Fundamental Study of Size Degradation Mechanism

of Agglomerates during Reduction*

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Synopsis
The mechanism of degradation of agglomerates during reduction is
studied with pellets made from powdery ingredients of chemical reagent
grade, and the changes in mineral phases due to certain oxides leading to
degradation, are examined quantitatively.
The results obtained are summarized as follows:
(1) Microscopic observations suggest that cracking occurs in the skeletal hematite and the calcium ferrite phases. Analysis by line-broadening measurements of X-ray diffraction reveals no strain both in the bulky and in the skeletal hematites regardless of the amount of alumina held in solid solution. Micropores are generated in magnetite as it is reduced from hematite to give rise to a stress when reduced at a low temperature, and stress concentration occurs around inclusions of small radius of curvature to cause cracking of skeletal hematite grains.
(2) The quaternary calcium ferrite is expected to be reduced to metallic iron in the blast furnace through dicalcium ferrite or wustite. Nonferrous oxides form gehlenite and j3-dicalcium silicate. Calcium ferrite is not only fragile but its amount to increase with the basicity under existence of A12O3.

(3) The amount of skeletal hematite depends mainly on the degree of supersaturation of iron ions in slag and on the dissociation temperature of hematite. The addition of TiO2 in sinters enhanced greatly the crystal growth of skeletal hematite in the case of induration at above THM, whereas bulky hematite at below THM.

I. Introduction

Disintegration of sinter, occurring on low tempera-
ture reduction, causes an increase in the permeability resistance at the shaft of the blast furnace and in the nonuniformity of gas flow, and exerts an unfavor-
able influence upon stable operation. Many studies
have been done on this phenomena clarifying that skeletal rhombohedral hematite, growing secondarily during the sintering process, is the cause of the cracking.1'2~ On the other hand, it is known that high basicity pellets degrade hardly upon low tem-

perature reduction.3~ Recently, several attempts4,5) have been made to control disintegration of sinters by decreasing the amounts of flux materials to ensure both the high reducibility and good high tempera-
ture properties. For this purpose, it is important to
clarify the mechanism of disintegration to produce high quality agglomerates.
The present report describes with synthesized min-
erals the behavior and the mechanism of disintegra-
tion by microscopic observations and by evaluating
lattice constants and the broadening of diffraction
lines of the crystals.
Also, it will report, for the first time, the amount
of skeletal hematite present at the induration step.

II. Experimental Procedure

1. Disintegration of Pellets

Ingredients of chemical reagent grade were mixed with ratios shown in Table 1 and granulated into balls of 13 mm in diameter. After being dried and pre-heated, two morphologically different hematites were

produced by two different induration procedures shown in Fig. 1. The resulting pellets were reduced at 550 °C for 60 min with a mixture gas (CO: 40 %, C02: 60 %). The polished samples of induration and reduction were microscopically observed.

2. Measurements of Lattice Constants

Various nonferrous oxides are contained in sinters, and skeletal rhombohedral hematite is considered as

the ` multi-component hematite ' transformed from multi-component magnetite. Consequently, there ex-ists the possibility that the resulting A1203, Ti02, or MnO, precipitated in hematites during cooling after sintering would cause the cracking.s) Thereupon, the change of lattice constants of hematite with A1203 held in solid solution was measured.

Oxides of chemical reagent grade were mixed so that the weight percentage of Fe203 was 77.5, Si02 4.5, Ca0 6.0, Mg0 2.0 and A1203 10.0. Each 0.5 g of the resulting powders was packed in a platinum envelope, heated in air following the induration pro-cedures mentioned below, and quenched in water.

Table 1. Composition of synthetic pellets. (wt%)

Fig. 1. Induration patterns for the pellets.

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Originally published in Tetsu-to-Hagane, 68 (1982), 1513, in Japanese. English version received August 26, Central Research Laboratory, Kobe Steel, Ltd., Wakinohama-cho, Chuo-ku, Kobe 651.

