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Metallic Iron Formation During Iron Ore Reduction

Contents

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Preface

Concerning the direct reduction, various methods have been proposed from of old. One of such methods is a prereduced pellet manufacturing which reduces green pellet of iron ore containing solid reductant, fine coke, coal, etc. It is reported that iron ores and solid reductants are finely ground, mixed in a suitable ratio and pelletized, but many kinds of iron ore indicate growth of fibrous metallic iron when reducing them in CO atmosphere. However, since a reduction behavior of iron ores is diversely influenced by internal (crystalline of iron ore, impurities, etc.) and external (types of reducing agents, heating method, etc.) conditions, an adequate knowledge is not still obtained. Therefore, it is essential to repeatedly experiment on iron ores with different mineral structures and properties and observe their reduction behaviours in details.

The objective of this study is to compare the reduction swelling phenomenon of ten kinds of iron ore with different locality, using three kinds of reductants (coke, charcoal, low temperature char), and to roughly classify the swelling property of iron ores by microscopic observation of mineral structure of these iron ores. The next objective is to investigate the conditions (types of solid reductants, addition of slag forming components, heating methods) capable of preventing the abnormal swelling while manufacturing prereduced pellets, and improving the quality of the pellets (strength, metallization ratio, fusibility).

Depending on the observation of mineral structure of iron ores, abnormal swelling is considered to be related to crystallization property. Therefore, in order to understand the essential qualities of abnormal swelling, it is needed to experiment not only the samples of natural iron ores, but iron oxid single crystals. Thus, six kinds of iron oxides single crystals were newly adopted as samples. The main objective of the study was to investigate the difference of reduction behaviors caused by reducing gases (H_2, CO), the growing process of fibrous metallic iron, and the effect of impurities (especially, Na, K, Ca) on the reduction by observing iron oxides in the process of reduction stereographically using a scanning electron microscope. Further, the next objective of the study was to discuss the growth mechanism of fibrous metallic iron, on the basis of the results crystallographic investigation about the reduction process of iron oxide single crystal by X-ray diffraction method (including Laue method) and the results of the reduction behavior observed by a scanning electron microscope.

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Chapter 1 Review:

Metallic Iron Formation during Iron Ore Reduction

Yoshinobu UEDA and Sogo SAYAMA

I. Abnormal Swelling of Iron Ore

In 1961, the pellet produced in the Marucona mine (the Republic of Peru) was introduced in Japan. This pellet which was separated by the magnetic separation method and whose concentrate was pulverized and sintered in the oxidation atmosphere, showed unique reducing properties which were not recognaized up to this time in the conventional charge for the blast furnace. For example, when these pellets were reduced in CO stream, they swelled like cotton and also when these pellets were reduced in a shaft furnace, they swelled and collapsed, interrupted ventilation of gas, and as a result the pressure loss increased abnormally.[1,2] In 1963–1964, some domestic blast furnace manufacturers imported the Marucona pellets and the tests were run on these pellets. The test results established that the pellets swell abnormally in process of reduction, and are not usable for the blast furnace. In 1964, at the 68th lecture meeting held by the Iron Steel Institute of Japan on the base of the mentioned above experience, a panel discussion was held under the title of "On Properties of the Pellets and their Use".[3,4] Thus the study about abnormal swelling of the pellets has advanced leadingly in our country.

Here we refer to the difference between normal swelling and abnormal swelling.[5] The normal swelling is a phase transformation from hematite of hexagonal structure to magnetite of cubic structure,[6] and the experiments by Edström,[7] using hematite-single crystal, reported that the coefficient of volume expansion of hematite in the process of reduction from Fe_2O_3 to Fe_3O_4 was 25%. And when the reduction process further proceeds from FeO (in the following FeO indicates Wustite $Fe_{1-y}O$, where Y hold concentration) to metallic iron (hereinafter, abbreviated to M. Fe), the volume of hematite single crystal shrunk reversely. The abnormal swelling is a phenomenon where the sample of iron ore swells greatly like cotton in the process of reduction from FeO to M. Fe, and coefficient of volume expansion reaches over 400 % under some conditions. It is obvious that this phenomenon has an ill effect on the blast furnace operation. It is considered to be said that abnormal swelling is briefly called "Swelling", and the expansion whose coefficient of volume expansion in the reduction process is more than 20 %, is called abnormal (abnormal or catastrophic) swelling.[8] In short, the expansion in the reduction process to Fe_3O_4 and FeO is not called abnormal swelling. Also, abnormal swelling is obviously observed when iron ore is reduced by CO, while it is generally not observed when the ore reduced by H_2.[9] However, it is also reported that the phenomenon of abnormal swelling is observed when the reduction is conducted by use of H_2 diluted with inert gas.[4)]

Some reasonings concerning the cause of abnormal reduction swelling proposed before and after the panel discussion held in 1964, are given as follows :

① Insufficient sintering
② Shortage of slag-forming components
③ Presence of γ-hematite phase
④ Presence of windmanstätten phase
⑤ Development of intergrowth in α-hematite phase
⑥ Generated gas pressure in fine ores
⑦ Weak bond strength of grains
⑧ Carbon precipitation reaction
⑨ Difference of the composition of reducing gases
⑩ Heating program
⑪ Presence of alkali salt
⑫ Growth of fibrous metallic iron

The estimated causes of abnormal swelling most recently published are as follows :

⑬ Presence of twin
⑭ Carbonization of formed iron and generation gas on the interface
⑮ Presence of CaO
⑯ Difference in basicity of the pellet

First, Kondo et al.[10)] established that on the phenomenon of normal swelling observed in the reduction process from Fe_2O_3 to Fe_3O_4, the reducing velocity in H_2 reduction corresponds with swelling, so that this swelling is dependent upon a crystal transformation to Fe_3O_4 caused by reduction of Fe_2O_3.

Next, as to the cause of abnormal swelling, many researchers paid attention to character of hematite, that is, to unstability of hematite.[11,12)] The following description relates to ① insufficient sintering considered to be the cause of abnormal swelling. Kodama et al.[2,13)] considered that the bond strength between the grains of the Marucona pellets is insufficient, and succeeded to prevent the abnormal swelling phenomenon by sintering the pellets at temperatures over 1300 °C. Yoshii[14)] also considered that insufficient sintering is one of the cause of collapsing of the Marucona pellets. Further, Kodama et al.[2,13)] considered that an amount of iron in the Marucona pellets is very high, that is, from 68.5 to 68.9 %, the volume of expansion is small, and consequently this fact might be possible to weaken the bond strenght. Kodama also clarified that from the experiment concerning ② slag forming components, the pellets sintered at a temperature of 1200 °C can be prevented from abnormal swelling by the addition of a proper quantity of CaO. In industries, bentonite is adopted as the additive, so that the properties of the Marucona pellets are now remarkably improved, and the tests are run in the blast furnace operation.[15,16,17] Adachi[18] also indicates that elevation of a sintering temperature is recognized by increasing the addition of bentonito for the purpose of improving the properties of the Marucona pellets. It is said that the pellets are slag-bonded by the addition of the slag forming components, and it is reported that resintering of the pellets at high temperatures may result in non-swelling of the pellets, because the grains of Fe_2O_3 grow up, strongly-bonded and the instable hematite is converted into stable hematite.[9]

What is the true nature of a instable hematite? Ishimitsu describes as follows.[9] Under the microscope, ③ phase estimated to be γ-Fe_2O_3 is observed in the swelled pellet. In the initial period of reduction, when almost all of the grain components were converted into Fe_3O_4, ④ the widmanstätten structures of Fe_2O_3 were observed in these pellets. It is considered that when the mineral components of the pellet exist as a crystallographically instable or metastable hematite, or as a transitional structure between hematite and α-hematite, and the above mentioned mineral is heated, the mineral components are readily converted into magnetite and then hematite liquates in the form of widmanstätten structure. However, Otake[11] regared the instability of hematite crystal structure as a result of ⑤ crystal growth of intergrowth. Thus, Otake established that these pellets are characterized by intergrowth structure of hematite, and under the high temperature microscope the reducing process proceeds rapidly along the boundary line in the intergrowth or parallel to the boundary line.[19,20] After this, ⑬ micro twin is found in the iron ore in which abnormal swelling occurs. Micro twin is also considered to be one of the factors of instability of hematite.[19,21]

As to the reasoning ⑥ generated gas pressure, generated gas CO_2 (its cross section area caluculated by BET method as 19.5 $Å^2$) is greater than the reaction gas CO (its cross section likewise 16.3 $Å^2$) [67], so that destruction occurs in the micro pores of the pellet.[9] The concept wherein ⑦ weakness of intergranular bond strength by removing O_2 in the reducing process led to destruction of the pellets,[9] is not developed theoretically after that. As to ⑧ carbon precipitation,[22] there exist also the concept that when fixed carbon is gasified, structual breaking may occur.[23] However, the phenomenon of carbon precipitation is not considered to be one of the causes of abnormal swelling.[4,9,61]

As to ⑨ the composition of reducing gas, abnormal swelling in process of H_2 reduction was not observed in the Marucona pellet.[2] Ishimitsu[9] presumed that no abnormal swelling occurs due to the strong H_2 reducing force, and also described that abnormal swelling is observed in the case of H_2-low partial pressure in the reducing condition.[24] About ⑩ heating program (test method), it is reported that a rate of pulverization of the Marucona pellets is lowered when reduction is carried out with increasing temperature either in the case of test of rotation reducing strength like Rinder-test or in the case of test of rotation strength after reduction like Gakushin-method, and the rate of pulverization is high when isothermal reduction is carried out at a temperature of 900 °C.[25] Also, Ishimitsu[9] states that a rapid reduction may cause abnormal swelling.

The effect of ⑪ alkali salt was experimentally denied in the early studies.[2,9] However, it is later proved that the presence of alkaline metals has a significant effect on acceleration of abnormal swelling. This fact will be described later.

By the detailed examinations by use of a optical microscope and by applying a scanning electron microscope, it is ascertained that the cause of abnormal swelling is ⑫ fibrous metallic iron generated in the reduction propess from FeO to M. Fe. The first presentation of the fibrous metallic iron related to the cause of abnormal swelling, was conducted by Yagi et al.[26] and Otake.[27]

Watanabe et al.[28] observe that a remarkable intergrowth structure[9,11,20] which can be seen in hematite of the Marucona pellets, accelerates reduction rate (reducing velocity). Abnormal swelliing is considered to be orginated in acceleration of rapid growth of fibrous metallic iron from Fe-phase in the process of rapid reduction. And the fibrous metallic iron is regarded as a kind of whisker.

Fuwa et al.[29] clarified that as the results of reduction experiments applied to six-teen kinds of iron ores and iron oxide reagents, the phenomenon of growth of fibrous metallic iron is recognized not only in the Marucona pellets, but in the other kind of ores. Also, they described that using CO-Ar mixed gas, the rate of swelling (swelling Index) tends to decrease with decreasing of CO flow rate, that is, with reducing the reduction rate. From these experimental results, it is proved that both the kinds of iron ores (for instance, hematite, magnetite, limonite) and the difference of the origin of deposit have no relation to abnormal swelling.

Watanabe et al.[21] state that even in the Rio-dose and Yanpi ores abnormal swelling was observed, and especially in the Yanpi ore abnormal swelling was observed in the same degree as the initial Marucona pellets. However, in this instance, an extreme development of the intergrowth structure observed in the Marucona pellets is not found.[11] In the case of the Rio-dose ore, a constant directional configulation structure of specularite grains can be seen, and in the case of the Yanpi ore, for example, micro twin is significantly developed. Also, this twin structure, like intergrowth structure, is considered to be obviously a factor which becomes a weak point and accelerates the reduction process. Further, in the case of abnormal swelling, it is emphasized that whether it may be pellet or ore, in the grains of ore, some substantially fine, regular structure are recognized.[30] Also, it considered that the

Marucona pellets resintered at 1300 °C, indicate no intergrowth structure of hematite, therefore no abnormal swelling occurs.[28)]

Ishimitsu et al.[31,32)] describe that when abnormal swelling occurs, generation of cracks in the pellets and fractionalization of every grain are needed before generation of fibrous metallic iron as a precondition. Kojima et al.[33)] also confirmed that fractionalization of the grains in the pellets wherein abnormal swelling occurs is observed in the initial reduction period. Further, using a scanning electron microscope, Kojima and the others confirmed that in the initial reduction period, intergranular combination is cut off, generation of cracks in the grains is observed and the degree of abnormal swelling is in close relation to the quantity of generated fibrous metallic iron, and when the single crystal of hematite is reduced to magnetite by use of CO-CO_2 mixed gas, the cracks being parallel to the (0001) face are observed.[37)]

Wenzel et al.[22)] think of the following three reasonings as the cause of abnormal swelling. These reasonings are ⑧ carbon precipitation, ⑫ growth of fibrous metallic iron, and ⑭ carbonization of generated iron. This is an idea that carbon in the iron crystal diffuses to the FeO/M. Fe interface and the pellets break down by the gas pressure generated on the said interface by the following reaction : FeO + CO/CO_2. There is also an opinion that a super pressure produced by gas generated in the sealed situation is the force led to collapse of the pellets.[42)] After that, Wenzel and the others[34,35)] observed fibrous metallic iron, using a scanning electron microscope and discussed its growth mechanism.[36)] This mechanism will be explained in next section.

Next, the influences of impuritues on the pellet are described. The influence of ⑪ alkalin metals on the granulated pellet using sea water was investigated by Kondo et al.[38)] It was confirmed that as a result of analyzing water soluble compound (NaCl) in slag and iron oxide separately, the iron oxide containing little Na minimizes coefficient of swelling, the slag extracts a part of Na from the iron oxide and it functions as a inhibitor of swelling. Also, coefficient of swelling is in close relation to Na volume contained in iron oxide phase, and if Na is less than 0.005 % normal swelling occurs and if it is greater than 0.03 %, abnormal swelling over about 300 % occurs.[39)]

The investigation of Ende et al.[40)] indicates that the pellets by the addition of 0–4 % $NaKCO_3$ may increase the coefficient of swelling with increasing alkali portion and finally the coefficient reaches over 400 %. Altering the composition of CO-CO_2 gas, swelling of the pellets in reduction was investigated. The result of the investigation clarified that the pellets containing alkali are ready to swell relatively in the process in which $Fe_2O_3 \rightarrow Fe_3O_4$ reduction proceeds, further swell a little in $Fe_3O_4 \rightarrow FeO$ reduction process, and swell again greatly in $FeO \rightarrow Fe$ reduction process. On the other hand, it was proved that the pellets containing no alkali, swell a little, and shrink in FeO→Fe reduction process. Lu[41)] also confirmed that abnormal swelling occurs by the addition of Na_2CO_3. Grebe[43)] decribes that the sintered ore containing 1–2 % alkali causes abnormal swelling.

It is reported that concerning ⑮ the presence of CaO, limestone is often added to the pellets as a binder to increase the pellet-strength, but if a small amount of CaO exists as a solid solution in the iron oxide, the crystal lattice is distorted, and this influences the behavior of the reduction swelling of the pellets,[44)] that is, in the pellets wherein 2 % CaO added to and sintered at a temperature of 900 °C, swelling above 200 % is observed, while the pellets which contain no CaO, indicate a shrinkage in diameter. Also, Bleifuss[45)] observed CaO as the cause of abnormal swelling. This problem will be described in the following section later on.

