

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

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**Abstract** – For the vapor-phase synthesis of iron particles from  $\text{FeCl}_2$  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  $1348.2 \text{ sec}^{-1}$  and  $159.1 \text{ KJ/mol}$ , 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 ( $\alpha\text{-FeOOH}$ ) 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  $\text{FeCl}_2$  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 cal-

culation 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-

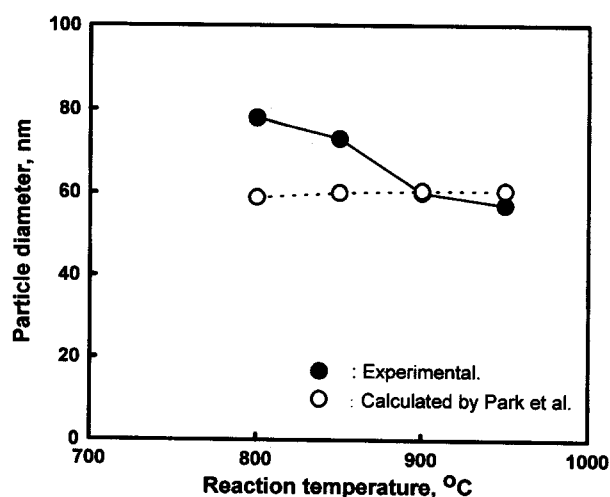


Fig. 1. Comparison of particle diameter calculated by Park et al. with experimental data.

( $\text{FeCl}_2$  feed rate=0.02 g/min;  $\text{H}_2$  feed rate=5 l/min; Ar feed rate=5 l/min)

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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.



The reduction of  $\text{FeCl}_2$  to iron rarely occurs in one step, but is more likely to occur in a series of steps. The iron chloride is reduced to  $\text{FeCl}$  radical first. The radicals then form a cluster represented by  $(\text{FeCl})_n$ , 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  $\text{FeCl}_2$ , scavenging of clusters and nuclei by particles, and also by coagulation between particles.

For a given conversion of  $\text{FeCl}_2$ , 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

$$I = 2 \left[ \frac{p_1}{\sqrt{2\pi m_1 kT}} \right] (n_1 v_1^{2/3}) \left[ \frac{\gamma_1^{2/3} v_1^{2/3}}{kT} \right]^{1/2} \exp \left[ -\frac{16\pi\gamma^3 v_1^2}{3(kT)^3 \ln^2 S} \right] \quad (2)$$

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,  $\gamma$  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

$$S = \frac{p_1}{p_\infty} \quad (3)$$

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

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

At a given number concentration ( $n_1$ ), by substituting  $p_1 = n_1 kT$  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  $T_2$ .

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

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

### 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,  $\beta$  and  $\Gamma$ .

$$I = \frac{a k^c n_1^2 A_1}{1 + \frac{1}{S} e^{-(E_1 - E_\infty)/RT} + \dots + \frac{1}{S^{N-1}} e^{-(E_2 + \dots + E_N - (N-1)E_\infty)/RT}} \quad (6)$$

$$E_i = (1 - \beta/i^\Gamma) E_\infty \quad (7)$$

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  $E_\infty$  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.

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

### 3. Arrhenius-Type Nucleation Rate Equation

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

$$I = A e^{-E/RT} C^* \quad (9)$$

where,  $E$  is the activation energy for nucleation,  $A$  is the pre-exponential 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  $\text{FeCl}_2$  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

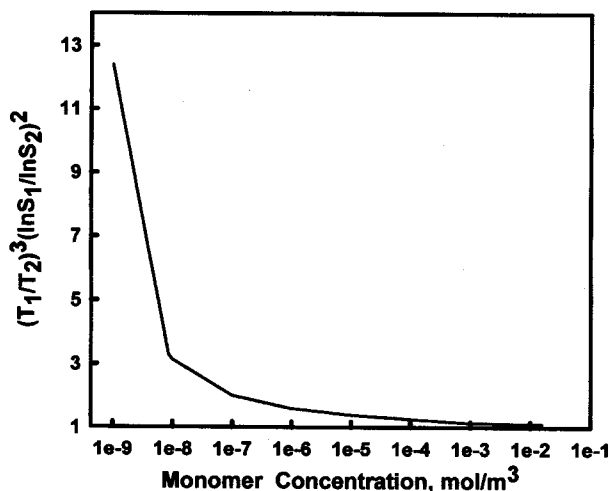


Fig. 2.  $(T_1/T_2)^3 (\ln S_1/\ln S_2)^2$  vs. monomer concentration.  
( $T_1=800^\circ\text{C}$ ,  $T_2=900^\circ\text{C}$ )

