Swelling of Iron Ore Pellets During Reduction*

*By Tasuku FUWA** and Shiro BAN-YA***

Synopsis

The extraordinary swelling of iron ore pellets during reduction was analyzed in a controlled CO-CO_2 *mixture at temperature from 600° to 1 200°C. In addition to the iron ore pellets, the pelletizing feed, several kinds of iron ore, and reagent grade ferric oxides were reduced under the same condition as the pellets.*

Most of swelling takes place in the stage of reduction from wüstite to metallic iron. The apparent volume change is related to the appearance of fibrous iron as the reduction product.

I. Introduction

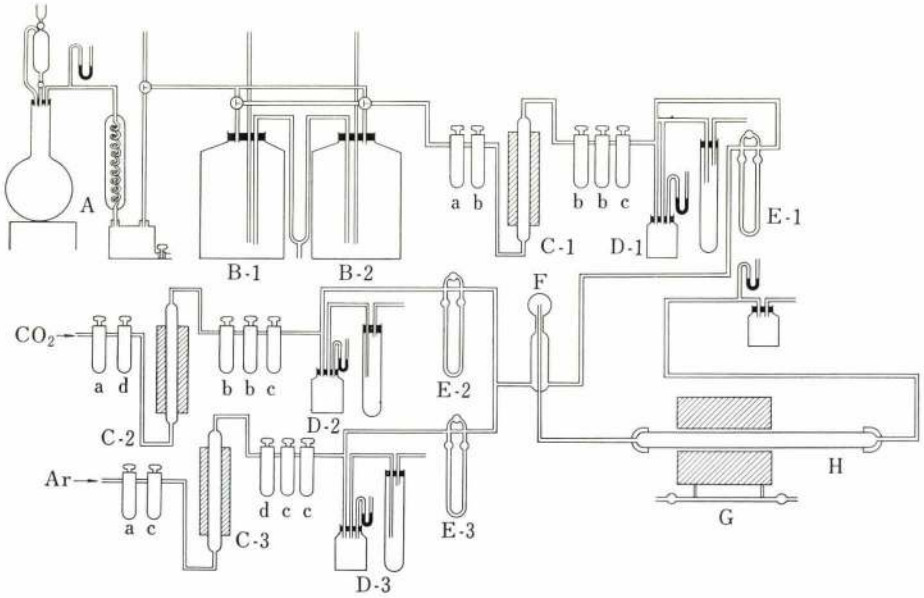
For the Japanese blast furnace which has increased her productivity by charging self-fluxing sinters, it has come into question whether iron ore pellets as the charging material for a blast furnace will have more advantages than sintered iron ore in the near future.

However, the first trial to charge iron ore pellets, imported from the Marcona Mining Company, to a blast furnace did not succeed as well as expected to improve operation and productivity. It was a problem to be solved promptly. So far it was disclosed phenomenally that during reduction pellets expanded and took powder form, and were not strong enough as blast furnace burden. The cause of swelling of Marcona pellets has been discussed as due to carbon deposition or formation of γ-hematite.[1] Watanabe and Yoshinaga[2] suggested the appearance of fibrous iron from wüstite to be related to the extraordinary swelling of the Marcona pellets. Matoba and Otake[3] observed previously fibrous metallic iron in reduced iron ores.

This paper will clarify the mechanism of swelling of iron ores, whose characteristic is not limited to the Marcona pellets. In other words, in general, pure iron oxide swells in the step from wüstite to metallic iron in process of reduction and becomes fibrous metallic iron under certain conditions.

II. Experimental Apparatus

The experimental apparatus for this work consists of the train for purification of CO, which was prepared from formic acid and concentrated sulphuric acid ; the train for purification of CO_2 from a cylinder (if necessary, this train was used for hydrogen instead of CO_2) ; the train for purification of argon from a cylinder by controlling flowrates of these gases, desired gas mixture could be supplied to the reaction tube. The reaction tube, which was made of a silica tube with 55 mm outer diameter and suited to be heated up to 1 300°C. During the course of this work, the reaction tube, shown in Fig. 2, was used for determination of bulk expansion of a pellet, instead of H in Fig. 1. The reaction tube is also made of a silica tube with 30 mm outer diameter. A pellet was set in a nickel crucible with a many-holed bottom. A concave nickel plate was put on the pellet upside-down. A 2 mm silica rod was attached to the nickel plate. Therefore, if the pellet expands during reduction, its expansion is measured by reading the top of the silica rod by means of a cathetometer. However, a pellet does not always



A : CO generator
B : CO holder
C : copper
D : flowrate adjuster
E : flowmeter
F : gas mixer
G : Kanthal resistance furnace
H : reaction tube
a : conc. H_2SO_4
b : soda-lime
c : P_2O_5
d : $CaCl_2$

Fig. 1. Experimental apparatus

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** Department of Metallurgy, Faculty of Engineering, Tohoku University, Sendai 980.

expand uniformly, rather it expands irregularly, and even the concave nickel plate disturbs its free expansion. Therefore, in order to measure the bulk expansion of the pellet, a nickel cup was designed as shown in Fig. 3. Instead of a vertical reaction tube, a horizontal reaction tube as shown in Fig. 1, was applied to the " cup test."

III. Experimental Procedure

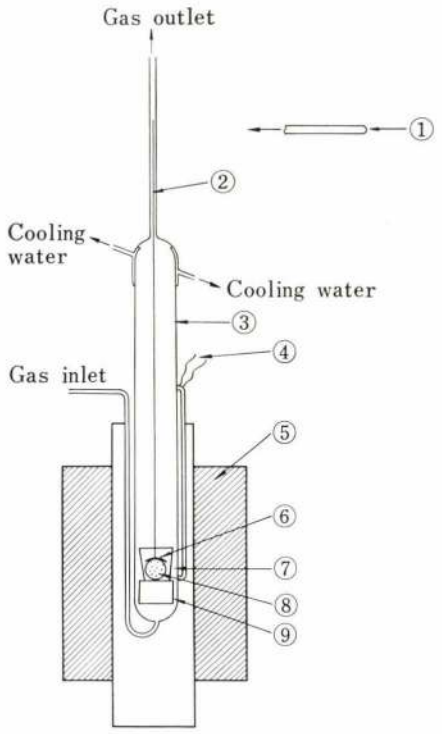
Iron ore pellets used for this work are a part of pellets shipped by the first boat from Marcona Mining Company and were chosen for comparatively spherical form of diameter 14~16 mm. The chemical composition of the pellets is shown in Table 1. They were heated previously to dry in the air at 500°C and have been kept in a desiccator.

