Relation between Sulfur Pressure and Sticking of Fine Iron Ores in Fluidized Bed Reduction

Shoji HAYASHI, Sougo SAYAMA¹⁾ and Yoshiaki IGUCHI

Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Aichi-ken, 466 Japan.

1) The Government Industrial Development Laboratory, Hokkaido, Tsukisamu-Higashi, Toyohira-ku, Sapporo, Hokkaido, 004 Japan.

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Fourteen kinds of iron ore fines (0.015–0.021 cm diameter) were reduced to iron in a laboratory batch fluidized bed with a 90%CO–10%CO₂ mixture (flow rate: 8 times the minimum fluidization velocity U_{mf}) at 700–900°C to investigate the relation between sticking behavior and sulfur activity in gas phase of bed during metallization (a_s), which could be evaluated from chemical analysis of sulfur species in exhausted gas, relative to iron/iron sulfide equilibrium.

Values of a_s obtained in all of tests were in the range of 0.01–1. The tests showing middle sulfur activities around 0.1, fell into sticking state soon after initial metallization, accompanied with long iron whiskers at higher temperatures. The tests showing activities other than the above conditions, induced short iron whiskers and porous or plain irons, indicating fluidized state until higher reduction degrees at lower temperatures. These temperature and sulfur activity dependences of product morphologies, which were in nearly agreement with authors' previous researches about abnormal swelling during reduction of iron oxide pellets prepared from reagent, corresponded to a sticking tendency of bed. These results give one reasonable idea by which the ore kind dependence of sticking can be interpreted.

KEY WORDS: iron ores; laboratory fluidized bed reduction; sticking; sulfur potential; iron morphology; temperature dependence; ore kind dependence.

1. Introduction

The fluidized bed reduction process of iron ores had developed as one of direct reduction processes in ironmaking. Recently it is also applicable to a pre-reduction process of ores within several smelting reduction processes as alternatives to blast furnace.^{1–3)} However, only a few successful operation have been found in an industrial scale. The cause is attributed to the most serious problem of defluidization of bed through sticking.^{4,5)} This had been detailed by some workers including Okura,⁶⁾ who observed that when the bed reached a defluidized state, numerous fine whiskers of iron were intertwined together with small connection. These phenomena are frequently found in several ores at higher temperatures such as 900°C. The temperature dependence of sticking is likely to coincide with a general tendency for whiskers to be formed with temperature. One of another troublesome problems is that this phenomena is strongly dependent upon the kind of ores.⁵⁾ However, these detailed mechanism remain unknown. Under these circumstance, many trials to avoid sticking had been made: addition of foreign materials such coke^{7,8)}; coating of MgO and carbon⁹⁾; etc. But, these methods are limited in some cases. Therefore, attempts to modify motion of bed by stirring,¹⁰⁾ rotation,¹¹⁾ and circulating¹²⁾ have been also continued in present time.

Present authors have investigated abnormal swelling during reduction in sulfur bearing gas using iron oxide pellets produced from reagent.^{13–15)} Main results were as follows: this swelling occurs due to appearance of fibrous metallic iron; the principal experimental condition to realize these phenomena is the intermediate reduction rate of wustite under the range of 0.01–1 as the sulfur activity in gas phase during metallization, a_s^* ; the maximum swelling occurs around 900°C and $a_s=0.1$ with long iron whiskers; and additives such as CaO promoting the abnormal swelling are operated as an assistant role regardless of any reduction history.

Based on above results, the reduction test of 14 kinds of iron ores with a CO–CO₂ mixture has been carried out in the present work using a laboratory batch fluidized bed reactor. The sulfur activity in gas phase of bed during reduction stage of wustite to metallic iron, which is derived from traces of sulfur present in ores, can be obtained from exit gas analysis. The sulfur activity dependence of sticking behavior in fluidized bed reduction of each ore was investigated in relation to the results such as morphology of metallic iron.