About ⑯ the basicity of the pellet, Gränse[46)] investigates the addition of the slag forming components and reported that coefficient of swelling reaches a maximum at the basicity of about 0.8. Concerning the similar problem, Nishida and the others[47)] state that when CaO/SiO_2 ratio of the pellet is especially equal to 0.5, swelling is observed. Kojima et al.[48)] drscribe that coefficient of swelling grows up remarkably around the basicity of 0.7 and the quantity of slag indicates a minimum at the basicity of 0.5–0.7 in accordance with the tendency of coefficient of swelling. Also, Nishida et al.[49,50)] reported that the pellets combined with calcium ferrite have a good reducing property and coefficient of swelling is very small. Further, about the properties of the pellets in the process of reduction, the generalization by Narita et al.[51)] is available.

The above mentioned sixteen reasonings about the causes of abnormal swelling were classified respectively and the contents of the reports and researches carried out up to this time were introduced. The main points clarified are summarized as follows:

a) Abnormal swelling depends upon the growth of ⑫ fibrous metallic iron in a reduction process FeO→Fe.

b) The ore and pellet caused abnormal swelling possess several characteristics known as ④ widmanstätten structure, ⑤ intergrowth, ⑬ twin and ③ γ-hematite, and wherein fine structures becoming weak points in reduction process are observed.

c) In order to prevent the pellets from abnormal swelling, ① sintering at over 1300°C, or ② the addition of an adequate amount of slag forming components is effective.

d) The cause of abnormal swelling is the presence of ⑪ alkaline metals (Na, K) and ⑮ alkali earth metal Ca as impurities. Also, ⑯ the basicity of the pellets relates to abnormal swelling.

e) Abnormol swelling is remarkably observed when ⑨ the reducing agent is CO gas, and it is not observed when the reducing agent is H_2 gas. However, in the diluted H_2 stream a certain degree of swelling is observed.

Besides the said facts, the most important factors are as follows :

f) Growth mechanism of fibrous metallic iron.

g) Observation of the ore structure in reduction process.

h) Behavior of elements as impurities and slag.

i) The king of reducing gases and the influence of solid reducing agent[66].

j) Crystallographical basic study of the reaction of iron oxide.[66]

Ⅱ. *Growth Mechanism of Fibrous Metallic Iron*

As the growth mechanism of fibrous metallic iron considered to be the greatest cause of abnormal reducing swelling of iron oxide, the two mechanisms are published. They are (1) tip growth mechanism and (2) base growth mechanism which are metioned in growth mechanism of whisker. In short, the difference between the two mechanisms is whether whisker grows on the tip or from the base. In order that whisker grows on the tip, a new atom must be adhered and supplied on the tip of whisker and in order that whisker grows from the base, a atom is needed to be added and supplied on the base.[52,53,54,55]

The growth of whisker from the tip is carried out by chemical reaction in the gaseous and dissolved conditions, or in the solid. For instance, when the halogenides which are ready to vaporized, are contained in gas phase, the produced substances are adhered on the tip of whisker. Besides this case, these are the method in which the chlorides such as NH_4Cl and $FeCl_3$ are added to iron ore and then H_2 reduction is carried out at 400–900°C,[56] and the method wherein whisker is obtained by H_2 reduction of $FeCl_2 . nH_2O$.[57] In the case of such tip growth, the screw dislocation in the direction of growth axis essentially functions, the growth of whisker is accompanied by phase change (Vapor→solid soltution→solid), and thermal decomposition.

There is also whisker generated without any phase change. This is called a proper whisker, for instance, observed in Ag, Au, Sn Ca, Cu, Fe, Mg, Pt, Zn, Pb, etc. It is confirmed by the electron microscopic observation that the generation of proper whisker is the base growth.[58]

The other example of the whisker growth from the base is the case of chloride being difficult to evaporate. The growth mechanism of whisker of Ag by reducing silver sulfide will be illustrated as follows. C. Wagner[59,60] illustrates this mechanism very briefly. After all, the reducing reaction by H_2 proceeds on the surface of AgS, and is removed as H_2S. When the surface reaction further proceeds, Ag^+ and e^- may be under supersaturation, and if nucleation is generated, they travel to the nucleus and then Ag^+ and e^- are bonded to become metallic silver. When the reaction continuously proceeds, Ag atoms are taken in the base of the nucleus, and whisker grows pushing up the nucleus.

About fibrous metallic iron which grows in the reduction process of iron oxide, Wenzel et al.[34,36] explain by use of the tip growth mechanism as follows. Concerning fibrous metallic iron, they suggest the two possibilities. One of the possibilities is that the reduced iron is under the adsorbed state at first on the surface of iron phase, and then the adsorbed iron travel to the growth point, the growth of directional whisker is brought up. The second possibility is that gaseous iron suboxide is produced on a newly reduced surface, and the iron phase in gas is separated by the change of the stability condition (gas component, temperature, pressure), thus the iron phase crystalizes on the growth point of whisker. This suboxide is an imaginary substance. However, also in the following reduction experiment of the ore of low quality, the observation is conducted on the base of generation of this suboxide. Namely, when the ore of low quality (bauxite residue Fe 35 %) was reduced at temperatures of 1300–1400°C using lignite, iron precipitated in the spherical form (1–3mm in diameter) on the tip.[35,36] In this case, it is also considered that iron traveled as the gaseous suboxide and precipitated on the sample surface. At the same time, the growth of gas phase of SiO_2 whisker is also obviously observed.

On the other hand, Fuwa et al.[61,62] describe on the base of the base growth mechanism as follows. Namely, they explain the growth mechanism of fibrous metallic iron using the analysis conducted by C. Wagner[59,60] of the growth mechanism of fibrous metallic silver in H_2 reduction process of silver sulfide. When oxygen is removed as CO_2 on the surface of wustite, in the process of reaction with CO, the concentration of Fe^{2+} ions and e^- in FeO layer increases gradually, and soon Fe^{2+} ions reach supersaturation. At this time, if iron nucleation is generated wherein nucleation is ready to occur, for example, in defects of crystal the supersaturated Fe^{2+} and e^- diffuse and travel in the direction of the nucleus according to the concentration gradient, and crystals of iron develop fibrously from the nucleus. The degree of supersaturation around the nucleus is too small to generate new nuclei, thus, it is described that the quantity of fibrous metallic iron principally depends upon the nature of the ore surface, number of iron nucleus, reduction velocity, diffusion coefficient of irons, and travel distance. Although the growth of fibrous metallic iron is not observed in the case of H_2 reduction, it is considered that even in the case of H_2 reduction the growth of fibrous metallic iron will be realized in principle, based on the results of study by Richardson et al.[63,64] However, the reducing conditions are considered to be narrowly restricted.

Gränse[46] like Fuwa et al.[61,62] also illustrated using the theory of C. Wagner[59,60], and Nicolle et al.[68] made an analysis of the mechanism, using a mathematical model.

Schaefer[65] illustrated the mechanism of abnormal swelling, using a model of H_2 reduction of magnetite as follows. With removing oxygen from the crystal surface by use of reducing gas, Fe^{2+} and e^- are supersaturated and the nucleation of metallic iron is generated on lattice defects. The supersaturated Fe^{2+} or e^- diffuses toward the produced nucleus, and then continuously precipitates and grows on the Fe nucleus. This precipitation of metals causes mechanical stress, and finally it leads to breaking of FeO matrix. The precipitation of Fe nuclei and accompanied breaking action are greatest when the diffusion of substances is restricted only in a few nuclei. When the number of generated nuclei is much, the quantity of accumulation of Fe on one nucleus becomes relatively small and the stress is divided proportional to the whole matrix. In this instance, the internal stress is considered to be smaller and to cause no abnormal swelling. Although this illustration does not touch the growth of fibrous metallic iron, the content is the same as the consideration on the base of the model about the neucleation and nucleus growth by Fuwa et al.61,62)

In the same way, referring to the base growth mechanism, Bleifuss45) regards Ca component as the cause of abnormal swelling, and explains the growth mechanism of fibrous metallic iron, using calcifellous magnetite as a sample. With proceeding the reduction, the concentration of Ca^{2+} on the surface of magnetite sample is increased. In such condition, generation of iron nuclei is restricted and only few iron nuclei are generated. It is considered that diffusion of Fe^{2+} ions occurs intensively on the iron uncleus, and the results fibrous metallic iron grows.

As mentioned above, any illustrations of the growth mechanism of fibrous metallic iron remain a stage of reasoning and they are also qualitative. However, it is indicated that the influence of various factors until now observed in every investigation should be studied in relation to the kind, number and distribution of lattice defects in the stage of reduction of wustite, and it is important.51) For the purpose, it is important that the detailed observation of mineral structure of hematite, magnetite, wustite and generated metallic iron is made, and next the growth mechanism is discussed. In order to attain the object, the author considers that the experiments performed using the single crystal whose face index is clear, are advantageous. Consequently, natural and synthetic hematite, magnetite single crystals should be used for this experiments.

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Chapter 2

Abnormal Swelling on Pellet during Prereduced Process

Sogo SAYAMA, Itsuma SEKIGUCHI and Yoshinobu UEDA

Synopsis

An investigation was made on the abnormal swelling during prereduced pellet firing. Ten kinds of iron ore and three kinds of solid reductant were tested. When pellets contained a reactive reductant, abnormal swelling occurred in some kinds of ore. This was found to be due to the growth of metallic filaments in the pellet, that grew abruptly in reduction at about 1000°C.

The swelling was related to the unstable phase during reduction, or this may be attributed to (1) the laminated structure, (2) strain within crystals, (3) weathering of ore, (4) incomplete recrystallization and so forth.

In experiments in which 2 % of pyrite or 1 % of sulphonic acid (S 15.9 %) was mixed with ores, an it was found that sulphur addition was effective to prevent from swelling. However, sulphur addition was detrimental to pellet quality, because the sulphur remains in the pellet after reduction.

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I. Introduction

A number of studies have been carried out to the present on degradation of sintered ore and swelling of natural ore during reduction. To clarify the mechanism, a special investigation was made in this paper with special regards to the state in the mineral phase. The authors have observed that when producing the prereduced pellets by mixing powdered iron ore with solid reductant, and sintering them, fibrous irons are grown, and as a result swelling occurs. And consequently a pellet product of a high quality could not be obtained. 10 kinds of the ores and 3 kinds of solid reductants were used for the experiments. It was confirmed that the abnormal swelling, cracking and high density sintering depends upon the different combinations of ore and solid reductant, and that the reduction of these ores must be conducted with special consideration to the characteristics of the ores. The results of experiments are as follows.

II. Materials and Methods for the Experiments

1. Ore Samples

The analytical values of all of the 10 ore samples are shown in Table 1. The characteristics of each ore will be explained in III. 2.

Table 1. Chemical compositions of ores (wt%)

Name of tested ores	T. Fe	FeO	SiO_2	Al_2O_3	CaO	MgO	S	C. W
Brazil	65.20	0.20	4.29	1.32	–	0.14	0.005	0.66
Swaziland	63.65	0.18	4.68	2.15	–	–	0.014	0.31
Hamersley	62.10	0.22	4.45	2.56	0.22	–	0.014	2.22
Portlady	61.19	0.20	1.63	3.30	–	0.10	0.052	5.45
Goldsworthy	65.85	0.08	3.30	1.25	0.10	–	0.125	0.72
Goa	62.95	3.70	2.07	2.61	0.10	0.20	0.025	2.50
Krivoy-Rog	58.52	3.15	15.62	1.04	0.30	0.18	0.032	0.69
Santafe	63.29	14.27	4.98	0.97	1.50	1.10	0.343	1.31
Marcona	63.22	15.29	5.08	0.82	1.08	1.76	1.606	0.82
Mosan	58.47	22.55	17.25	0.42	0.71	0.59	0.034	0.64

2. Carbon Material Sample

Three Kinds of solid reductants were used ; metallurgical coke, charcoal and lignite char (char). Proximate analysis of these solid reductants are given in Table 2, and the Chemical compositions of the reductant ashes are given in Table 3. The coke is characterised by high fixed carbon content, the charcoal by high volatile matter, and the char by high sulphur concentration. Compared to the ashes, the charcoal has alkali content.

3. Compacting of Green Pellet

After mixing pulverized ore and carbon material (−400 mesh, 100 wt%) using a grinder, and moistening with about 10 wt% water, the mixture was compressed and molded with a

Table 2. Proximate analysis of reductants (wt%)

Reductants	Moisture	Volatile matter	Fixed carbon	Sulphur	Ash
Coke	0.5	2.3	83.2	0.40	13.6
Charcoal	1.3	11.9	73.2	0.06	3.5
Lignite char	5.7	5.8	77.5	1.03	9.2

Table 3. Chemical compositions of reductants ashes (wt%)

Reductants	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
Coke	47.2	23.3	17.5	2.4	4.2	0.23	0.53
Charcoal	2.9	7.6	2.3	7.4	60.5	1.38	5.82
Lignite char	15.2	16.9	12.9	3.8	25.8	0.22	0.02

die. A green pellet weighing about 3 g was molded under a pressure of 320 kg/cm^2. The pellet is 14.0 mm in diameter and about 5 mm in height. Table 4 shows the weight percent of −400 mesh pulverized ore, apparent specific gravity and porosity of the dried green pellet, including 10 wt% of carbon material. In addition, the compression process was done at a molding pressure of 320 kg/cm^2, consequently, the influence of the compresion pressure on porosity was not studied. Further, the pulverized ore and the carbon material were mixed by a grinder for 15 minutes. The ores were pulverized during mixing, at a weight percent of −400 mesh grain size increased by about 3 percent.

Table 4 Size analysis of tested ores and apparent specific gravity and porosity of dried pellets.

Name of tested ore	−400 mesh of powdered ore (wt%)	Dried pellet*					
		Contain 10% of coke		Contain 10% of charcoal		Contain 10% of lignite char	
		Apparent specific gravity	Porosity (%)	Apparent specific gravity	Porosity (%)	Apparent specific gravity	Porosity (%)
Brazil	83.2	2.74	37.5	2.49	42.8	2.56	41.3
Swaziland	56.6	2.68	38.5	2.55	41.1	2.52	42.1
Hamersley	61.1	2.76	34.4	2.51	40.0	2.59	38.2
Portlady	55.7	2.59	37.6	2.38	42.2	2.31	44.1
Goldsworthy	58.8	2.62	40.3	2.33	46.6	2.38	45.7
Goa	71.7	2.76	37.4	2.47	43.6	2.55	41.9
Krivoy-Rog	86.3	2.77	36.0	2.49	42.1	2.54	41.1
Santafe	77.9	2.77	36.3	2.35	45.6	2.60	40.1
Marcona	79.1	2.84	36.8	2.47	44.8	2.64	40.9
Mosan	89.8	2.53	40.1	2.27	45.8	2.26	46.2

* Average value of seven pellets.

4. Reducing Method

To dehydrate the pellets in a muffle oven, the temperature was increased to 400°C at a rate of about 5 °C/min, and kept constant for 30 minutes. When dehydrating, the state of pellets changed as follows. Magnetites are oxidized and the analytical values of FeO decreased by about 30%. While the coke used as internal carbon material is almost not oxidized, the charcoal or char is oxidized and is decreased by about 3 vol.%. Phyrite is also oxidized and the sulphur content decreases by about 30 %.

Two of pellets and external carbon material were placed in a crucible of stainless steel (40 mm in diameter, 70 mm in height), which was suspended in a vertical tube furnace (60 mm in inner diameter, 300 mm in heating length) and reduced. After blowing N_2 gas (200 ml/min.)

through the tube furnace and after a fixed reducing time, the crucible was removed into the atmosphere and cooled. While cooling, the possibility of the reduced pellets being reoxidized was present. But, the problem was not considered, because the pellets had an external 50 mm layer of carbon material.

