Evaporation rate of molten copper in argon and nitrogen gas flow and characteristics of condensed particles

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Abstract. Copper has been levitation-melted in room temperature Ar and N2 gas flows to investigate the evaporation rate and characteristics of condensed particles. The evaporation measured experimentally increased with the increases of the temperature of the levitated Cu, and the gas flow rate. The site, the concentration and temperature at the vapor condensation in the gas film around the levitated Cu was analysed using the temperature distribution and the critical supersaturation concentration of Cu vapor. There was a linear relationship between the calculated and the experimentally obtained evaporation rates. The calculated evaporation rate was larger than the experimentally measured rate. The condensed particles were metallic Cu. When the temperature at the vapor condensation site was lower than the melting point of Cu, the vapor condensed as a solid phase, and the solid particles did not grow with collision-coalescence of the particles. Therefore, the size of them was not influenced by the temperature of levitated Cu and the gas flow rate. When the temperature at the condensation site was higher than the melting point, the size of them was increased by the distance which was the difference in the position at the melting point and the vapor condensation.

1. Introduction

One of the methods for preparing ultrafine particles of metals and alloys is a low pressure gas evaporation method [1]. In this method, a metal is evaporated and metal vapor condenses under reduced pressure. It has been already known that the size of the particles obtained with this method increases with an increase in atmospheric pressure. However, there are scarecely any research in which particles are produced at atmospheric pressure. On the other hand, studies of the evaporation rate in a gas stream are mostly performed in a high-temperature gas stream, and there are few studies in a gas stream at lower temperature than that of the evaporated substance. Evaporation in gas proceeds through a continuous process of evaporation, vapor diffusion, condensation and particle growth. Thus, these four processes for the evaporation in a low temperature gas stream completes in the gas film on the surface of substance [2]. Particle size is influenced by the vapor condensation site and so on in the gas film. Recently, high temperature process such as a plasma process has become easily available. It is also important to investigate the evaporation phenomenon at high temperatures.

The evaporation rates and characteristics of the condensed particles of molten Al and Fe in a stream of argon gas at room temperature were investigated in previous works [3-7]. Temperature ranges for aluminum and iron were 1873 K to 2273 K, and 2173 K to 2273 K respectively. The temperature of the
iron vapor condensation was below the melting point of iron. Whereas condensed particle size of iron was unchanged with temperature of levitation-melted iron, gas flow rate and so on, the particle size of aluminum was influenced by them. Then, as one of a series of fundamental studies of evaporation of metal in room temperature gas stream, evaporation of copper of which melting temperature was between Al and Fe was investigated in this study.

2. Experimental

Figure 1 depicts the main part of the experimental apparatus [3,5]. The levitation melting apparatus was a high frequency induction furnace (130 kHz, 60 kW, Hitachi Kokusai Electric). The temperature of the levitated specimen was measured through the prism by a two-colour thermometer (Chino, IR-FL2), and was manually controlled at less than plus or minus 10 K. The flow rate of the gas was adjusted by a mass flow controller. The purities of an Ar and a N₂ gases used were 99.99 vol% and 99.9995 vol% respectively. These gases were passed through the two columns (Nikka Seiko) to eliminate water vapour and oxygen gas included as impurities. Those contents were less than 2 ppb. The sample of Cu was cut from a cylinder rod with purity of 99.9 wt% by a fine cutting device. Cut sample was ground by emery paper to remove oxide layer on the sample. Finally, sample weight was adjusted to be 2.20 ± 0.05 g by cutting with a nipper.

The Cu sample was levitation-melted in Ar or N₂ gas stream. The levitated sample melted 60 s later after turning on the power. Ten seconds later, evaporation from the sample was observed. This time was set as the starting time. The rise in temperature was kept constant to measure the evaporation weight from the sample weight. After the temperature of the levitated copper was kept constant for a predetermined time, the sample was dropped onto a water-cooled copper mold which was inserted from the end of the reaction tube.