2. Experimentals

2.1. Specimens

Chemical compositions of test ores are shown in

* In this work, a_s is defined as $(P_{COs}/P_{CO})/(P_{COs}/P_{CO})_e$, where $(P_{COs}/P_{CO})_e$ is the gas ratio under iron and iron sulfide equilibrium.^{13,16)}

Table 1. Each of these ores is crushed, screened with water, and dried at 150°C to prepare particles of 0.015–0.021 cm diameter. The table also shows main mineral phases detected by a powder X-ray diffraction method. Sayama *et al.*¹⁷⁾ had indicated characteristics of ores A–J as below.

Ore A shows a typical lamellar structure, which is subjected to dynamic metamorphism. Hematite is a compacted ore and its crystals are arranged with directionality. The crystal also tends to crack into a plate form. Goethite is not observed, but a small amount of quartz exists as gangue. Ore B is massive and contains mainly hematite. The grain boundary shows a mosaic structure. The structure of ore C is similar to that of ore B. The ore includes a small amount of goethite. Ore D contains an abundance of goethite, coexisting with hematite. Hematite is porous and the grain boundary is indistinct. In ore E columnar developed hematites are observed. Grain boundaries of such kinds of crystals are clearly observed, but the ore is not stratified, differing from Brazil ore. The deposit of ore G is considerably folded and subjected to a strong metamorphism. The ore contains hematite and a large amount of quartz. In ore H hematite is developed in magnetite. The deposit which is a contact metasomatism deposit akin to the Marcona deposit, abounds in alkali components and contains pyrite too. In ore I, an abundance of pyrite is observed and the ore presents a structure similar to that of Santafe ore. Ore J contains porous magnetite. But, hematite cannot be observed. This ore is classified under banded ore deposits that had been subjected to dynamic metamorphism. The ore contains much quartz as gangue.

2.2. Experimental Procedure

Batches of 20 g of ore were reduced under fluidized state in a stainless steel tube (2.2 cm inner diameter) with a 90%CO–10%CO₂ mixture at 700–900°C. The bed is supported by a distributor with opening

of 105 µm. The experimental apparatus is constructed as shown in Fig. 1. The temperature of bed is monitored by a thermocouple at its center. The bed is held by nitrogen much enough to fluidize during ascending and descending periods between room and reaction temperatures. For the purpose of following the reaction level of ore during reduction, a portion of off-gas is always flowed bypassing into an oxygen sensor using a zirconia solid electrolyte with a reference of air. For example, Fig. 2 shows the electric motive force of the sensor (EMF) obtained during reduction of ore A (Brazil ore). This variation of EMF, which is analogous to those measured by Sheasby and Gransden,¹⁸⁾ informs roughly the reduced level of ore. Based on this EMF observation, the gas exhausted by reduction beyond wustite stage is introduced to SO₂ absorbents *via* an oxidizing furnace, where the total sulfur species are deter-

Fig. 1. Experimental apparatus.

Table 1. Chemical composition of iron ore. (wt%)

Name	Ore	T.Fe	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	S* ²	Na ₂ O* ²	K ₂ O* ²	Main mineral phases* ³
Brazil	A	65.20	0.20	4.29	1.32	—	0.14	0.0034	0.005	0.003	H
Swaziland	B	63.65	0.18	4.68	2.15	—	—	0.0058	0.018	0.019	H
Hamersley	C	62.10	0.22	4.45	2.56	0.22	—	0.0164	0.018	0.012	H
Portlady	D	61.19	0.20	1.63	3.30	—	0.10	0.0253	0.009	0.010	H, G
Goldsworthy	E	65.85	0.08	3.30	1.25	0.10	—	0.0200	0.028	0.010	H
Krivoy-Rog	G	58.52	3.15	15.62	1.04	0.30	0.18	0.0110	0.013	0.016	H, Q
Santafe	H	63.29	14.29	4.98	0.97	1.50	1.10	0.1183	0.029	0.030	M, H
Marcona	I	63.22	15.29	5.08	0.82	1.08	1.76	1.441	0.063	0.051	M, H, P
Mosan	J	58.47	22.55	17.25	0.42	0.71	0.59	0.0290	0.012	0.030	M, Q
Mt. Newman	K	61.48	0.29	6.47	2.76	0.06	0.06	0.0113	0.014	0.037	H
Dempo	L	62.60	2.04	2.44	2.26	0.03	0.08	0.0320	0.014	0.032	H, G
Romeral	M	66.25	28.42	3.91	0.81	1.23	0.79	0.0670	0.031	0.026	M
Rio Doce*	O	62.31	0.46	5.82	1.26	0.15	0.13	0.0102	0.007	0.007	H, Q
Taharoa*	S	56.85	18.57	2.96	3.68	1.51	3.55	0.0181	0.015	0.012	M