$^\circ\text{C}$  and  $900^\circ\text{C}$  for Fe monomer concentrations ranging  $10^{-9}$  to  $10^{-2}$  mol/m<sup>3</sup>. The effect of temperature on nucleation rate depends on the value of  $(\delta-1)$  in Eq. (5). If it is negative or  $\delta$  is less than 1.0, the nucleation rate will increase with increasing temperature. Otherwise, it decreases with temperature increase. Substituting  $800^\circ\text{C}$  for  $T_1$  and  $900^\circ\text{C}$  for  $T_2$  in Eq. (5),  $\delta$  was calculated for the various Fe monomer concentrations. The result is shown in Fig. 2. The value of  $\delta$  came out to be greater than 1.0 over the entire range of concentrations in discussion. As can be seen in Eq. (5),  $\delta$  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  $(\delta-1)$  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.

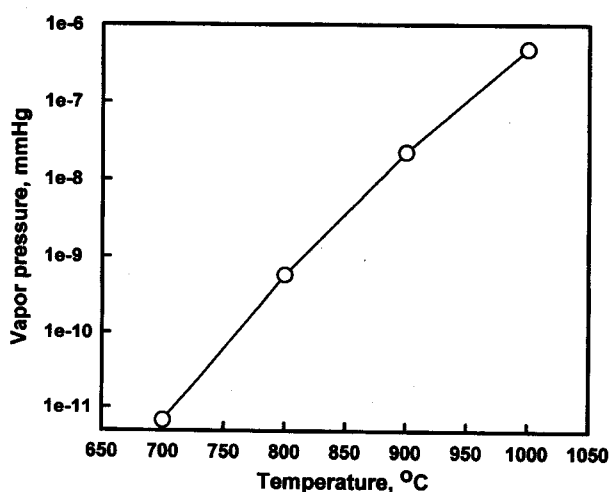


Fig. 3. Vapor pressure of Fe with temperature.

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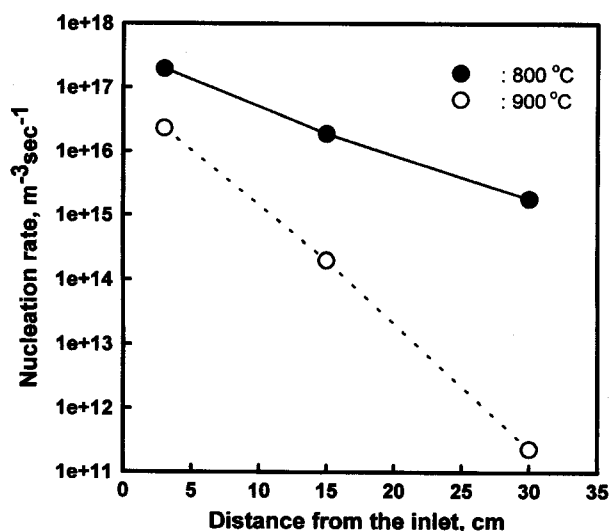


Fig. 4. Comparison of nucleation rates between 800 and  $900^\circ\text{C}$ .  
( $\text{FeCl}_2$  feed rate, 0.02 g/min;  $\text{H}_2$  flow rate, 5 l/min; Ar flow rate, 5 l/min)

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  $900^\circ\text{C}$  using the Park et al.'s model with the classical nucleation theory, under an operating condition of the  $\text{FeCl}_2$  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  $800^\circ\text{C}$  are higher than at  $900^\circ\text{C}$ , 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<sup>3</sup>, nucleation rates were calculated at 800 and  $900^\circ\text{C}$  with