![Figure 1. Schematic of main part of experimental apparatus.](image1)

![Figure 2. Change in weight of evaporated Cu with time. Tₛ is the temperature of levitated Cu.](image2)

The particles for the observation of a TEM (transmission electron microscope, Hitachi, H800) with an electron diffraction device were collected at the end of the reaction tube by placing a collodion film bound copper mesh in the exhausted gas mixture for a moment. The particles for measuring the contents of nitrogen and oxygen and analysing the crystal structure were collected by adhesion on a filter for a vacuum cleaner. Both the particles for a TEM and for measuring content and structure were collected in a gas stream. The time that the former particles are in contact with air was sorter than that of the latter.
The size of the particles, which were photographed with TEM, was measured by the image analyzer (Nireco, LUZEXIII). More than 500 Particles were investigated. The particles that were attached to each other were classified as isolated particles. The content of nitrogen in the particles was measured by extracting nitrogen in a He gas (Horiha, EMGA-1300). Crystal structure was analysed using XRD (X-ray diffractometry, Rigaku, RINT-2200).

The experiments were carried out to investigate the effect of temperature (1993 K – 2493 K) of the levitated copper while keeping the gas flowrate (1.67~25.0 ×10⁻⁵m³s⁻¹ (NTP (normal temperature and pressure))) on both the evaporation rate and the characteristics of the condensed particles.

3. Results

3.1 Evaporation rate

Figure 2 showed the change in the evaporated weight of levitation-melted sample with time. In this figure, the evaporated weight was given by dividing the weight loss with initial surface area of the levitated Cu. The initial surface areas of the levitated Cu for 1993 K, 2093 K, 2193 K, 2293 K, 2393 K, 2443 K, and 2493 K were 1.94×10⁻⁴ m², 1.96×10⁻⁴ m², 1.98×10⁻⁴ m², 2.01×10⁻⁴ m², 2.04×10⁻⁴ m², and 2.05 ×10⁻⁴ m² respectively. However, the surface area decreased by approximately 13 % when the weight loss by evaporation was maximum. The evaporated weight linearly increased with time at each temperature. The straight lines did not pass through the origin of this figure. This indicated that it took time for the sample to reach the predetermined temperature after the evaporation was castle observed visually. The evaporated weight in the N₂ gas flow also increased linearly with time. The gradients of theses straight lines expressed the evaporation rates respectively. The evaporation rate increased with the temperature rise. Here, the evaporation rate was the production rate of condensed Cu particle.

Figure 3 shows the influence of gas flow rate on the evaporation rate. Generally, the experimental evaporation rates, \( W_{\text{obs}} \), increased with an increase in the gas flow rate, \( Q \). In addition, the evaporation rate in N₂ gas flow was larger than that in Ar gas flow, and its dependency of gas flow rate was larger than that in Ar gas flow rate.

The comparison of the evaporation rates in the Ar and the N₂ gas flow at the same temperature and gas flow rate was shown in figure 4. The evaporation rate in the N₂ gas stream was approximately 1.27 times larger than that in the Ar gas stream.

**Figure 3.** Influence of gas flow rate, \( Q \), on evaporation rate obtained experimentally, \( W_{\text{obs}} \).

**Figure 4.** Comparison of the evaporation rates in Ar, \( W_{\text{obs,Ar}} \), and N₂ gas flow, \( W_{\text{obs,N₂}} \).
Figure 2 showed the change in the evaporated weight of levitation-melted sample with time. In this figure, the evaporated weight was given by dividing the weight loss with initial surface area of the levitated Cu. The initial surface areas of the levitated Cu for 1993 K, 2093 K, 2193 K, 2293 K, 2393 K, 2443 K, and 2493 K were 1.94×10⁻⁴ m², 1.96×10⁻⁴ m², 1.98×10⁻⁴ m², 2.01×10⁻⁴ m², 2.04×10⁻⁴ m², and 2.05×10⁻⁴ m² respectively. However, the surface area decreased by approximately 13% when the weight loss by evaporation was maximum. The evaporated weight linearly increased with time at each temperature. The straight lines did not pass through the origin of this figure. This indicated that it took time for the sample to reach the predetermined temperature after the evaporation was cast observed visually. The evaporated weight in the N₂ gas flow also increased linearly with time. The gradients of these straight lines expressed the evaporation rates respectively. The evaporation rate increased with the temperature rise. Here, the evaporation rate was the production rate of condensed Cu particle.

