Korean J. Chem. Eng., **16**(1), 64-68 (1999)

EFFECT OF TEMPERATURE ON PARTICLE SIZE FOR VAPOR-PHASE SYNTHESIS OF ULTRAFINE IRON PARTICLES

Kyun Young Park† **and Hi Jae Jeong**

Department of Chemical Engineering, Kongju National Univ., 182 Shinkwandong, Kongju, Chungnam 314-701, Korea

(*Received 12 May 1998 • accepted 15 October 1998*)

Abstract – For the vapor-phase synthesis of iron particles from $FeCl_2$ at temperatures ranging from 800 to 950 °C, the reason is sought why the model based on the classical nucleation theory brought an increase of particle size with temperature increase, in reverse to experimental observation. The nucleation rate according to the classical theory should decrease with a temperature increase, due to the decrease of super-saturation ratio resulting from the increase of vapor pressure. The decrease of nucleation rate ultimately leads to an increase of particle size. Yang and Qiu's nucleation theory was applied in place of the classical theory. However, the same result as with the classical theory was obtained: the nucleation rate decreased with the temperature increase. Finally, an Arrhenius-type nucleation rate equation was introduced. The preexponential factor and the activation energy for nucleation were determined to be 1348.2 sec^{-1} and 159.1 KJ/mol, respectively. With these values put into Park et al.'s model, good agreement was obtained in temperature dependence of particle size between model prediction and experimental data.

Key words : Particle Size, Vapor-Phase Synthesis, Iron Particles

INTRODUCTION

The hydrogen reduction of goethite (α-FeOOH) obtained by precipitation from aqueous solutions of iron salts has been the major route to commercial production of metallic iron powders used for high-density recording media. Otsuka et al. [1984] reported that ultrafine iron powders could be obtained by hydrogen reduction of ferrous chloride vapor. Further experimental studies followed to investigate the effect of various operating variables on the particle size distribution of iron powders resulting from the reduction of $FeCl_2$ vapors [Park et al., 1991, 1998]. Their experimental data indicate that the average diameter of primary particles of the iron decreased with an increase of reaction zone temperature from 800 to 950 °C, as shown in Fig. 1. Using the classical theory [Friedlander, 1977] for nucleation rate and the method of moments [Lee et al., 1984] to solve the general dynamics equation, a model has been developed to calculate the particle size for the vapor-phase synthesis of iron powders [Park et al., 1996]. In contrast to experimental observations, the model gave a slight increase in the particle size with temperature increase.

In the present work, the reason is sought why the model based on the classical nucleation theory brought the increase of particle size with temperature increase, and two attempts have been made to improve the model so that the experimentally observed relationship between particle size and temperature can be predicted. One is to replace the classical nucleation theory with the nucleation theory by Yang and Qiu [1986]. The classical theory assumes that the nucleus is large enough to form a surface, and requires the surface tension in the calculation of the nucleation rate. For materials like iron, the vapor pressure of which is too low for the nucleus to form a surface, the application of the classical theory would therefore be misleading. By comparison, Yang and Qiu's theory eliminates the use of surface tension; it may be suitable for gas to solid transitions where surface tension is ambiguous. The other attempt is to employ an Arrhenius-type equation for nucleation rate. The two parameters, preexponential factor and activation energy for nucleation, are determined to best fit measured particle sizes. This approach is well known but has never been applied to the vapor phase synthesis of solid par-

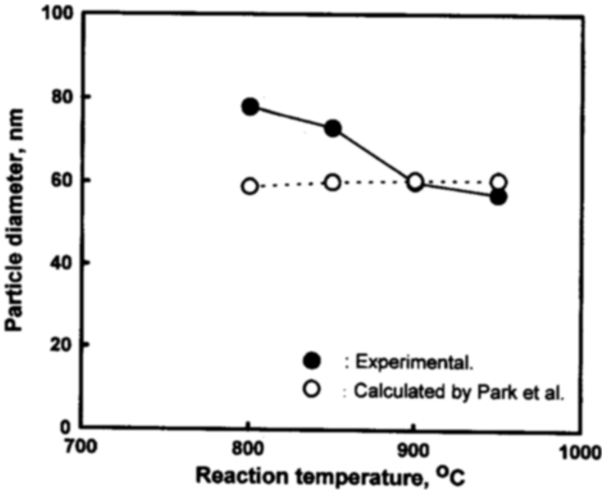

Fig. 1. Comparison of particle diameter calculated by Park et al. with experimental data.
($FeCl_2$ feed rate=0.02 g/min; H_2 feed rate=5 *l*/min; Ar feed rate=5 *l*/min)

---

†To whom correspondence should be addressed.
E-mail : kypark@knu.kongju.ac.kr

ticles, as far as is known.