Ⅲ. *Structure of Ore Samples*

1. X-ray Diffraction Test

The results of these tests are as follows. In the Hamersley, Portlady and Goa crude ores goethite was observed, which disappeared after dehydration of the ores. The reducing experiments were conducted also on the ores which were roasted at a temperature of 1000°C for one hour in the atmosphere and subsequently underwent a change of crystalline structure. The results of the X-ray tests of these roasted ores will be described later. When roasting the ores, magnetite was almost oxidized to hematite.

The peak of (0006) mirror index of hematite is observed clearly, especially in the Brazil ore. This peak dose not disappear even after roasting at a temperature of 1000°C.

2. Microscopic Observations

Characteristics of the mineral structures of the tested ores are as follows :

(1) Brazil

This ore shows a typical lamellar structure, which was subjected to dynamic metamorphism. Hematite is a compact ore and its crystals are arranged with directional properties. The crystal also tends to crack into a plate form. The results of the X-ray diffraction tests show that this ore has a strong peak of (0006) crystal face in comparison with the other ores, and that the crystals are developed in the direction of c plane. As described by Yamada et al.[1)] by X-ray diffraction, it was confirmed that a directional arrangement in a specified direction is developed in the massive ore. Goethite is not observed, but quartz exists as gangue. In photo. 1(a) is shown the ore structure, and a grain boundary is distinctly observed.

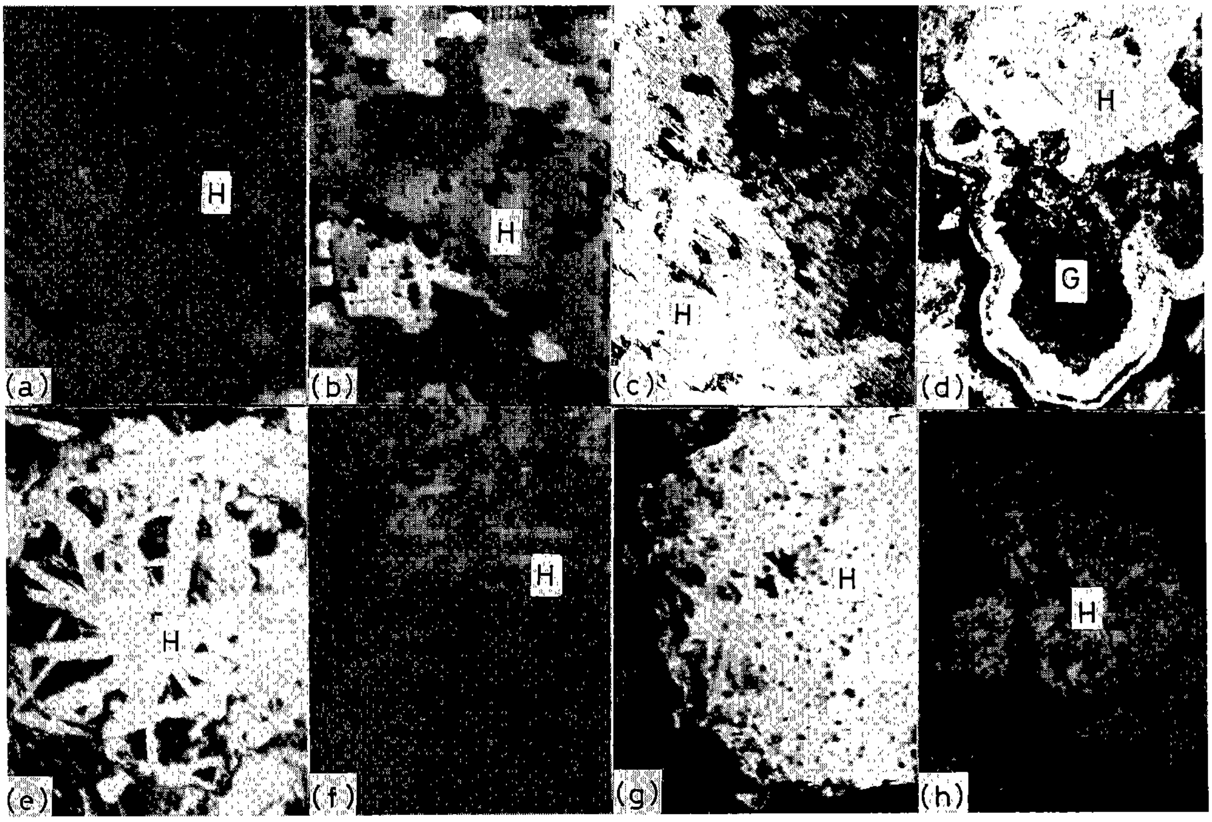
(2) Swaziland

This ore is massive. The grain boundary shows a mosaic structure, shown in Photo. 1(b). This hematite ore general shows a structure which differs from Brazil ore.

(3) Hamersley

The structure of this ore is similar to that of the Swaziland ore. Although goethite can be observed in this ore by X-ray diffraction, the boundary between hematite and goethite was often observed under a microscope. The presence of these minerals is given in Photo. 1(c).

(4) Portlady



H : hematite G : goethite
(a) Brazil, + nicol (b) Swaziland, + nicol (c) Hamersley (d) portlady (e) Goldsworthy, + nicol
(f) Krivoy-Rog, + nicol (g) Santafe, + nicol (h) Marcona roasted at 1000°C, + nicol

Photo. 1. Micro structure of tested ores.

This ore contains an abundance of goethite, coexisting with hematite. It is especially seen that the perimeter of circular grain is weathered into goethite. Hematite is porous and the grain boundary is indistinct. Photo. 1(d) shows the existing state of goethite.

(5) Goa

Hematite is weathered into goethite. This ore abounds in magnetite, forming eutectic crystals with hematite. Observing the hematite grains, grain boundaries with direction properties similar to intergrowth, are observed.

(6) Goldsworthy

Columnar developed hematites are observed. Grain boundaries of crystals of this kind are clearly observed, but ore is not stratified, differing from Brazil ore. The structure is shown in Photo. 1(e). The massive ore shows a grain boundary which is similar to that of the Swaziland ore.

(7) Krivoy-rog

From the geologic map[2), it can be seen that this deposit is considerably folded and subjected to a strong dynamic metamorphism. The Krivoy-rog mine has produced magnetite and hematite, containing an bundance of quartz as gangue. In this experiment only magnetite was used. Hematite is massive, and the grain boundary is also very fine and relatively clear. Most hematites present a structure, closely allied to the intergrowth. Photo. 1(f) shows such intergrowth.

(8) Santafe

Hematite is developed in magnetite. The grain boundary of hematite is generally indistinct. Photo. 1(g) shows the development of hematite. The deposit which is a contact metasomatism deposit akin to the Marcona deposit, abounds in alkali components and contains pyrite too.

(9) Marcona

In this ore, an abundance of pyrite is observed and the ore presents a structure similar to that of Santafe ore.

(10) Mozan

The ore contains porous magnetite. But, hematite has not been observed. According to Asano's investigation[3)], this ore is classified under banded ore deposits that has been subjected to dynamic metamorphism. The ore contains much quartz as gangue.

(11) Ore Roasted at a Temperature of 1000°C

Only hematite is observed as a mineral. Under a polarization-microscope the grain boundary can be generally clearly observed compared with that of crude ores. The intergrowth structures are generally observed in the Portlady and Goa ores, but the intergrowth of hematite are seen prominently developed in two or three directions, regarding this Watanabe et al.[4)] reported that they had observed in the Marcona pellet, this was not recognized in ore roasted. In this experiment, roasting of the ores in the atmosphere was dared at a temperature of 1000°C. It is considered that hematite was under the state in which due to lower rosting temperature recrystallization could not entirely realized. Photo. 1(h) shows the structure of the marcona ore roasted at 1000°C, but the intergrowth is indistinct. Further, microtwin that Watanabe et al.[5)] observed, could not be recognized in any of the cases.

Ⅳ. Results of the Experiments

1. Determination of the Reduction Conditions

It is necessary to determine the quantity of internal reductant, reduction temperature etc. before undertaking the experiment. Placing the pellets, made from both the Brazil and Hamersley ores and 20 wt% of various internal carbon materials into a crucible, which was suspended without the external carbon materials in N_2 atmosphere of a vertical tubular furnace, and the loss in quantity was measured by a balance. The results demonstrated that when the pellets are heated at 1200°C, the reduction ceases in about 20 minutes. This result coincides with that of the experment which Kunii et al.[6] performed by an external reductant method. When using char as the carbon material, the strength of the pellet decreased remarkably at the time of dehydration at 400°C for 30 min. As a result it was difficult to insert 20 % of char.

Judging from the results of preliminary experiment, the so-called combined internal and external solid reductant method in which internal carbon materials are kept within 10 wt% and the shortage of carbon material was filled with external carbon, was employed. According to the results of the experiments of the combined method, carried out by Kunii et al.,[7] it is necessary to heat the pellets at a temperature of 1200°C for 30 min. for sufficient metallization. Although the reduction is expected to be insufficient, in this experiment, the reduction time was controlled within 25 min. In all reducing temperatures, and the properties of the pellets were compared with each other. The maximum reduction temperature was determined to be 1250°C.

2. Reactivity of Carbon Materials

Kunii et al.[8] reported that the properties of the reduced pellets can be differentiated by the type of carbon material. This report also describes that the reactivity of carbon material, namely, the gasification velocity had an effect on the reducing reaction, this was proportional. In order to compare the reactivities of three kinds of carbon materials, the boat experiment was carried out to determine the weight-loss of carbon material by reacting of carbon material with CO_2 gas. 3 g of −400 mesh carbon material was placed in a boat, which was inserted into a tube furnace (30 mm in inner diameter). And then, CO_2 gas was charged at a rate of 100 cc/min into the furnace. After a lapse of time, the boat was transferred to the low-temperature part of the furnace and then cooled. By weighing the carbon material together with the boat, the loss of the carbon material was measured. Fig. 1 shows the reaction rate of various carbon materials at 1000°C in the case of the carbon materials except ash is 100 wt%.

According to the results of the measurements, reactivity of te char with CO_2 gas was highest, and that of the charcoal was somewhat lower. However, the reactivities of these carbons showed the same tendency. As illustrated in Fig. 1 however, the coke reacted with CO_2 gas very slowly and the reaction advances only up to about 20 % within the reaction time (10 min) by which time the reaction of char was nearly completed.

3. Grain Size of External Carbon Material

In order to investigate the effect of grain size of external carbon materials on the pellets of 4 kinds (Brazil, Swaziland, Marcona and Mozan pellets) mixed with internal carbon (coke) materials, the behavior of coarse (−14 mesh) and fine (−250 mesh) coke was compared.

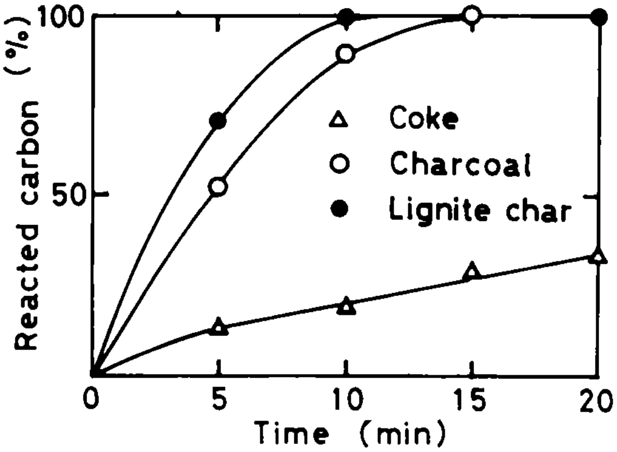


Fig. 1. Specific reaction rate of various reductants with CO_2 at 1000°C.

The crucible in which the pellets charged with 10 % of internal coke and external coke, was suspended in a vertical furnace heated at temperatures of 1150 and 1250°C, and then the pellets were reduced by rapid heating for 25 min. Diametral swelling index of pellets after the reduction are given in Table 5.

This shows that with respect to the grain size of the external cokes, grain size of −14 mesh is preferable to the density of reduced pellets. To investigate the reson for the lower density of pellets when the grain size of external cokes is fine, microscopic observations were made. The microstructures of the Swaziland and Mozan pellets are given in Photo. 2. When the external coke is −14 mesh, the above two pellets generate a large liquid phase (Photo. 2(a), (c)). When the grain size of the coke is −250 mesh, on the other hand, linkage of grains is weak (Photo. 2(b), (d)). This can be attributed to the fact that when the coke is fine grained and high in its reactivity, a small amount of liquid phase due to high reducing velocity to M. Fe is developed. Consequently, it can be seen that the liquid phase is

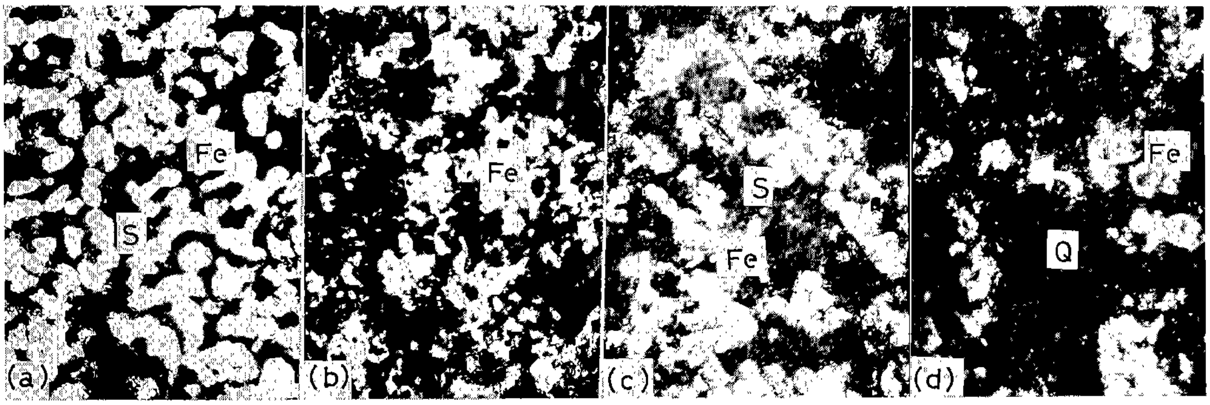
Table 5. Effect of coke size on swelling index of reduced pellets (%)

Coke size	−14mesh		−250mesh	
* * *	1150℃	1250℃	1150℃	1250℃
Brazil	6.5	−10.7	12.8	− 5.7
Swaziland	−10.0	−14.2	0.0	−12.1
Marcona	−10.7	−20.7	− 0.7	−10.0
Mosan	− 4.2	−12.8	6.4	− 4.3

Reducing time : 25 min

* Reducing temperature

* * Name of tested ores



Fe : metallic Fe. Q : quartz. S : silicate glass.
(a) Swaziland, coke −14 mesh (b) Swaziland, coke −250 mesh
(c) Mosan, coke −14 mesh (d) Mosan, coke −250 mesh.

Photo. 2. Microstructure of reduced pellets with different external reductant size reduced at 1250°C for 25min. x400

also related to the sintering of the reduced pellets. The external carbon material probably has an optimum grain size with regards to its reactivity and an optimum contact area with the pellets. However, in this paper the detailed study on optimum grain size was not carried out. As a result, in the case of using external carbon material, the grain size of −14 mesh was adopted for all the three carbon materials.

4. Kinds of External Carbon Materials

The study that Kunii et al.[8)] carried out regarding the internal carbon method, describes that by using carbon materials such as weak coking coal, or thermaly subjected coal of a higher reactivity than coke, the compression strength of the pellet decreased. Thus, it can be said that the quality of the pellets are affected by the reactivity of carbon materials. Therefor, the effect of various internal and external carbon materials on the quality of pellets were investigated by the use of the combined method.