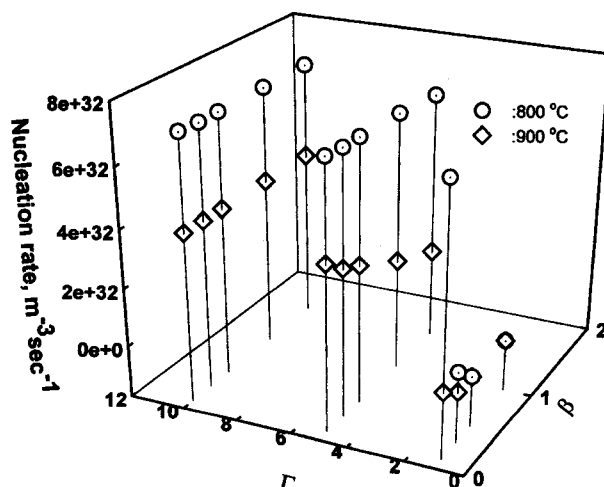


Fig. 5. Nucleation rate for monomer concentration of  $10^{-9}$  mol/m<sup>3</sup> with varying  $\beta$  and  $\Gamma$ .

varying  $\beta$  and  $\Gamma$ . Fig. 5 shows the comparison of nucleation rates between 800 and 900°C for the monomer concentration of  $10^{-9}$  mol/m<sup>3</sup> with  $\beta$  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<sup>3</sup> 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  $2.44 \times 10^{-5}$ ,  $4.40 \times 10^{-5}$ ,  $12.3 \times 10^{-5}$  and  $18.4 \times 10^{-5}$  sec<sup>-1</sup>, 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<sup>-1</sup> 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

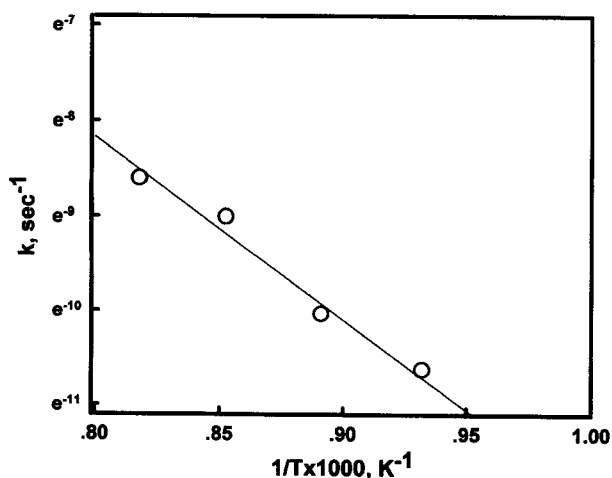


Fig. 6. The Arrhenius plot for nucleation rate constant.

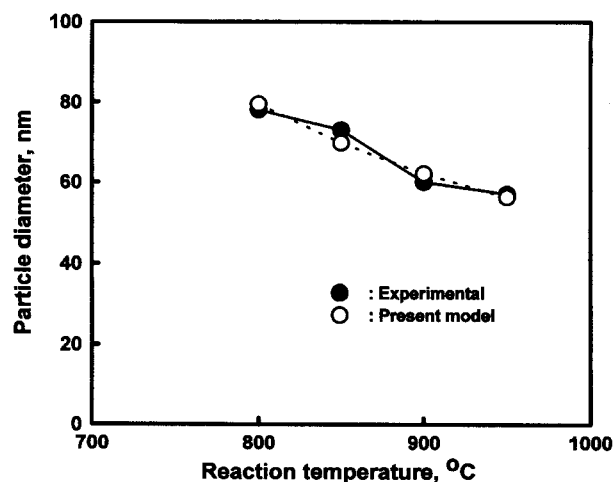


Fig. 7. Comparison of particle diameter calculated by present model with experimental data.

(FeCl<sub>2</sub> feed rate=0.02 g/min; H<sub>2</sub> feed rate=5 l/min, Ar feed rate=5 l/min)

would be improbable for the hydrogen reduction of FeCl<sub>2</sub>. 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.

### CONCLUSION

For the vapor-phase synthesis of iron particles from FeCl<sub>2</sub>, 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.

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## NOMENCLATURE

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

## Greek Letters

$\alpha$	: parameter in Eq. (5)
$\beta$	: adjustable parameter in Eq. (7)
$\Gamma$	: adjustable parameter in Eq. (7)
$\gamma$	: surface tension [ $\text{Kg m}^{-1} \text{sec}^{-1}$ ]
$\delta$	: parameter in Eq. (5)

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