One pellet was taken for making a run, weighed, and measured in diameter at four places with the average taken as the pellet diameter. The pellet in the nickel crucible was set in the reaction tube, and the experimental train was replaced by argon with the flowrate 100 cc/min. Then the furnace, previously heated to a given temperature, was made hotter to heat the reaction tube. After the temperature became steady at a given temperature, argon stream was switched to reducing gas with the flowrates 100 and 200 cc/min. Then the temperature and expansion were observed every 10 min for 4 hr. As the reducing gas, CO, H_2, CO-CO_2 mixture, and H_2-propane mixture were used at temperatures from 600° to 1 200°C. Then the reaction tube was cooled in the argon stream to room temperature. The pellet after reduction was weighed and its diameter at four different places was measured again. Bulk expansion will be given as follows:

$$\text{Bulk expansion } (\%) = \text{Apparent volume change } (\%) = (V_a - V_i)/V_i \times 100 \quad \cdots\cdots(1)$$

where, V_a is the volume of a pellet after reduction, and V_i is the initial volume of a pellet before reduction.

The nickel cup test was applied, based on the results obtained by the above mentioned experimental procedure, in order to clarify the relationship between deformation of iron ore particles and degree of swelling during reduction. Several different sizes of cups were prepared; as far as the cup of dimensions shown in Fig. 3 is concerned, one with an inner volume of about 4 cm^3 was used and the result of the cup test gave a good reproducibility. For the cup test, not only the Marcona pellet but also the Marcona pelletizing feed was used, with chemical composition as shown in Table 1. And the screen analysis of the pelletizing feed is shown in Fig. 4 and Table 2.



① Cathetometer
② Silica glass rod
③ Reaction tube
④ Thermocouple
⑤ SiC resistance furnace
⑥ Conical nickel plate
⑦ Nickel crucible
⑧ Iron ore pellet
⑨ Alumina tube supporter

Fig. 2. Reaction tube

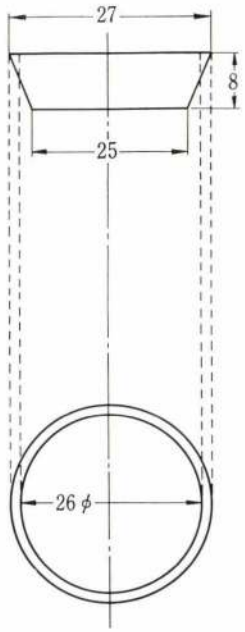


Fig. 3. Nickel cup (mm)

Table 1. The chemical composition of Marcona pellet and the pelletizing feed

	T.Fe	FeO	Fe_2O_3	SiO_2	CaO	Al_2O_3	MgO	MnO	TiO_2	Cu	P	S	Ni	Cr
Pellet *A*	67.78	1.09	95.69	0.85	0.11	0.25	0.32	0.04	0.006	0.029	0.012	0.012	0.012	0.004
Feed	67.29	1.42	—	2.04	0.32	0.41	0.67	—	0.09	0.022	0.014	0.073	—	—

The experimental procedure of the cup test was just the same as mentioned above, except for use of the nickel cup in a horizontal reaction tube instead of a vertical one.

For the pelletizing feed, about 10 g feed was filled in a nickel cup. After reduction, the bulk expansion of a reduced sample was calculated from the shape, the average diameter and height of expanded feed being measured.

IV. Experimental Results

In Fig. 5, some typical curves of the vertical diameter charge plotted against time, are shown. For the first 10 min the vertical diameter change was not large, but was followed by rapid increase, and then stayed at a constant value. However, as mentioned above, a pellet does not swell uniformly. Even concave nickel plate disturbs the free expansion of a pellet. Therefore, apparent volume change was calculated from the diameter of the comparatively spherical swollen pellet.

In Fig. 6, apparent volume changes during the reduction of the Marcona and Erie pellets was compared. The Erie pellet shows a maximum 15% volume increase, while the Marcona pellet shows about 280% volume change. Both curves for Marcona pellets in Figs. 5 and 6 show a steep increase after 30 or 40 min of reduction, which is related to the reaction from FeO to metallic iron.

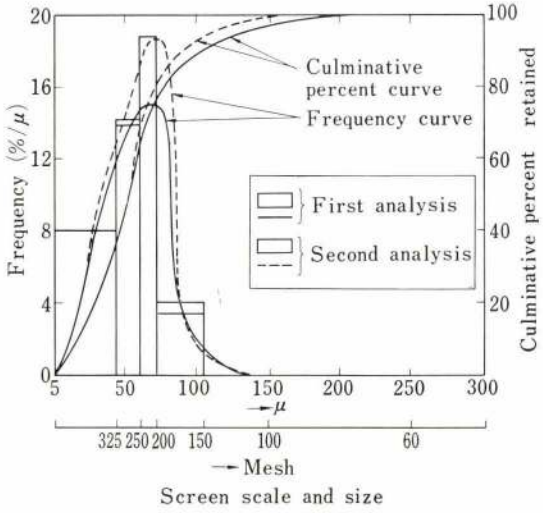


Fig. 4. Screen analysis for Marcona pelletizing feed

Table 2. Screen analysis for Marcona pelletizing feed

Screen scale (Mesh)	1st analysis (%)	2nd analysis (%)
+60	0.2	0.1
60 to 100	2.2	0.4
100 to 150	5.8	5.6
150 to 200	12.6	10.5
200 to 250	18.0	22.5
250 to 325	25.0	25.6
−325	36.2	35.4

Sample taken : 500 g (dried at 120°C)
JIS Screen : 5 hr

In Fig. 7, the apparent volume change of the pellet was shown when a pellet was reduced in the following reducing gases at temperatures from 600° to 1 200°C : CO and H_2 reduce a pellet to metallic iron ; 50%CO-50%CO_2 mixture reduces to wüstite (" FeO ") ; 90%CO_2-10%CO mixture reduces to