1981. © 1982 ISIJ

(838) Research Article

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To achieve equilibrium, they were held for 60 min at 1 250 or 1 300 °C. For cooling, they were held for 60 min at 1 400 °C and cooled at 5 °C/min on the average to be quenched from 1 250 and 800 °C, re-spectively.
Lattice constants of the resulting powdery speci-mens were calculated using the extrapolation method of Nelson and Riley.7)
In the meantime, the behavior of solid solution A1203 in hematite during heating and reduction in a blast furnace was studied as follows. An oxide (chem-ical reagent grade) mixture of 90 wt% Fe203 and 10 wt% A1203 was heated in air for 6.5 hr at 1 300 °C and quenched. The resulting hematite wtih A1203 in solid solution was heated for 2 hr in air either at

500 or at 600 °C and quenched. The powdery hema-tites thus obtained were used for measurements of

lattice constants by X-ray diffractmetry. Also, the lattice constants of powdery magnetite were measured as reduced at 600, 700, 800 and 900 °C for 2.5 hr from the solid solution, and quenched from the same temperature with the reduction.

3. Measurement of the Strain of Crystals
Strains were evaluated from line-broadening mea-surements of X-ray diffraction lines for crystals of hematite, which were different in existence of alumina in solid solution and were observed to be morphologi-cally different due to the different crystal growth. Diffraction was done with monochromic CuK~ to

eliminate errors occurring in doublet separation of Ka. All the diffraction experiments were done with a tube loading of 45 kV and 160 mA, and by the fixed time method of step scanning with a step width of 2/100 deg using a set of slits, where D.S, was 1 /2 deg, R.S. 0.15 mm and 5.5. 1 /2 deg.
To suppress generation of calcium ferrite, ingredi-ents of chemical reagent grade were mixed and com-pressed by a hydrostatic force of 5 000 kg/cm2 to disks of 25 mm~b in diameter, whose basicity was 0.7 as shown in Table 2. The resulting bodies were in-durated in two heat patterns as follows :
Skeletal hematites of proper size were made by heating at 1 350 °C for 10 min in N2 atmosphere to make iron oxides as magnetite, and by introducing air to oxidize and cool the disk at a rate of 10 °C/min

to 1 250 °C, which was maintained for 5 min. Bulky hematites were made with the Pattern I in Fig. 1. The resulting natural surfaces of the fired bodies were used for X-ray diffraction.
Furthermore, the strain of magnetites reduced from hematites was evaluated quantitatively. For that purpose, commercial pellet was ground to powder,

from which magnetite was eliminated by magnetic separation, then the residual was immersed in HCl (1 + 1) at 60 °C for 1 hr to dissolve away calcium fer-rite, silicate slag and slag minerals.8~ The hematite thus obtained was reduced by a mixture gas to mag-netite; the gases used were CO/C02=40/60 at 550

°C, CO/C02=30170 at 700 °C, CO/C02=20/80 at
800 °C and CO/C02=20/80 at 900 °C.

4. Reduction of Calcium Ferrite

Quaternary calcium ferrite having A1203 and Si02 in solid solution were synthesized as shown in Fig. 2 to be reduced for 3 hr between 500 °C and 1 000 °C by appropriate gas to obtain the pseudo-equilibria.

5. Amounts of Minerals of Quaternary Systems Amounts of minerals at equilibrium of relevant temperatures were obtained for specimens made of ingredients of chemical reagent grade, where the weight percentage of T.Fe was 61.0, that of non-ferrous oxide (MgO, A1203, Ti02) 1.0 and the sum of CaO and Si02 11.79; at the same time, the basicity was changed from 0.6 to 1.8. Each specimen was packed in a platinum envelope and fired in air for 1 hr at 1 250 or 1 350 °C in a siliconit furnace, then quenched in water. Minerals were evaluated by point analysis with • EPMA, and the amounts of min-erals were calculated by taking material balance be-tween the weight ratios of the sample and the values determined in the point analysis.9~

III. Results

1. Disintegration and Mineral Phases
Photographs 1 and 2 show microstructures of the two kinds of pellets indurated by the two patterns of Fig. 1 and reduced. Difference in the induration pattern led to different characteristic morphologies of hematite : bulky on the Pattern I and skeletal rhom-bohedral on II. Hematite of pellet B contained 1,32 wt% of A12O3 when I, but 1.50 wt% when II, a slight-ly higher content as detected by EPMA, though this had no great significance to the experiment.

