Experimental Study of the Antiactivation of Reduced Pellets at Low Temperatures*

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Synopsis

It is generally recognized that iron oxide pellets reduced by hydrogen at lower temperatures are easily reoxidized in an air atmosphere even at room temperature.

However, pellets slightly reoxidized by the inert gas of a lower oxygen potential showed inactive behaviours. Very thin oxide layer of the thickness less than 9 Å was formed on the pore surface of the pellet during reoxidation with nitrogen-oxygen gas mixture of below 1% oxygen. When the oxygen content in the gas mixture was below 1%, the degree of reoxidation was nearly 0.9% independent of the oxygen potential. But if the oxygen content exceeded 1%, the degree of reoxidation increased rapidly with the oxygen content.

It was also shown that the rate of reoxidation was controlled by the diffusion of oxygen through the boundary and the reacted shell layers. Therefore, the exposure time necessary for antiactivation could be calculated and it was dependent on the oxygen potential.

Furthermore, when the resistance of the gas transport was negligibly small, the rate of reoxidation was represented by the logarithmic rate law.

I. Introduction

It is well known that the reduced pellets are easily reoxidized in the air at room temperature. Especially, the pellets reduced at lower temperatures ignite in the air.

Nevertheless, the reoxidation behaviours of reduced pellets have not yet been studied sufficiently. In order to prevent the ignition of sponge-iron powders reduced at lower temperatures, the treatment in an inert gas of extremely low oxygen potential is known¹⁾ to be effective. But the necessary oxygen potential and the treating time for antiactivation have not been clarified yet. The authors investigated the reoxidation behaviours of reduced pellets in order to know the conditions necessary for the antiactivation and also to clarify the mechanism of such antiactivation.

Fig. 1. Effect of the oxygen content on the reoxidation of reduced pellet (Oxygen content: over 10%, temperature: 25°C)

From the view point of iron and steel industry, the pellets are generally reduced at higher temperatures, however, the pellets reduced at lower temperatures are particularly interested in the present study.

II. Materials

In the present work, all the experiments were carried out with hematite pellets prepared by balling of oxide particles and igniting at 1300°C for 6 hr in the air. The porosity of the pellets was 18 to 28% and the pore surface areas were 11 to 13 sqm per gram.

III. Experimental Procedure

All the rate measurements were made with the same balance system which had been used in the previous works.²⁾ The sensibility of the balance is 0.5 mg. The pellet was suspended from the balance in a reaction tube heated by an electric resistance furnace.

The reaction tube made of silica was 33 mm ID and 1000 mm long, and its lower part was packed with alumina particles to preheat the reaction gas. A Pt-Pt-13% Rh thermocouple covered with a 6 mm silica protection tube was inserted from the bottom of reaction tube to the position 5 mm below the sample.

The reduction and reoxidation of the pellets were carried out in series. The pellet was weighed, put in a basket made of platinum wire and suspended from the balance. While the pellet was heated to a desired reduction temperature, the atmosphere in the reaction tube was purged with nitrogen. Hydrogen was then introduced and the weight loss was recorded at adequate time intervals. After the pellet was completely reduced to sponge iron, it was cooled down to the reoxidation temperature in the same atmosphere and then the atmosphere in the reaction tube was

Fig. 2. Effect of the oxygen content on the reoxidation of reduced pellet (Oxygen content: below 1%, temperature: 25°C)

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purged with nitrogen. To remove oxygen contained in commercial grade nitrogen as an impurity, so as to prevent the slightest reoxidation, nitrogen from a cylinder was flowed through the packed bed of copper chips which was reduced frequently by introducing hydrogen. Accordingly, any oxygen could not be detected by gas chromatograph with high sensibility. Then, nitrogen containing some amount of oxygen was introduced and the weight increase was measured by the balance at adequate time intervals.

IV. Experimental Results

1. Reoxidation of Reduced Pellets under Several Oxygen Potentials at Room Temperature

Pellets reduced by hydrogen at 520°C were reoxidized at room temperature with nitrogen containing various amounts of oxygen, 29 ppm to 40%. The reoxidation curves obtained are given in Figs. 1 and 2. As shown in these figures, if the reduced pellets are reoxidized with the gas of lower oxygen concentration, below 1% oxygen, the reoxidation does not proceed over 1.0% independent of the oxygen potential. On the other hand, in the case of oxygen potential higher than 5% oxygen, the reoxidation proceeds with increasing oxygen potential. It is also observed that the reoxidation proceeds up to 1.0% more rapidly with increasing oxygen potential. The detailed description on the relationship between the degree of reoxidation and the oxygen potential is referred to section IV. 5. Here, the degree of reoxidation is defined as the percentage of oxidation up to ferric oxide.

2. Heat Evolved by Reoxidation

Since the oxidation of metallic iron is exothermic and the reduced pellet has a large reaction interface area, the temperature change during the reoxidation must be taken into account for the investigation of reoxidation behaviours.