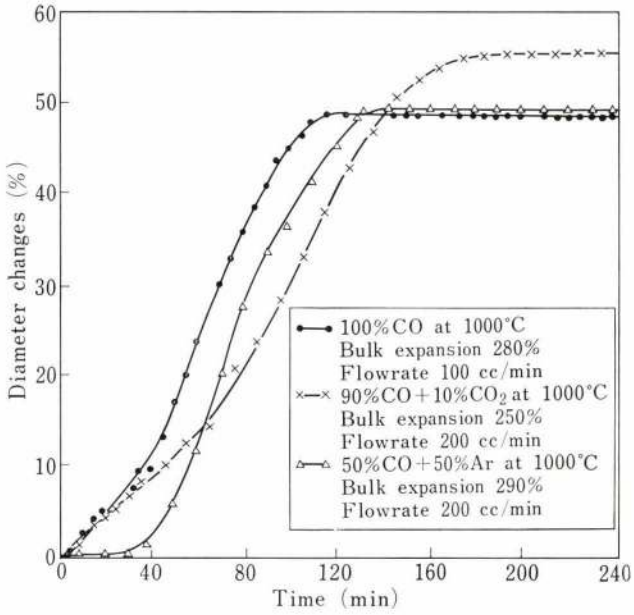


Fig. 5. Diameter changes of Marcona pellet in process of reduction

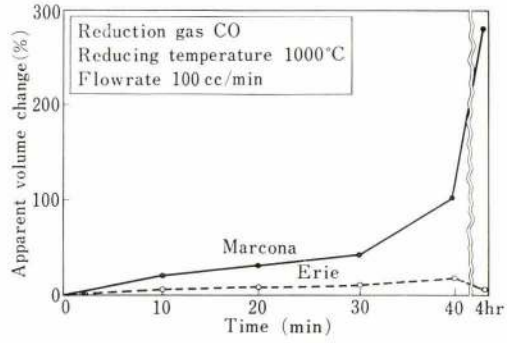


Fig. 6. Volume change of pellet in process of reduction

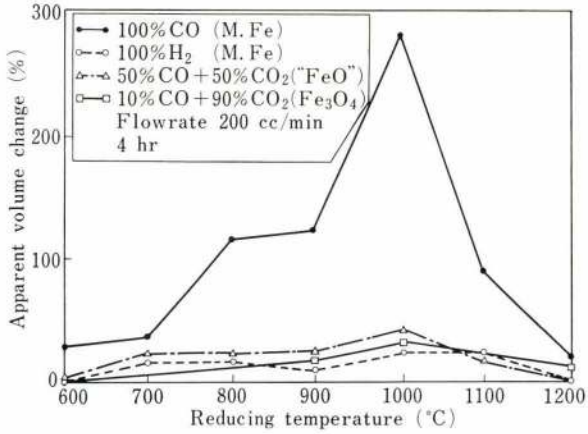


Fig. 7. Relation between temperature and apparent volume change

Fe_3O_4. There was about a 20% increase in the apparent volume change of a pellet which was reduced to metallic iron in the hydrogen stream. The maximum volume change was observed at 1 000°C. At a temperature higher than 600°C, Fe_2O_3 is reduced to metallic iron through the stages of Fe_3O_4 and "FeO." Therefore, by controlling the ratio of carbon monoxide to carbon dioxide, the Marcona pellet was reduced in a given gas mixture for 4 hr at 1 000°C, at which the maximum volume change was observed. The results obtained are shown in Fig. 8, which clearly shows that a large part of the extraordinary swelling of the Marcona pellet takes place in the stage in which "FeO" is reduced to metallic iron. In the ranges of Fe_3O_4 and "FeO," the volume change increases with higher CO-mixtures and was at a maximum at 15 and 20~35% respectively. In the CO-CO_2 mixture equilibrated with stable Fe_3O_4 or "FeO" at 1 000°C, the reaction of carbon deposition does not occur. Nevertheless the fact that a 15~35% swelling was observed in the magnetite and wüstite range, shows that swelling is not directly caused by carbon deposition, as will be explained later.

In order to check the effect of the rate of reduction on the apparent volume change, a pellet was reduced at 1 000°C in the CO-stream with 50, 100, and 200 cc/min for 4 hr, but it was not found to change phenomenally. Therefore, in order to reduce it further, the CO-argon mixture with 200 cc/min, in which 5, 10, and 15%CO was mixed, was applied to reduce a pellet at 1 000°C. The results obtained are shown in Fig. 9. A higher mixture than 15%CO does not affect reduction much differently from 100%CO. However, a lower CO-mixture shows lower volume increase. In order to make sure the effect of the carbon deposition on the swelling, the carbon content of the reduced pellet was determined as shown in Table 3 and Fig. 9. A hydrogen-propane mixture was also used to reduce the pellet for 4 hr at 1 000°C. From these results it can be seen that the carbon deposition is not directly related to the cause of swelling. Also it was clarified that the swelling of the pellets is caused by the lowering of the bulk density, and it is not like volume expansion of the metal caused by lowering its true density.

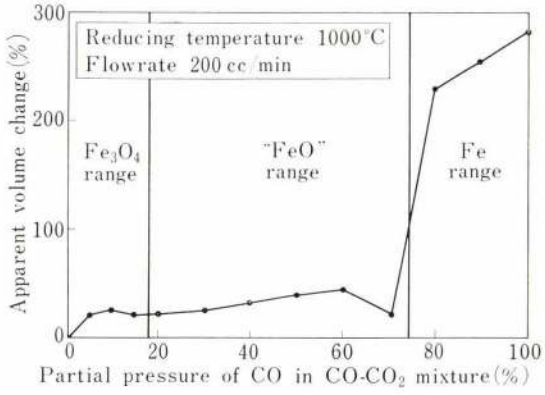


Fig. 8. Effect of the gas composition of CO-CO_2 mixture on the apparent volume change

However, extraordinary swelling did not occur in the Erie pellets. Therefore, in order to ascertain whether it is a characteristic phenomenon of the Marcona pellets, or whether it is related to the origin or occurrence of the iron ore, the cup test was applied to the Marcona pellet and pelletizing feed in 100~200 cc/min CO-stream at 600°~1 200°C for 4~5 hr. The results obtained are shown in Fig. 10 and Photo. 1. Photograph 2 is a microscopic picture of the pelletizing feed before reduction, and Photos. 3~11 are the pictures of a part of the reduced pelletizing feed and pellets taken through microscopy. These pictures show the apparent change of the shape of the initial grains. According to the cup test, the pelletizing feed swells most between 800°~1 000°C, the biggest swelling taking place at 900°C, while it occurs at 1 000°C in pellets. At 1 100°~1 200°C, the tend-

Table 3. Carbon content in reduced pellet

Reducing gas	Temperature (°C)	Carbon content (%)	Apparent volume change (%)
100%CO	1 000	0.09	280
100%CO	600	3.30	30
50%CO 50%CO_2	1 000	0.01	39
50%CO +50%CO_2	600	0.02	4.2