Table 2. Composition of synthetic pellets.

Fig. 2, Experimental procedure for

of calcium ferrite.

pseudo-equilibriation

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No disintegration occurred in pellet A for indura-tion Pattern I, whereas cracks were observed around the skeletal hematite phases for Pattern II. Cracks were seen to have developed around silicate slag in-clusions in hematite crystals and penetrated through the silicate slag extending to several hematite crystals. Directions of the cracks were various, and micropores were observed in magnetite reduced from hematite. Cracks parallel to the circumference of the pellet were observed in calcium ferrite in pellet B, Pattern I.

Such cracks were restricted to the parts in the radial direction where surrounding hematite grains were re-duced and were arrested at the part consisting of mag-netite grains. Many cracks also occurred in skeletal hematite and calcium ferrite phases in Pattern II.

2. Behavior of A1203 in Solid Solution of Hematite

Figure 3 shows the lattice constants of hematite under equilibrium and for two different cooling con-ditions. The lattice constant at equilibrium decreases

Photo. 1.
Photomicrographs of
cracking in the speci-
men A.

Photo. 2.
Photomicrographs of
cracking in the speci-
men B.

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with increasing temperature, indicating the solution of A1203. The amount of A1203 held in solid solu-tion was estimated to be 4.4 wt% at 1 300 °C on the

basis of lattice constant reported by Atlas and Sumi-da.10~ Also, the amounts of A1203 soluble in hematite as quenched from 1 250 and 800 °C for the cooling shown in Fig. 3 were estimated to be 4.7 wt%. This may be taken as clarifying that no precipitation of A1203 had occurred during cooling. From this, fur-ther, it may be said that no alumina precipitation will occur in the commercial sintering process, because it is far closer to quenching than the present experi-mental conditions.

However, it may be that the alumina held in solid solution in the hematite can yet precipitate during heating and reduction in blast furnace. Lattice con-stants of hematite and magnetite for various heating and reduction processes are shown in Fig. 4. Virtual-ly no change is seen in the hematite lattice constant nor in the magnetite lattice constant, and the lattice constant of magnetite reduced at 600 °C corresponds to 10.6 wt% alumina solution from the report by Atlas and Sumida.10> Consequently, the alumina held in solid solution in hematite of commercial sin-

ters and pellets may be considered to stay in solution during the heating and reduction process; commercial products have far less alumina solid solution in the hematite than these specimens of the present study.

3. Lattice Distortion on Induration and Reduction

1. Lattice Distortion of the Hematite Crystals
There may exist differences in lattice distortion be-tween the two kinds of hematite, one of which is the skeletal crystal growing rapidly at a high temperature and the other is the bulky crystal growing slowly. An attempt was made by X-ray diffraction to evaluate the lattice distortion of the hematite crystals having different morphologies and solid solution aluminas. In general, line-broadening of a diffraction peak is caused by diminution of crystal size and by lattice distortion, and is related by Hall's equation.11 The strain can be calculated from the slope of the line and

the size of crystallites by tak
cepts at the vertical axis.
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j3: half peak breadth due solely to the crys-tallites (rad)
l : characteristic wave-length of X-ray (cm) 0: diffraction angle (deg)
r : effective size of crystallite (cm)
7 : stress (dynf cm2)
Eh : Young's modulus in the h direction (dyn/ cm2).
des the line-broadening due to crystallites effect
ned above, there are other influencial factors
the apparatus itself. Estimation of the half-
readth bdue to apparatus was done as shown
5 using Si of 99.9 % purity and 250 to 200 expected to have little strain and little size of
were obtained by separating b from Values
ed half-peak breadth values B using Jone's cor-curve12~ which shows the relation between ~f B

. Figure 6 shows the experimental results for
to crystallites different in morphology and in olution alumina. The contents of alumina in

to crystals grown through the two processes 1 about 2 wt% as determined by EPMA. The ning for each lattice plane is small regardless specimens, and no relation to Eq. (1) is ob-between the values of (012) and (024) planes. his, it may be concluded that no lattice distor-

Fig. 3. Behavior of solute alumina
cooling.

in hematite through

Fig. 4. Behavior of solute alumina in hematite during heat-ing and reduction.