When the raw pellet was prepared, the hot junction of Pt-Pt-13% Rh thermocouple was settled so as to be in the center of the pellet. Then the raw pellet was heated in the air at 1 300°C for 6 hr.

The pellets prepared were reduced by hydrogen at 500°C and then reoxidized in various oxygen potentials at room temperature.

Fig. 3. Temperature changes of reduced pellets by reoxidation with nitrogen-oxygen gas mixture of various oxygen content. Figures in parentheses show diameters of pellets.

The temperature change was recorded automatically during reoxidation. The results are shown in Fig. 3 where the diameters of pellets are given by the number in parenthesis.

The highest peak of the temperature curve during the reoxidation became higher and sharper, and the time to reach the peak became shorter with increasing oxygen potential. Below 1% oxygen, the temperature rises were relatively small.

3. Microscopic and X-ray Analysis of Reduced Pellets Reoxidized in Various Oxygen Potentials at Room Temperature

In order to analyse the process of reoxidation, cross sections of the pellets reoxidized in various oxygen potentials were observed.

Macroscopic inspection of the fracture surface shows that an light gray inner core is surrounded by a dark gray outer shell of oxide layer, when the oxygen potential is higher than 5%. A typical figure is shown in Photo. 1.

The thickness of the macroscopic oxide layer increases with increasing oxygen potential above 5% oxygen. When the pellets were reoxidized in lower oxygen potentials such as below 1% oxygen, the cross section was observed to be apparently uniform like the core shown in the Photo. 1. The interface between the outer shell and the inner core seems to be parallel to the surface. This fact suggests that the rate of oxidation of metallic iron on the pore surface is rapid as compared with the diffusion rate of oxygen in the reoxidized shell layer. Therefore, the reoxidation of reduced pellets might proceed topochemically.

Furthermore, microscopic observation shows that the macroscopic oxide shell layer consists of the thin oxide film on the pore surface and the metallic iron inside of this film. In the inner core, however, any microscopic oxide layer could not be observed. The

Photo. 1. Cross sectional view of a pellet reduced by hydrogen at 520°C and reoxidized by nitrogen-oxygen gas mixture at room temperature

A: Macroscopic oxide shell layer
B: Transitional shell layer
C: Inner core

pellets reoxidized in the oxygen potential below 1% show no more microscopic oxide film. It was also clarified that the visual colour of the macroscopic oxide shell might vary with the thickness of microscopic oxide films.

The typical microphotograph of the macroscopic oxide shell is shown in Photo. 2.

The identification of metallic iron, wustite, magnetite and hematite in both parts was made by X-ray diffraction, using iron target, and the results obtained are listed in Table 1.

Hematite was detected only for the pellet reoxidized in such higher oxygen potential as 40% oxygen and magnetite was seen for any pellet reoxidized in the oxygen potential higher than 5%. For the pellets reoxidized in the oxygen potential less than 1% and also the inner cores reoxidized in the oxygen potential higher than 5%, nothing was observed except metallic iron.

4. Reoxidation of Reduced Pellets at 100° to 300°C under Lower Oxygen Potentials

As mentioned in section IV. 1, it is evident that if the reduced pellets are reoxidized to a definite degree under lower oxygen potentials, they are not further reoxidized.

It is generally recognized³⁾ that the rate of oxidation of metallic iron obeys the logarithmic rate law at lower temperatures and the parabolic rate law at higher temperatures. Concerning the transition temperature from the logarithmic to the parabolic rate law, a close agreement among earlier works was not necessarily obtained. However, it is obvious⁴⁾ that the

Photo. 2. Microphotograph of the oxide layer of a reoxidized (by 20% oxygen-nitrogen gas mixture) pellet which was reduced at 520°C, showing microscopic oxide layer and metallic iron

Table 1. X-ray analysis of reduced pellets reoxidized by various oxygen concentration

Partial pressure of oxygen (atm)	Outside layer	Inner core
0.40	Fe, Fe ₃ O ₄ , Fe ₂ O ₃	Fe
0.30	Fe, Fe ₃ O ₄	Fe
0.25	Fe, Fe ₃ O ₄	—
0.20	Fe, Fe ₃ O ₄	Fe
0.10	Fe, Fe ₃ O ₄	

logarithmic rate law is applicable to the initial stage of the oxidation of iron at the temperature in the neighbourhood of A₁ transformation point of iron.

The authors⁵⁾ have already shown that the logarithmic rate law is valid to the reoxidation of iron powders reduced by hydrogen.

According to the logarithmic rate law, at room temperature the reoxidation proceeds very rapidly at first and its rate decreases after a definite period as if the further reoxidation was stopped. Therefore, the present results that the reoxidation of reduced pellets seems to stop at a definite degree of reoxidation may be resulted from the fact that the oxidation of metallic iron on the pore surface obeys the logarithmic rate law.