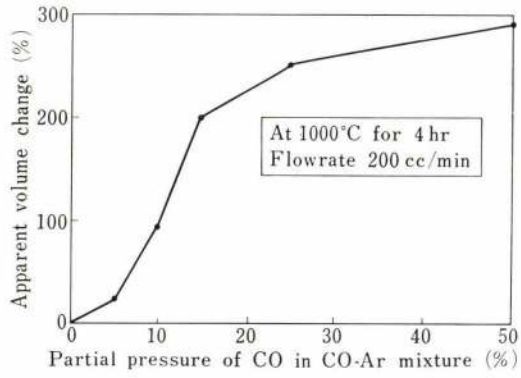


Fig. 9. Effect of rate of reduction on apparent volume change

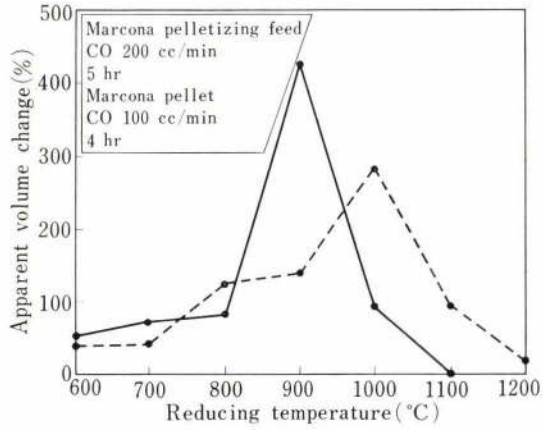


Fig. 10. Effect of reducing temperature on apparent volume change

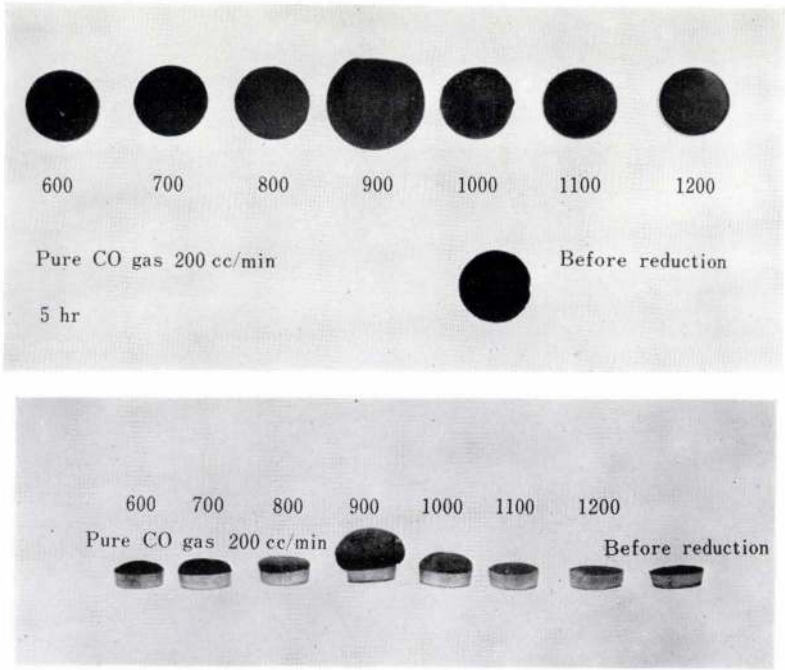


Photo. 1. The cup test for the Marcona pelletizing feed

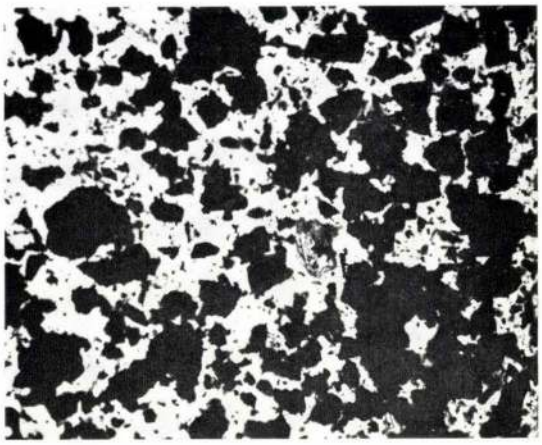


Photo. 2. Marcona pelletizing feed (before reduction) (×100) (2/3)

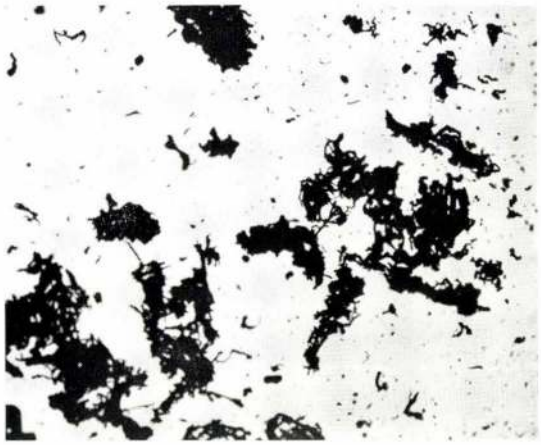


Photo. 4. Marcona pelletizing feed (CO 200 cc/min, 900°C, 5 hr) (×100) (2/3)

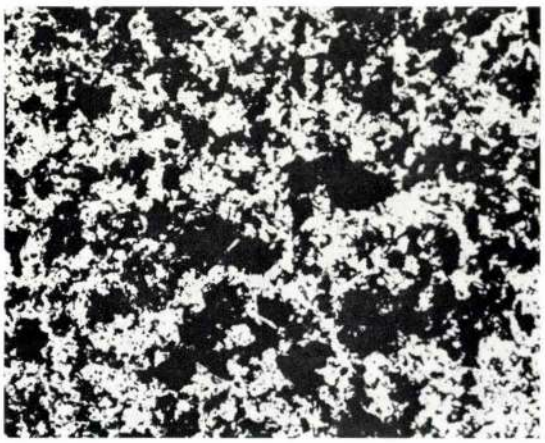


Photo. 3. Marcona pelletizing feed (CO 200 cc/min, 800°C, 5 hr) (×100) (2/3)

Photo. 5. Marcona pelletizing feed (CO 200 cc/min, 1 000°C, 5 hr) (×100) (2/3)

ency was observed for the swollen bulk to shrink because of sintering as shown in Photos. 6, 7, and 11.