In Table 6 are given the diametral swelling indices of the pellets, reduced at a temperature of 1250°C for 25 min using coke and charcoal as carbon material, and charging 10 wt% of internal carbon material.

In Table 6 it was clearly demonstrated that various ores show swelling over the diameter (14.0 mm) of the green pellets by using charcoal as the internal carbon material. Charcoal, used internally or externally, is inferior to coke because of the density of pellets. As mentioned in Ⅳ.3, the densiy of pellets decreases when the grain size of the external carbon materials is fine. Consequently, it can be said that the strength of pellets tends to decrease when the reactivity of carbon material is high.

Table 6. Swelling index (%) of tested ores during reducing tests with different internal or external reductant.

Internal reductants / External reductants / Name of tested ore	Coke		Charcoal	
	Coke	Charcoal	Coke	Charcoal
Brazil	−10.7	−2.8	0.7	6.7
Swaziland	−14.2	−10.7	−10.7	−10.0
Hamersley	−19.3	−8.6	−2.8	−1.4
Portlady	−18.6	−8.6	1.4	8.6
Goldsworthy	−21.4	−13.6	−7.8	−8.6
Goa	−15.7	−5.7	7.1	10.0
Krivoy-Rog	−14.2	−7.1	−0.6	7.1
Santafe	−19.3	−17.8	−17.8	−17.8
Marcona	−20.7	−19.3	−12.8	−12.8
Mosan	−12.8	−8.6	0.0	5.6

Reducing time : 25 min   Reducing temperature : 1 250°C.

5. Reduction Tests at Each Temperature

Table 6 also shows that five kinds of Brazil, Portlady, Goa, Krivoy-rog, Mozan ores have a stronger swelling property compared with the other ores, reduced under the same conditions. From hematite ore a Brazil pellet of strong swelling property, a Swaziland pellet of weak swelling proserty were chosen. From magnetite ore a Mosan pellet of strong swelling property and a Marcona pellet of a weak swelling property were chosen. Those pellets were rapidly heated at each temperature for 25 min. In Fig. 2 are given the bulk density (apparent specific gravity), total Fe-content and total metallization grade of these pellets. The type of internal and external carbon materials were the same.

According to the results of this experiments, the bulk density decreases at a temperature of an order of 950 to 1050°C in all cases. When using coke as reductant, the density of pellets begins to increase at a temperature of 1050°C with the formation of metallic iron, and the density of pellets is higher than of the pellets in the case of using other carbon materials. When the charcoal is used as the reductant, the formation of metallic iron begins at 950°C and the density of the Brazil and Mozan pellets decreases remarkably. When char is employed as the reductant, the formation of metallic iron occurs suddenly at a temperature of 1050°C, but the degree of density falls between cases of using coke and charcoal.

The structures of pellets were as follows at each temperature.

(1) Brazil

When using coke as the reductant, most of the pellets are converted to wustite at a

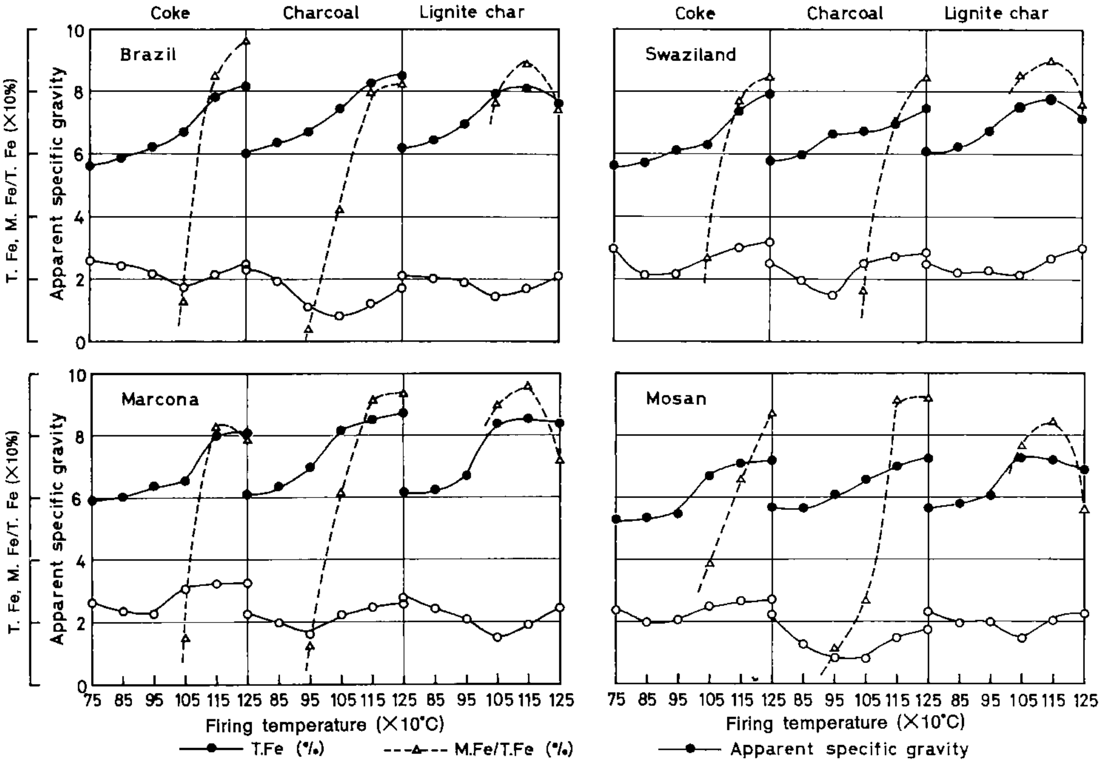
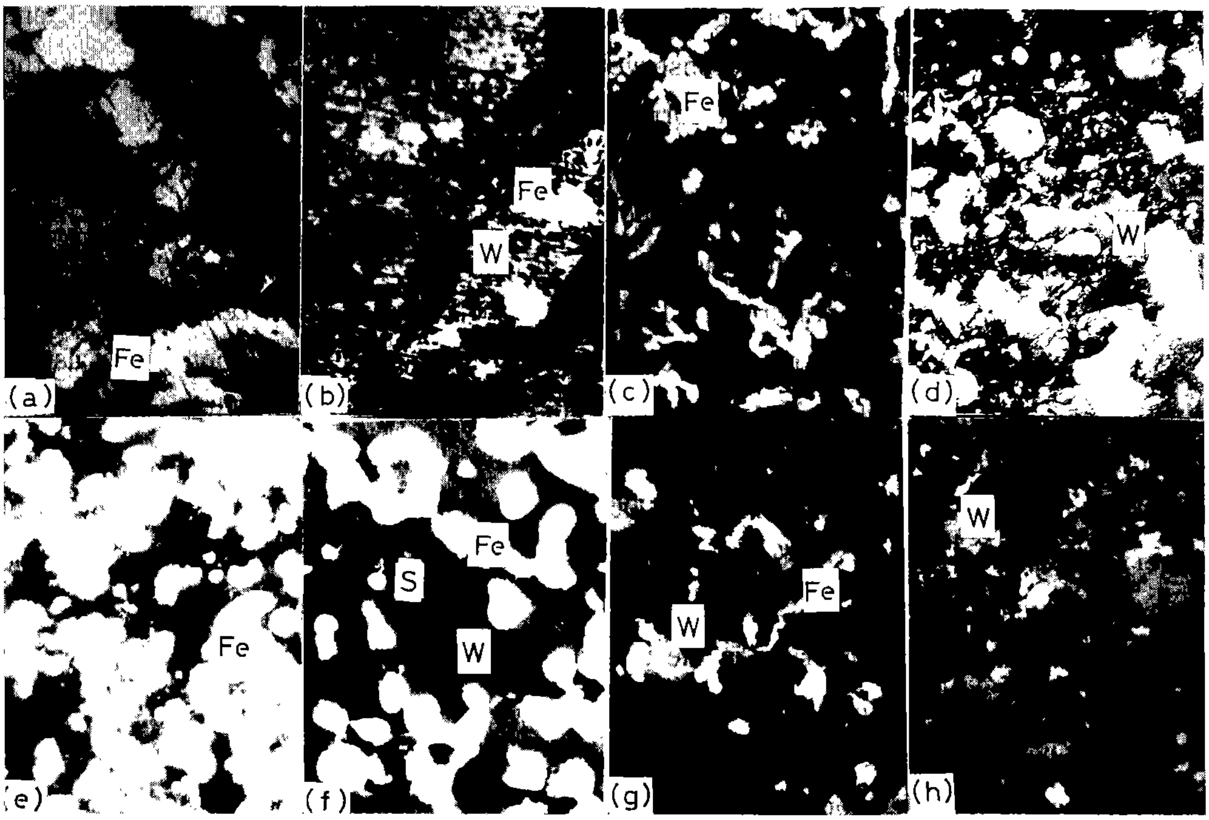


Fig. 2. Fe content and apparent specific graving of pellets when reduced with different reductants at each temperature for 25 min. Size of external reductant was — 140 mesh and the kind of external reductant was the same to internal one.

temperature of 950°C and a part of wustite startes to convert into metallic iron at 1050°C (Photo. 3(a)). When charcoal was used, magnetite begins to be formed into compact hematite grains at a temperature of 750°C and the hematite grains are converted to fine grains. It is observed that a part of the wustite grains change into metallic iron at 950°C (Photo. 3(b)), and then a characteristic fibrous metallic iron is formed at 1050°C. The fibrous metallic irons are sintered together at a temperature of 1150°C (Photo. 3((c)). When char is used as a reductant, fine grained megnetite is formed at 750°C, metallic irons are formed at 950°C, large amounts of metallic irons are formed at 1050°C, but the fibrous irons are not observed. Also, at a temperature of 1250°C, a considerable liquid phase develope. Further, when using char as the reductant, the formation of liquid phase is often observed in common with the other iron ore pellets.

(2) Swaziland

When using char as the reductant, numerous voids are observed in the wustite grains, formed at a temperature of 950°C. The metallic irons are formed in part of the surface of wustite at a temperature of 1050°C (Photo. 3(d)).



Fe : metallic Fe. W : wustite. S : silicate glass.
(a) Brazil, coke, 1050°C. (b) Brazil, charcoal, 950°C. (c) Brazil, charcoal, 1050°C. (d) Swaziland, coke, 1050°C. (e) Marcona, lignite char, 1150°C. (f) Marcona, lignite char, 1250°C. (g) Mosan, charcoal, 950°. (h) Mosan, lignite char, 950°C.

Photo. 3 Microstructure of reduced pellets with different reductants reduced at different temperatures for 25min. x400

When charcoal is used as a reductant, magnetite is formed at a temperature of 750°C, but in this case the disintegration of the fine grains dose not occur such as seen in Brazil pellets. At 950°C, a part of wustite begins to be converted to metallic iron, but the fibrous irons are not observed. When char is used as a reductant, the pellets are almost changed to magnetite at 750°C and metallic irons are formed at 950°C.

(3) Marcona

When using coke as the reductant, metallic irons are formed at a temperature of 1050°C, and when charcoal or char is used, metallic irons are formed at 950°C. When char is used, the metallic irons are sintered with one another at a temperature of 1150°C (Photo. 3(e)), but many minerals besides the metallic irons are sintered in a complicated state at 1250°C (Photo. 3(f)).

(4) Mosan

When using coke as the reductant, metallic irons are developed from wustite at a temperature of 1050°C. When using charcoal, the swelling of pellets is large at 950°C and many fine fibrous irons filments are observed (Photo. 3(g)). When char is used as the reductant, fine metallic irons are also formed at 950°C, but fibrous irons are not observed (Photo. 3(h)).

Summarizing the above mentioned structural obsrvations, it is clearly shown that when coke of a low reactivity is used, metallic irons are formed at 1050°C, but the coke reacts very slowly and even at a temperature of 1150°C a part of the coke still remains intact.

When charcoal or char is used, it reacts rapidly and the internal carbon materials are almost consumed at 1050°C. Metallic irons are developed at 950°C, but when using charcol in the Brazil and Mozan pellets, fibrous irons are formed at the same temperature (at 950°C) and the pellets swell remarkably at about 1000°C. When using char, fibrous substance is not observed in spite of its high reactivity such as seen in charcoal. In the same way as coke, the degree of swelling of the pellets is very low. When using charcoal as the internal carbon material, swelling is not observed in the Swaziland and Marcona pellets. With regards to these carbon materials, for instance, when coke is used as the reductant, the pellets do not swell, but when comparing char with charcoal, which have the same reactivity, fibrous metallic irons are remarkably developed and the pellets swell only when the char is used. The fact can not be explained, the difference arises from the reactivity of carbon material.

It is already known that the fibrous irons grew at the time of reduction of the Marcona pellet. According to recent studies[4,5], the fibrous irons mentioned above can be regraded as the same as the fibrous irons which are recognized at the reduction of other ores.

The above mentioned studies are concerned mainly with the CO reduction of pellet. In this paper we have found that under certain reduction conditions, fibrous irons are formed abnormally even if the reduced pellets are heated with carbon material of high reactivity ; as a result the pellets swelled. This swelling of pellets interferes with the manufacturing of pellets of high density and of high strength.

The results of observing fibrous irons by a scanning electron microscope are given in photo. 4. As described by Kojima et al.[9] in their observations of pellet reduction, the fibrous metallic irons show a entwined state and that the crystal habit of fiber is not clear. Therefore, this fibrous metallic iron is expected to be a material which differs somewhat from whiskers. This fibrous Metallic iron often becomes pyrophorous when the cooling is insufficient (about 100°C). As described by Okura et al.[10] in their experiments with sponge iron reduced at low temperature, the crystals are considered to be unstable and active. The abnormally swollen pellet is liable to be reoxidized and unfavorable to the strength, and the quality of the iron product is at a disadvantage.

When green pellets are reduced at 1250°C, a considerable amount of liquid phase is

Reducing temperature : 1150°C, Reductant : charcoal

Photo. 4 Metallic iron filament in reduced pellet of Brazil ore. x3000

observed in all cases. This tendency becomes remarkable especially when char is employed as the reductant, and the quantity of metallic iron decreases and the analytical value of FeO becomes higher as compared with the reduction at 1150°C. For example, the results of analyzing the liquid phase of the Marcona reduced pellet by EPMA when using char as reductant are as follows : Fe 49.6 %, SiO_2 27.2 %, Al_2O_3 1.5 %, MgO 11.8 %, CaO 8.8 %. This result is probably due to the insufficiency of reducing gas flow, in this case numerous wustite phases are observed.

6. Reduction of Roasted Ores

An investigation was conducted on the reduction of the ores which were subjected to roasting at least once. The ores roasted at a temperature of 1000 or 1300°C for 1 hour were used as the test sample. These roasted ores were rapidly reduced at 1250°C, usig char as carbon material. In Table 7 are the diametral swelling index of these reduce pellets. Further, in order to compare the roasted ores with the crude ores, the swelling indices of crude ores are given in Table 7.

From this table, it is clear that when the ores are roasted at a temperature of 1000°C before pelletizing and reduced, the degree of swelling of the pellets is higher than that of the non roasted ore pellets. When the pellets are roasted at 1300°C, the swelling index of the pellets also becomes lower than that of the pellets roasted at 1000°C.

7. Reducing Velocity

As described in Ⅳ.5, the density of the pellet decreases at a temperature of about 1000°C. Therefore, when reducing the pellet, it is necessary to shorten the duration time of

Table 7. Swelling index of pellets when reduced with charcoal at 1250°C for 25 min. Ores were roasted before pelletizing.

