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Morphological Effect of Hematite on the Synthesis of Fayalite in Reducing Atmosphere

Eung-Keuk Lim and Myung-Soo Kwon

College of Engeineering, Seoul National University

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환원성 분위기에서의 규산철의 합성에 미치는 산화 제2철의 형태학적 효과에 관한 연구

임 응 극·권 명 수

서울대학교 공과대학

요 약

철(II)이온을 안정화 하기위하여, 2산화 규소와, 구상, 입방체상및 침상의 서로 다른형태의 산화 제 2 철로 부터규산철을 합성하였다.

메타놀증기로 포화시킨 질소까스를 튜브로에 도입시켜 얻은 환원성 분위기속에서, 1140°C에서 1165°C의 온도범위에서, 가스유속을 0.13 및 0.25l/min. 로서, 환원시간 4—150 분동안 고상반응을 진행하였다.

반응생성의 동태를 오르자트 가스분석으로 점토하였으며, 생성물의 확인은 X-선 회절시험및 감량정량에 의하였으며.

결과는 다음과 같다·1:1.1 의 몰비로 혼합한산화제 2 철과 2 산화 규소의 경우, 가스유속이 0.13l/min 일때, 규산철 합성반응시간은 구상, 입방체상및 침상산화철에 있어서 각기 18—27분, 10—16분 및 6—7분으로 구상의 경우가 범위가 가장넓었다. 또한, 반응속도는 산화제 2 철의 조면적의 평방근에 비례하였고 반응시간의 평방근에 역비례하였다.

1. Introduction

In the steel industry, the system Fe-Si-O is of great importance due to the formation of FeO-SiO_2 slag with the fluxing phenomena thereon and many works on them have been reported.[1],[2],[3],[4],[5] But, most of the studies are mainly on either the fusion behaviour or impurity effects on reduction. Aiso, fayalite has been known to be formed above or below the fusion point hitherto[1]

In the caramic field, iron oxide has been used as a stain in the celadon glaze whose subtle greenish-grey colours are believed to be originated from Fe^{++}–O–Fe^{++} combinations owing to the ferric to ferrous conversion during the reduction period.[12] To obtain the ferrous state solely, the reduction to wüstite was studied with different shapes of hematite.[8] But because wüstite is not stable below 570°C. the method to preserve the metastable ferrous form is required. Hence, one of the main purposes is to stabilize ferrous state through the formation of stable compound, fayalite.

Fayalite, $2FeO.SiO_2$ or Fe_2SiO_4, is the only crystalline iron silicate compound in the system of FeO–SiO_2 according to Bowen and Schairer who confirmed the

non-existence of $FeSiO_3$ as a crystalline system.[4] With forsterite, Mg_2SiO_4, fayalite makes a continuous solid solution to constitute the olivine series, $(Mg, Fe)_2SiO_4$, where SiO_4^{-2} groups exist independently, that is, nesosilicate, which results in hcp-like dense atomic packing with rather high hardness and density. Consequently, forsterite has a high m. p. of 1890°C. But, as smaller Mg ions are replaced by larger ferrous ions, the cation-oxygen bonds become weaker. Hence, the m. p. of fayalite is 1205°C, which means fayalite will be a suitable constituent in the glaze.

Many methods to form reducing atmosphere have been developed these days. Berg used charcoal to make a CO generator and dropped 2.5 to 10% methanal solution in the furnace.[8] Also, C_4-hydrocarbon instead of liquid vapour was proposed for tunnel kiln by Metzel et al.[8] Ostrovsky sintered fayalite in the presence of water vapour.[7] A. Gorgeu obtained fayalite by heating a mixture of ferrous chloride and silica in a current of hydrogen charged with steam.[1] According to W. A. Bone et al, methanal was decomposed into CO and H_2 in the combustion tube at 800 ~900°C, where small amount of CH_4 is produced, too.[9]

So. in this study, the lately developed method of Berg[6] was adopted: introducing N_2 gas as a carrier gas saturated with methanal vapour into the furnace with the advantage of controling the flow rate of carrier gas to change the furnace atmosphere with ease.

