determined. A simple operating map for nanoparticle synthesis was presented. The results may serve as a guide for design of experimental studies on the effect of process parameters on nanoparticle characteristics.

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1. Introduction

A variety of metal nanoparticles are made today for a spectrum of niche applications. The production methods are rather versatile and a great development has been achieved during the past few years. Among different existing methods, condensation of the corresponding metal vapors is the predominant technology for synthesis of metal nanoparticles [1]. The process is so-called inert-gas consolidation (IGC) method with which Gleiter and co-workers [2] first generated the materials that demonstrated the exciting properties of nanostructured materials [3]. In this method, a metal is typically vaporized into a low density gas by Joule heating, although other ways of evaporation such as thermal plasma [4] and laser ablation [5] are also being used. Vapors migrate from the hot source into a cooler gas by a combination of convective flows and diffusion. The decreasing temperature leads to a far more rapid decrease in the equilibrium vapor pressure and correspondingly high supersaturation [3]. At high supersaturation, the vapors rapidly nucleate, forming very large numbers of extremely small particles. The particles then grow by Brownian coagulation [6]. The product particles are generally collected by thermophoretic deposition. In order to enhance the deposition efficiency, a substrate surface cooled with liquid nitrogen may be used. The production rate is typically low, i.e., in the order of 1–2 kg per day [7]. Recently, some modifications such as forced gas flows [1] were proposed for production of large quantities of nanoparticles by IGC method. The other changes were concerned with the introduction of different evaporation sources to adopt for different starting materials such as high melting point materials [8] or gaseous precursors [9].
A glance through the literature reveals that direct evaporation of metals from heated crucibles into a gas has been widely studied [6,7,10–17]. The production of nanoparticles of bismuth, aluminum, antimony, lead, copper, palladium, and silver has been exclusively examined. However, little systematic work has been devoted to process control in order to improve overall process performance and powder characteristics since the price of metal nanopowders is still very high [1]. In fact, the IGC system is far from optimal for large-scale production of nanoparticles. Therefore, as the technology improves and the product prices become competitive, the need for optimum process design and engineering will rise. As there are many complex processes to consider in the formation of clusters, the design of a production unit is largely an empirical task. In order to understand how particle characteristics could be improved it is necessary to identify the physical variables determining the particle nucleation and growth in vapor phase. These variables can be related to the experimentally controllable process parameters such as evaporation temperature, overall pressure, type of gas convection and chamber geometry in order to optimize the process performance. The outcomes can be used as a design guide for implementation of a gas condensation reactor for controlled deposition of size-selected clusters. To achieve such a goal, a systematic study was performed in the present work on the synthesis of silver and copper–tin nanopowders by vapor condensation process. Silver was especially used because there are many data available in the literature. The metals were heated by a small temperature-regulated crucible and their metal vapors were rapidly quenched on the surface of a liquid nitrogen tank at a reduced atmosphere of argon gas. The influence of the source temperature, evaporation rate, and the argon pressure on the average particle size and particle shape was studied. Scanning and transmission electron microscopy (SEM and TEM) and X-ray diffraction (XRD) methods were used to characterize the produced nanoparticles. In this paper, the kinetics and mechanisms of particle formation and growth in the vapor phase is addressed according to the results of experiments and the theoretical principles of the process.

2. Experimental

Fig. 1 shows a schematic of the inert-gas condensation unit used for the production of nanopowders. The apparatus consists of five basic units: a processing chamber, vacuum pumps and gages, a Mo crucible and RF generator, a liquid nitrogen tank as cold finger, and gas supply unit. A large stainless steel cylinder (diameter 0.55 m, height 0.5 m) was fitted to stainless steel endplates and evacuated to a pressure of approximately 10⁻⁵ torr by a diffusion pump. After an appropriate outgassing, the pumping line was closed and reduced atmosphere of inert argon gas (99.999% purity) was introduced into the cylinder. In order to reduce the oxygen level, gas purging and evacuating was repeated three times. Afterwards, the pressure of chamber was kept constant in the range of 1–100 torr by feeding the argon gas into the chamber. The crucible was then heated under quasi-equilibrium conditions, i.e., constant temperature and pressure. The vertical distance of the evaporation source to the cooled substrate was 0.05 m.