Name of tested ores \ Roasting tem.	1000℃	1300℃	Not roasted
Brazil	21.2	3.5	6.7
Swaziland	− 5.7	− 7.2	−10.0
Hamersley	7.1	− 7.2	− 1.4
Portlady	3.6	7.1	8.6
Goldsworthy	2.8	− 3.6	− 8.6
Goa	7.1	− 3.6	10.0
Krivoy-Rog	7.1	0	7.1
Santafe	− 7.2	0	−17.8
Marcona	14.2	10.6	−12.8
Mosan	28.4	0	5.6

pellets at about 1000°C as short as possible. To ascertain this, reducing tests were carried out under the following four types of elevated temperature conditions.

A. The crucible was placed into a 1000°C furnace and then kept constant for 20 min.;

B. After maintaining the crucible at a temperature of 1000°C for 20 min., this temperature was elevated at a rate of 10°C per minute up to 1250°C and kept constant for 25 minutes;

C. The crucible was placed in a 900°C furnace, and the temperature was elevated at a rate of 10°C per min. up to 1250°C and then kept constant for 25 minutes;

D. The crucible was placed in a 1250°C furnace and kept constant for 25 minutes.

The measured swelling indices of the reduced pellets (Brazil, Swaziland, Marcona and Mozan) were given in Table 8. When using char as the reductant, ores of high swelling property (Brazil and Mozan ores) show a considerable swelling under condition A. Even if the temperature is elevated to condition B and the ore was reduced, these ores were not sintered, and pellets of high density were not obtained. From these results, it is evident that if the reduction conditions which tend to cause a swelling are maintained for a long time, pellets of high quality were not obtained by reduction using a rotary kiln and furthermore by reduction in a static state. Condition C generally tends to accelarate the sintering process faster than the rapid heating under condition D. However, there is an exception when Brazil ore was used with coke as the reductant.

In case of the ore of weak swelling (Swaziland, Marcona), even if the carbon material was changed for another and the conditions (B, C, D) were different, the obtained densities of pellets show no great difference.

Table 8. Swelling index of reduced pellets with various reductantf under several heating patterns (%).

Name of tested ores	Heating patterns / Reductants	1000°C 20 min	1000°C 20 min ↓10°C/min 1250°C 25 min	900°C ↓10°C/min 1250°C 25 min	1250°C 25 min
Brazil	Coke	7.1	2.8	− 1.4	−10.7
	Charcoal	42.9	37.1	− 4.2	6.7
	Lignite char	10.7	0.0	−10.7	− 3.5
Swaziland	Coke	0.0	− 7.8	−15.7	−14.2
	Charcoal	− 3.5	− 9.9	−13.5	−10.0
	Lignite char	1.4	− 9.3	−15.0	−12.8
Marcona	Coke	0.0	−13.6	−15.7	−20.7
	Charcoal	3.6	−10.0	−12.8	−12.8
	Lignite char	3.6	−15.6	−14.3	−13.6
Mosan	Coke	1.5	− 8.5	−13.6	−12.8
	Charcoal	28.6	28.6	0.0	5.6
	Lignite char	3.6	−16.3	−10.6	−10.0

These above mentioned results show that in order to manufacture pellets of high strength, it is essential to pass through 1000°C as quickly as possible. Also, favourable conditions for elevating temperatures depends on the type of carbon materials and kind of ores. This seems to be caused by the fact that the progress of reduction is closely related with the sintering mechanism, and that this relation determines the ultimate quality of pellets.

V. Study of Abnormal Swelling

1. Mineral phase of Iron Ores

The abnormal reductivity of iron ores has been investigated hitherto from a point of view of mineral structure. For instance, Watanabe et al.[5] showed that some regular structures (intergrowth, twin) are generally observed in a fine order when pellets swell abnormally. Likewise regarding micro twin, it is estimated that some external pressure producing internal stress in the crystal would exist. Ishimitsu[11] says in his consideration regrading heat degradation that the constituent mineral of the ore was subjected to dynamic metamorphism or heavy pressure action caused by the dead load of the ore deposit, and was naturally strained. Fuwa et al.[12] considered that the abnormal swelling is a general pheonomenon which developed in case of reducing relatively pure, fine ores by CO-gas, and the reason why some ores do not show abnormal swelling is attributable to th nature, quantity and the state of impurities contained in ores caused by the difference of the origin of iron ore deposit. Ishimitsu et al.[13] estimate that in process of swelling, the separation of each grain and development of fine grains are required as an essential condition before formation of the fibrous structures. Further, regarding the abnormal swelling phenomenon, they indicated that the raw materials are possessed of some special basic factors which bring about the swelling. Regarding this basic factor, Ishimitsu et al. pointed out a instability of the mineral phase, but came to no definite conclusion.

The authors also think that the reason why the fibrous metallic irons are formed and why the ores show swelling in the process of pellet reduction, can be traced to the origine of the ores. In other word imperfection of crystallization, amorphous state of goethite by dehydration and instability of mineral phase such as hematite and magnetite may be attributed to the cause. However, our studies have not yet reached the stage of drawing deductions beyond the opinions of the above mentioned researchers.

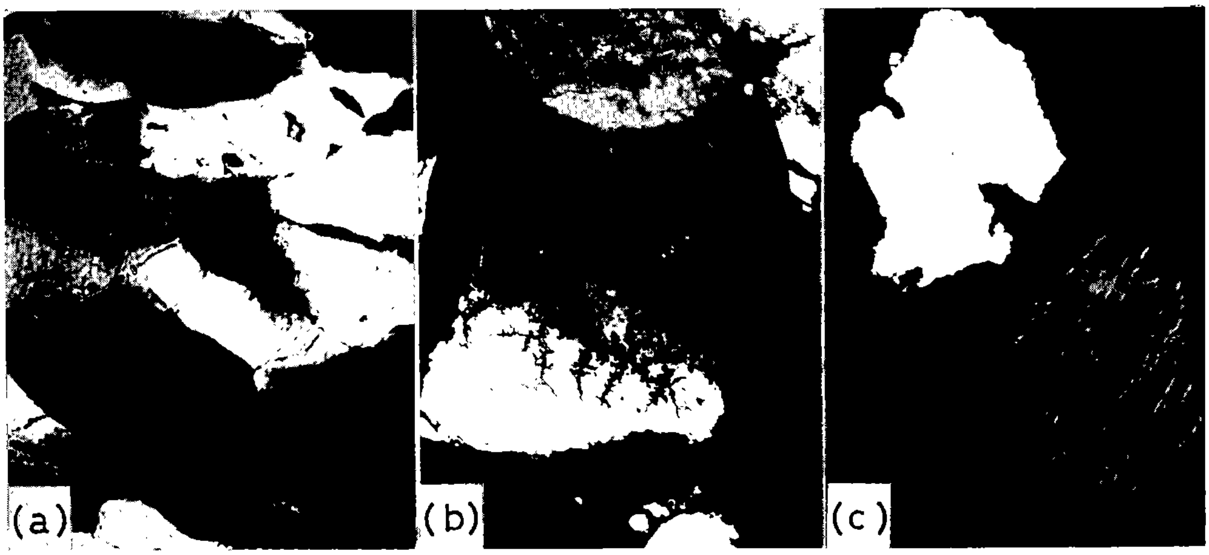
With reference to the 10 different species of ores below, the authors have classified the causes of swelling into several groups by some supplementary experiments.

(1) Ores of high swelling index

The Brazil ore in which the grains are arranged in a specific direction, cause cracks by heating by the difference of heat dilatation. According to Yamada et al.[1] the specific surface area increases due to pulverization which resulted in the reduction velocity to become faster, can be related to the abnormal swelling.

It is expected that the Portlady and Goa ores contain much goethite, and that hematite underwent a considerably intensive weathering and become instable. As one of the reasons heating and dehydration occurs and amorphous hematite is formed, and owing to its activity the reduction progresses rapidly.

The Kriboy-rog and Mozan ores were subjected to dynamic metamorphism. Consequently, it can be also assumed that within the crystals strains are produced. Ishimitsu et al.[11], reported that iron oxides which are capable of detecting the presence of strains in opaque minerals, have not yet been found. But, useing chemical analysis and X-ray diffraction, it was clearly shown that these two ores contain an abundance of quartz. Therefore, by separating this quartz by the gravity concentration method and making a thin leaf of quartz, microscopic observations were carried out. The results are given in photo. 5(a), (b). From the photo., it is clear that the two ores show clearly a abnormal extinction under polarization of light and the presence of strains in quartz crystals were confirmed. As a result, it can be expected that in iron oxide internal strains exist, produced by the stress similar to that in the quartz crystal. If the presence of this stress is an actual fact this stress itself could be a cause of heat cracking, and the main factor of the progress of abnormal



(a) Krivoy-Rog. (b) Mosan. (c) Brazil. x400

Photo. 5 Ertination stage of quarts included in iron ores. +nicol

reduction is due to the weak points in the crystals.

In quartz which was contained in Brazil ore that was subjected to dynamic metamorphism, an examination was made under a microscope. The results are shown in photo. 5(c). In this case, granification is not advanced, and the direction of extinction is clear and no strain is observed. Consequently, we can not discuss the strains in the iron ore crystal merely from the observations on the co-existent quartz. With special reference to this, Watanabe et al. report that the Rio. Doce (Brazil) ore which was subjected to intensive metamorphism, did not have any micro twins.

(2) Ore of Weak Swelling index

The Swaziland ore is massive and its grain boundary is of mosaic structure. The Goldsworthy ore has numerous developed columnar grains and a clear grain boundary. Refering to the regularity of structure of the two ores, no noteworthy findings are seen.

Harmersley ore contains goethite, but this ore is characterized by the fact that hematite and goethite are clearly separated unlike Portlady and Goa ores. Further, the grain boundary of hematite in general show a mosaic structure. Accordingly, with special reference to swelling, it is important to investigate the degree of weathering of the hematite, or the state of its grain boundary rather than the quantity of goethite.

As mentioned above, the investigation of the ores of weak swelling index is not sufficient. It can be seen that most of these ores are massive and somewhat irregular in their structures. On the basis of the fact that the fibrous materials are generated from the wustite phase, a discussion on the relation between its cause and the crude ore structure will be important.

However, an investigation of the reduction of wustite phase is considered to be more important.

(3) Non-Swelling Ores

Santafe and Marcona ores have their origine in metasomatic deposits, containing large alkali-components and pyrite of high sulphur. The Marcona pellet was first noted as the pellet which brought about abnormal swelling, but the sample used for the present experiments did not show any swelling. This seems to be a contradiction. It is noted that magnetite ores are extremely rich in sulphur, compared with the other ores. Under a microscope, magnetite shows that most of sulphur exists as pyrite. Further, it was confirmed that the presence of pyrite could prevent abnormal swelling. The particulars will be explained in VI. 1.

2. Roasted Ores

As mentioned in IV. 6, when ores roasted at a temperature of 1000°C or 1300°C are used as the sample, the reduced pellets of the roasted ores show a much higher swelling than that of the reduced pellets from the crude ores. One of the reasons for this is due to the fact that as a result of roasting the ores at 1000°C the progress of recrystallization is not sufficient and the crystals are in a unstable state. The ores which are mixed with carbon materials and heated to the reduced pellets, after roasting at a temperature of 1300°C, show a lower degree of swelling compared with that of the ores roasted at 1000°C. This is due to the fact that crystals were stabilized by roasting at a high temperature.

Kodama et al.[14] described that the oxidized pellet, roasted sufficiently at 1300°C, does not swell when the pellet reduced is by CO. However, in case of reduction of the green pellet, even if the ore is roasted at a temperature of 1300°C, the binding force between the grains is wesk, and up to a certain degree swelling will be inevitable, because the reduction is conducted merely in the state of consolidating the pulverized ore and carbon mixture into briquette. Nakazawa et al.[15] also confirmed similar results in the reducing experiment of the oxidized pellets, pulverized and molded under pressure.

In V. 1, Marcona and Santafe ores were classified under non-swelling ores, but the Marcona causes a abnormal swelling when calcining the reduced pellet after roasting it at 1000°C. This abnormal swelling is due to the disappearance of most sulphurs and the oxidation of magnetite to hematite. On the other hand, the Santafe ore show a weak swelling even in case of roasting at 1000°C. The difference from Marcona ore should be attributed to the oxidized hematite phase (see Table 7).

3. Generation of Cracks

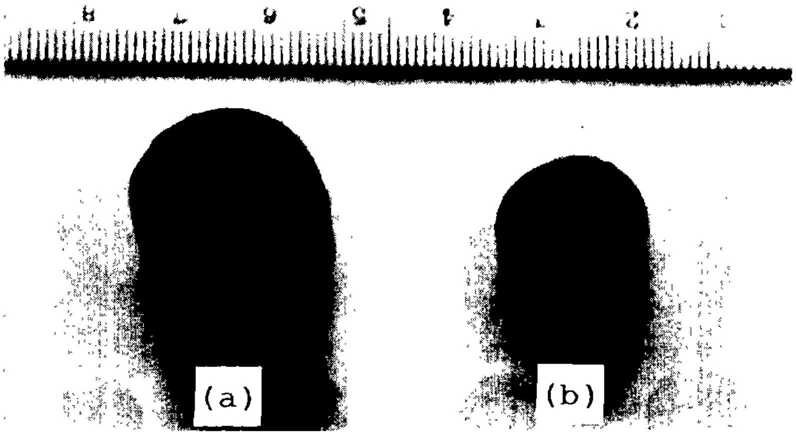
Brazil ore show swelling when reducing it with charcoal, while it produces cracks when reducing by coke. In the case of reducing the Brazil ore, cracks come out very remarkably compared with the other ores. When reducing in a spherical ball state (a pan type pelletizer used) instead of briquette, the cracks are formed in pomégranate shape. This property is considerd to be related to heat cracking, but a detailed study was not carried out.

Ⅵ. *Prevention of Abnormal Swelling and Generating of Cracks*

1. Addition of Sulphur

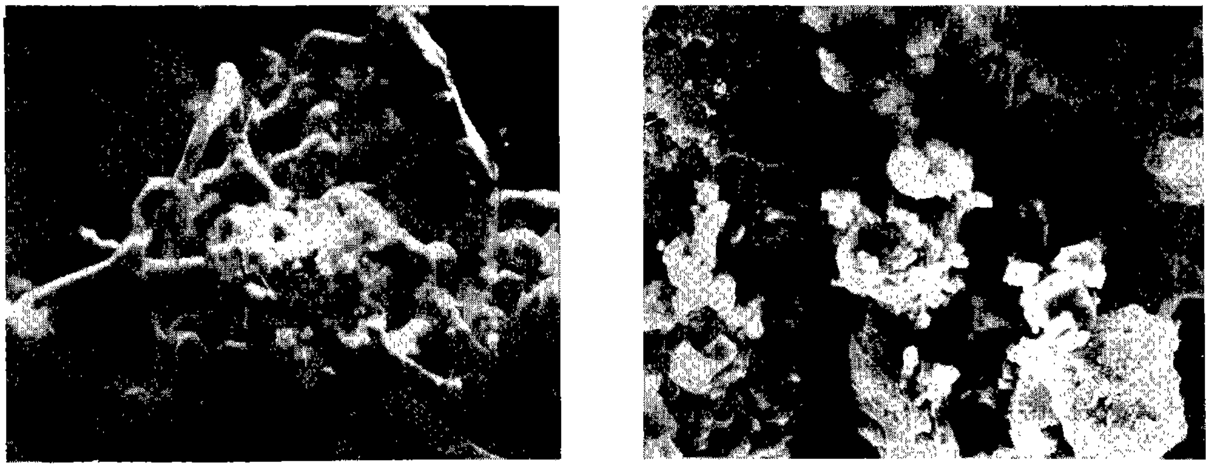
When green pellets were made from Marcona ores roasted at 1000°C, the charcoal as internal and external carbon materials, were reduced at a temrerature of 1000°C for 20 min, and the pellets swell more than 50 % in a diametral direction. Although Marcona crude ores do not show swelling, the same ores roasted at 1000°C swell considerably. The reson is due to oxidation of magnetite to hematite and the decrease of sulphur content of pyrite. This assumption was already described in *V*. 1 of this paper. In order to investigate the effect of sulphur on swelling, the ore roasted at 1000°C was mixed with 2.2 % of pyrite (S 1.14 %) and then heated to reduce pellets using charcoal as carbon material. At this point, no swelling was observed (see Phote. 6). The results of survey on the structure of these pellets by a scanning electron microscope were given in Photo. 7. From this. Photo. 7, it is clear that when reducing the Marcona roasted ore useing charcoal as the carbon material, the formation of fibrous iron is restrained.