Figure 3 shows the influence of gas flow rate on the evaporation rate. Generally, the experimental evaporation rates, \( W_{\text{obs}} \), increased with an increase in the gas flow rate, \( Q \). In addition, the evaporation rate in \( \text{N}_2 \) gas flow was larger than that in \( \text{Ar} \) gas flow, and its dependency of gas flow rate was larger than that in \( \text{Ar} \) gas flow rate.

The comparison of the evaporation rates in the \( \text{Ar} \) and the \( \text{N}_2 \) gas flow at the same temperature and gas flow rate was shown in figure 4. The evaporation rate in the \( \text{N}_2 \) gas stream was approximately 1.27 times larger than that in the \( \text{Ar} \) gas stream.

3.2 Characteristics of particle
3.2.1 Composition of particles

TEM image of condensed particles was shown in figure 5. The particles were sphere in shape. Some particles contacted each other, other particles were isolated. Generally, plenty of consolidated particles were observed when the temperature of the levitation-melted copper was relatively low, or when the gas flow rate was relatively high. The particles did not have metallic luster and had reddish colour.
Figure 6 shows the relation between the nitrogen content, $C_N$, in the particles and the temperature of levitated copper. Generally, the nitrogen content in the particles decreased with increasing temperature irrespective of gas species. The nitrogen content in the particles was less than approximately one-tenth of the nitrogen content in Cu$_3$N (6.84 wt%). The nitrogen content of the particles prepared in argon stream was smaller than that in nitrogen gas. Because the Ar gas did not include N$_2$ gas, the copper particles could not react with N$_2$ in the evaporation and condensation process. As described earlier, the particles were exposed to the air when they are collected. At that time, the particles were considered to have reacted with N$_2$.

This figure also depicted the nitrogen content of the levitated copper. The nitrogen content of the copper melted in the Ar gas flow could not be detected. The nitrogen content of the levitation-melted copper in the N$_2$ gas stream indicated the solubility of N$_2$ gas in the molten copper. The solubility for 1 atm of N$_2$ gas pressure is expressed as the following equation [8]:

$$\ln [\text{mass}\% N] = -(7406/T) - 5.863$$

(1)

Figure 7 shows the relation between oxygen content, $C_O$, in the particles and the temperature of levitated Cu. The particles were prepared in 8.3×10$^{-5}$ m$^3$/s of the gas flow rate.

Figure 7 shows the relation between the oxygen content, $C_O$, in the particles and the temperature of levitated copper. Generally, the oxygen contents in the particles decreased with increasing temperature irrespective of gas species. The oxygen content of the particles prepared in argon stream was
approximately 10% smaller than that in nitrogen gas. In addition, the oxygen content of the particles was less than approximately one-half of the content in the Cu₂O (11.2 wt%). The oxygen content in the levitated Cu increased with increasing the temperature.

As shown in figure 6 and figure 7, the nitrogen content in the particles and the levitated Cu increased with increasing the oxygen content in them respectively. The temperature dependency of the relationship in the oxygen and nitrogen contents in the particles were different from the dependency in the levitated Cu. As described earlier, no oxide and nitride were not detected from the XRD and the electron diffraction detected no nitride and oxide. The oxygen and nitrogen seems to be forcibly dissolved in copper.

3.2.2 Mean particle diameter

The particle size distribution is shown in the figure 8. The value of the vertical axis of this figure represents the number-based ratio in percent. The distribution showed a distribution with one mode. Therefore, the mean particle size becomes a representative value of the distribution.

Figure 9 and Figure 10 show the influence of the temperature of the levitated Cu and the gas flow rate on the mean particles size respectively. Generally, the mean size increased with the temperature rise, and decreased with the increase in the gas flow rate. As shown in figure 2 and figure 3, the evaporation rate increased with the temperature rise and with increasing the gas flow rate. Therefore, the temperature and gas flow rate on the horizontal axis in figure 9 and figure 10 correspond qualitatively to the evaporation rate. Accordingly, there was no correlation between the mean size and the evaporation rate.
4. Discussion

4.1 Evaporation rate

Because the details of analysis of the evaporation rate have been described in previous work, they will be briefly described here. The outline of the model is as follows: According to the film theory for fluid-solid system [12], a stagnant gas film exists around a body in forced fluid flow. Vapor condenses in the gas film [8,10].