Many evaporations of silver and copper–tin alloy have been performed using the built IGC reactor. When an appropriate quantity of nanopowders had been produced, the heating system and vacuum pumps were turned down, and the chamber was disassembled. The particles were collected by brushing them off the cooling cylinder. The
characterization of the produced nanoparticles was performed by SEM, TEM and XRD. For SEM analysis, a dilute suspension of the nanoparticles and high purity acetone in volume ratio of 1–100 was prepared in an ultrasonic bath. Then, one drop of the suspension was put on a small sheet and dried. The prepared specimens were then studied by using a Philips XL30 SEM. Similar procedure was afforded for TEM analysis on 300 mesh carbon coated copper grids. However, the suspension was diluter, i.e., a volume ratio of 1–1000 was used. The size and morphology of the particles were determined using a high resolution Philips CM200 TEM.

3. Results

3.1. Shape and crystal structure of the nanoparticles

Fig. 2 shows representative SEM micrograph of the synthesized nanoparticles. These particles were produced at 1460 K at reduced atmosphere of argon with 1 torr pressure. It appears that the as-synthesized particles are generally near spherical in shape with very small average particle size. However, the particles are stick together in clusters and formed agglomerates. This is probably an electrostatic effect as well as an artifact of the drying of the aqueous suspension. Here, it is pertinent to point out that formation of sinter necks between the tiny particles is likely to occur. This is attributed to the clean particle surfaces that facilities the growth of the porous powders by welding the particles together in the course of production [10]. Anyway, this clustering clearly makes an evaluation of the particle size troublesome. This problem can be evaded by using high resolution transmission electron microscopy. Fig. 3 shows TEM images of silver and copper–10 wt% tin nanoparticles produced at 1 torr argon pressure. The evaporation temperature was 1460 and 1523 K for the silver and the copper–tin alloy, respectively. The nanoparticles look almost spherical, and this is equally true, irrespective of constituent elements, i.e., silver or copper–tin, and the particles size. Nevertheless, the pictures also illustrate the formation of crystal habit in some of the tiny particles. The diffraction pattern of the nanoparticles is shown in Fig. 4. Analysis of the diffraction rings revealed that the crystal lattice of silver nanoparticles is the same as the bulk silver (Table 1). However, the diffraction rings of the copper–tin alloy...
3.2. Effect of processing condition

Some runs were performed by evaporation of the metals at different evaporation temperatures \( T_{\text{evp}} \) and chamber pressures \( P \). Table 2 reports the average particle size determined by the high resolution TEM. It is apparent that larger particles were formed at higher evaporation temperatures and the gas pressures. TEM image of the silver particles produced at \( T_{\text{evp}} = 1297 \) K and \( P = 0.1 \) torr is shown in Fig. 5. As seen, the particle diameter is about 7 nm that is almost one-third of the size of silver particles produced at \( T_{\text{evp}} = 1460 \) K and \( P = 1 \) torr (Fig. 3(a)). Fig. 6 shows the particle size versus the ratio of \( T_{\text{evp}} \) to \( P \). The results obtained by Turker [10] on silver nanopowders and Braqvist [6] on aluminum nanoparticles were also included in the diagram for comparison. Since the coagulation is a significant and often prevailing mechanism of metal particle growth [19], the slope of the lines \( m \) is dictated by the coagulation rate. This observation is important in description of the mechanism and kinetics of particle formation in the vapor condensation method. This will be addressed briefly in the following section. Anyway, the results suggest that lowering the overall pressure decreases the rate of nucleate growth by coagulation, leading to finer final particles. Similar result is obtained as the evaporation temperature is decreased.