It was confirmed that an addition of pyrite prevents swelling. Thus, the experiments on the effec of an addition of 2.2 % of pyrite on swelling were carried out on four kinds of crude



(a) no addition of pyrite (b) added 2.2wt % of pyrite

Photo. 6. Effect of pyrite addition on swelling, in case of Marcona ore oxidized and desulfurized at 1000°C in air. Pellets were reduced with charcoal at 1000°C for 20min.



(a) no addition of pyrite (b) added 2.2wt % of pyrite ×2000

Photo. 7. Microstructure of pellet shown in Photo. 6.

ores (Brazil, Swaziland, Marcona, Mozan). Provided that the ores are rapidly heated at 1250°C by using charcoal as carbon material, the effect of the addition of pyrite on swelling was compared with that of non-addition of pyrite. The results are shown in Photo. 8. From the Photo., it was clearly confirmed that in Marcona containing a high percentage of sulphur, the influence of pyrite addition does not appear, but in the other ores, contractions of the ores are seen, and the effect of pyrite addition could be clearly confirmed.

Fine et al.[16] have already described that pyrite addition has an effect on increasing the strength of reduced pellets. In this case, the effect of pyrite addition is attributed to the fact

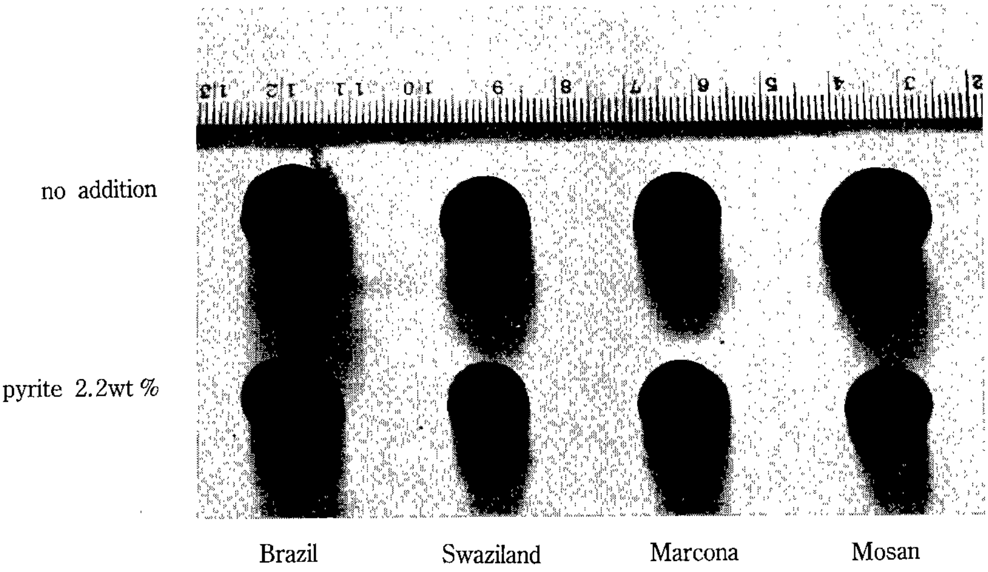


Photo 8 Effect of pyrite addition on swelling for various ores. Pellets were reduced with charcoal at 1250°C for 20min.

that a liquid phase of sulfide is generated at a low temperature, and diffusion of irons become easy and as a result sintering advances steadily. Further, they described that besides the addftion of pyrite, introduction of H_2S gas is also effective.

The authers have established that besides pyrite the addition of 0.8 wt% sodium pitch-sulfonic acid (S 15.9 wt%) prevents pellets from swelling. It was also confirmed that when the green pellets, added with and without sodium pitch-sulfonic acid, were reduced in the same crucible, the pellets witout sodium pitch-sulfonic acid also did not show any swelling. From this result, it can be seen that mixing of the gaseous sulphur with the reducing atmosphere can be effective in the same way as an addition of pyrite. However, after reducing the pellets, about 50 % of added sulphur remains in the pellets, so that an addition of sulphur is undesirable from a view point of quality of pellets.

As described by Fine et al.,16) the effect of sulphur on the increase of the reduced strength can be attributed to the fact that besides the development of a liquid phase with lower melting point, growth of fibrous iron is suppressed. Namely, it is expected that when reduced from wustite to metallic iron, the ions diffuse into the nucleus of metallic iron and as a result, the metallic iron grows in the fiber form. If sulphur exists at this stage, this sulphur will be adsorbed onto the surface of the iron rich wustite, so that rapid nucleus growth of metallic iron will be checked and the fibrous structure of metallic iron may not be formed. However, in what manner sulphur is adsorbed, is not unknown as yet.

When reducing the pellets at various temperatures (*IV*.5) by the use of charcoal and char of even reactivity, abnormal swelling was observed only when charcoal was used. One of the reasons is considered to be a difference of sulphur content of carbon material, and alkali content.11) The difference of volatile matter8) are considered to be the reasons likewise.

2. Addition of Lime

Kodama et al.14) described that sufficient firing at a temperature of 1300°C when the oxidized pellet was produced and an addition of SiO_2 and CaO are effective as a preventive of swelling in the reducing process. As a addition agent, CaO is more effective. The adove mentioned adthors considered that addition of CaO strengthen the bond of the grains. The authors assumed that a large quantity of FeO was produced when producing the reduced pellets, and a liquid phase form readily when slag forming components are abundant, may have a great influence on the reducing process of pellets. Thus, the experiments were carried out with CaO addition.

The reduced pellets, mixing the four kinds of ores (Brazil, Swaziland, Marcona and Mozan) with 4.4 wt% of reagent $CaCO_3$ (CaO 2.5 wt%), and the same pellets without reagents, were reduced respectively and compared with each other. Cokes were used as internal and external carbon materials. A rapid reduction was conducted at a temperature of

1250°C for 20 minutes. The experimental resuits are given in photo. 9.

In these experiments, prevention of the pellets from cracking was achieved especially in the Brazil ore, and the diametrical compression strength of pellets increased from about 40 kg up to 70 kg by the addition of lime. The relationship of the type, quantity, basicity of the addition agent for increasing the pellet strength with the rate of metallization, and the problem of desulfrization is an important theme for further investigation.

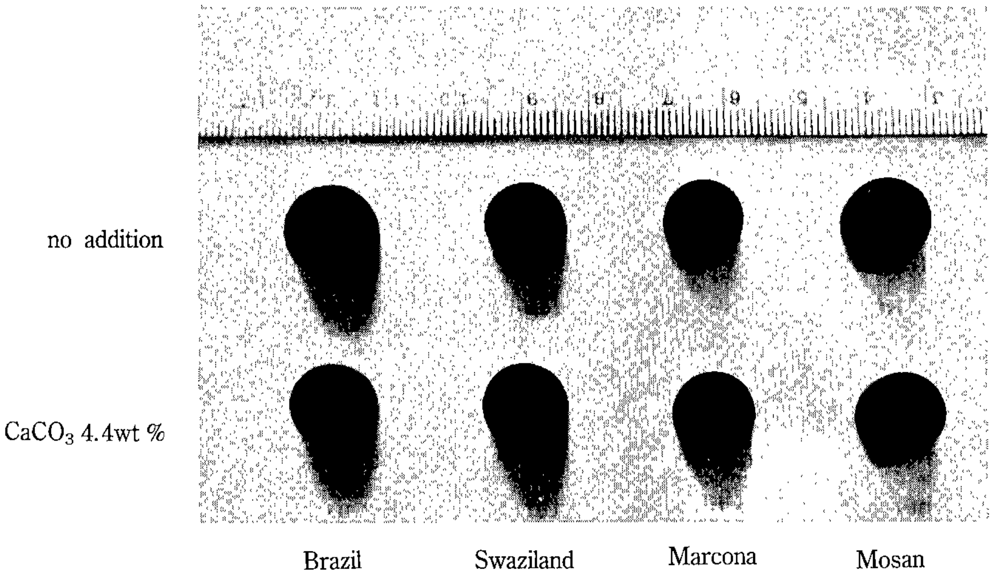


Photo 9 **Effect of $CaCO_3$ addition on cracking for various ores. Pellets were reduced with coke at 1250°C 20min. Effect was remarkable for Brazil ore, but was not notable for others.**

Ⅶ. *Summary*

(1) When producing the prereduced pellets by the combined reductant method, some ores cause abnormal swelling by useing of carbon material of high reactivity. The reason can be attributed to the formation of fibrous iron in progress of rapid reduction.

(2) The fibrous irons are generated at a temperature of around 1000°C in large quantities. In order to produce the reduced pellets of high density, it is necessary that the temperature be elevated so that the duration time of 1000°C or thereabouts may be as short as possible.

(3) Formation of fibrous iron is considered to be related to the instability of minerals in the reduction process. The ores of a strong swelling is considered to be caused by the following factors : a fixed directional development of crystal, intensive stress within the crystal, and the presence of goethite. The ores of a weak swelling-index often show an irregular structure. The discussion of the relation of fibrous iron formation with the mineral phase is still unclarified.

(4) Swelling property of the ores roasted in the atmosphere is generally stronger than that of crude ores. The reason may be attributed to the fact that the recrystallization progress of hematite is not sufficient and hematite is in an unstable state.

(5) The addition of sulpur can prevent the pellets from abnormal swelling. The addition of pyrite or sulfonic acid, instead of sulphur, is also effective. The reason why the presence of sulphur prevents the growth of fibrous metallic iron, is due to the fact that sulphur is adsorbed onto the surface of the iron rich wustite, and consequently the rapid nucleus growth of metallic irons is checked. Another reason is the formation of of liquid phase at relativery low temperatures.

(6) Addition of CaO also can prevent the reduced pellets from development of cracks. The reason is considered to be the easy generation of liquid phase and the subsequent increase of bonding force between the grains.

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Chapter 3

Effect of the Addition of $Ca(OH)_2$, SiO_2, and Pyrite on the Shrinkage and the Metallization of Pellets Containing Coke during Firing

Sogo SAYAMA and Yoshinobu UEDA

Synopsis

Investigation has been caarried out on the effect of $Ca(OH)_2$, SiO_2, *and pyrite addition on the shrinkage and the metallization of pellets during the reduction in coke bed.*

Four kinds of iron ore were used as test materials. The mixed powder of the test materials with fixed amounts of $Ca(OH)_2$, SiO_2, *and pyrite, and 10wt% of coke was pressed in a die to make green pellets. The pellets were embeded in a crucible charged the coke powder to be reduced in vertical tube furnace at the temperature of 1200 to 1300°C.*

$Ca(OH)_2$ *addition to the pellets was very effective for shrinkage because of the formation of a large amount of liquid phase in the pellets, and also for metallization because of the prevention of fayalite formatioon. The necessary amount of* $Ca(OH)_2$ *for the improvement of shrinkage and metallization depends on the origin of ore used and the reduction conditions. At a reducing temperature of 1250°C, for example, it was found that the addition of about 4wt% of* $Ca(OH)_2$ *was generally effective owing to the formation of slag containing a large amount of CaO.*

Prereduced pellets added CaO can be expected to have high fusibility in the melting process of pellets, because metallic iron is surrounded by slag with a low melting point and low content in FeO.

SiO_2 *addition was not favorable either from the viewpoint of strengthning and of the metallization of the pellets. Only 0.2wt% of pyrite was effective in pellet shrinkage, and pellet strength increased. However, desulphurization was needed because of remains of high percentage of sulphur after reduction.*

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I. Introduction

The self-fluxing pellets with the lime made by heating in oxidizing atmosphere have been produced in large amounts because of the high reducibility. In the same way, in the production of iron using prereduced pellets, CaO addition is expected to improve the reducibility of the pellets. Tanaka, Ohba, Ozawa, Kamiya, and Tanaka have previously reported on their experimental results regarding to the iron production using green ball bound by cement and bentonite.[1] Kihlstedt reported on the agglomeration of iron ore concentrate of cold-bound ball containing lime, because the reducibility and the strength of lime-bound pellet during reduction are high in comparison with the sintered pellets.[2] But they did not study on the detail behaviour of slag-forming materials in reduction.

The present authors have reported that an appropriate amount of lime addition prevents the cracking of the pellets and promotes their shrinkage.[3] In the present work, the mechanism of the reduction of prereduced pellets adding $Ca(OH)_2$ was investigated, and it was found that the addition of CaO improves the metallization of the pellets. Further, the effects of the addition of SiO_2 and pyrite were also studied.

The fusibility of the prereduced pellets has been investigated in our second report.[4]

Ⅱ. Materials and Method

1. Experimental Material

Four kinds of iron ore from Brazil, Swaziland, Marcona, and Mosan, and coke as reducer were used in the experiments. The chemical compositions of the ore are shown in Table 1.

Table 1. Chemical compositions of orea and porosity of green pellets

Tested ores	Chemical compositions (wt%)								Porosity of green pellets (%)
	T. Fe	FeO	SiO_2	Al_2O_3	CaO	MgO	S	C.W.	
Brazil	65.20	0.20	4.29	1.32	–	0.14	0.01	0.66	37.5
Swaziland	63.65	0.18	4.68	2.15	–	–	0.01	0.31	38.5
Marcona	63.22	15.29	5.08	0.82	1.08	1.76	1.61	0.82	36.8
Mosan	58.47	22.55	17.25	0.42	0.71	0.59	0.03	0.64	40.1

2. Experimental Method

The given amounts of Ca $(OH)_2$, SiO_2 and pyrite were mixed with the finely pulverized iron ore and 10wt% of coke. Mixed powder with 10wt% of water was pressed to make green pellets in a die with the pressure of 320 kg/cm^2. The size and weight of green pellet were 14.0 mm in diameter, 5 mm in height, about 3 g in weight.

The green pellet after dehydration was embeded in a stainless steel crucible (40 mm in diameter, 70 mm in height) together with coke (−14 mesh). The crucible was placed in a vertical tube furnace which was preheated at the reducing temperature of the pellets. After the reduction the crucible was cooled to room temperature.

The porosity of the green pellet containing 10wt% of coke is also shown in Table 1.