Hematite has a variety of α-, γ-, ε- and amorphous forms And that, α-Fe_2O_3 has spheroidal, cubical, acicular shape according to Stephens.[8] Differences among those forms lie in those of the surface area, which lead to different reactivities. In this study, spheroidal, cubical and acicular forms of hematite were used with silica as starting materials to obtain the proper conditions of producing fayalite along these morphological differences.

2. Experiment

As regards Fe_2O_3, Columbian Carbon Co.'s MAPIC O was used; Red 567, EG80 and Red 516-Dark as spheroidal, cubical and acicular respectively. And regarding SiO_2, Kanto Chemical Co.'s silicic anhydride was used. Fe_2O_3 and SiO_2 were sufficiently mixed with the molar ratio of 1 to 1.1. Then, they were molded under the pressure of 400kg/cm². To exclude the volatile organic matter, those molded were calcinated at 600°C for 20min. Like this, samples were prepared in the form of a pellet with dimension of 10mm×20mm×5mm and weighed to 0.1mg. with the chemical balance. Then, samples were placed in a refractory boat, which was inserted into the center of the tube in the furnace.

Apparatus used for this experiment is just same as Lim's device[8]. Operations were proceded at the gas flow rate of 0.13 and 0.25*l*/min over a temperature range of 1140°C to 1165°C during the reduction period of 4 to 150minutes. The reduced products were guenched into the deaerated distilled water(Q) and dried, then weighted with the chemical balance. Those products were ground and examined by X-ray diffractometer (JEOL) under the same condition with 35 KV, 18mA Geiger counter, Mo-Kα radiation, Zr filter and 2°/min. scanning speed over the range of 2θ from 5° to 35°.

3. Results and Discussion

According to H. Steffe[1], the sintering temperature of iron silicate is around 1165°C and above 1170°C, fusion broke out according to a preliminary test. So, 1165°C was adopted as upper limit. As a preliminary test, raw sample, 1000mg of spheroidal Fe_2O_3 and SiO_2 with mixing ratio of 1:1 was analyzed with TGA

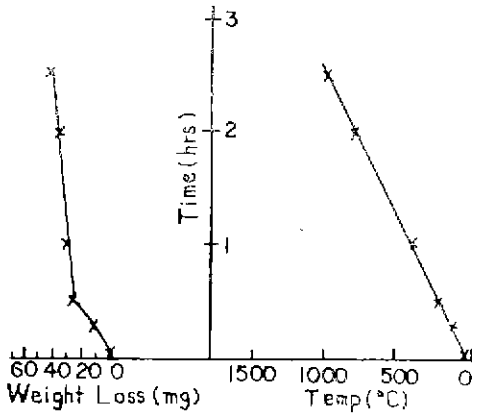

Fig. 1. TGA analysis of raw sample

(STANTION, LONDON) at 400°C/hr in the atmospheric condition. Over the temperature range of 200 to 1000°C, 1.5mg was lost.

In other words, oxygen was considered to be released, because that sample did not include any organic matter. Hence, in this study, samples were directly inserted into the tube at the reduction temperatures. Gas flow rates were determined by means of Orsat gas analysis in the preliminary experiment. P_{CO_2}/P_{CO} ratio of the furnace atmosphere was plotted in Fig. 2. Curve A is for 1170°C and 1l/min., B for 1160°C and 1l/min, C for 1140°C and 0.25l/min, D for 1150°C and 0.13l/min, and curve E is for 1165°C and 0.13l/min.

According to L. S. Darken[5], the range of log P_{CO_2}/P_{CO} lies between 0.5 and 0.4 for the stable phase of fayalite, which means the lower limit of P_{CO_2}/P_{CO} will be around 0.4. As gas flow rates, 0.13l/min. and 0.25l/min. were adopted in the present study. Below the lower limit, metallic iron appeared.