Assuming that the levitation-melted sample is sphere, the steady state evaporation rate of the sphere in forced convection with equimolar interdiffusion is expressed as:

\[
\dot{W} = M_{Cu} \cdot D_{Cu} \left( 1 + \frac{r_n - r_s}{r_s} \right) \frac{C_s - C_n}{r_n - r_s}
\]

where \( \dot{W} \) is the evaporation rate [kg mol\(^{-1}\) s\(^{-1}\)], \( M_{Cu} \) molar atomic weight of Cu (kg/mol), \( D_{Cu} \) the interdiffusion coefficient of Cu vapor and the gas system (m\(^2\)/s), \( C \) the concentration of Cu vapor (mol/m\(^3\)), and \( r \) the radial distance from the center of levitated Cu (m). Subscript \( s \) is the surface of the levitated Cu, and \( n \) the vapor condensation. In order to calculate the evaporation rate, we must know the concentration, position, and the temperature at vapor condensation.

\[
Nu = 2.0 + 0.6Re^{1/2}Pr^{1/3}
\]

Figure 11. Distributions of temperature and concentration of Cu vapor in gas film.

The temperature distribution around the levitated sample is determined as follows. First, the temperature film thickness is determined using the following Rantz and Marshall’s equation which represents heat transfer around the sphere in forced convection [9].
Next, the temperature distribution in the gas film was determined from the following equation using the temperature of the levitated Cu.

$$\frac{T - T_b}{T_s - T_b} = \frac{1/r}{1/r_s} - \frac{1/r_b}{1/r_s}$$

(4)

where subscript b is the gas bulk. The temperature distribution of the main part is shown in figure 11. The film thickness of temperature is given by subtracting $r_s$ from $r_b$.

The nucleation rate, $I$ (m$^{-3}$s$^{-1}$), given by Becker, Dörning, and Zeldovich [10] is as:

$$I = n_1 \frac{\alpha p_{Cu}}{\rho_{Cu} k_B T} \left( \frac{2\sigma_{Cu} M_{Cu}}{\pi N_A} \right)^{1/2} \exp \left\{ -\frac{16\pi \sigma_{Cu}^2 M_{Cu}^2 N_A}{3R T^3 \rho_{Cu} (\ln \alpha)^2} \right\}$$

(5)

where $n_1$ is the number concentration of monomar vapor (m$^{-3}$), $p$ the vapor pressure (Pa), $M$ the molecular weight (kg/mol), $N_A$ the Avogadro constant (mol$^{-1}$), $k_B$ the Boltzmann constant (J/K), $\alpha$ saturation ratio (-), $\rho$ the density (kg/m$^3$), and $\sigma$ the surface tension (N/m). When the temperature is once set, the physical property values such as the surface tension are determined. $I/n_1$ becomes a function of the supersaturation ratio, $\alpha$. $I/n_1$ is calculated at each temperature. Figure 12 shows the relation between $I/n_1$ and the supersaturation ratio at each temperature. Generally, after $I/n_1$ gradually increased with increasing the supersaturation ratio, it steeply increased with the ratio. The supersaturation ratio at 0.1 of $I/n_1$ at each temperature, this point almost corresponded to the point where $I/n_1$ increased steeply, was defined as the critical supersaturation ratio above which nucleation occured. This point corresponds to the point where $I/n_1$ starts up rapidly.

Using the critical supersaturation ratio and vapor pressure at each temperature, the critical supersaturation concentration, $C_{ss}$, is calculated, and shown in figure 11. The tangent line is drawn from the surface concentration, $C_s$, toward the curve, $C_{ss}$. It is assumed that Cu vapor was condensed at the concentration, $C_{ss}$, and position, $r_{ss}$, of the contact point.