Ⅲ. Results and Discussion

1. $Ca(OH)_2$ Addition

In Fig. 1, the effects of the addition of pure $Ca(OH)_2$ up to 7wt% on the change of the diameter, the total Fe content and the metallization ratio of pellets are shown about the reduction times of 20, 30 and 60 min at 1250°C. As an example of experimental results, Fig. 2 shows the diameter, the total iron content, and metallization ratio of the pellets reduced at 1200°C for 20, 30 minutes, and of the pellet reduced at 1300°C for 30 minutes. It was shown that an increase in the addition of $Ca(OH)_2$ lowers the iron grade of the reduced pellets. However, it was found that the effects of $Ca(OH)_2$ addition on the metallization ratio and pellet diameter depend upon the origin of the ore and reducing condition. The effect of the origin of

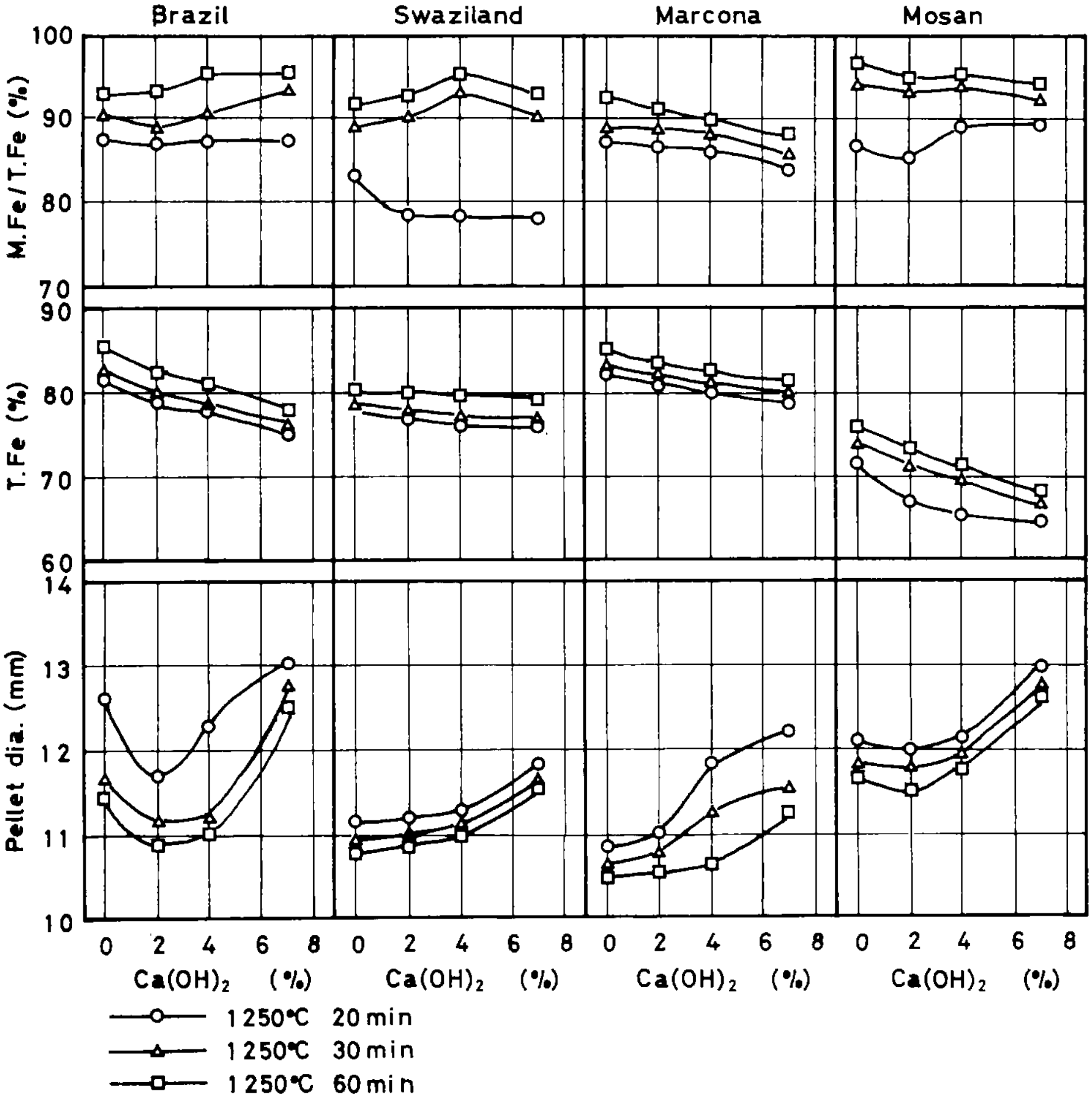


Fig. 1. Effects of $Ca(OH)_2$ addition on Fe content and diameter of pellets reduced at 1250°C

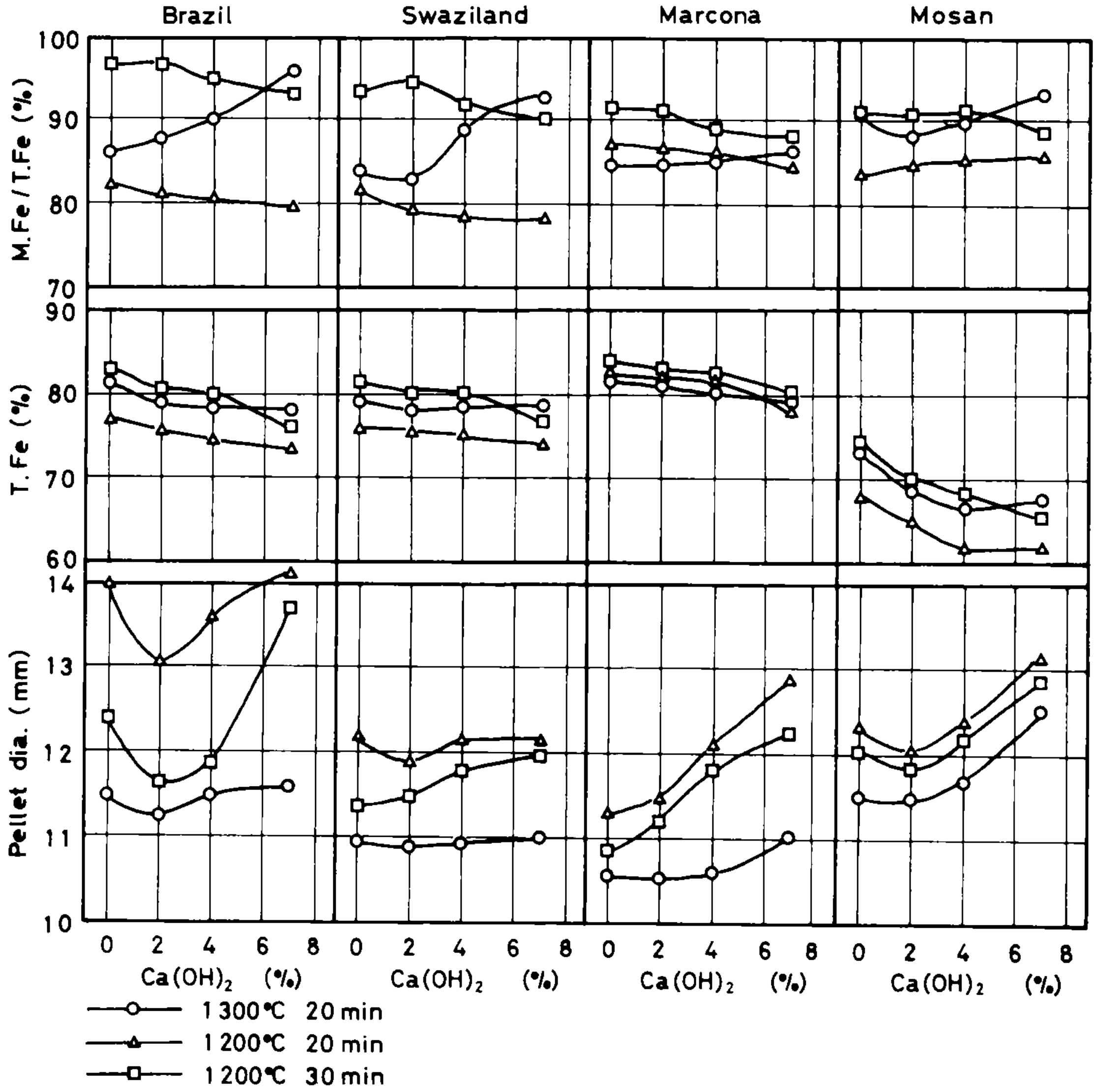
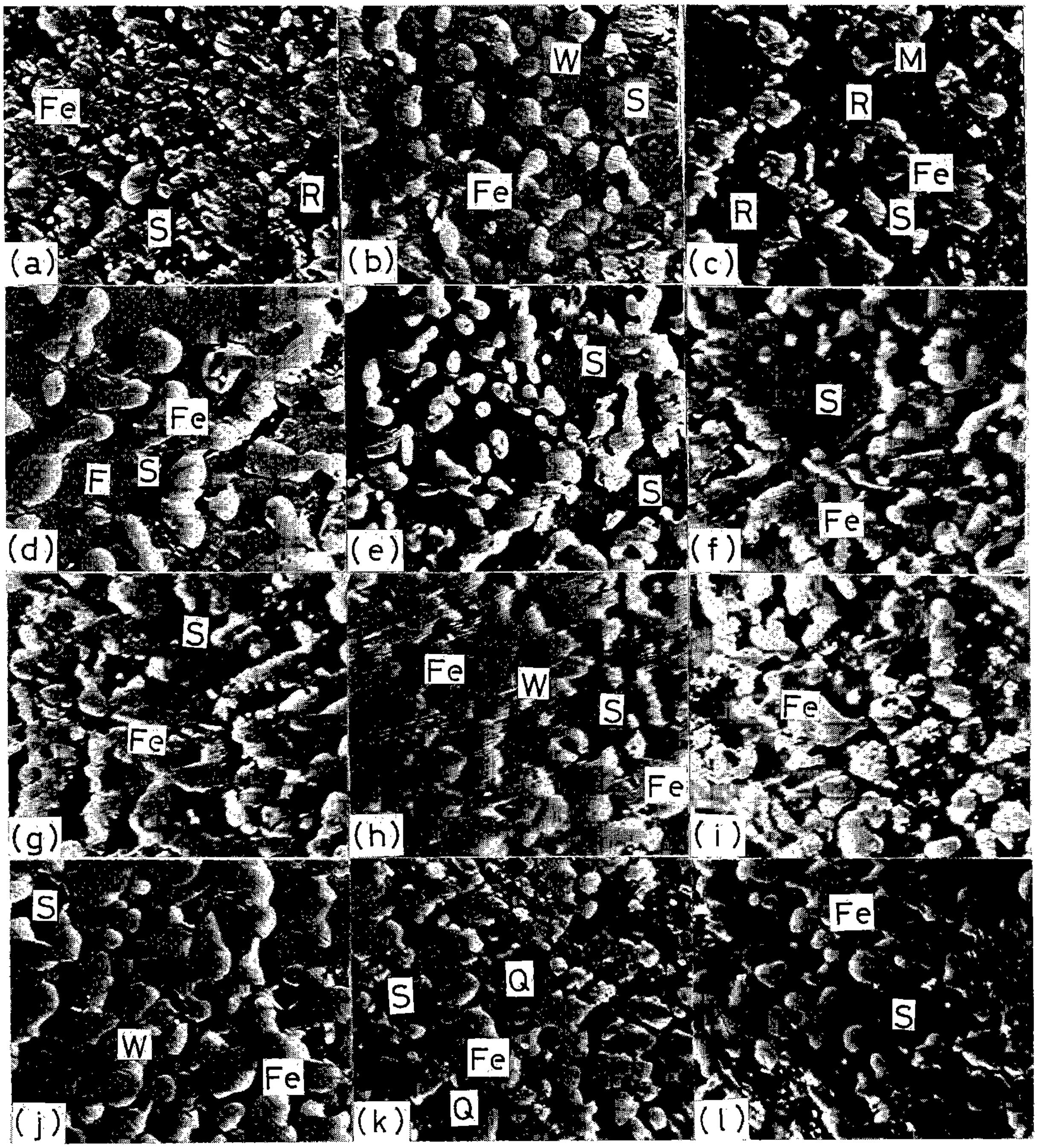


Fig. 2. Fe content and diameter of pellets containing various amount of $Ca(OH)_2$ reduced at 1200°C and 1300°C.

ore will be discussed in the following section.

(1). Brazil Ore

The prereduced pellets of Brazil ore often cracked during reduction, but the formation of cracks decreases with the addition of 2 to 4wt% of $Ca(OH)_2$ and the prereduced pellets show the shrinkage of diameter. The microstructures at the center of the pellet reduced for 20 min at 1250°C are shown in Photo. 1, in which 1(a) and (b) are non-addtion and 2wt% addtion of $Ca(OH)_2$ respectively. Acoording to the results it was recognized that the 2wt% added pellets showed better formation of slag bonds, and the shrinkage of the pellets proceeded. When the amount of added $Ca(OH)_2$ increased to 7wt%, the volume of liquid phase decreased and shrinkage of the pellet did not proceed (Photo. 1(c)). In order to clarify why the volume



Fe : metallic Fe. W : wustite. S : silicate glass. F : fayalite. Q : quartz. M : fine reaction products. R : resin. (a) Brazil, $Ca(OH)_2$ 0%, 1250°C, 20min. (b) Brazil ore 2% $Ca(OH)_2$, 1250°C, 20min. (c) Brazil ore 7% $Ca(OH)_2$, 1250°C, 20min. (d) Brazil ore 0% $Ca(OH)_2$, 1300°C, 20min. (e) Brazil ore 7% $Ca(OH)_2$, 1300°C, 20min. (f) Swaziland ore 0% $Ca(OH)_2$, 1250°C, 60min. (g) Swaziland ore 4% $Ca(OH)_2$, 1250°C, 60min. (h) Marcona ore 0% $Ca(OH)_2$, 1200°C, 20min. (i) Macona ore 4% $Ca(OH)_2$, 1200°C, 20min. (j) Macrona ore 4% $Ca(OH)_2$, 1300°C, 20min. (k) Mosan ore 0% $Ca(OH)_2$, 1250°C, 30min. (l) Mosan ore 4% $Ca(OH)_2$, 1300°C, 30min.

Photo. 1 Microstructure of inner part of reduced pellets containing various amount of $Ca(OH)_2$. x400 of the liquid phase decreased with increasing CaO contents, the distribution of CaO in the pellet was observed by a X-ray microanalyzer. As clearly seen in Photo. 1 (c), a considerable amount of fine particles with the diameter of approximate 10 μ or much smaller were dispersed. The compositions of this substance were not uniform and changed with the position of analysis by a X-ray microanalyzer. The approximate compositions of this substance were 8%FeO, 50%SiO_2, 12%Al_2O_3 and 28%CaO. Thus, this substance seemed to be a reaction product with a high melting point, because the bond in the pellets was not strengthened.

In the reduction of the green pellets for 30 min at 1200°C, it was recognized that the volume of the formation of liquid phase becomes small and the metallization ratio decreases with increasing the addition of $Ca(OH)_2$. The observation on the microstructure of the pellets revealed that fine reaction products increases with increasing the addition of $Ca(OH)_2$. The approximate compositions of this substance produced during the reduction at the addition of 4wt% of $Ca(OH)_2$ were 12%FeO, 52%SiO_2, 11%Al_2O_3 and 20%CaO. Accordingly it is surmised that the metallization ratio becomes low because of the reduction of FeO in this substance.

It was shown that the metallization ratio in the reduction of green pellets at 1200°C for 30 min was higher than that at 1250°C for 30 min. It is surmised that the increase of the volume of the liquid phase at a higher reducing temperature results to the lowering of the passage of the reducing gas and the metallization ratio becomes lower.

The volume of the liquid phase was still large even when 7wt% of $Ca(OH)_2$ was added at 1300°C. The structure of the pellets reduced for 20 min with non-addition and addition of 7wt% of $Ca(OH)_2$ are compared in Photos. 1(d) and (e). The approximate compositions of the liquid phase in Photos. 1(d) and (e) were respectively 71%FeO, 28%SiO_2, 4%Al_2O_3 and trace CaO, and 10%FeO, 45%SiO_2, 6%Al_2O_3 and 36%CaO. These results indicate that when $Ca(OH)_2$ is not added, fayalite is formed and FeO content in liquid phase is high, but when $Ca(OH)_2$ was added, the FeO content of the liquid phase is lowered, and the increasing tendency of the metallization ratio is observed.