In order to ascertain whether or not the logarithmic rate law might be valid to the reoxidation of reduced pellets, the pellets reduced at 520°C were reoxidized

Fig. 4. Logarithmic plots of reoxidation curves of reduced pellets, reoxidized by nitrogen-oxygen gas mixture containing 1% oxygen at 100° to 300°C

Fig. 5. Relations between the reoxidation temperature and the initial reoxidation degree of reduced pellet with gas containing 1% oxygen

in the nitrogen containing 1% oxygen at 100°, 200°, and 300°C, and the results obtained are shown in Fig. 4 with a semi-log scale. Except the initial stage, it is clear that linear relationships may hold at each temperature. That is, the logarithmic rate law is applicable to the later stage. Now, it is defined that the degree of initial reoxidation is that at which the logarithmic rate law begins to hold. In Fig. 5, the degrees of initial reoxidation obtained from Fig. 4 are shown as Arrhenius-type plots. It shows that the degree of initial reoxidation increases with increasing reoxidation temperature, especially above 100°C.

5. Effect of the Oxygen Potential on the Degree of Reoxidation

The relationship between the degree of initial reoxidation and the oxygen potential in the range of 29 ppm to 40% oxygen is shown in Fig. 6. It is obvious that although the degree of initial reoxidation increases with oxygen concentration in the cases more than 5% oxygen, it becomes nearly constant at the oxygen concentration below 1% independent of the oxygen potential.

It is reasonable to consider that the degree of initial reoxidation increases with increasing oxygen potential, due to the temperature rise of the pellet by the heat of oxidation which accelerates reoxidation. If the oxygen potential is lower than 1%, the temperature rise is negligibly small and its effect on the reoxidation becomes also negligible. Therefore, it seems that the degree of initial reoxidation is nearly constant below 1% oxygen at room temperature. Even in the oxygen potential above 5%, if the temperature rise could be prevented, the degree of reoxidation would not increase and show the similar values as in the case of lower oxygen potential below 1%.

Considering that the inner structures of the reoxidized pellets in the oxygen potential below 1% are observed to be uniform microscopically, it seems that any part of the pellet should absorb a definite content of oxygen and show no more increase of reoxidation.

Since the degree of reoxidation depends on the temperature rise during the reoxidation, the range of the oxygen potential where the degree of reoxidation is constant may also depend on the characteristics of heat conduction surrounding the sample such as the heat conductivity of gas.

Fig. 6. Relation between the reoxidation degree of reduced pellet (reduced at 520°C) and the oxygen content at room temperature

It was also recognized that the pellet reoxidized in a lower oxygen potential was not further reoxidized even in a higher oxygen potential. Consequently, the pellets slightly reoxidized in the oxygen potential below 1% are regarded as to be antiactivated.

6. Antiactivation of the Pellets Reduced at Various Temperatures

It is quite clear that the pellets reduced at 520°C are antiactivated by reoxidizing in the low oxygen potential below 1% oxygen. Now, in order to ascertain the effects of reducing temperature on the degree of initial reoxidation, the pellets reduced at a temperature in the range of 400° to 690°C were reoxidized in the oxygen potential of 0.1% oxygen. The results are shown in Fig. 7 in which the degree of reoxidation decreases rapidly with increasing reduction temperature below 600°C but gradually decreases above 600°C.

7. Amount of Oxygen Absorbed per Unit Surface Area of the Pellets Reduced at Various Temperatures

In order to obtain the amount of oxygen absorbed

Fig. 7. Relation between the reoxidation degree of reduced pellet and the reduction temperature

Fig. 8. Specific surface areas of pellets reduced at various temperatures

per unit surface area of reduced pellets, specific surface areas of the pellets reduced at various temperatures were measured by applying the BET equation for adsorption isotherms of nitrogen at -195°C . The relationship between the specific surface area and reduction temperature is shown in Fig. 8 in which the area decreases linearly with increasing reduction temperature. This is in good agreement with the previous work.⁵⁾

Now, if the composition of oxide layers could be analysed, the thickness of such layers would be calculated from the amount of oxygen absorbed per unit area. However, this composition can not be determined by X-ray analysis as described in section IV. 3, and the thickness of oxide layer was therefore calculated by Eq. (1), assuming the oxide layer to be a simple iron oxide, that is, wüstite, magnetite, or hematite where their densities are 5.261 g/cm^3 , 5.136 g/cm^3 and 5.73 g/cm^3 ,³⁾ respectively.

$$x \cdot 10^{-8} \cdot d_{\text{oxide}} \cdot \frac{yM_{\text{O}}}{M_{\text{Fe}} + yM_{\text{O}}} = \frac{F}{S_w} \cdot \frac{3M_{\text{O}}}{2M_{\text{Fe}}} \quad \text{.....(1)}$$

The results are shown in Fig. 9. The maximum thickness is obtained when the pellets are reduced at nearly 520°C independent of the kind of iron oxide, and the value obtained is approximately $9\text{ \AA}$.