PARTICLE GROWTH

The formation of iron particles by hydrogen reduction of ferrous chloride can be represented by the following equation.

$$FeCl_2(v) + H_2(g) \rightarrow Fe(s) + 2HCl(g) \tag{1}$$

The reduction of $FeCl_2$ to iron rarely occurs in one step, but is more likely to occur in a series of steps. The iron chloride is reduced to FeCl radical first. The radicals then form a cluster represented by $(FeCl)_2$, which eventually grows to a stable nucleus by coagulation between clusters with Cl atoms being removed further. Once the nucleus or smallest particle of iron is formed, it is then grown by the surface reaction of $FeCl_2$, scavenging of clusters and nuclei by particles, and also by coagulation between particles.

For a given conversion of $FeCl_2$, the particle size becomes smaller as the number of particles increases. The number of particles is controlled by the nucleation rate and the coagulation rate. The particle size increases with decreasing nucleation rate and with increasing coagulation rate. A temperature increase in the reaction zone would increase the coagulation rate with an order of 0.5 to 1.0 with respect to the temperature [Fuchs, 1964], thereby acting in the direction toward increasing the particle size. The experimental result [Park et al., 1991] that the particle size decreased with the temperature increase implies that the nucleation rate must have increased to such an extent that the decrease of particle size by increased nucleation dominated over the increase of particle size due to enhanced coagulation.

NUCLEATION RATE

1. Classical Theory

According to the classical theory, the nucleation rate is calculated by

$$I = 2\left[\frac{p_1}{\sqrt{2\pi m_1 kT}}\right](n_1 v_1^{2/3})\left[\frac{\gamma v_1^{2/3} v_1^{2/3}}{kT}\right]^{1/2} \exp\left[-\frac{16\pi\gamma^3 v_1^2}{3(kT)^3 \ln^2 S}\right] \tag{2}$$

where p_1 is the partial pressure of Fe monomer, m_1 is the mass of monomer, k is the Boltzmann constant, n_1 is the number concentration of monomer, γ is the surface tension of iron, v_1 is the volume of monomer, and S is the super-saturation ratio.

The super-saturation ratio(S) can be represented by

$$S = \frac{p_1}{p_\infty} \tag{3}$$

where, p_∞ is the vapor pressure of bulk iron. The following equation [Shelton, 1983] is introduced to estimate the vapor pressure.

$$\log p_\infty(\text{mmHg}) = -\frac{21080}{T} + 16.89 - 2.14\log(T) \tag{4}$$

At a given number concentration (n_1), by sustituting $p_1 = n_1 kT$ into Eq. (2), one can obtain Eq. (5) relating the nucleation rate (I_1) at the temperature of T_1 to the nucleation rate (I_2) at T_2.

$$\frac{I_1}{I_2} = \exp\left[\frac{\alpha}{T_1^3(\ln S_1)^2}(\delta - 1)\right] \tag{5}$$

where, $\alpha = \dfrac{16\pi\gamma^3 v_1^2}{3k^3}$, $\delta = \left(\dfrac{T_1}{T_2}\right)^3\left(\dfrac{\ln S_1}{\ln S_2}\right)^2$

2. Yang and Qiu's Theory

By Yang and Qiu's theory, the nucleation rate is calculated by Eqs. (6) and (7) which do not involve the surface tension, but two adjustable parameters, β and Γ.

$$I = \frac{a\, k^c\, n_1^2 A_1}{1 + \frac{1}{S} e^{-(E_2 - E_\infty)/RT} + \cdots + \frac{1}{S^{N-1}} e^{-(E_2 + \cdots + E_N - (N-1)E_\infty)/RT}} \tag{6}$$

$$E_i = (1 - \beta/i^\Gamma)\, E_\infty \tag{7}$$

where, a is an accommodation factor, k^c is the condensation rate constant, n_1 is the monomer concentration, A_1 is the surface area of monomer, S is the supersaturation ratio, E_i is the activation energy for vaporization for cluster size i, and E_∞ is the activation energy for vaporization under the vapor pressure of bulk iron.