The results of the cup test for the Marcona pellet, as shown in Fig. 10, were just the same as the results obtained in the vertical reaction tube.

The reason why the maximum swelling temperature is shifted is considered to be the difference of bonding strength among grains against the swelling force by the deforming of the grains. It might be easier to swell unsintered grains rather than for sintered grains at lower temperature under the same reducing condition.

According to microscopic observation of the reduced

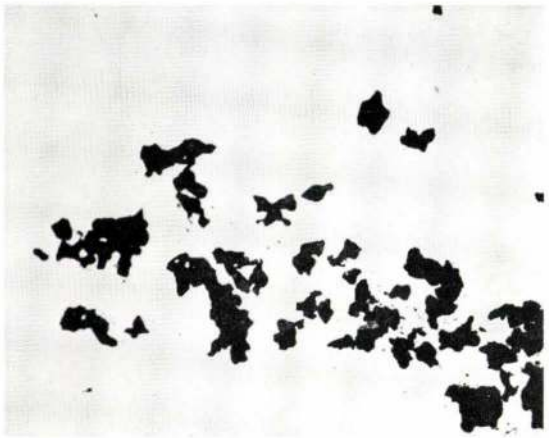


Photo. 6. Marcona pelletizing feed (CO 200 cc/min, 1 100°C, 5 hr) (×100) (2/3)

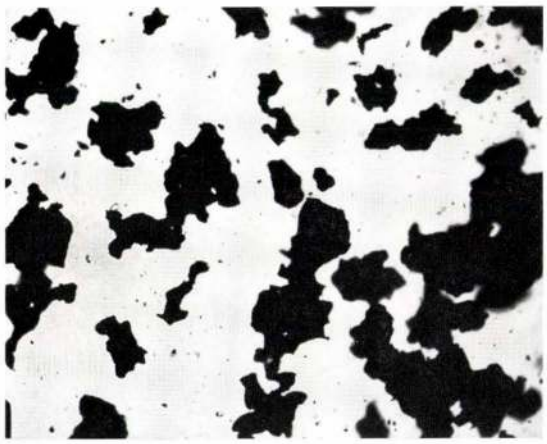


Photo. 7. Marcona pelletizing feed (CO 200 cc/min, 1 200°C, 5 hr) (×100) (2/3)

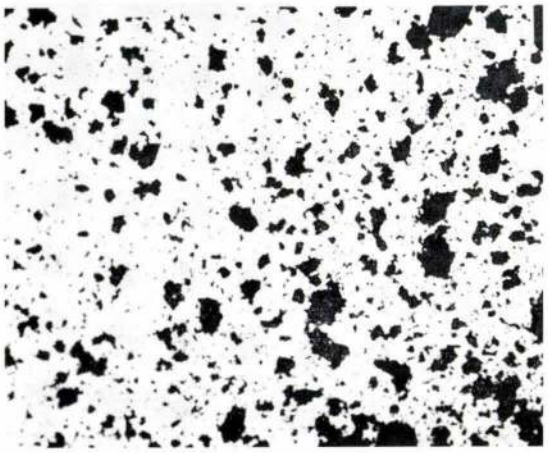


Photo. 8. Marcona pellet (CO 100 cc/min, 800°C, 4 hr) (×100) (2/3)

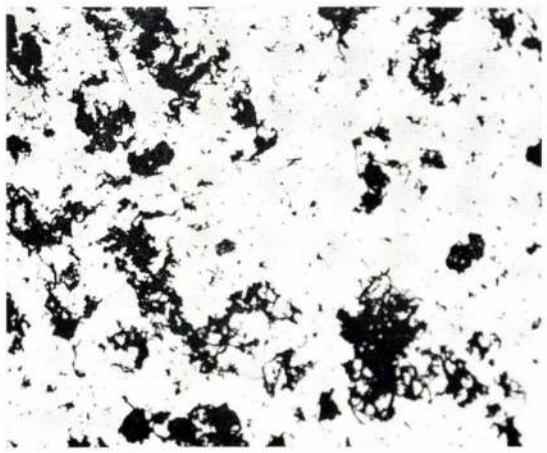


Photo. 9. Marcona pellet (CO 100 cc/min, 900°C, 4 hr) (×100) (2/3)

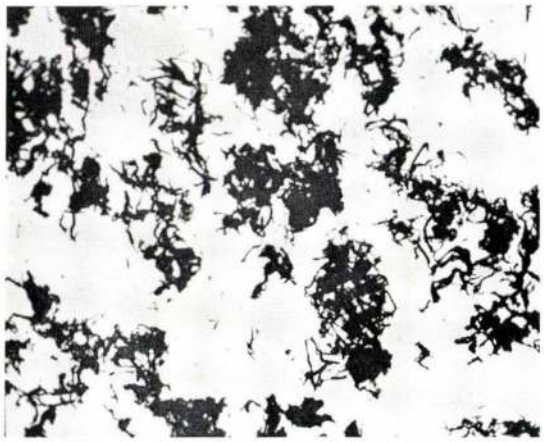


Photo. 10. Marcona pellet (CO 100 cc/min, 1 000°C, 4 hr) (×100) (2/3)

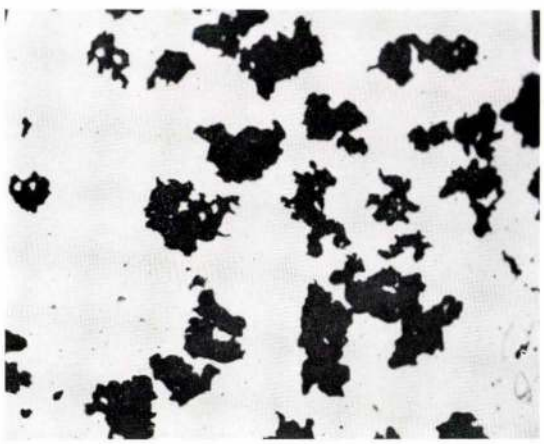


Photo. 11. Marcona pellet (CO 100 cc/min, 1 100°C, 4 hr) (×100) (2/3)

pelletizing feed at 600°C, it seemed to leave the shape of the original grain with little change though it was reduced to metallic iron. In the picture of the reduced pelletizing feed at 700° and 800°C (Photo. 3), a little fibrous metallic iron appears from grains. In the reduced pelletizing feed at 900° and 1 000°C, the initial shape of original grains disappears and deforms to fibrous metallic iron as shown in Photos. 4 and 5, in which fine fibrous iron at 900°C aggregates to thicker fibrous form at 1 000°C. In the reduced pelletizing feed at 1100° and 1 200°C, fibrous iron decreases and sinters together as Photos. 6 and 7 show.