V. Discussions

As described in section IV. 4, the logarithmic rate law is valid for the later stage of the reoxidation of reduced pellets as the oxidation of metallic iron. Accordingly, if the oxygen supply is enough to the reaction interface, the reoxidation rate of the reduced pellet would also obey the same logarithmic rate law. Since the reduced pellet, however, is porous and has a large specific surface area, oxygen molecule must diffuse inside the pores from the gas bulk to reach the reaction interface. Furthermore, the reduced pellets are more strongly affected by the exothermic reaction of

Fig. 9. Relation between the reduction temperature of pellet and the calculated thickness of oxide layer of reduced pellets, reoxidized by gas containing 0.1% oxygen at room temperature

oxidation due to the large reaction interface. Those factors are different from the oxidation behaviour of metallic iron. In the present work, the analyses of the reoxidation process were carried out when a remarkable temperature increase of the pellet was not observed by reoxidation in a low oxygen potential.

1. Reoxidation Rate of Metallic Iron on the Pore Surface of Reduced Pellets

It is reasonable to consider that the oxidation rate law of metallic iron should also be applied to the reoxidation of metallic iron on the pore surface of a reduced pellet. In our previous work,⁵⁾ it was shown that the logarithmic rate law was valid to the later stage of the reoxidation of reduced iron-powders, and it was also valid for the reduced pellets, as described in section IV. 4. It is generally accepted that the logarithmic rate law is valid to the oxidation of metallic iron at lower temperatures and also to the initial period of the oxidation at higher temperatures.

According to the Mott's theory,⁶⁾ the logarithmic rate law can be applied to the oxidation of metals whose oxides are ion conductors and also electron insulators. Namely, the rate of oxidation is limited by the rate of electron transfer. Electrons can penetrate through the oxide layer by tunnelling effect of quantum mechanics without going over the energy barrier. The probability of passing through is represented by $\exp(-x/x_0)$. The rate of growth of oxide layer is proportional to this probability and is represented by Eq. (2).

$$dx/dt \propto \exp(-x/x_0) \quad \text{.....(2)}$$

Integrating Eq. (2), Eq. (3) is obtained

$$x = x_0 \log(t + t_0) - x_0 \log t_0 \quad \text{.....(3)}$$

When $t \gg t_0$, Eq. (3) becomes

$$x = x_0 \log t - x_0 \log t_0 \quad \text{.....(4)}$$

Substituting Eq. (1) into Eq. (4), it becomes

$$F = k \log t - k \log t_0 \quad \text{.....(5)}$$

$$k = S_w \cdot d_{\text{oxide}} \cdot \frac{yM_{\text{Fe}}}{M_{\text{Fe}} + yM_{\text{O}}} \cdot \frac{2}{3} \cdot 10^{-6} \cdot x_0 \quad \text{.....(6)}$$

Fig. 10. Temperature dependence of the rate constant for reoxidation of reduced pellet as shown by the logarithmic law

Since the increase of the weight is approximately proportional to the thickness of the oxide layer, it is linearly proportional to the logarithmic value of reoxidation time. The results in the present work satisfy the logarithmic rate law, as mentioned in section IV. 4.

It is suggested from the above theory that x_0 depends on the temperature, but not on the oxygen potential. Applying the results shown in Fig. 4, the values of k were estimated as 0.363, 1.08, and 3.50 (—), respectively. They satisfied approximately the Arrhenius-type relation, as shown in Fig. 10. The apparent activation energy was estimated to be 4.8 kcal/mol which was slightly larger than the value obtained for the reoxidation of reduced iron-powders which was 3 kcal/mol, but remarkably less than that for the oxidation of iron plate, 21.7 kcal/mol, reported by Measor *et al.*⁴⁾

2. Reoxidation Rate of Reduced Pellets

As described in section IV. 4, the reoxidation process of the reduced pellets is analysed by separating into the initial stage and the later one. Here, the present results show that the logarithmic rate law can be applied to the later stage. It is generally recognized that this law is applicable to the oxidation of metallic iron at lower temperatures and to the initial period of the oxidation of metallic iron at higher temperatures.

According to the logarithmic rate law, a metallic iron is rapidly oxidized to a definite degree of reoxidation. In this case, the rate of reoxidation reaction of metallic iron on the pore surface may be very rapid.⁶⁾

Therefore, it is concluded that the rate limiting step in the initial stage of the reoxidation of reduced pellets should be the gas diffusion process both in the boundary layers and in the reoxidized shell layers of reduced pellets, or the both processes of the gas diffusion and the reoxidation of the pore surface, but not the oxidation process on the pore surface.