Fig. 3. shows weight loss-reduction time plot in case of spheroidal hematite with the gas flow rates of 0.13l/min. and 0.25l/min. at 1165°C and 1140°C, where

$$F=\left(\frac{\text{Weight loss}}{\text{Weight of input sample}}\right)\times\left(\frac{\text{M. W. of } Fe_2O_3+1.1\times\text{M. W. of } SiO_2}{\text{M. W. of oxygen}}\right) \quad (1)$$

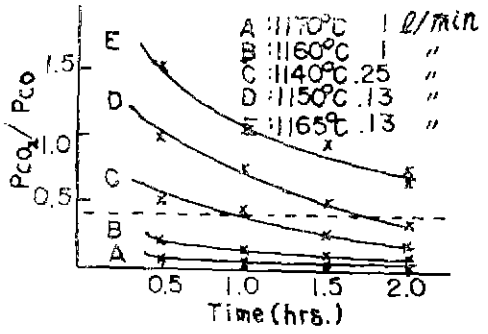

Fig. 2. P_{CO_2}/P_{CO} ratio of the furnace atmosphere.

F is the number of oxygen molecule lost per 226g of reactant sample.

$$Fe_2O_3+1.1\ SiO_2 \xrightarrow[\Delta]{CO,\,H_2} 2FeO\cdot SiO_2+0.1SiO_2+\frac{1}{2}O_2\uparrow \quad (2)$$

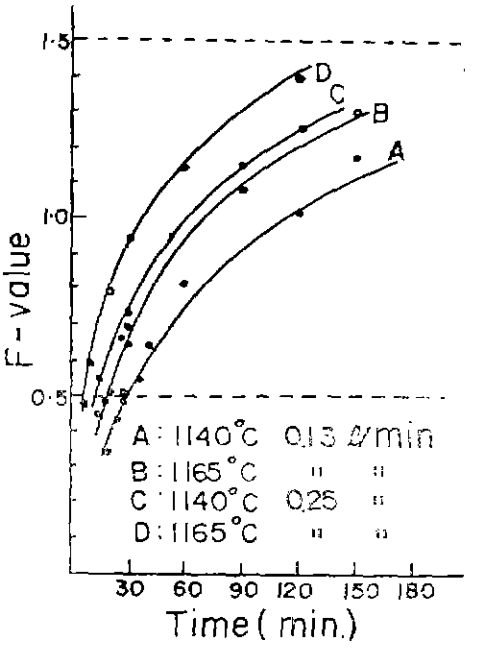

Fig. 3. F–t plot of spheroidal series.

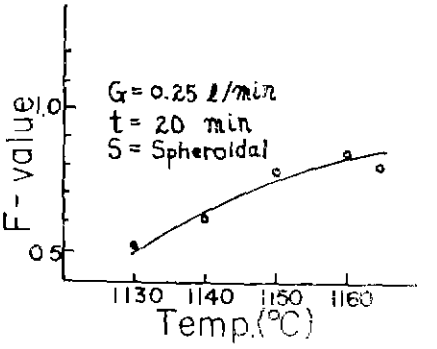

Fig. 4. F–T plot of spheroidal hematite

By eq. (2), F value which corresponds to the formation of fayalite will be 0.5. while 1.5 corresponds to complete reduction of Fe_2O_3 to matallic Fe. For the reduction time of 20 min and the gas flow rate of 0.25l/min., F-Temperature plot is shown in case of spheroidal hematite in Fig. 4.

Fig. 5. shows F values as a function of reduction period in the neighborhood of 0.5 in case of spheroidal, acicular and cubical hematite. Optimum F-value was found to be 0.5 by means of X-ray diffractometer. X-ray patterns are shown in Fig. 6 and 7.

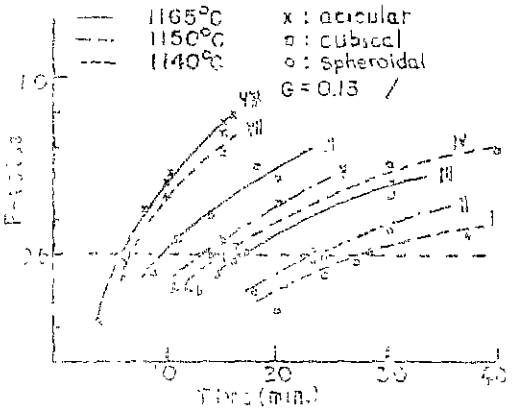

Fig. 5. F-t plot at G=0 13l/min.