Ores A–M: Ref. 17)

* : Kobe Steel, Ltd.

*²: 150–210 µm, Alkali contents are those soluble in hot HCl solution.

*³: H; Hematite, M; Magnetite, G; Goethite, Q; Quartz, P; Pyrite

Fig. 2. Variation of EMF, pressure, and pressure drop during reduction.

mined by means of acidimetry using NaOH solution (JIS K2541-1984). Thermodynamical consideration¹³⁾ shows that COS is most stable as sulfur species in present reduction condition, so that $P_{\text{COS}}/P_{\text{CO}}$ in bed is evaluated as a mean value during gas sampling assuming that gas phase in bed is under Fe/FeO equilibrium.¹⁹⁾ This comes from that present EMF measurement cannot assess the exact oxygen pressure in bed. The sticking time, t_s (s), as seen in the figure, can be detected from both abrupt changes of an oscillating total pressure in upstream of gas and pressure drop through bed. After sticking, the ore bed is cooled until room temperature. Fractional reduction of ores, R , is measured by the reoxidation method (950°C for 3.5 h in air), based on the complete oxidation of total iron in ores.

3. Experimental Results

3.1. Gas Volume Dependence

Substitution in the equation of minimum fluidization velocity, $U_{mf} = \rho_s g d^2 / 1650 \mu$,²¹⁾ derived from the equation of Wen and Yu,²⁰⁾ of the density of solid $\rho_s = 5.26 \text{ g/cm}^3$, the particle diameter $d = 0.021 \text{ cm}$, and the nitrogen viscosity $\mu_{N_2} = 4.53 \times 10^{-4} \text{ g/cms}$ gives $U_{mf} = 3.05 \text{ cm/s}$ at 900°C. This value agreed with the minimum fluidization velocity measured with nitrogen at 900°C, $U_{mf}^* = 3.15 \text{ cm/s}$. Because $\mu_{\text{CO}} = 4.58 \times 10^{-4}$ and $\mu_{\text{CO}_2} = 4.26 \times 10^{-4} \text{ g/cms}$ at 900°C,²²⁾ U_{mf} using a $\text{CO}-\text{CO}_2$ mixture should be in nearly agreement with U_{mf}^* using nitrogen. For example, a nitrogen gas volume of 1.5 l/min at room temperature is corresponding to a linear velocity at 900°C of 26.3 cm/s (8.3 times U_{mf}^*). Because Froud number becomes $Fr = U^2/gd = 39.1 > 1$ for this condition, a bubbling type fluidization bed will be operated in the present work.