Fig. 5. Half peak breadths of the powdered si licon.

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tion is present in any of those hematite crystals.
2. Stress of Reduced Magnetite
It has been clarified by Terui et al.13~ that low tem-perature degradation of sinters occurs when hematite is reduced to magnetite, especially in a low tempera-ture range from 500 to 550 °C. In this work a quan-titative relationship is obtained between the reduction temperature and the strain occurring when hematite in a commercial pellet is reduced to magnetite.
The relations in Fig. 7 were drawn using Hall's equation (1). Although the lines were drawn be-tween the data points of the (220) and the (440) planes, points of the other lattice planes fell nicely on these lines. Therefore, the magnitude of strain may be said to be almost of the same order for the other

planes. The sizes of magnetite were from 1 200 to 3 200 A, the sizes which are larger than the lower limiting crystallite size for the use of Eq. (1).
The effect of reduction temperature on the strain of magnetite is shown in Fig. 8. The value of the strain of reduction at 550 °C is about 0. 10, and it decreases with increasing temperature.
By direct observation of the process from hematite to magnetite on natural and artificial single crystals or sintered polycrystals using high voltage electron microscopy, Swann and co-workers14~ have revealed that the reduction mechanism differs by the tempera-ture. Their report shows that columnar narrow tun-nels are generated in magnetite resulting in expansion when reduced at from 400 to 650 °C, whereas above 800 °C the basal plane of hematite is transformed to the (111) plane of magnetite.
Observation by SEM was done on the magnetites reduced from the hematite of commercial pellet. Micropores were seen to have been generated in the magnetite on low temperature reduction as shown in Photo. 3(B) and have developed with reduction as shown in Photo. 3(C). Here, it may be noticed that micropores are aimed in one direction. However, they are not generated upon high temperature reduc-tion as shown in Photo. 3(D). The point analysis of the hematite by EPMA indicated the existence of A12O3 in solid solution to 0.35 wt%, TiO2 to 0.23, and CaO to 0.27; they will affect the volumetric dif-fusion of Fee. However, judging from the values of

strain and the SEM images, the present authors con-clude the reduction mechanism of Swann applies well in this range of impurity content,

4. Reduction of Quaternary Calcium Ferrite
Calcium ferrite in agglomerate has been proposed to be the solid solution of CaO . SiO2 and CaO 3 (AI,Fe)2O3.9> Because of solution of A12O3 and SiO2, further, reduction equilibria of the quaternary cal-cium ferrite is expected to be different from that of the ternary system15~ of Fe, Fe2O3 and CaO.
Figure 9 shows the pseudoequilibria of the qua-ternary calcium ferrite reduced for 3 hr in a gas with a wide range of CO/CO2 mixing ratios and at tem-peratures from 500 to 1 000 °C. It indicates that the quaternary calcium ferrite is reduced to iron through dicalcium ferrite or wustite in the range of gas com-positions and temperatures of blast furnace, and that nonferrous oxides are formed into dicalcium silicate

and gehlenite. The reaction rate is very slow under 650 °C with no appreciable change.
Consequently, it may be concluded that the cracks in the calcium ferrite phases in Photo. 2(I) were not caused by the phase change itself but by the stresses

Fig. 6. Analysis of line-broad
ous hematites.

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Fig. 7. Analysis
netites.

of line-broadening measurements of mag-

Fig. 8. Effect of
magnetite.

reduction temperature on the strain of

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occurring in the surrounding hematite crystals as they were reduced to magnetite.