From Fig. 6 and Fig. 7, the points where F value were 0.5 in Fig. 3 and Fig. 5, were found to be best. It is evident from Fig. 6-3 and Fig. 6-4 in case of spheroidal series, from Fig. 7-3 and Fig. 7-4 in case of cubical series and from Fig. 7-6 and Fig. 7-7 in case of acicular series. On account of rather incomplete quenching, excess SiO_2 of β-quartz state was transformed into the α-quartz and wüstite appeared tracely. Hence, from Fig. 5. the best conditions to produce fayalite were 18 to 27min., 11 to 16min., and 6 to 7 min. in case of spheroidal, cubical and acicular hematite respectively at the gas flow 0.13l/min. over the temperature range of 1165°C to 1140°C Also following behaviours can be believed to occur:

$$2\left(Fe\begin{matrix}O\\O\end{matrix}Fe+2(O=Si=O)\right) \tag{3}$$

$$\xrightarrow[\Delta]{CO,H_2} Fe=O+Fe\begin{matrix}O-Fe\\O\\O-Fe\end{matrix}O+2(O=Si=O)+$$

$$\frac{1}{2}O_2\uparrow \text{ (in } CO_2 \text{ or } H_2O) \tag{4}$$

$$\xrightarrow[\Delta]{CO,H_2} 4Fe=O+2(O=Si=O)+\frac{1}{2}O_2\uparrow \text{ (in } CO_2 \text{ or}$$

$$H_2O) \tag{5}$$

$$\xrightarrow[\Delta]{CO,H_2} 4[\cdots Fe\cdots O]+2[\cdots O\cdots Si\cdots O] \tag{6}$$

$$\xrightarrow[\Delta]{CO,H_2} 2\left(Fe\begin{matrix}O\\O\end{matrix}Si\begin{matrix}O\\O\end{matrix}Fe\right) \tag{7}$$

$$\xrightarrow[\Delta]{CO,H_2} 4Fe+2(O=Si=O)+2O_2\uparrow \text{ (in } CO_2 \text{ or } H_2O)$$

(8)

Input thermal energy is dilivered in the form of phonons into the sample and vibrates Fe-O and Si-O bonds. As the dissociation energy of Fe-O bond (98 kcal/mole) is much smaller than that of Si-O bond (192kcal/mole)[10],[11], Fe-O bonds open first so that oxygen erupts out and diffuses to the surface of reducing atmosphere. Eqs. (4), (5) and (6) are based upon Fig. 6-2 and 6-3. In eq. (6), Fe-O and Si-O bonds open together, before fayalite is formed in eq. (7). Excess reduction of eq. (8) is shown in Fig. 6-8.

By the way, F is the function of mixing ratio(X), gas flow rate (G), temperature (T), reduction period (t), shape of hematite (S) and particle size (R).

$$F=f(X,\ G,\ T,\ t,\ S,\ R) \tag{9}$$

Particles of reactants were ground to pass through 44 mesh screen to fix constantly. Hence, in the present study, X, G and R were assumed to be constant. Therefore, $F=f(T,\ t,\ S)$ (10)

Shapes of particles are characterized by those surface areas (A) and so, functions of surface area (A).

$$F=f(T,\ t,\ A) \tag{11}$$

Surface areas (A) of α-Fe_2O_3 are about 3.0, 10 and 5.0m^2/g in case of spheroidal, acicular and cubical shapes respectively [8]

Fig. 9 is the log-log plot of Fig. 3 and Fig. 5. From the figure, log F is assumed to be a linear function of log t.

$$\log F=\log C_1+C_2\times\log t \tag{12}$$

C_2 was found to have a approximate value of 0.5 for all curves.

$$F=C_1t^{0.5} \qquad (0<t<150) \tag{13}$$

And from eq. (11).

$$F=f(T,\ A)t^{0.5} \tag{14}$$

Surface area (A) is related to diffusion distance (x), whose depth is shortened as A increases, that is, A is assumed to be function of $1/x$). Hence, the increase of surface area causes more diffusion to the surface, which improves the reactivity of the process.