Gas volume dependence of t_s values was examined

Fig. 3. Relation between gas volume and sticking time.

at 900°C using ore O (Rio Doce ore). The result is shown in Fig. 3. The values decrease with increasing gas volume until 1.0 l/min and reach nearly a plateau at 1.5 l/min. Sticking of each experiment seems to occur at initial metallization stage due to $R = 0.30-0.32$. These results suppose that the reduction until wustite stage of ore O below a condition of 1.0 l/min probably progresses under gas supplying control and that the reduction at a condition of 1.5 l/min will proceed with some of chemical reaction resistances between gas and solid. Because the reduction from original ore until wustite stage is generally faster than that after the stage, the latter reduction in the range of 1.0–1.5 l/min will proceed with more resistances for both processes of reaction and diffusion within ore particles, meaning lowering of gas utilization. But, the gas volumes of 1.0 and 1.5 l/min were selected as main ones. This is owing to the cause that the experiments by much volume enabling more intensive stirring of bed is more favorable for ascertaining the difference among sticking of ores.

As the values of a_s , corresponding to $P_{\text{COS}}/P_{\text{CO}}$, is almost constant with increasing gas volumes, as seen in Fig. 3, the desulfurization rate of ore O would be controlled by gas starvation.

3.2. Relation between Reduction Behavior and Sulfur Activity

Ores were reduced in gas volumes of 1.0 and 1.5 l/min at 900°C. The relations between the value of t_s or the partial reduction time under fluidization and $\log a_s$ are plotted together with fractional reduction in parentheses, as shown in Figs. 4 and 5. The iron morphology observed under SEM after partial reduction is shown in Fig. 6 for the condition of 1.5 l/min at 900°C.* In most of cases, fibrous irons are formed. They are classified into *L*, *M*, and *S* type iron whiskers, according to their lengths rather than numbers.

Concerning Fig. 5, ore S of $\log a_s = -1.96$ was under fluidization without whiskers ($R = 0.44$). Ore B of $\log a_s = -1.11$ formed *S* type iron whiskers with sticking ($R = 0.42$). Ore O of $\log a_s = -0.62$ gave *L* type iron whiskers to stick ($R = 0.31$), indicating the shortest value of t_s . Ore I of $\log a_s = -0.22$ presented *S* type iron whiskers to stick, having a relatively larger

* Ores D, O, and I referred to Figs. 9(c), 10(c), and 11(c).

Marks *L*, *M*, *S*, and *N* are explained in Fig. 6.
 Parentheses: Fractional reduction

Fig. 4.
 Sulfur activity dependence of reduction behavior at 900°C
 (1.0 l/min).

Marks *L*, *M*, *S*, and *N* are explained in Fig. 6.
 Parentheses: Fractional reduction

Fig. 5.
 Sulfur activity dependence of reduction behavior at 900°C
 (1.5 l/min).

Fig. 7.
 Sulfur activity dependence of reduction behavior at 800°C
 (1.5 l/min).

value of $R=0.46$. Ore M stuck in spite of occurrence of plain irons as shown in Fig. 6(j). This is likely owing to the formation of active surface. The variations of t_s values and iron morphologies with $\log a_s$ in case of 1.0 l/min as indicated in Fig. 4 are in nearly agreement with those in case of 1.5 l/min (Fig. 5) except larger values of t_s as a whole. Such a sulfur activity dependence of iron morphology, as expected, also corresponds to the authors' previous results¹³⁾ that abnormal swelling during reduction of wustite pellets with CO-CO₂ mixtures existed in the range of 0.01–1 of a_s accompanied with iron whiskers.

Fig. 7 shows the results at 800°C, in which ores B and J are joined as those being fluidized. Ore J forms no whiskers in spite of a favorable condition of intermediate a_s and shows the slow reduction ($R=0.40$) due to magnetite ore. Ore I stuck regardless of no whiskers ($R=0.48$), probably attributed to the active surface of porous iron. Excepting larger values of t_s at 800°C than at 900°C, the sulfur activity dependence of iron morphology at the former temperature is roughly similar to that at the latter. Moreover, the values of R are greater at 800°C than at 900°C as a whole, resulting in a less sticking tendency.