The expression for critical nucleus size (n) is obtained by equating the condensation and vaporization rates of the critical nucleus.

$$n = \left(\frac{\beta E_\infty}{R\,T \log S}\right)^{1/\Gamma} \tag{8}$$

3. Arrhenius-Type Nucleation Rate Equation

The nucleation is treated as a chemical reaction, and its rate is represented by an Arrhenius-type equation.

$$I = A\, e^{-E/RT} C^* \tag{9}$$

where, E is the activation energy for nucleation, A is the preexponential factor, and C^* is the cluster concentration. The nucleation rate is assumed to be first order with respect to cluster concentration. When the critical nucleus or smallest particle consists of n iron atoms, the number of iron atoms composing embryonic clusters would be in the range 2 to (n-1). In the present study, however, the number is assumed to be n/2 for all clusters, for simplicity. Then, by stoichiometry, the molar rate of formation of the clusters would be 2/n times that of $FeCl_2$ consumption and the nucleation rate be half the cluster formation rate. These relationships are incorporated into the model of Park et al. [1996] to determine by iterations the activation energy for nucleation (E) and the preexponential factor (A) which best fit the particle sizes measured by Park et al. [1991].

RESULTS AND DISCUSSION

1. Temperature Dependence of Nucleation Rate with Classical Theory

Using Eq. (5), nucleation rates were compared between 800

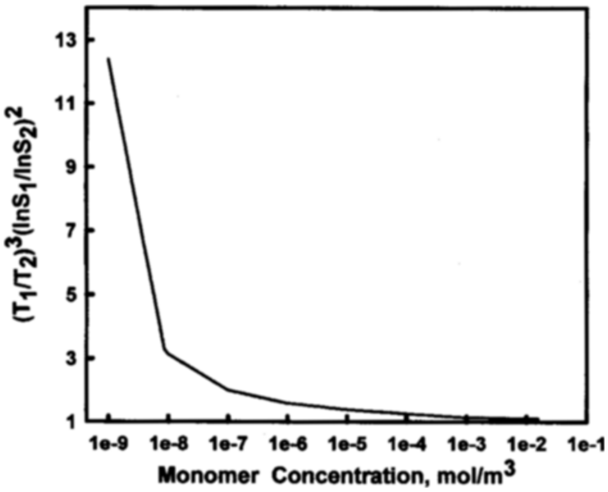

Fig. 2. $(T_1T_2)^3$ $(\ln S_1/\ln S_2)^2$ **vs. monomer concentration.**
(T_1=800 °C, T_2=900 °C)

°C and 900 °C for Fe monomer concentrations ranging 10^{-9} to 10^{-2} mol/m^3. The effect of temperature on nucleation rate depends on the value of (δ-1) in Eq. (5). If it is negative or δ is less than 1.0, the nucleation rate will increase with increasing temperature. Otherwise, it decreases with temperature increase. Substituting 800 °C for T_1 and 900 °C for T_2 in Eq. (5), δ was calculated for the various Fe monomer concentrations. The result is shown in Fig. 2. The value of δ came out to be greater than 1.0 over the entire range of concentrations in discussion. As can be seen in Eq. (5), δ is composed of two terms. The first term, $(T_1/T_2)^3$, decreases with temperature, while the second one, $(\ln S_1/\ln S_2)^2$, increases with temperature since the super-saturation ratio decreases due to a corresponding increase of the vapor pressure of iron, as shown in Fig. 3. For the case in discussion, the second term dominated and the value of (δ-1) became negative, indicating the nucleation rate would decrease with temperature increase. The resultant decrease of nucleation rate must have led to an increase of particle size, as shown by the model employing the classical nucleation theory.