Iv. Discussin

1. Stress Concentration in the Skeletal Hematite

The results mentioned above indicate that the main cause of cracking of the skeletal hematite lies not in the lattice distortion on induration or on precipita-tion of A12O3 but in the morphology. Inazumi16~ pointed out this fact and postulated further that the cracking would be caused by morphology of inter-growth of the skeletal hematite in a parallel direction and by the difference in expansion due to difference in the reaction rate between the hematite and the inclusion, which might be magnetite, calcium ferrite, or silicate slag.
In this paper the present authors have considered
the cracking of the skeletal hematite from a viewpoint of mechanics. Consider an infinite plate containing a circular inclusion that is under a tensile stress of o

as shown in Fig. 10(A). The periphery of the inclu-sion is cohesive with the circular hole edge of the plate.17) Stresses arising within the plate (6,) and the inclusion (6I) will differ with the ratio of Young's modulus of shear modulus, and of Poisson's ratio of the plate and the inclusion, E, G, v, and E', G', v', respectively. For convenience we will assume that v and v' are both 0.25. Then, of the Lame's constants,
A becomes equal to p, and A' to p'.
The stress distribution depends on the ratio of G/G',
which is shown in Fig. 10(B) as 1/2. The maximum
stress of Qp lies at the point A whose value is 1.5 o.
It is -0.25 Qo at the point B, where the reversal of

Photo. 3. Change in the magnetite morphology by the change in the reduction temperature as observed by SEM.

Fig. 9. Pseudo-equilibrium diagram of the quaternary cal-cium ferrite during reduction.

Fig. 10. Stresses occurring under a tensile force in
containing a round inclusion.

a plate

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sign is to be noticed. The stress reaches a maximum value for the distribution on the y axis and decreases when departing from the point A to approach a'o. The a I, on the other hand, is zero at the point B and is 0.75 oo at point A, indicating release of the stress at A.
The relation between stress concentration a(= roA/ ao) and the ratio of the shear modulus is shown in Fig. 10(C). It indicates that QI is small when the inclusion is soft, namely, a small G'/G, while o is large. The ratio of the shear modulus was calculated from the room temperature values18~ of quartz glass and magnetite and found 0.37, i.e., 1.7 in terms of the stress concentration factor a.
Now, of the three candidate inclusions of Inazumi's, magnetite may be excluded because it is no inclusion at all for the case at hand, but magnetite inclusions often coexist with silicate slag, and in this case modulus of elasticity is supposed to be intermediate of the two. Calcium ferrite is also regarded probable because its modulus of elasticity is supposed to be smaller than that of magnetite. Therefore, the cracking of the skeletal hematites may be visualized as occurring under the stress that concentrates at the boundary between the magnetite and the inclusion. Forms and orientations of the actual inclusions may be various, and stress concentration increases as the radius of curvature at the head of the inclusion becomes smaller.

This will induce the cracking to develop in various directions in the skeletal hematite phase.

2. Stress Distribution in a Pellet
Stress is generated in a pellet due to the expansion
on reduction of hematite to magnetite. The stress distribution was analyzed quantitatively based on the following model. The pellet is postulated to be a bo radius sphere, whose inner core of b radius is un-reduced, while whose outer shell is reduced to mag-netite. The basic equation should be that of thermal stress, because whatever the causes of expansion may be, the mechanical state may be described by thermal expansion. We next assume that as reduction pro-ceeds the entire shell is heated to a same temperature, while the central core stays at the temperature of ini-tiation since the pellet is reduced topochemically. A solution for thermal stresses in a sphere under a tem-perature gradient in the radial direction in the spheri-cal coordinates is obtained analytically.19> For this
case equations are obtained as follows using a bound-
ary condition that arr=0 at xr=1.

x = kG3 1 -1 ....(2) when C<xr arr(G, x)

x3

aoe(C, xr) - Q = -kC3 1 2x3 --1 ...(3)
r when C > xr irr(C) - goo = a~~ = k(1- C3) ...(4)
k = 2a•E•t/3(1-v) ....(5)

where, C: bi/bo (-)
xr : r/bo (-)
bo : radius of the pellet (cm)
b2: radius of the unreduced core (cm)

a : coefficient of linear expansion (1 /°K)
E: Young's modulus (dynf cm2)
t: temperature difference between the shell
and the core (°K)
v : Poisson's ratio (-).
Equation (4) indicates that the stress in the un-reduced core are those of hydrostatic pressure, be-cause stresses are the same everywhere and in every direction of r, 8 and w. Calculations were carried out on the stress distribution for values of C of 0.8 and