No.	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)
Ore	A	B	C	E	G	H	J	K	L	M	S
$\log a_s$	-1.30	-1.11	-0.55	-0.66	-0.56	-0.39	-0.50	-0.80	-0.55	-0.36	-1.96
*	<i>M</i>	<i>S</i>	<i>S</i>	<i>M</i>	<i>L</i>	<i>S</i>	<i>S</i>	<i>M</i>	<i>L</i>	<i>N</i>	<i>N</i>
**	<i>St</i>	<i>St</i>	<i>St</i>	<i>St</i>	<i>St</i>	<i>St</i>	<i>St</i>	<i>St</i>	<i>St</i>	<i>St</i>	<i>F</i>

* Product morphology; Long and short iron whiskers named *L* and *S* type iron whiskers, respectively.
M type iron whisker means middle one.

Mark *N* means porous or plain iron, including the state prior to metallization.

** *St*: Sticking, *F*: Fluidization.

Fig. 6. External views of partial reduced ores at 900°C (1.5 l/min).

Fig. 8 shows the results at 700°C. Inside low sulfur activities, ores K, L, and D were joined as those under fluidization other than ores S and B, despite that ore K formed *S* type iron whiskers. These ores indicate higher reduction degrees except ore S of iron sand ($R=0.13$). Inside high sulfur activities, ore I was fluidized besides ore J. Within the field between both above activities, as expected, iron whiskers of *S* type were formed for a few ores, leading to sticking of bed.

Table 2 summarizes the variations of product morphology and fluidization state with temperatures. The temperature dependence of iron morphology for

typical ores is shown as below. Ore D having middle activities diminishes the formation of fibrous irons with decreasing temperatures as shown in Fig. 9, to be under fluidization at 700°C. However, ore O having the same activity as ore D stuck even at 700°C due to *L* type iron whiskers as shown in Fig. 10, to be in lower reduction level of $R=0.31-0.43$ at all temperatures. It is also found that the whiskers become finer at low temperatures. Ore I having higher sulfur activities suppresses the formation of whiskers as shown in Fig. 11 with more reduction degrees than ore O, indicating the fluidization state at 700°C.

Fig. 8. Sulfur activity dependence of reduction behavior at 700°C (1.5 l/min).

Table 2. Product morphology and fluidization behavior.

Ore	700°C	800°C	900°C	
	1.5 l/min	1.5 l/min	1.0 l/min	1.5 l/min
A	S, St	S, St	S, St	M, St
B	N, F	N, F	S, St	S, St
C	S, St	S, St	S, St	S, St
D	N, F	S, St	L, St	L, St
E	N, St	S, St	S, St	M, St
G	S, St	S, St	L, St	L, St
H	S, St	S, St	S, St	S, St
I	N, F	N, St	S, St	S, St
J	N, F	N, F	S, St	S, St
K	S, F	S, St	S, St	M, St
L	N, F	M, St	L, St	L, St
M	M, St	M, St	N, St	N, St
O	L, St	L, St	L, St	L, St
S	N, F	N, F	N, F	N, F

Marks L, M, S, N, St, and F are referred to Fig. 6.

Portlady (Ore D), (1.5 l/min)

No.	Red. temp.	R	log a_s	*	**
(a)	700°C	0.64	-0.77	N	F
(b)	800°C	0.41	-0.98	S	St
(c)	900°C	0.37	-0.58	L	St

*, **: Referred to Fig. 6.

Fig. 9. External views of partial reduced ores.

Rio Doce (Ore O), (1.5 l/min)

No.	Red. temp.	R	log a_s	*	**
(a)	700°C	0.33	-0.75	L	St
(b)	800°C	0.43	-0.66	L	St
(c)	900°C	0.31	-0.62	L	St

Fig. 10. External views of partial reduced ores.

3.3. Relation between Sulfur in Ore and Its Potential

Relation between the initial sulfur content in ore ($\%S_0$) and the sulfur activity during metallization a_s is plotted at 900°C as shown in Fig. 12. Both variables have some relation each other for both gas volumes, except ore S showing the lowest value of a_s .