Exactly the same tendency was observed in the pellets reduced at 600°~1 200°C as shown in Photos. 8 (800°C), 9 (900°C), 10 (1 000°C), and 11 (1100°C).

These results show that the magnitude of swelling corresponds to the occurrence and growth of fibrous metallic iron, and that extraordinary swelling of the Marcona pellet and feed as large as 200~400% of the initial state is caused by growth of fibrous metallic iron.

On the other hand, microscopic observation of the reduced pellets remaining in the state of magnetite and of wüstite shows that initial shape of grains does not much change without fibrous shape.

In order to catch the initial state and growth of fibrous metallic iron, 100~150 mesh Marcona pelletizing feed was used for the cup test. The feed was reduced in the CO-stream at 900°C for one hour. Then the sample was taken from the center of different layers as Fig. 11 shows, and Photos. 12, 13, 14, and 15 of layers from bottom to top show the growth of fibrous metallic iron.

Effect of the size of grain on the apparent volume change was studied. Marcona pelletizing feed has the size distribution as shown in Fig. 4, and was classified into fractions of 60 mesh and over, 60~100 mesh, 100~150 mesh, 150~200 mesh, 200~250 mesh, 250~325 mesh, and under 325 mesh. Each fraction was used

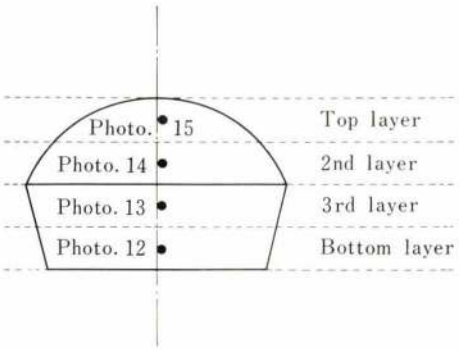


Fig. 11. Location of sample taken in reduced pelletizing feed

Photo. 12. Marcona pelletizing feed taken from bottom layer (CO 200 cc/min, 900°C, 1 hr) (×100) (2/3)

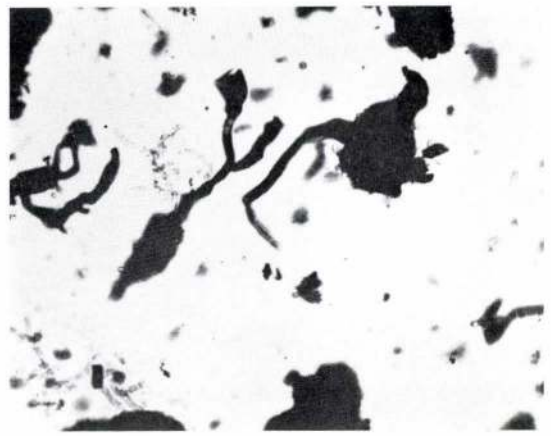


Photo. 13. Marcona pelletizing feed taken from 3rd layer (CO 200 cc/min, 900°C, 1 hr) (×400) (2/3)

Photo. 14. Marcona pelletizing feed taken from 2nd layer (CO 200 cc/min, 900°C, 1 hr) (×400) (2/3)

Photo. 15. Marcona pelletizing feed taken from 1st layer (CO 200 cc/min, 900°C, 1 hr) (×400) (2/3)

for the cup test in the CO-stream of 100 cc/min at 900°C for five hours. The results obtained are shown in Fig. 12. The apparent volume change is different depending upon fractions of size of the pelletizing feed. It is large in the range of 150~325 mesh, and maximum in 200~250 mesh. The fact that a large part of the Marcona pelletizing feed is distributed in these size ranges, which show large apparent volume change, is considered to be a cause of extraordinary swelling of the Marcona pellets. All reduced pelletizing feed becomes completely fibrous metallic iron as shown in Photo. 16 (150~250 mesh) and Photo. 17 (under 325 mesh). Though fibrous iron from the 200~250 mesh feed and the 150~200 mesh feed seems to be a little thicker compared with the others, as a whole, the size of the grains in these ranges before reduction seems to have little relation to the growth of fibrous metallic iron. From time to time big fibrous iron was observed, but in general the fibrous iron is very fine. Most of them are 3~5 μ thick and 40~120 μ long. In cases where the feed was reduced at 1 000°C instead of 900°C the length of fibrous iron was not different, 40~120 μ, but its thickness was about 5~12 μ.

As far as the Marcona pellet or the pelletizing feed is reduced by CO, the reduced sample easily becomes fibrous metallic iron, and shows large bulk volume change. However, as Fig. 7 shows, when these samples are reduced by hydrogen, their apparent volume change is not large. In several papers[4),5)] it was reported that the Marcona pellet during reduction by hydrogen shows little volume change. However, from Fig. 7 the following tendency could be observed: though the apparent volume change observed was a maximum of 20%, maximum change was apt to occur at about 1 000°~1 100°C. According to microscopic observation, most of the reduced pellet in hydrogen stream seems not to change initial shape much, but a slight tendency to produce fibrous iron was observed at 1 000° and at 1 100°C (as shown in Photo. 18).

If the extraordinary swelling occurs in the stage from wüstite to metallic iron during reduction and it is caused by growth of fibrous iron, it could be found in other types of iron oxide. Therefore, as Table 4 shows, the cup test under the conditions of the CO-stream of 100 cc/min at 900°C for five hours was applied to 16 kinds of iron oxide, including hematite, magnetite, limonite, and mill scale and chemical reagent. Lump ore was ground to under 100 mesh. Powder form ore was not treated. The sample was filled up in the cup, where bulk density was as close as possible to 2.5 g/cm^3.