Furthermore, as described in section IV. 1, the rate of initial reoxidation of reduced pellets increases with increasing oxygen potential. This fact also suggests that the initial stage of the reoxidation of reduced pellets is mainly controlled by the gas diffusion, and that the rate constant, k , is independent of oxygen potential.

It is well known⁷⁾ that the gas-solid reaction proceeds topochemically when the rate of chemical reaction at the interface is remarkably rapid and the gas diffusion is rate controlling. This is confirmed by the macroscopic observation of the cross sections of reduced pellets reoxidized in the oxygen potential above 5%.

If it is assumed that the reoxidation rate of the reduced pellet should be controlled by the gas diffusion in the gas boundary and the reoxidized shell layers, the rate equation can be given by Eq. (7), where the reoxidation model is shown in Fig. 11.

$$\frac{1}{D_e} \left[\frac{1}{2} \{1 - (1-R)^{2/3}\} - \frac{1}{3} R \right] + \frac{R}{3k_f r_0} = \frac{C_{O_2}^b - C_{O_2}^r}{d_{\text{iron}} \cdot \alpha \cdot r_0^2} \cdot t \quad \text{.....(7)}$$

Fig. 11. Reoxidation model

Fig. 12. Relation between $[\frac{1}{2} \{1 - (1-R)^{2/3}\} - \frac{1}{3} R]/R$ and t/R shown in Eq. (11) for No. 3

Since oxygen molecules react with iron atoms and disappear at the reaction interface, the number of molecules in the gas phase decreases at the reaction interface. Hence, bulk flow occurs from the bulk gas phase toward the reaction interface.

The rate of oxygen transfer by bulk flow and diffusion can be calculated from the following equation, assuming quasi-stationary state.

$$J_{O_2}^d + J_{O_2}^e = C_0 \cdot \frac{D_e}{r_0} \cdot \frac{r}{r-r_0} \cdot \ln \frac{C_0}{C_{N_2}^r} \quad \text{.....(8)}$$

On the other hand, the rate of diffusion through shell layer is given by Eq. (9), neglecting bulk flow.

$$J_{O_2}^d = \frac{D_e}{r_0} \cdot \frac{r}{r-r_0} \cdot C_{O_2}^r \quad \text{.....(9)}$$

The ratio of the diffusion flux to the total transfer flux is expressed by Eq. (10).

$$J_{O_2}^d / (J_{O_2}^d + J_{O_2}^e) = \frac{C_{O_2}^r - C_{O_2}^r}{C_0 \ln (C_0 / C_{N_2}^r)} \quad \text{.....(10)}$$

The relation given in Eq. (10) shows that $J_{O_2}^d / (J_{O_2}^d + J_{O_2}^e)$ may gradually approach unity, namely $J_{O_2}^e$ may approach to zero, when the concentration of oxygen $C_{O_2}^r$ approaches to zero. The transfer of oxy-

Table 2. Effective diffusion coefficient D_e and mass transfer coefficient k_f in the reoxidation of pellets

No.	$C_{O_2}^b$ (mol/cm ³)	α (mol-oxygen/ g-atom-iron)	r_0 (cm)	d_{iron} (g-atom/cm ³)	D_e (cm ² /sec)	$D_e/D_{N_2-O_2}$	k_f^{expt} (cm/sec)	k_f^{calc} (R.M.) (cm/sec)	k_f^{calc} (S.T.) (cm/sec)
1	4.18×10^{-7}	7.09×10^{-3}	0.662	5.16×10^{-2}	0.054	0.25	0.26	0.809	0.728
2	8.61×10^{-8}	7.15×10^{-3}	0.620	5.05×10^{-2}	0.079	0.37	0.81	0.847	0.760
3	4.51×10^{-8}	8.48×10^{-3}	0.633	4.74×10^{-2}	0.079	0.37	0.72	0.835	0.749
4	2.17×10^{-8}	6.93×10^{-3}	0.608	5.04×10^{-2}	0.065	0.31	0.51	0.843	0.756
5	1.19×10^{-9}	5.92×10^{-3}	0.576	5.08×10^{-2}	0.067	0.32	1.10	0.892	0.803

gen by bulk flow may be practically negligible at the oxygen potential less than 1%.

As mentioned above, it is observed that any part of the reduced pellet is reoxidized to a definite degree of reoxidation.