The amount of sulfur gasified during reduction from ore to wustite stage, which has no influence to morphology of iron, was determined for 8 kinds of ores (900°C, 1.0 l/min). The average ratios of the gasification before wustite stage against that beyond

the stage amount to 1.4–1.8 for ores C, D, G, K, and O (hematite ore), and 3.3–7.8 for ores H to J (magnetite ore).

4. Discussion

4.1. Sulfur Potential

The results in Fig. 12 can be explained as follows. As the desulfurization rate of ore O having a low sulfur content as described in Sec. 3.1 would be controlled under gas starvation, the chemical reaction

Fig. 11. External views of partial reduced ores.

Marcona (Ore I), (1.5 l/min)

No.	Red. temp.	<i>R</i>	log <i>a_s</i>	*	**
(a)	700°C	0.44	−0.09	<i>N</i>	<i>F</i>
(b)	800°C	0.47	−0.23	<i>N</i>	<i>St</i>
(c)	900°C	0.46	−0.22	<i>S</i>	<i>St</i>

Fig. 12. Relation between sulfur activity and sulfur content in ore at 900°C.

between sulfur species in ore and gas might be apparently under equilibrium, suggesting that a_s is proportional to $(\%S)_0$. As expected, the gradient between both variables shown in Fig. 12 seems to be nearly unity in the range of $\log (\%S)_0 < -1.8$. However, the gradient gradually becomes less than unity over this content. This fact suggests an increment of chemical reaction resistance including relatively lowering of reaction areas for the desulfurization of ore. For the case of ore I containing a large amount of pyrite, if the chemical reaction rate is enough great and gangues are inert, the results of $a_s=1$ in gas phase should be realized under the existence of metallic iron. However, the actual results reveal that $a_s < 1$. Nevertheless, it is probably that the reduction of each ore proceeds under the value close to a_s obtained in this figure.

According to authors' basic research,²³⁾ it is expected that sulfur species chemisorbed on solids such as reduced iron might control markedly iron morphology, being dependent upon the sulfur potential. Consequently, it may be necessary to examine their adsorption behavior on solid phases and their interfaces and to observe in detail the phenomena related to nucleation and growth of metallic iron.

4.2. Comparison of Sticking and Swelling Phenomena

A series of authors' studies¹³⁻¹⁵⁾ about abnormal swelling indicated that the swelling depends on length rather than number of iron whiskers. On the other hand, Langston and Stephens²⁴⁾ had studies self-agglomeration during fluidized bed reduction and presented that the tendency for particles to stick together (stickiness) is directly proportional to their adhesive force and surface area of contact, and inversely proportional to their momentum. Presumably, the longer the whiskers (as seen in Fig. 6(e)) and the higher the surface activity of iron, the more intensive the adhesive force. The area of contact possibly increases with increasing both length and number of whiskers. Because the momentum is constant in case of a definite gas volume, the former two variables probably control the stickiness.

As described in Sec. 3.2, most of fibrous irons of *L* type were found around intermediate a_s , where the bed was easily stuck with less values of t_s and *R*. In the cases other than these a_s , *S* type iron whiskers and porous or plain irons were formed to give slightly larger values of t_s and *R* and to realize the fluidization state at lower temperatures. As a conclusion, the temperature and sulfur activity dependences of t_s and *R* agree with those concerning the swelling behavior of pellets described in the beginning.¹³⁻¹⁵⁾

The result that iron morphology produced from many kinds of iron ores depends on sulfur activity in gas phase cannot be almost found out in other studies, which might present one of mechanisms interpreting clearly difference of sticking behavior among various kinds of ores.

4.3. Effects of Other Factors on Reduction Behavior

Fuwa and Ban-ya²⁵⁾ had carried out the gaseous reduction of various iron ores and reported that the formation of fibrous iron occurred frequently in most of ores more and less and did not depend on the kind of iron oxides such as hematite, magnetite, and rimonite. Similar results would be also found out in this work using a number of ores containing hematite, magnetite, and goethite as a single or mixed phases (Tables 1 and 2). Neuschütz and Hoster¹⁾ had reduced 10 kinds of ores in fluidized state with a 90% CO–10% H₂ mixture at 800°C and presented the same result as above.