As shown in Table 4, most of the oxides after reduction increase their apparent volume, and reduced samples have fibrous metallic iron, though the degrees of volume change are different with the amount of

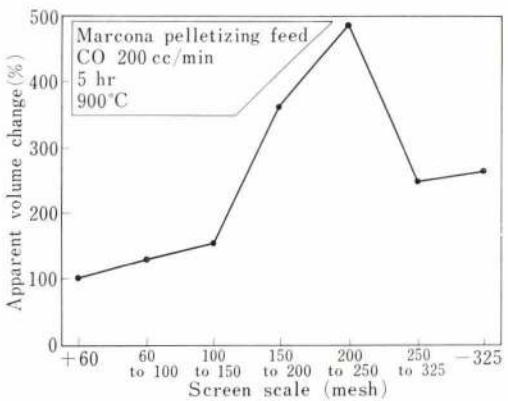


Fig. 12. Effect of size of grain on apparent volume change

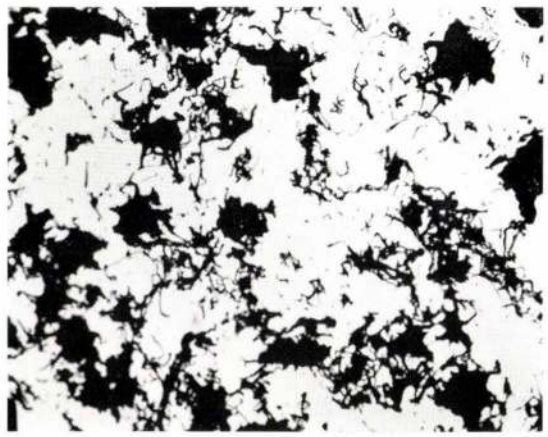


Photo. 16. Marcona pelletizing feed under 150 to 200 mesh (CO 200 cc/min, 900°C, 5 hr) (×100) (2/3)

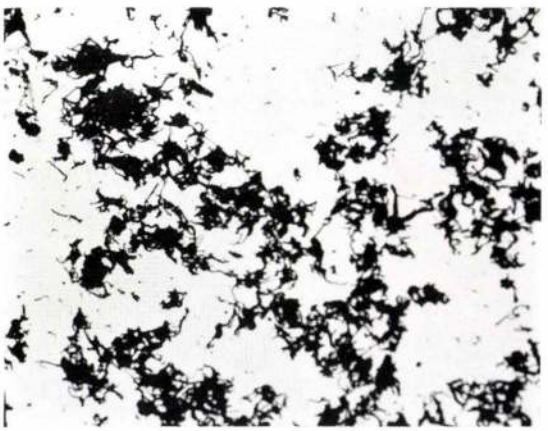


Photo. 17. Marcona pelletizing feed under 325 mesh (CO 200 cc/min, 900°C, 5 hr) (×100) (2/3)

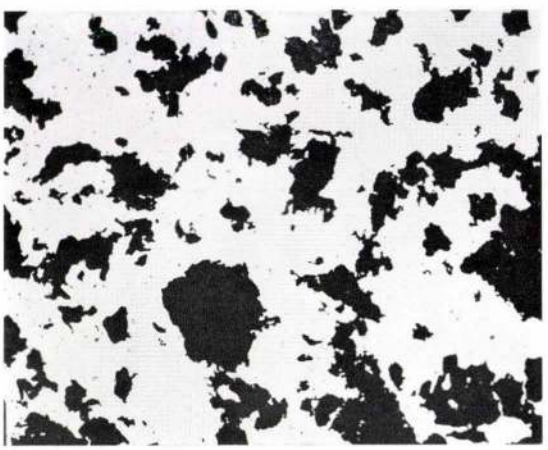


Photo. 18. Marcona pellet (H_2 100 cc/min, 1 100°C, 4 hr) (×100) (2/3)

fibrous iron observed. However, hematites from Utah, U.S.A., and from Zungun, Malaysia, and laterite from the Philippines were exceptions. These three did not show fibrous metallic iron and showed little volume change.

Excluding these three among the 16 samples, it was generally observed that the amount of apparent volume change corresponds to the amount of fibrous metallic iron.

From these results obtained, it will be concluded that extraordinary swelling is not a special phenomenon limited only to Marcona pellet or pelletizing feed ; it is independent of the geological occurrence or mineralogical origin of iron oxide samples, and it is considered to be a general tendency among iron oxides which do not contain certain kinds of impurities (maybe, as the form of solid solution).

In three kinds of iron ore which do not show the general tendency, there is a common characteristic that alumina contents in them are higher than in others. As the Marcona pellet and feed contain about 0.25～0.41% alumina, they were heated up to 1 300°C and held at 1 300°C for two hours. Then the cup test was applied to them at 900°～1 000°C. As expected, they did not swell and did not show any more fibrous metallic iron. The role played by alumina has been checked by the addition of alumina to Kahlbaum-chemical pure Fe_2O_3, which showed large growth of fibrous iron after reduction by CO (Photo. 19). The series of this work is not yet completed, but so far the results obtained confirm the above conclusion.

The addition of silica to pure iron oxide is also helpful to avoid or decrease swelling.

According to the study of metallic iron whisker, it is easier to get iron whisker from halides. Therefore, the whisker of metallic iron is prepared by reduction of iron ore at 400°～900°C in hydrogen stream,[6] after addition of NH_4Cl or $FeCl_3$ to iron ore. Marcona pelletizing feed contains 0.3%NaCl, because sea water has been used for washing at the plant. Therefore, the effect of NaCl content in feed on the growth of fibrous iron was checked. After the NaCl content in feed was lowered to 0.08% by washing, it was applied to the cup test. However, a difference of the amount of fibrous iron after reduction was not observed, as an effect of different content of NaCl.

From the foregoing experimental work, the following conclusions may be drawn with regard to the extraordinary swelling of the Marcona pellet. Carbon deposition is not directly related to abnormal swelling. There is an idea that γ-hematite will participate in swelling. However, γ-hematite is unstable above 550°C, while unusual swelling takes place at temperatures higher than 600°C. Therefore, the γ-hematite theory was discarded. Furthermore, 0.3%NaCl does not affect swelling.

In order to decrease swelling of the pellet, it is helpful to heat and hold the pellet at 1 300°C, or to add Al_2O_3 or SiO_2 to pellet feed and heat it at 1 200°C.