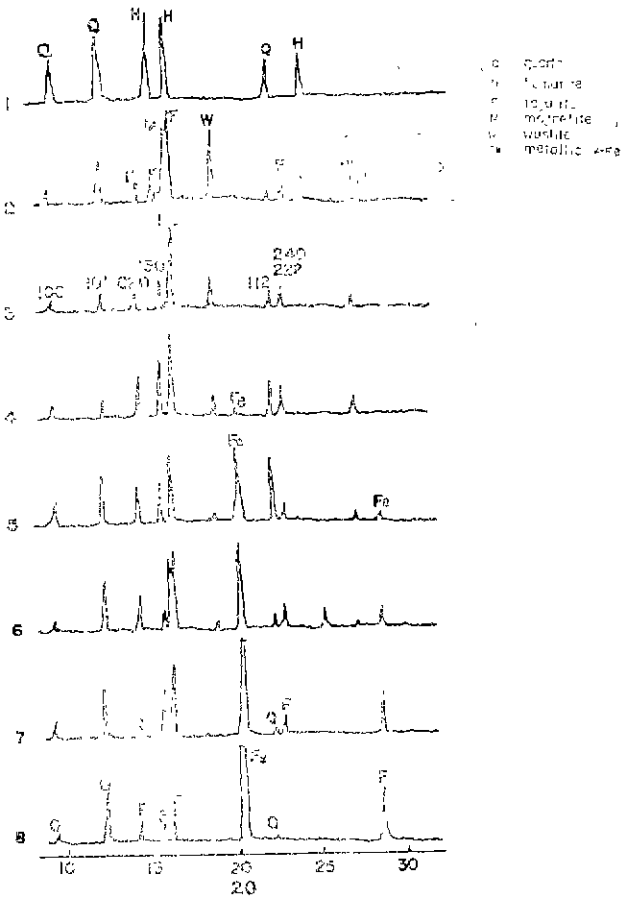

Fig. 6. X-ray patterns of spheroidal series at $G=0.13l$/min.

1 : raw sample
2 : F=0.391
3 : F=0.467
4 : F=1.535
5 : F=0.648
6 : F=0.825
7 : F=1.065
8 : F=1.170

Therefore, the range of synthesis is made narrower.

$$F=f(T,\ 1/x)t^{0.5} \tag{15}$$

$$=f(D_0\exp^{-Q/RT},\ 1/x)t^{0.5} \tag{16}$$

From eq. (16), a dimensionless group. $\frac{\sqrt{Dt}}{x}$ can be deduced.

Hence, $F=f\left(\frac{\sqrt{D_0\exp(-Q/RT)t}}{x},\ 1/x\right)$

$$=\alpha'\left(\frac{\sqrt{D_0\exp(-Q/RT)t}}{x}\right)^{\beta}(1/x)^{\gamma} \tag{17}$$

From eq. (16), $\beta=1$.

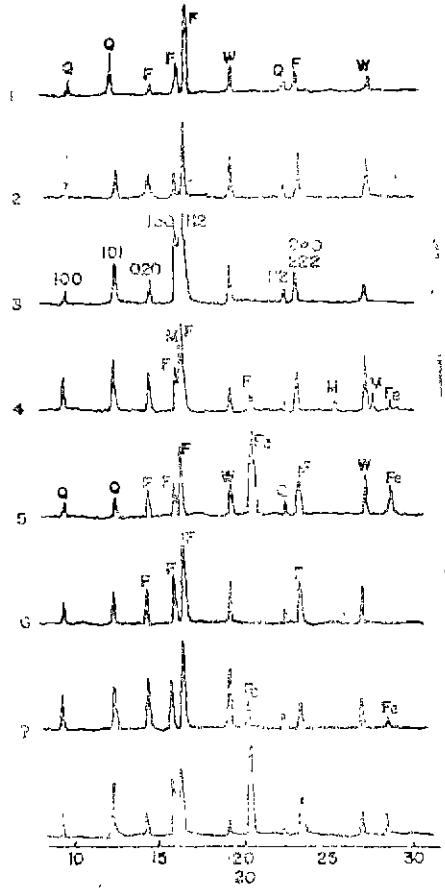

Fig. 7. X-ray patterns of cubical and acicular series at $G=0.13l$/min.