Oxygen potential in equilibrium with iron and magnetite, 1.63×10^{-92} mol/cm³, was substituted into $C_{O_2}^r$ which was negligibly small as compared with $C_{O_2}^b$. Then, the rate equation becomes as follows.

$$\frac{1}{D_e} \left[\frac{1}{2} \{1 - (1-R)^{2/3}\} - \frac{1}{3} R \right] + \frac{R}{3k_f r_0} = \frac{C_{O_2}^b}{d_{\text{iron}} \cdot \alpha \cdot r_0^2} \cdot t \quad \text{.....(11)}$$

Dividing Eq. (11) with R , Eq. (12) is obtained.

$$\frac{\frac{1}{2} \{1 - (1-R)^{2/3}\} - \frac{1}{3} R}{R} = \frac{D_e \cdot C_{O_2}^b}{d_{\text{iron}} \cdot \alpha \cdot r_0^2} \cdot \frac{t}{R} - \frac{D_e}{3k_f r_0} \quad \text{.....(12)}$$

When the gas diffusion through either the reoxidized shell or the gas boundary layer, or through both of them may control the rate of reoxidation, there is a linear relation between $[1/2\{1 - (1-R)^{2/3}\} - 1/3R]/R$ and t/R . Effective diffusivity and mass transfer coefficient can be calculated from the slope and the intersection of the straight line obtained by Eq. (12). The reoxidation curves in the present work satisfied the relation of Eq. (12) and shows a linear relationship, as shown in Fig. 12.

The calculated values of D_e and k_f are listed in Table 2. It is obvious from this table that D_e and k_f are approximately constant independent of the oxygen potential.

Applying the value of the gas diffusivity in the system N_2-O_2 , $D_{N_2-O_2}=0.212$ cm²/sec⁸⁾ at 25°C, the values of $D_e/D_{N_2-O_2}$ are also calculated and are shown in Table 2.

Concerning the value of k_f , it can also be calculated from the correlations of dimensionless numbers, that is, Ranz-Marshall relation shown in Eq. (13) and Steinberger-Treyball relation given by Eq. (14).

$$Sh = 2.0 + 0.6Re^{1/2} \cdot Sc^{1/3} \quad \text{.....(13)}$$

$$Sh = 2.0 + 0.343Re^{0.62} \cdot Sc^{0.41} \quad \text{.....(14)}$$

The results are listed in Table 2 together with the above values.

VI. Conclusions

The pellets reduced at lower temperatures ignite if

they are exposed to an air atmosphere, as the sponge iron powders reduced at the similar condition. In order to reveal the reoxidation phenomena and to prevent the ignition, the reoxidation of reduced pellets was investigated at room temperature over the range of oxygen potential, 29 ppm to 40%.

The reoxidation behaviours of the reduced pellets are different from the oxidation of metallic iron. Namely, the oxygen molecules must diffuse through the pore to reach the pore surface where the reaction occurs and also the reoxidation is strongly influenced by the temperature increase due to the heat of oxidation itself, as the specific reaction interface is larger than the metallic iron plate. In the present work, the following conclusions were obtained from the analysis of the rate of reoxidation for the former case.

(1) If the reduced pellets are reoxidized to a definite degree of reoxidation further reoxidation does not proceed even in the higher oxygen potentials.

(2) While the degree of final reoxidation increases with increasing oxygen potential when the potential is higher than 5% oxygen, it shows, however, constant values independent of the oxygen potential in the case lower than 1%. The degree of reoxidation for a lower oxygen potential may be determined by the characteristics of the reduced pellet.

(3) The results that the degree of reoxidation increases with increasing oxygen potential above 5%, could be interpreted by the temperature rise due to the heat of reaction which promotes the reoxidation, especially above 100°C. The degree of reoxidation would show the definite value if the temperature rise could be prevented by the sufficiently rapid cooling.

(4) The rate of reoxidation is controlled by the gas diffusion through the gas boundary and the reoxidized shell layers. Therefore, the time required for the antiactivation of reduced pellets can be calculated from the model for gas diffusion controlling.

(5) The results that the reoxidation seems to stop after a slight reoxidation up to a definite degree in the lower oxygen potential such as below 1% would be interpreted by the logarithmic rate law which is valid for the rate of reoxidation.

(6) The macroscopic oxide shell layer is formed when the pellets are reoxidized in the oxygen potential above 5%. This oxide shell layer is composed of the microscopic oxide film and the metallic iron remained beneath the film. The macroscopic inner cores are apparently composed of the metallic iron alone, so far as by X-ray and microscopic examinations, as observed on the pellets reoxidized below 1% oxygen.

Appendix

Jost⁹⁾ has derived the rate equation of bulk flow and diffusion for the gas-solid reaction.

The rate equations for bulk flow and diffusion in the reaction (1) have been derived under the boundary conditions of reoxidation.

Now, consider the system in which gas molecules reach the reaction interface and react with solid reactant as described by the reaction (1).

Here, r is defined as the radius of unreacted core of a pellet which has the radius r_0 and ρ is also defined as the radial variable. Since gas molecules consumes at the reaction interface, gaseous reactant is transported to the interface by both diffusion and bulk flow. The flow rates are derived by assuming the quasi-stationary state.