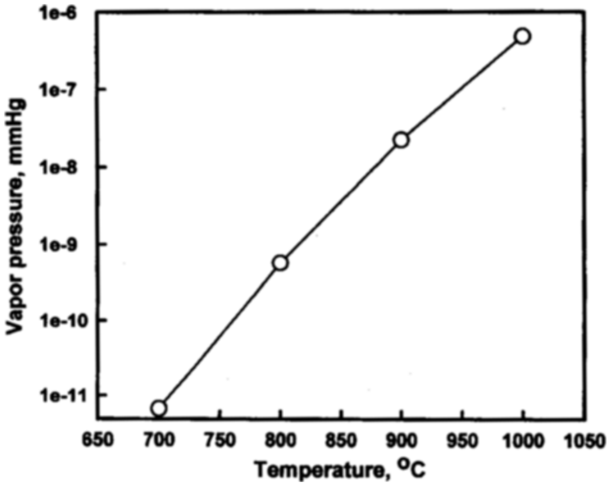

Fig. 3. Vapor pressure of Fe with temperature.

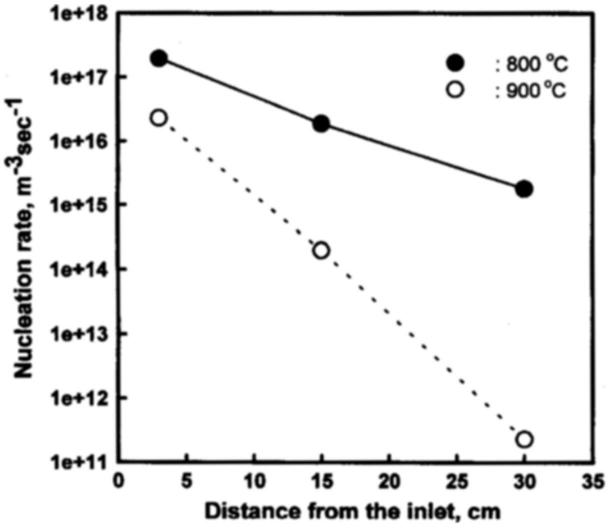

Fig. 4. Comparison of nucleation rates between 800 and 900 °C.
($FeCl_2$ feed rate, 0.02 g/min; H_2 flow rate, 5 *l*/min; Ar flow rate, 5 *l*/min)

The comparison above was made under the same monomer concentration. The distribution of the monomer concentration in the reactor, however, may be different between the two temperatures. Taking this into account, the nucleation rates were calculated along the reactor for the two temperatures of 800 and 900 °C using the Park et al.'s model with the classical nucleation theory, under an operating condition of the $FeCl_2$ feed rate at 0.02 g/min and the hydrogen and argon flow rates at 5 L/min, respectively. The nucleation rates in the center of the reactor vs. the distance from the inlet are shown in Fig. 4. As can be seen in the figure, the nucleation rates at 800 °C are higher than at 900 °C, consistent with the result shown earlier.

2. Temperature Dependence of Nucleation Rate with Yang and Qiu's Theory

For Fe monomer concentrations of 10^{-2}, 10^{-5}, and 10^{-9} mol/m^3, nucleation rates were calculated at 800 and 900 °C with

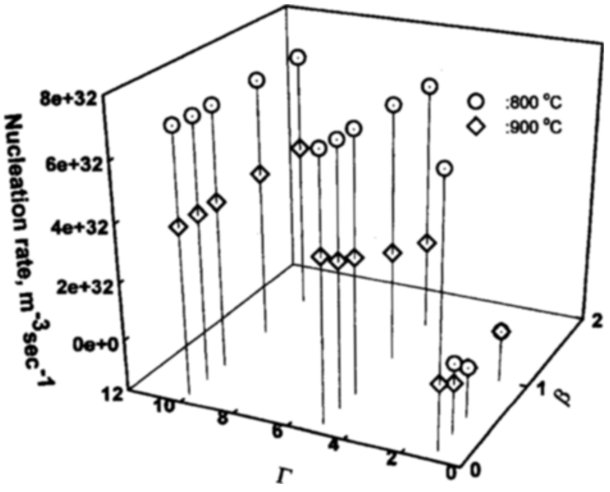

Fig. 5. Nucleation rate for monomer concentration of 10^{-9} mol/m^3 with varying β and Γ.

varying β and Γ. Fig. 5 shows the comparison of nucleation rates between 800 and 900 °C for the monomer concentration of 10^{-9} mol/m^3 with β varied over the range 0.1 to 1.0. The nucleation rate at 800 °C turned out to be greater than that at 900 °C, the same result as with the classical nucleation theory. A further increase of the concentration to 10^{-5} and 10^{-2} mol/m^3 exhibited the same temperature dependence. Though Yang and Qiu's theory differs from the classical theory in that it does not require the surface tension for calculation of nucleation rate, their theory involves the supersaturation ratio, similarly as in the classical theory; this may be the reason why Yang and Qiu's theory gave a temperature dependence of nucleation rate similar to that with the classical theory.