1. Cubical, F=0.469
2. Cubical, F=0.450
3. Cubical, F=0.497
4. Cubical, F=0.562
5. Cubical, F=0.749
6. Acicular, F=0.470
7. Acicular, F=0.554
8. Acicular, F=0.865

$$E=\alpha'\left(\frac{1}{x^{\gamma'}}\right)\times\sqrt{D_0\exp(-Q/RT)}\,t^{0.5} \tag{18}$$

Also, surface area, A is given in the dimension of area per unit mass.

$$A=\frac{L^2}{M}=\frac{L^2}{\rho L^3},\qquad \text{where } \rho \text{ is density}$$

$$\text{or}\quad A=\frac{1}{\rho L} \tag{19}$$

Eq. (19) can be rewritten as $A=\delta/x$ (20)

Substituting eq (20) into eq (18) and rearranging

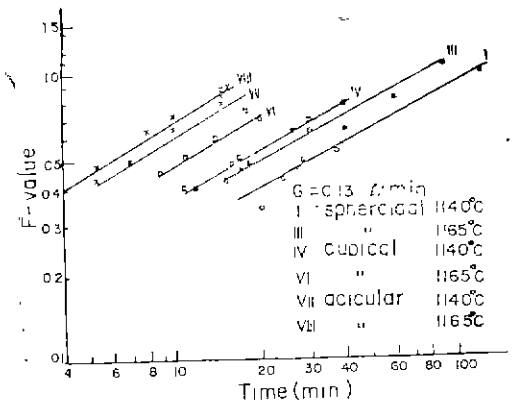

Fig. 8. F-t plot in log-log scale

them,

$$F=\alpha A^{b}\sqrt{D_0\exp(-Q/RT)}\ t^{0.5} \quad (21)$$

Again, diffusion coefficient, $D=D_0\exp(-Q/RT)$ is assumed to be unaffected by shape variation.

From Fig. 8,

$F=0.118t^{0.5}$: III with spheroidal at 1165°C (22)

$F=0.154t^{0.5}$: VI with cubical at 1165°C (23)

$F=0.208t^{0.5}$: VIII with acicular at 1165°C (24)

As $f=\alpha A^{b}\sqrt{D_0\exp(-Q/RT)}$,

$$f_{sp}:f_{cu}:f_{ac}=(A_{sp})^{b}:(A_{cu})^{b}:(A_{ac})^{b} \quad (25)$$

and $f_{sp}:f_{cu}::f_{ac}=0.118:0.154:0.208$(from eq (22), (23) and (24))$=1:1.31:1.77$. (26)

By trial and error, it is assumed that b is 0.5.

Then, $A_{sp}:A_{cu}:A_{ac}=f_{sp}^{2}:f_{cu}^{2}:f_{ac}^{2}$

$=1^2:1.31^2:1.77^2$

$=1:1.72:3.14$

$=3:5.16:9.42$ (27)

This ratio has a good agreement with observed value of 3:5:10. Therefore,

$$F=\alpha A^{1/2}\sqrt{D_0\exp(-Q/RT)}\,t^{1/2} \quad (28)$$

where α is a proportionality constant.

Differentiating eq. (28),

$$\frac{dF}{dt}=0.5\alpha A^{0.5}\sqrt{D_0\exp(-Q/RT)}\ t^{-0.5} \quad (29)$$

So, instantaneous reduction rate is inversely proportional to 0.5th power of reduction time.

4. Conclusion

The reduction rate (dF/dt) is found to be proportional to arround 0.5 th power of reduction period (t) regardless of shape of hematite and to 0.5 the power of surface area (A):

$$dF/dt \propto A^{0.5}t^{-0.5}$$

Optimum synthetic conditions of fayalite are as follows: the molar ratio of Fe_2O_3 to SiO_2 is 1:1.1 and the gas flow rate, 0.13l/min. at the range of 18-27, 10-16 and 6-7min. in case of spheroidal, cubical and acicular hematite respetively over the temperature range of 1165 to 1140°C.

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