0.5, whose results are shown in Fig. 11.
The r-direction stress is tensile within the already reduced zone, increasing inwardly through the zone and also as reduction proceeds. Therefore, the un-reduced core is under a tensile stress.
On the other hand, the stress in the ti-direction is compressive, which increases inwardly through the zone but decreases with the progress of reduction. The shearing stress, therefore, is maximum at the boundary between the reduced zone and the unre-duced core, becoming zero inside the latter due to the stress of hydrostatic pressure. Consequently, if a pel-let can be assumed to be homogeneously isotropic, cracking should not occur in the core, however large the compressive stress may become with the advance of reduction, but should be considered to be generated by the tensile stress or by the shearing stress acting on the boundary.
Calculations were carried out by substituting the physical constants for the case of Photo. 2(I). The expansion a • t was estimated by the value of strain obtained by the line-broadening measurement, the volumetric percentage of hematite present, and the porosity. The value of Err turned out to be only 7 kgf/mm2 and a06--2 x 103 kgf/mm2 when values of Young's modulus and the shearing modulus of the [111] direction were used. It may be concluded that the calcium ferrite is fragile to be cracked in the parallel direction to the pellet's periphery by arr. If skeletal hematite exists under the stress like this, the tensile stress at the point A in Fig. 9(B) is a sum of a • o rr and - j9 • a'oo when stress concentration factor j9 is defined as a00/co. It may be concluded, therefore, that large contribution of the term -l3a aBe to the tensile stress induces cracking of skeletal hematite.

Fig. 11. Stress distribution in a sphere.

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3. Growth of the Skeletal Hematite and Influence of J'fon-ferrous Oxides

As mentioned above, the disintegration is depen-dent on the amount of skeletal hematite, that of bulky hematite, porosity, and the existence of the calcium ferrite. Thereupon the effect of nonferrous oxides on the amounts of those minerals were examined.
It has been said that the skeletal hematite in a

fluxed sinter grows rapidly with the transformation of magnetite during the cooling process, coexisting with melts at the transformation temperature TJHM between a hematite and magnetite. Inazumi has pointed out that the addition of Mg0 is effective in decreasing the degradation since it lowers THM,16)
In a sinter pellet, the hematite in question pre-cipitates in a morphology of dendritic, skeletal, or bulky crystals. The relative abundance of these crys-tals depends on a balance between the two-dimen-sional nucleation rate, the number of the screw dis-locations and the degree of supersaturation.20) Con-sequently, it is possible for the skeletal hematite to grow without transformation from magnetite.
This point was examined with specimens made of powders of chemical reagent grade: specimens com-posed of 78.6 wt% Fe203, 12.1 % CaO, and 9.3 % Si02 and weighing 0.5 g each were packed individual-ly in a platinum envelope and heated in air in an electric furnace at 1 360 °C for 10 min, then cooled at a rate of 20 °C/min. On the way of cooling, they were quenched in water from temperatures designated in Photo. 4. As shown in Photo. 4(A) only hematite and silicate slag existed at 1 360 °C. Photograph 4(B) shows that polycrystalline hematites containing slag inclusions grew by connecting each other. This may be attributed to a low degree of supersaturation attained in the inner part because of the slow cooling rate and of the existence of many crystals. Photo-graph 4(C) shows a crystal growing under a high cool-ing rate existing near the platinum foil and completely surrounded by slag. Here, it may be seen that, first,