Finally, the inter-diffusion coefficient at mean temperature between the surface and the vapor condensation site is calculated from Chapman-Enskog’s first approximation [11].

The relationship between the calculated and the experimentally obtained evaporation rates is shown in figure 13. There was a good liner relation between the calculated and experimental evaporation rates irrespective of the temperature, the gas flow rate, and the gas species. The calculated evaporation rate was approximately two times larger than the experimental evaporation rate. In the case of evaporation of Al, the calculated evaporation rate of Al in a He or an Ar gas stream was approximately 1.1 and 1.8 times larger than the experimental evaporation rate respectively [3]. In the case of Fe evaporation, the calculated and the experimental evaporation rates in an Ar gas stream agreed well each other [5]. Therefore, it can be said that this model roughly explains the evaporation phenomena.

Thickness of the film for mass transfer is given from Rantz and Marshall’s equation which represents mass transfer around the sphere in forced convection [9]. This equation is as:

$$Sh = 2.0 + 0.6 Re^{1/2} Sc^{1/3}$$

(6)

where $Sh$ and $Sc$ are the Sherwood and Schmidt numbers respectively, and are dimensionless numbers. In figure 11, the point, $C_{sM}$, represents the position of the film thickness. In addition, generally, the thickness of the gas film for the mass transfer is smaller than that for the heat transfer. Assuming that the Cu vapor condensed at $C_{sM}$, that is, Cu vapor does not condense in the gas film, the calculated evaporation rate was approximately one third of the experimental evaporation rate. Therefore, it can be said that Cu vapor condensed in the gas film.
4.2 Particle size

Figure 14 shows the relation between the mean particle size and the temperature at the vapor condensation. When the temperature at the condensation was below the melting point of Cu, the mean particle size was unchanged with the temperature. When the temperature was above the melting point, the mean particle size increased with the temperature rise. The condensed particles are liquid when the vapor condenses above the melting point. Therefore, the particles are easy to grow by collision-coalescence.

As shown in figure 11, the difference from the position of the melting point of Cu to the position of the vapor condensation was defined as the distance of the particle growth, $\delta p$. Figure 15 shows the relationship between the particle growth distance and the average particle diameter is shown in the figure. The negative growth distance is due to the presence of the condensation position where the radius is smaller than the melting point position. The negative growth distance is due to the vapor condensing...
where the radius is larger than the melting point position. The correlation between the distance and the mean particle size was better than the relationship between the melting point and the mean particle size. In practice, the size and frequency of the condensed particles seem to have an effect, so further study is needed for grain growth.

In the case of Fe evaporation, because the temperature of the iron vapor condensation was below the melting point of Fe, the particle size was constant. In the case of evaporation of Al, because the temperature of the Al vapor condensation was higher than the melting point of Al, the particle size increased with an increase in the growth distance. The condensation temperature of Cu vapor became higher or lower than the melting point depending on the experimental conditions. The results of this study were consistent with previous results.

In addition, the distribution of the particles were expressed by the Weibull distribution with the shape parameter of 1.15 to 3.06. Generally, this parameter relates the range of the particle distribution. The parameter shows the tendencies to decrease with the temperature rise, and to increase with the increase in the gas flow rate. Therefore, the range became wide with the temperature rise, and narrow with the increase in the gas flow rate.

5. Conclusion

Copper was levitation-melted in an argon or nitrogen gas stream to study experimentally the evaporation rate and the characteristics of condensed particles. Both of them were analysed with using the model where the Cu vapor condenses in the gas film. The results and discussions were summarized as follows:

The evaporation rate increased with increasing the temperature of the levitated Cu and the gas flow rate. The evaporation rate in N2 gas flow was larger than that in Ar gas flow. The rate calculated from this model was approximately two times larger than the experimental rate irrespective of the temperature of the levitated Cu, the gas flow rate, and gas species.

The condensed particles were spherical metallic copper. When the temperature at the condensation of vapor was below the melting point of Cu, the mean particles size was almost constant. When the temperature was above the melting point, the mean size increased with the increase in the distance of particle growth.

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