4. Discussion

The mechanism of nanoparticle formation in the inert-gas condensation process includes nucleation, particle growth, particles coagulation and coalescence. The processing condition dictates which of these mechanisms have vital role on the particle characteristics. In this process, the metal atoms effused from the source will rapidly lose their energy by collision with gas atoms. Therefore, the nucleation process is performed homogenously in the vapor phase as regard the collision mean free path is very short, i.e., in the order of 100 nm. If a steady-state cluster formation and distribution is considered, the nucleation rate depends on the supersaturation of metal vapor in the gas phase, \( S \) [3]

\[
J \propto \exp \left( \frac{-\sigma^{3}}{\ln^{2}S} \right)
\]

where \( \sigma \) is the surface tension. The free energy barrier against nucleation is also a function of \( \sigma \) and \( S \) as follows [6]

<table>
<thead>
<tr>
<th>Crystal plane</th>
<th>111</th>
<th>002</th>
<th>022</th>
<th>113</th>
<th>222</th>
<th>004</th>
<th>133</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring diameter (nm)</td>
<td>5.3</td>
<td>6.1</td>
<td>8.7</td>
<td>10.2</td>
<td>10.6</td>
<td>12.3</td>
<td>13.4</td>
</tr>
<tr>
<td>Lattice parameter (Å)</td>
<td>2.359</td>
<td>2.044</td>
<td>1.435</td>
<td>1.231</td>
<td>1.180</td>
<td>1.022</td>
<td>0.938</td>
</tr>
<tr>
<td>Lattice parameter of bulk silver (Å)</td>
<td>2.362</td>
<td>2.050</td>
<td>1.442</td>
<td>1.230</td>
<td>1.183</td>
<td>1.021</td>
<td>0.936</td>
</tr>
</tbody>
</table>

\[ a \] The diffraction pattern taken under high resolution TEM.

\[ b \] Deduced from Ref. [18].
\[ \Delta G^* = \frac{16}{3} \pi \frac{\sigma^3}{(\rho RT \ln S)^2} \]  

where \( \rho \) is the particle density, \( R \) is the gas constant, and \( T \) is temperature. Since the supersaturation of metal vapor is caused by the collision of the metal atoms with the gas atoms, the amount of undercooling determines the supersaturation and thus the nucleation process. It is known that the value of vapor phase undercooling depends on the evaporation temperature. Therefore, according to the temperature dependence of the vapor pressure of materials, it is possible to estimate the supersaturation in the gas phase. Fig. 7 shows the supersaturation of silver vapor in the gas phase dependent on the evaporation temperature for different evaporation temperatures \( T_{evp} \). Data of silver equilibrium pressure have been taken from Ref. [20].

\[ \ln P \text{ (mmHg)} = -\frac{14,400}{T} - 0.85 \log T + 11.7 \]  

As the difference between the evaporation temperature and the gas phase is very high, it is likely that nucleation begins very abruptly and proceeds at a very high rate. For instance, an undercooling of 400 K at the evaporation temperature of 1297 K results in a supersaturation value in the order of \( 10^5 \). According to known classification [19], the nucleation process is considered negligible when supersaturation exceeds \( 10^6 \). Fig. 8 shows the critical undercooling to fulfill this requirement as a function of the evaporation temperature. The nucleation barrier and the
critical diameter of embryonic particles at the evaporation temperature of 1293 K are also shown in Fig. 9. As the critical diameter of embryonic particles and the nucleation energy barrier are extremely low, an undercooling of the order of few hundred degrees leads to the formation of large number of very fine particles. These particles serve as sink for additional vapor, quickly reducing the supersaturation and quenching additional nucleation.