3. Arrhenius Equation for Nucleation Rate

The nucleation rate represented by Eq. (9) was incorporated in the model of Park et al. [1996] to examine the effect of temperature on the particle size. Assuming the number of Fe atoms constituting the critical nucleus at five, the nucleation rate constants at 800, 850, 900 and 950 °C were obtained by trial and error so that particle sizes calculated by the model fit the measured particle sizes. They were 2.44×10^{-5}, 4.40×10^{-5}, 12.3×10^{-5} and 18.4×10^{-5} sec^{-1}, respectively. An Arrhenius plot was drawn from these data, as shown in Fig. 6. The preexponential factor and the activation energy for nucleation were determined to be 1348.2 sec^{-1} and 159.1 KJ/mol, respectively. With these values put in the model, good agreement was obtained in temperature dependence of particle size between model prediction and experimental data, as shown in Fig. 7. When the number of iron atoms constituting the nucleus was increased to 10, 50 and 100, the corresponding activation energies were 161.7, 161.6 and 161.0 KJ/mol, respectively. This indicates that the number of iron atoms up to 100 has little effect on the activation energy.

With the classical theory and the Yang and Qiu's theory as well, the supersaturation ratio, defined by the ratio of the partial pressure of iron monomers to the vapor pressure of iron, plays a critical role in determining the nucleation rate and ultimately the particle size. By those theories, the presence of iron monomers is implicitly assumed. As discussed earlier, however, the presence of iron monomers in any significant quantity would be improbable for the hydrogen reduction of $FeCl_2$. The classical theory further assumes that the nucleus has a clear surface, which appears not valid for the case in discussion. By comparison, the Arrhenius equation for nucleation rate does not involve those impractical assumptions. It requires measurements of particle size at a few temperatures to determine the two parameters, preexponential factor and activation energy. Once those parameters are determined, the equation can then be used for calculations in the whole range of temperatures.

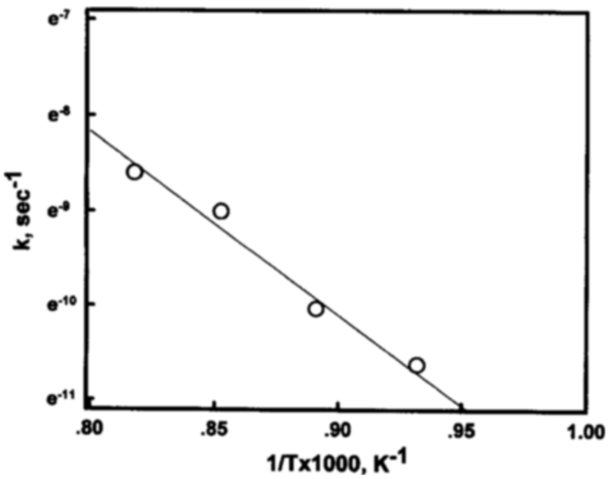

Fig. 6. The Arrhenius plot for nucleation rate constant.

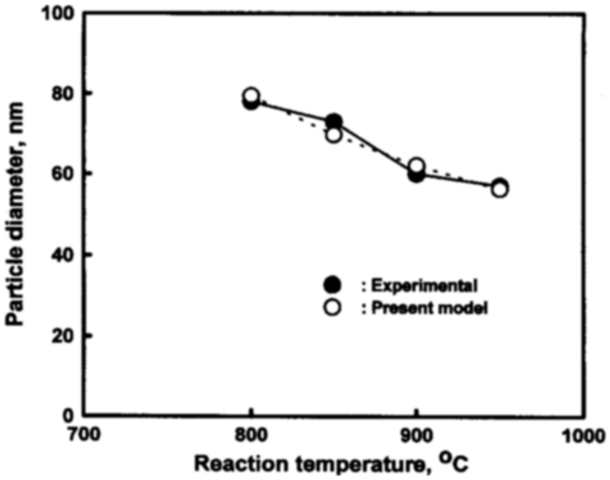

Fig. 7. Comparison of particle diameter calculated by present model with experimental data.
($FeCl_2$ feed rate=0.02 g/min; H_2 feed rate=5 *l*/min, Ar feed rate=5 *l*/min)