Miyagawa *et al.*⁵⁾ reduced 8 kinds of ores in fluidized state with a 80%CO–20% H_2 mixture at 850°C and claimed that ores with high alumina content did not stick due to inhibition of sintering metallic iron by alumina. In the present work using a CO–CO₂ mixture, the sticking behavior of ore at 700°C had a relation with the alumina content as indicated in Fig. 13, despite no relation at higher temperatures. Excepting ores J and S being under a reduced state prior to metallization, the beds stick below 1.3 % Al₂O₃ and fluidize above 2.1 % Al₂O₃. Ore I could fluidize due to an high a_s . Ore C would stick due to an intermediate a_s . It is known that traces of alumina dissolved in wustite promotes the formation of dense iron,^{26,27)} different from the action of sulfur inducing porous iron. So that, in order to investigate the results of Fig. 13, it will be important to clarify characteristics of alumina in ores and the relationship between alumina and sulfur for product morphology.

Kobayashi *et al.*²⁸⁾ reduced in CO base gas Wabush ore (Fe₃O₄, 0.016 % S) and Mt.-Wright ore (Fe₃O₄, 0.007 % S), whose alumina contents were in low level for both ores, and observed fibrous irons in the former ore. This result may be able to be explained by different amounts of sulfur species gasified from ores. They also observed numerous iron whiskers for chemical reagent Fe₂O₃ (0.01 % SO₄). This suggests that the reduction had proceeded under a middle sulfur activity. Assuming that both reactions of reduction and desulfurization during metallization of the reagent in CO at 900°C occur alike under gas starvation control a_s becomes 0.11.

de Haas *et al.*²⁹⁾ reduced magnetite ores with a 40%CO–60%N₂ mixture at 900°C, and observed markedly fibrous irons by the addition of 5–50 ppm SO₂. Because P_{CO}/P_{CO_2} in gas is calculated to be 1.8×10^{-5} – 1.8×10^{-4} based on the same assumption as above, their sulfur activity range coincides with this work.

Previous studies revealed that alkali has a smaller effect than sulfur for producing iron whiskers.^{13,15)} The alkali species existing in ore which enhances the

formation of whiskers is probably binding with iron oxides, not with silica.¹⁵⁾ The former can be analyzed by means of hot hydrochloric acid extraction as shown in Table 1. Because most of these contents (Na₂O+K₂O) are in much lower levels except ore I, it will be not necessary to take into account alkalis for morphology change in spite of the coexistence condition of alkali and sulfur markedly favorable to the whisker formation.¹⁵⁾

5. Conclusion

The values of the sulfur activity in bed during metallization of ore (a_s), which had a corresponding relation with sulfur content in each ore except Taharoa ore, was in the range of 0.01–1 for all of tests. Many of reduction tests were fell into a sticking at higher temperatures with iron whiskers. The conditions around a middle activity ($a_s=0.1$), where long iron whiskers (L type) appeared at 900 and 800°C and short iron whiskers (S type) at 700°C, led to a sticking soon after initial metallization. The conditions showing the activities less and more than the above condition, where iron whiskers of S type and porous or plain irons were observed, presented a fluidization state with higher reduction degrees at lower temperatures.

The sulfur activity and the temperature dependences of iron morphology agreed nearly with those of abnormal swelling studied early by authors. As a whole, the sticking tendency of bed coincided with the iron morphology change. Though these results had no relation with the kind of iron oxides in ores, those obtained at 700°C were certainly concerned in alumina content of ore.

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Marks L, M, S, and N are referred to Fig. 6. Reduction time of each test is shown in Fig. 8.

Fig. 13. Effect of Al₂O₃ content on reduction behavior at 700°C.

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