If the supersaturation is limited, the rate of particle formation would be reduced, leading to lower initial number concentrations. The nucleuses can then grow to larger size as additional material is deposited on the surfaces of the growing particles. Since the relative range of particle sizes will decrease as the particle grow, the distribution of the nanoparticle size must be narrow as cited by Okuyama et al. [21] and Flagan and Lunden [3]. In the present experiments, narrow particle size distribution was not obtained (Figs. 3 and 5). Therefore, the supersaturation and thus nucleation was very high. In this case, the particle growth had to be performed due to Brownian coagulation, i.e., the collision of nucleuses resulted in particle growth. The Brownian coagulation rate, i.e., freely molecular process, can be expressed as a function of the particle content within the flow (C) as follows [19]

$$v_{cog} = -K \cdot C^n$$  \hspace{1cm} (4)

where $K$ is coagulation rate constant that equals to $7 \times 10^{-14}$ m$^2$.s$^{-1}$ for most metals and alloys. $n$ also equals to 1.83 for Brownian coagulation. The particle content within the flow is a function of the partial pressure of the vapor phase ($P_{vap}$) and temperature. By simple ideal gas assumption, it can written

$$C = \frac{NRT}{P_{vap}}$$  \hspace{1cm} (5)

where $N$ is the particle mass concentration in the flow. It is known that diffusion of the vapors from the hot source into surrounding low density gas varies inversely with overall pressure [3]. Hence, to account the effect of the overall pressure ($P$), we assume that $P_{vap}$ is a constant fraction of $P$. By substituting this relation into Eq. (4) and then combining with Eq. (5), it is determined that the isothermal rate of particle growth strongly depends on the overall pressure

$$v_{cog} = -K' \left(\frac{1}{P}\right)^n$$  \hspace{1cm} (6)

Consequently, the particle size of nanopowders produced by the vapor condensation method should have a strong dependence on the overall pressure. Fig. 10 shows the operating map of silver nanoparticle synthesis by the inert-gas condensation method. To generalize the processing map and make it useful for design of experimental studies for different material systems, normalized pressure (the ratio of overall pressure to the metal vapor pressure) and normalized
temperature (the ratio of evaporation temperature to the boiling point of the material) were used. It is noticeable that a decrease in the normalized pressure results in production of finer particles. It is known that lowering the pressure increases vapor dispersion and dilution, thereby lowering the volume concentration of particulate materials produced by condensation and slowing their growth by coagulation [3]. In contrast, at the higher pressures the coagulation rate is improved, leading to faster growth of the nucleuses and thus formation of larger particles. Here, it is important to point out that to increases the mass throughput of particles of a given size, the residence time of the nucleuses would have to be decreased to limit growth at the higher pressures.

To produce finer particles, the evaporation temperature could also be decreased. It is evident that the density of particles within the gas phase increases as the source temperature is increased. Consequently, the collision frequency of the particles becomes higher, i.e., coalescence occurs more frequently. This leads to the formation of larger particles at higher evaporation temperatures. Nevertheless, decreasing the evaporation temperature, or equivalently evaporation rate, decreases the mass throughput of the particles. Therefore, in a reactor which primary growth mechanism is coagulation, operating at elevated pressures or temperatures is only beneficial when a short growth time is fulfilled. This objection can be achieved by proper design and implementation of a gas condensation cluster source, e.g., utilization of forced gas flows in the process [1].

5. Conclusions

In the present work, the kinetics and mechanisms of nanoparticle synthesis by the vapor phase condensation method was studied. To understand the influence of process parameters on the product particle characteristics, silver and copper–tin nanopowders were produced by the inert-gas condensation process. The produced particles had near spherical shape with relatively wide particle size distribution. Crystal habit was also observed in larger nanoparticle. The mechanism of nanoparticle formation was emphasized as homogenous nucleation, coagulation, and coalescence. The nucleation rate was found to be very fast due to high supersaturation value induced by the collision of the metal atoms to the surrounding gas atoms. The condensation mechanism for the growth of nucleuses, i.e., deposition of metal atoms on the surface of growing particles, was not undertaken as rate controlling stage as regard the produced nanoparticles had relatively wide distribution. However, coagulation and coalescence of the particles were found to be as dominant growth mechanisms in the synthesis process. According to these mechanisms, the evaporation temperature and chamber pressure have a strong influence on the particle size. Based on the experimental results, a simple operating map for nanoparticle synthesis was presented. The outcome of this research work might be useful for establishing a design route for experimental studies on the nanoparticle characteristics.

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References