the main trunks were developed growing dendritical-ly and three-dimensionally, filling the interdendritic spaces. Then the beginning of the layer growth led to the formation of skeletal crystals as shown in Photo. 4(D). Although it is possible for the skeletal crystals to grow by this process, microscopic observations revealed qualitatively that it was easier for the crystals to grow by transformation of magnetite for a wide quantity range of slag and the cooling rate.
As mentioned earlier, formation of skeletal hema-tite is complicated by the amount of slag present, viscosity of slag, the amount of magnetite coexisting with slag, and the cooling rate. Further, nonferrous oxides may exert some effect on the amount of skeletal hematite. This was examined with specimens of quaternary system synthesized out of powders of chemical reagent grade and brought to equilibrium by heating at 1 250 or 1 350 °C, with a view that the difference in iron content between the two might serve as a driving force for crystal growth.
A result of ternary system of Fe203, Ca0 and Si02 is obtained as a standard state shown in Fig. 12. It is seen that there exists little difference in iron con-

tent at a low basicity, whereas it increases above a basicity of 1.4. The effect of Mg0 is shown in Fig.
13. It is seen that the amount of slag does not in-crease even for a high basicity and at 1 350 °C; only an increase of magnetite transformed from hematite is revealed. Since addition of Mg0 leads to decrease of the total amount of hematite and to growth of the skeletal hematite, it is effective for suppressing the degradation. The effect of A1203 is shown in Fig.
14. The growth of the skeletal hematite is suppressed since the calcium ferrite precipitates from hematite and from the melt in the presence of A1203 at a high basicity. Some of the hematite is consumed in the generation of the calcium ferrite during cooling at a basicity of 1.8, whereas near 1.4 hematite growth is easier. Figure 15 indicates that the effect of Ti02 is similar to the standard result. The large difference

Photo. 4.
Growth of skeletal hematites from
the system of hematites and silicate
slag.

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in the iron content between the two slags at a high value basicity and the stability of hematite due to the high of THM lead to fast growth of hematite crystals into the skeletal morphology during cooling in the case of induration at above THM to form a large

amount of magnetite by transformation. On the con-trary, in the case of induration at below THM, the growth of hematite is restricted, and the degradation will be suppressed. In the meantime, the increase of the amount of bulky hematite improves the reduc-ibility of sinters. Suppression of degradation and im-provement of reducibility by thus be achieved by decreasing A12O3 and adding TiO2.

V. Conclusions

The mechanism of the disintegration with speci-mens prepared from powdery ingredients of chemical reagent grade was clarified by X-ray analysis of lat-tice distortion of hematites different in morphology and in the amount of A12O3 held in solid solution, and by X-ray analysis of the state of solution of A12O3.
(1) No lattice strain was detected in crystals either
in the skeletal or the bulky morphology. The A12O3 held in solid solution did not induce lattice distortion

in either case. No precipitation of A12O3 occurred during the process of cooling and reduction to mag-netite, the A12O3 being held in solid solution in hema-tite at high temperatures of actual sintering process. Moreover, the skeletal hematite having no A12O3 in solid solution also degraded. These facts and theo-retical stress analysis lead to a conclusion that the main cause of the cracking of the skeletal hematite lies in this particular morphology, such that the stress arising on reduction is concentrated at the boundary between magnetite and inclusion where the radius of curvature is small to crack the inclusion.

(2) The quaternary calcium ferrite, which is re-duced to iron through dicalcium ferrite or wustite in blast furnace, was found not only to be very fragile but its amount to increase with the basicity under existence of A12O3. Nonferrous oxides are formed

into dicalcium silicate and gehlenite.
(3) The amount of the skeletal hematite was seen to depend mainly on the supersaturation of iron in slag and on the THM, the transformation temperature of hematite. Further, the addition of TiO2 in sinters enhanced greatly the crystal growth of skeletal hema-tite in the case of induration at above THM, whereas it enhances the growth of bulky hematite at below THM.

Fig. 12. Phase relations at equilibrium specimen.

of the standard

Fig. 13. Phase relations at
taming specimen.

equi librium in the Mg0-con-

Fig. 14. Phase relations at
taming specimen.

equilibrium in the A1203-con-

Fig. 15. Phase relations at
taming specimen.

equilibrium in the Ti02-con-

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