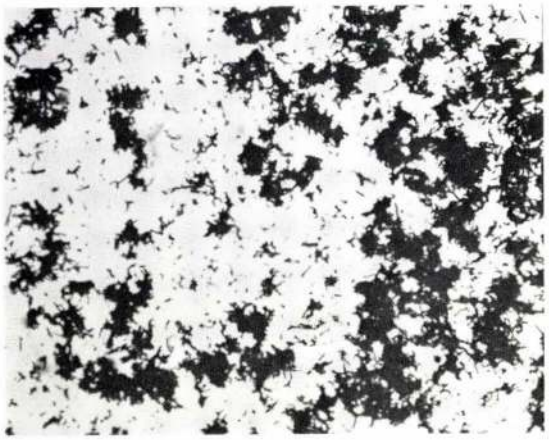


Photo. 19. Kahlbaum-ferric oxide (CO 200 cc/min, 900°C, 5 hr) (×100) (2/3)

Table 4. The cup test for swelling of iron oxides

Iron oxide	Genesis of deposit	Size for test	Apparent volume change (%)	Growth of fibrous metallic iron
Magnetite (Marcona)	Contact metasomatic deposit	Fine grain	430	Very large
Hematite (Goa)	Residual deposit	−100 mesh	176	Large
Magnetite (Vancouver)	Contact metasomatic deposit	−100 mesh	172	Large
Limonite (Kutchan)	Sedimentary iron ore deposit	Fine powder	103	Very large
Hematite (Anzan)	Contact metasomatic deposit	Fine grain	100	Large
Mill scale		−100 mesh	84.8	Medium
Magnetite (Kamaishi)	Contact metasomatic deposit	−100 mesh	79.2	Medium
Magnetite (Hangkong)	Contact metasomatic deposit	−100 mesh	54.0	Medium
Hematite (Johole)	Metasomatic deposit	−100 mesh	24.2	Small
Iron sand (Tanegashima)	Placer iron ore deposit	−100 mesh	26.6	Small
Iron sand (Aomori)	Contact metasomatic deposit	−100 mesh	21.9	Small
Hematite (Utah)	Contact metasomatic deposit	−100 mesh	17.6	None
Hematite (Dungun)	Residual deposit	−100 mesh	12.9	None
Laterite		Fine grain	3.1	None
Fe_2O_3 (Schering-Kahlbaum)		Fine powder	88.5	Very large
Fe_2O_3 (Junsei)		Fine powder	40.1	Very large

Not only the Marcona pellet but also iron oxide which contains little impurities show unusual swelling and growth of fibrous metallic iron.

V. Discussion

From Photos. 12~15, the process of formation and growth of fibrous metallic iron could be supposed. As Photo. 12 shows, several rises are observed on the surface of iron ore. And these projections grow while reduction proceeds. Then the original form of the grain disappears with the growth of fibrous iron. These processes could be interpreted on the same basis as C.Wagner[7),8)] analyzed the mechanism of the reduction of sulphide to metal.

Wüstite " FeO " is an NaCl-type crystal structure, but in the wüstite range, the Fe/O ratio is always somewhat less than the ideal stoichiometric ratio because of the presence of cation vacancy and cations in a higher valence state, *i.e.* ferric ion. Therefore, the ratio of ferrous ion to ferric ion and the concentration of O^{2-} are determined by the oxygen potential of the atmosphere around the wüstite. In the process of oxidation and reduction of iron, it is considered that the mobility of ferrous ion is larger compared with the mobility of oxygen ion, and ferrous ion plays a major role in the above reactions. According to Richardson and co-workers,[9),10)] the mobility of ferrous ion is affected by temperature and estimated to be about a hundred times larger at above 900°C than at 600°C.

In order to interpret the growth of fibrous metallic iron, the mechanism discussed by C. Wagner in conjunction with the formation of a fine filament of silver during reduction of silver sulphide with hydrogen will be applied.

Figure 13 is the model for the reduction process of wüstite by carbon monoxide. In the first stage of the reduction process at every point on the surface of wüstite, carbon monoxide reacts with oxygen so that excess ferrous ions and electrons are formed and the surface will become supersaturated with respect to ferrous ions and electrons. Though the ferrous ions and electrons migrate in order to form metallic iron, it is necessary for them to be captured by a nucleus at nucleation site on the surface. Ferrous ion and electron in the vicinity of metal nuclei diffuse toward the original nuclei, which are pushed outward by them. Thus fibrous metallic iron grows. The formation of a number of nuclei on the surface will be determined by the nature of the surface, temperature, and the rate of reduction. However, if once nuclei form, supersaturation near the nuclei will be too small to form other nuclei. Therefore, the amount of fibrous iron depends upon the size of grain, the number of nuclei in a grain, the rate of chemical reaction at the surface on the grain, the diffusion coefficient of ion, and the distance from nuclei whose ion should migrate.

According to the results of the reduced pellet in hydrogen stream, as mentioned above, no large growth of fibrous iron was observed. However, from the experimental works by Richardson and co-workers,[9),10)] it is possible in principle to reduce iron oxide to fibrous iron with hydrogen, though the reducing conditions are very limited. The results of reduction of 0.01 mm wüstite film on iron plate with hydrogen by Richardson and his co-workers, were that a very thin film of iron formed on the surface, but its growth soon ceased ; then the reduction proceeded outwards from the interface between the iron plate and wüstite. That is, the thickness of the inner iron core increased, instead of metallic iron forming from the surface inward at the outer surface at 900°C, while spongy metallic iron formed at the outer surface of the wüstite at 700°C. At 900°C ferrous ion and electron diffuse in the layer of wüstite, and metallic iron grows at nuclei on the iron plate just as in the reduction of iron oxide by CO.

Heating the pellet or pelletizing feed or pure iron oxide with the addition of alumina or silica, above 1 200°C, decreases the abnormal swelling of specimen. The observed phenomena will be interpreted that bentonite of a sort, or impurities of iron ore, alumina and silica added diffuse into the surface of iron oxide and disturb the form of nucleus available for nucleation of ferrous ion on the surface of iron oxide.

VI. Conclusion

The extraordinary swelling of the Marcona pellet which became a serious problem for blast furnace operation, is not the special characteristic of Marcona iron ore or of a pellet made from it. Pure iron oxide has a tendency to grow fibrous metallic iron in process of reduction from wüstite to metallic iron.

In order to avoid the unusually large swelling of the pellet during reduction, it is helpful to reheat the pellet above 1 200°C if pelletizing feed contains alumina and silica.

Acknowledgements

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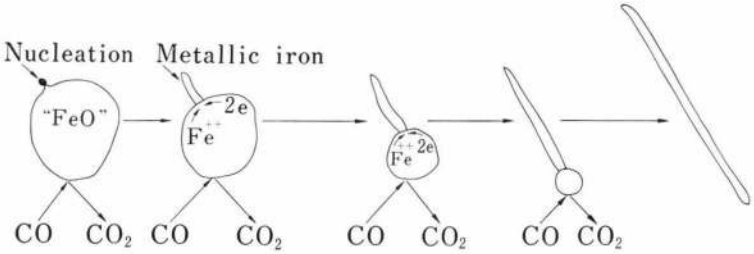

Fig. 13. Model for growth of fibrous iron

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