The convection of gas flow in the direction of $+\rho$ is given by Eq. (2)

$$v\rho^2 = v_0r_0^2, \quad v = v_0 \cdot \frac{r_0^2}{\rho^2} \quad \dots\dots\dots(2)$$

The diffusion rate is represented by Eq. (3),

$$J_1^d = -D_e \cdot \frac{\partial C_1}{\partial \rho}, \quad J_2^d = -D_e \cdot \frac{\partial C_2}{\partial \rho} = D_e \cdot \frac{\partial C_1}{\partial \rho} \quad \dots(3)$$

and the flow rate due to the bulk flow is also shown by Eq. (4).

$$J_1^c = C_1v = C_1v_0 \cdot \frac{r_0^2}{\rho^2}, \quad J_2^c = C_2v = C_2v_0 \cdot \frac{r_0^2}{\rho^2} \quad \dots\dots\dots(4)$$

Therefore, the total flow is expressed by Eq. (5)

$$J_1 = -D_e \cdot \frac{\partial C_1}{\partial \rho} + C_1v_0 \cdot \frac{r_0^2}{\rho^2} \quad \dots\dots\dots(5a)$$

$$J_2 = D_e \cdot \frac{\partial C_1}{\partial \rho} + C_2v_0 \cdot \frac{r_0^2}{\rho^2} \quad \dots\dots\dots(5b)$$

$$J_1 + J_2 = (C_1 + C_2) \cdot v_0 \cdot \frac{r_0^2}{\rho^2} = C_0v_0 \cdot \frac{r_0^2}{\rho^2} \quad \dots\dots\dots(5c)$$

Taking the mass balance within the shell layer of radius ρ and thickness $d\rho$, the time-dependent diffusion equation for component 1 is

$$\begin{aligned} \frac{\partial C_1}{\partial t} &= -\text{div}(J_1) \\ &= D_e \left[\frac{\partial^2 C_1}{\partial \rho^2} + \frac{2}{\rho} \cdot \frac{\partial C_1}{\partial \rho} \right] - \frac{v_0r_0^2}{\rho^2} \cdot \frac{\partial C_1}{\partial \rho} = 0 \quad \dots\dots\dots(6) \end{aligned}$$

Here, $\partial C_1/\partial t$ is equal to zero for a quasi-stationary state.

In the case C_1 depends on ρ alone and Eq. (7) is obtained instead of Eq. (6)

$$\rho^2 C_1'' + C_1'(2\rho - \beta) = 0 \quad \dots\dots\dots(7)$$

where dashes denote differentiation with respect to ρ and the length β is given by Eq. (8).

$$\beta = v_0r_0^2/D_e \quad \dots\dots\dots(8)$$

Eq. (7) can be solved under the following boundary conditions:

$$(J_2)_0 = 0, \quad \rho = r \quad \dots\dots\dots(9a)$$

$$C_1 = 0, \quad \rho = r \quad \dots\dots\dots(9b)$$

$$(J_1)_{r_0} = (J_1)_r \cdot \frac{r^2}{r_0^2} \quad \dots\dots\dots(9c)$$

Substituting Eq. (5b) into Eq. (9a), then

$$D_e \left(\frac{\partial C_1}{\partial \rho} \right)_r = -C_2^r \cdot v_0 \cdot \frac{r_0^2}{r^2} \quad \dots\dots\dots(10)$$

and substituting Eq. (5a) into Eq. (9c) and using Eq. (9b), Eq. (11) is obtained.

$$-D_e \left(\frac{\partial C_1}{\partial \rho} \right)_{r_0} + C_1^{r_0} \cdot v_0 = -D_e \left(\frac{\partial C_1}{\partial \rho} \right)_r \cdot \frac{r^2}{r_0^2} \quad \dots(11)$$

Putting C_1' in Eq. (7) equal to ξ , then

$$\frac{d \ln \xi}{d \rho} = \frac{\beta - 2\rho}{\rho^2} \quad \dots\dots\dots(12)$$

and integrating between r_0 and ρ , Eq. (13) is obtained.

$$\ln \frac{\xi}{\xi_0} = \frac{\beta}{r_0} - \frac{\beta}{\rho} - 2 \ln \frac{\rho}{r_0} \quad \dots\dots\dots(13)$$

$$\frac{\xi}{\xi_0} = \left(\frac{r_0}{\rho} \right)^2 \exp \left(\frac{\beta}{r_0} \right) \exp \left(-\frac{\beta}{\rho} \right) \quad \dots\dots\dots(13a)$$

Substituting Eq. (8) into Eq. (13a), then

$$\left(\frac{\partial C_1}{\partial \rho} \right)_r = \left(\frac{\partial C_1}{\partial \rho} \right)_{r_0} \cdot \frac{r_0^2}{r^2} \exp \left(\frac{v_0r_0}{D_e} \right) \exp \left(-\frac{v_0r_0^2}{rD_e} \right) \quad \dots(14)$$