CONCLUSION

For the vapor-phase synthesis of iron particles from $FeCl_2$, the nucleation rate according to the classical theory decreased with the temperature increase, due to the decrease of supersaturation ratio resulting from the increase of vapor pressure. This can explain why Park et al.'s model based on the classical nucleation theory brought an increase of particle size with temperature increase. Yang and Qiu's nucleation theory showed the same tendency on temperature dependence of nucleation rate as with classical theory, although it does not involve surface tension and therefore appears suitable for the synthesis of iron particles where the surface tension of the nucleus is ambiguous. The nucleation rate equation of Arrhenius type provided good agreement in particle size between model prediction and experimental data. This approach requires measurements of particle size at a few temperatures to determine the two parameters, preexponential factor and activation energy. Once those parameters are determined, the Arrhenius equation can then be used for particle size predictions over a broad range of operating conditions.

ACKNOWLEDGMENT

The authors thank the Korea Research Foundation for supporting the project which motivated this work and Eun Joo Bae for her help in the preparation of the manuscript.

NOMENCLATURE

A : preexponential factor
A_1 : surface area of monomer [m^2]
a : accommodation factor for condensation
C^* : cluster concentration [mol/m^3]
E : activation energy for nucleation [J/mol]
I : nucleation rate [sec^{-1}]
k : Boltzmann constant [$Kg\ m^2\ sec^{-2}\ K^{-1}$]
k^c : condensation rate constant [$m\ sec^{-1}$]
m_1 : mass of monomer [Kg]
n_1 : number concentration of monomer [m^{-3}]
p_1 : partial pressure of Fe monomer [Pa]
p_∞ : vapor pressure of bulk iron [Pa]
S : super-saturation ratio
T : temperature [K]
v_1 : volume of monomer [m^3]

Greek Letters

α : parameter in Eq. (5)
β : adjustable parameter in Eq. (7)
Γ : adjustable parameter in Eq. (7)
γ : surface tension [$Kgm^{-1}sec^{-1}$]
δ : parameter in Eq. (5)

REFERENCES

Friedlander, S. K., "Smoke, Dust and Haze," Wiley, New York (1977).

Fuchs, N. A., "The Mechanics of Aerosol," Pergamon Press, New York (1964).

Lee, K. W., Chen, H. and Gieseke, J. A., "Log-Normally Preserving Size Distribution for Brownian Coagulation in the Free-Molecule Regime," *Aerosol Sci. and Tech.,* **3**, 53 (1984).

Otsuka, R., Yamamoto, H. and Yoshizawa, A., "Preparation of Ultrafine Particles of Nickel, Cobalt and Iron by Hydrogen Reduction of Chloride Vapor," *Nippon Kagaku Kaishi,* 869 (1984).

Park, K. Y., Jang, H. D. and Choi, C. S., "Generation of Ultrafine Iron Powders by Gas-phase Reduction of Ferrous Chloride with Hydrogen," *J. Aerosol Sci.,* **22**, s113 (1991).

Park, K. Y., Jang, H. D. and Choi, C. S., "Vapor-phase Synthesis and Characterization of Ultrafine Iron Powders," *Aerosol Sci. and Tech.,* **28**, 215 (1998).

Park, K. Y., Oh, E., Kim, S. and Jang, H. D., "Modeling of Particle Growth in the Manufacture of Ultrafine Inorganic Powders by the Gas-phase Reaction-Application to the Manufacture of Ultrafine Iron Powders," *HWAHAK KONGHAK,* **34**, 534 (1996).

Shelton, R. A., "Smithhells Metals Reference Book," 6th ed., edited by Brandes, E. A., Butterworth and Co., Ltd. (1983).

Yang, C. H. and Qiu, H., "Theory of Homogeneous Nucleation: A Chemical Kinetic View," *J. Chem. Phys.,* **84**, 416 (1986).