From Eqs. (10) and (11), the following equation is obtained.

$$D_e \left(\frac{\partial C_1}{\partial \rho} \right)_{r_0} = C_1^{r_0}v_0 - C_2^r \cdot v_0 = -C_2^r \cdot v_0 \quad \dots\dots\dots(15)$$

From Eqs. (11) and (14), Eq. (16) is obtained.

$$C_1^{r_0} \cdot v_0 = D_e \left(\frac{\partial C_1}{\partial \rho} \right)_{r_0} \left[1 - \exp \left(\frac{v_0r_0}{D_e} \right) \exp \left(-\frac{v_0r_0^2}{rD_e} \right) \right] \quad \dots\dots\dots(16)$$

Substituting Eq. (16) into Eq. (15), it becomes

$$C_1^{r_0} \cdot v_0 = -C_2^r \cdot v_0 \left[1 - \exp \left(\frac{v_0r_0}{D_e} \right) \exp \left(-\frac{v_0r_0^2}{rD_e} \right) \right] \quad \dots\dots\dots(17)$$

Solving Eq. (17) for the exponentials and taking logarithms, Eqs. (18) and (19) are finally obtained.

$$\frac{v_0r_0}{D_e} - \frac{v_0r_0^2}{rD_e} = \ln \frac{C_1^{r_0} + C_2^{r_0}}{C_2^{r_0}} \quad \dots\dots\dots(18)$$

$$v_0 = \frac{D_e}{r_0} \cdot \frac{r}{r-r_0} \cdot \ln \frac{C_1^{r_0} + C_2^{r_0}}{C_2^{r_0}} \quad \dots\dots\dots(19)$$

Changing ρ into r_0 and substituting Eq. (15) into Eq. (19), Eq. (20) is obtained.

$$J_1 = -D_e \left(\frac{\partial C_1}{\partial \rho} \right)_{r_0} + C_1^{r_0} \cdot v_0 = (C_1^{r_0} + C_2^{r_0}) \cdot v_0 \quad \dots(20)$$

and substituting Eq. (19) into Eq. (20), one obtains

$$J_1 = C_0 \cdot \frac{D_e}{r_0} \cdot \frac{r}{r-r_0} \ln \frac{C_0}{C_{2^0}^r} \dots\dots\dots(21)$$

Next, the flow rate can be calculated by the diffusion alone, neglecting bulk flow. Eq. (22) is obtained from Eq. (3).

$$J_1^d = \frac{D_e}{r_0} \cdot \frac{r}{r-r_0} \cdot (C_1^r - C_1^{r_0}) \dots\dots\dots(22)$$

Substituting Eq. (9b) into Eq. (22), Eq. (23) is obtained.

$$J_1^d = \frac{D_e}{r_0} \cdot \frac{r}{r-r_0} \cdot C_1^{r_0} \dots\dots\dots(23)$$

Nomenclature

C :	gas concentration (mol·cm ⁻³)
C_0 :	total concentration of gas (mol·cm ⁻³)
d_{iron} :	apparent density of iron in the reduced pellet (g·atom·cm ⁻³)
d_{oxide} :	apparent density of iron oxide in the reoxidized pellet (g·cm ⁻³)
D_e :	effective diffusivity (cm ² ·sec ⁻¹)
$D_{\text{N}_2\text{-O}_2}$:	gas diffusivity in the system N ₂ -O ₂ (cm ² ·sec ⁻¹)
F :	reoxidation degree (%)
G_1 :	gas reactant
J :	flux of mass transfer (mol·cm ⁻² ·sec ⁻¹)
k :	rate constant of logarithmic rate law (—)
k_f :	mass transfer coefficient in the gas film (cm·sec ⁻¹)
M_{O} :	atomic weight of oxygen
M_{Fe} :	atomic weight of iron
r :	radius of unreacted core (cm)
r_0 :	radius of pellet (cm)
R :	ratio of the reoxidation degree at t to the initial reoxidation degree (—)
R_e :	Reynolds number

S_1 :	solid reactant
S_2 :	solid product
Sc :	Schmidt number
Sh :	Sherwood number
S_w :	specific surface area (cm ² ·g-iron ⁻¹)
t :	reoxidation time (sec)
t_0 :	characteristic time (sec)
v :	flow rate (cm ³ ·cm ⁻² ·sec ⁻¹)
x :	thickness of oxide layer (cm)
x_0 :	characteristic length (cm)
y :	number of oxygen atoms combined with one atom of iron
α :	initial reoxidation degree expressed in the unit (mol-oxygen·g-atom-iron ⁻¹)
ρ :	variable showing the distance from the center of pellet (cm)

Subscripts and Superscripts

1:	reactive gas
2:	inert gas
c :	bulk flow
d :	diffusion
e :	equilibrium
expt:	experimental value
calc:	theoretically calculated value

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