(2). Swaziland Ore

Within the additions of 0 to 4wt% of $Ca(OH)_2$ the pellets showed a large shrinkage. When the amount of the addition increased to 7wt%, the shrinkage was retarded similarly to the Brazil ore.

In the case of the reduction for 30 and 60 min at 1250°C, the metallization ratio of the pellets adding $Ca(OH)_2$ is high. The structures of the inner part of the pellets reduced for 60 min at 1250°C with and without the addition of 4wt% of $Ca(OH)_2$ are shown in Photos. 1 (f) and (g). The approximate compositions of the liquid phase without the addition of $Ca(OH)_2$ were

67%FeO, 22%SiO_2, 9%Al_2O_3 and trace CaO, and those with the addition of $Ca(OH)_2$ were 8%FeO, 40%SiO_2, 20%Al_2O_3 and 20%CaO. The latter showed a higher progress of reduction. Further, when the pellets were reduced for 20 min at 1300°C, the FeO content in the liquid phase decreased with increasing the addition of $Ca(OH)_2$.

(3). Marcona Ore

By the addition of $Ca(OH)_2$ the shrinkage of the pellets was retarded, and further the lower metallization ratio was obtained. This ore contains approximately 3wt% of basic slag-forming materials. Even in the non-addition of $Ca(OH)_2$ the formation of liquid phase was large at the reduction for 20 min at 1200°C, and the shrinkage of pellets proceeded (Photo. 1 (h)). But, when 4wt% of $Ca(OH)_2$ was added, the volume of liquid phase decreased (Photo. 1 (i)).

In the reduction of the pellets for 20 min at 1300°C the volume of the liquid phase was large, even when 4wt% of $Ca(OH)_2$ was added. However, a large amount of wustite was observed in the inner part of the pellets because the passage of reducing gas was not good, and the metallization ratio did not increase (Photo. 1(j)). Thus, it may be said that in Marcona ore containing such high basic slag-forming materials, the effect of $Ca(OH)_2$ addition improving the shrinkage and the metallization of the prereduced pellets is limited.

(4). Mosan Ore

This ore contains approximately 17wt% of SiO_2, which is very high in comparison with other ores used as test sample. The addition of 2wt% of $Ca(OH)_2$ promoted a tendency for shrinkage. Little changes were observed on the metallization ratio even in the addition of $Ca(OH)_2$ at the reduction of 30 or 60 min and 1250°C. The structures of the inner part of the pellets reduced for 30 min at 1250°C with non-addition and with the addition of 4wt% $Ca(OH)_2$ are shown in Photos. 1 (k) and (l). According to this, when $Ca(OH)_2$ was not added, a considerable amount of non-reacted SiO_2 surrounded by liquid phase remained. When 4wt% of $Ca(OH)_2$ was added, the liquid phase which have the approximate compositions of 15%FeO, 50%SiO_2, 3%Al_2O_3, 3%MgO and 18%CaO increased, and non-reacted SiO_2 decreased. Thus, with the increase of liquid phase containing FeO, the metallization ratio showed a slight decreasing tendency.

When the pellets were reduced for 20 min at 1300°C, the FeO content in the liquid phase of the pellets adding 2wt% of $Ca(OH)_2$ was approximately 40wt%, but the approximate compositions of the liquid phase in the pellets adding 7wt% were 7%FeO, 50%SiO_2, 3%Al_2O_3, 4%MgO and 30%CaO, and the metallization ratio increased because of the decrease of FeO content in the liquid phase.

2. Reduction Processes at Various Reducing Conditions

It was observed that when the Brazil and Swaziland ores were reduced at a relatively lower temperature (1200°C, 30 min) generation of a liquid phase was low, and the metallization ratio was relatively high. However, since a lower reducing temperature it does not improve the sintering of fine ores in the pellets, a higher reducing temperature is profitable for shrinkage of the pellet.

In order to investigate the reducing condition in which the pellet of high metallization ratio and of high density can be achieved, the experiment was made using the Swaziland ores added with 2 wt% $Ca(OH)_2$ so that generation of the liquid phase increases in its quantity in the reducing process (shown in Fig. 2). To discuss the effect of the reducing condition on pellet quality, reduction experiments were made under several heating conditions shown in Table 2. Summarization of these results and the observation of the pellet structure were as follows :

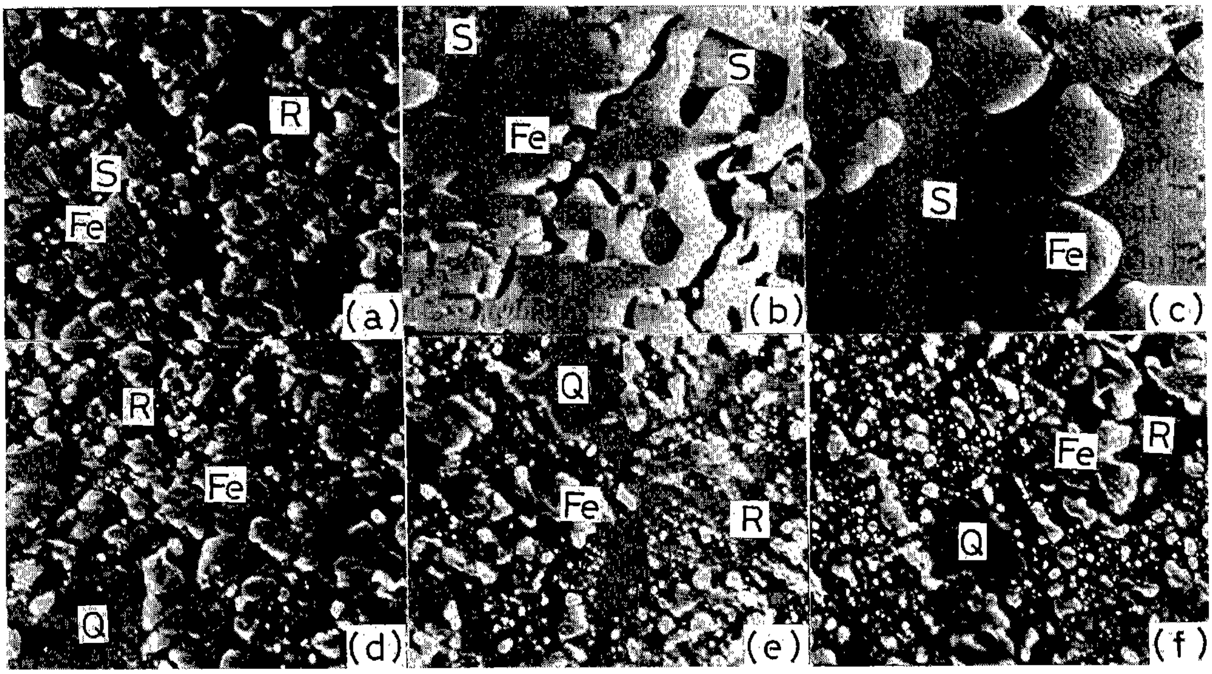
Table 2. The effect of the heating pattern on the quality of reduced pellets

Heating pattern	T. Fe (wt%)	MFe/T.Fe (%)	Pellet dia. (mm)
1250℃ 30 min	78.2	90.1	11.0
1250℃ 120 min	79.2	92.9	10.8
1150℃·120 min	80.2	93.3	11.4
1150℃ 120 min→ 1250℃ 120 min	81.6	98.1	11.3

Tested ore : Swaziland ore added 2 wt% of $Ca(OH)_2$

(1) Photo. 2 (a), (b) and (c) show respectively the structures of the pellets reduced at a temperature of 1250°C for 120 minutes. As shown in those pictures, the pellet reduced at 1250°C has a triple core structure. The structure was composed of two phases ; metallic iron and silicate glass. In the outer part of the pellet, the metallic iron is fine in size and the reduction of FeO in the liquid phase was well advanced (about 2–4 wt% FeO). In the intermediate part, wide layers of the metallic iron are formed, while the inner part indicates the structure in which metallic iron appeared like an island in the liquid phase of higher FeO content (about 55%). Because a thick layer of metallic iron is formed in the intermediate part of the pellet, contact of the inner liquid phase with the reducing gas and the outer liquid phase of lower FeO is shut down and the reducing process is difficult to advance forward.

(2) When the reducing pellet shows the triple core ptructure, the reduction may be considered to progress forward in the following mechanism. In the outer part, the reduction progressed forward relatively sooner until the iron oxide is reduced to metallic iron, and clearance



Fe : metallic Fe. S : silicate glass. Q : quartz. R : resin. (a) 1250°C 120min, outer part. (b) 1250°C 120min, middle part. (c) 1250°C 120min, inner part. (d) 1150°C 120min, inner part. (e) 1150°C 120min~1250°C 120min, outer part. (f) 1150°C 120min~1250°C 120min, inner part.

Photo. 2. Microstructure of Swaziland pellets containing 2 wt% of $Ca(OH)_2$ produced under different reducing conditions. x400

between the metallic iron particles are filled with the liquid phase containing a smaller amount of FeO. Under such conditions, the reducing gas can not penetrate into the liquid phase of the central part through pores. Therefore, the reducing process of the central part advances slowly and the reduction of iron oxide reaches FeO, so that a large quantity of the liquid phase is generated. Thus, the reduction prevails only in the surroundings of the liquid phase. As a result, it is considered that concentration gradient of Fe^{++} is produced between the central liquid phase and the layer of metallic iron in the intermediate part, and Fe^{++} is transported to the interface by diffusion and reduced by CO, so that the layer of metallic iron grows in the intermediate part by high mobility of Fe^{++} in liquid phase.

(3) Photo. 2(b) illustrates the central part structure of the pellet reduced at 1150°C for 120 minutes. In this case, generation of the liquid phase is little and reducing process advances up to the central part.

(4) Photo. 2 (e) and (f) show the outer and central part structures of the pellet reduced at 1250°C for 120 minutes after being reduced at 1150°C for 120 minutes. The liquid phase is low at outer and central parts, the metallization ratio becomes higher and shrinkage of the pellet advanced a little.

(5) To increase the metallization ratio and the density of the pellet, reduction should be performed with restraining the generation of the liquid phase at relatively lower temperatures, and next a heating method should be adopted to advance the reduction and sitering at high temperature. In this case, the generation of the liquid phase is relatively hampered and the sintering by liquid phase dose not improve forward. Consequently, it is needed to investigate in detail the hot reduction property of the pellet such as strength during reducing process for the improvement of pellet quality..

3. SiO_2 Addition

Kodama et al. reported that SiO_2 addition was also favourabe for the prevention of swelling[3]. Figure 3 gives the results of the reduction of pellets adding pure SiO_2 of 0, 2, 4 and 7wt% at 1250°C for 30 min. With the increase in SiO_2 addition, the shrinkage of the pellets

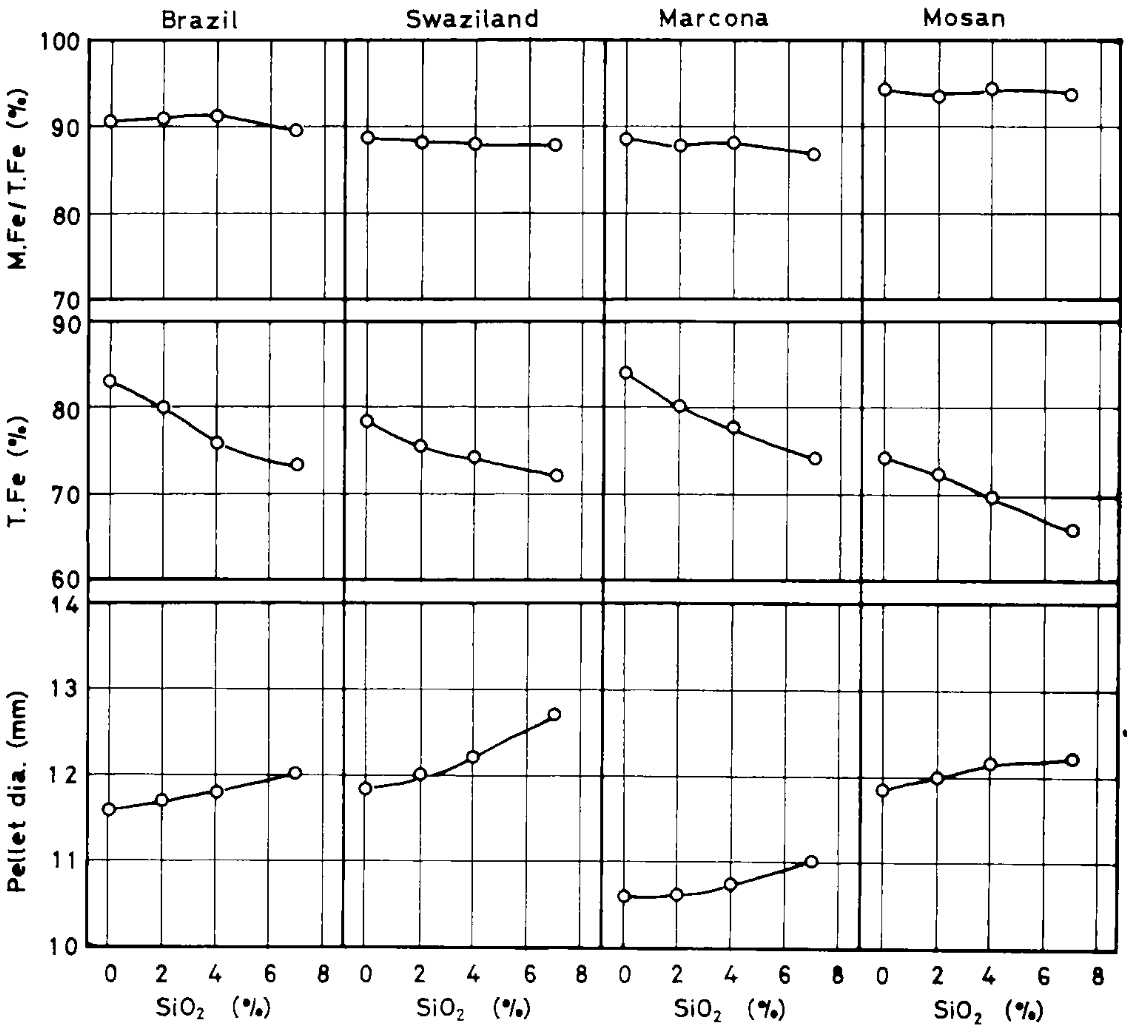


Fig. 3. Effects of SiO_2 addition on Fe content and diameter of pellets reduced at 1250°C for 30 min

was retarded, and no change was observed in metallization ratio. Namely, no effect of SiO_2 was observed. By a microscopic observation, the lare amount of non-reacted SiO_2 was observed and the volume of liquid phase did not increase. Kodama, Shigemi, Ono, Horio, and Azuma[5] reported that the bond of oxidized pellet was strengthened by an addition of SiO_2. However during the firing of the prereduced pellets, both processes of reduction and sintering proceed simultaneously. Therefore, the bond of the pellets should be naturally different from that of the oxidized pellets studied by Kodama *et al.*[5]

4. Pyrite Addition

Fine and Schluter[6] reported that, when pyrite was added to the pellets, its density increases during the reduction due to the formation of the liquid phase of low melting point. The influence of pyrite addition was studied by using the four kings of ore samples, namely, Brazil ore, 2wt% $Ca(OH)_2$ added Brazil ore, Swaziland ore and Mosan ore, excluding Marcona

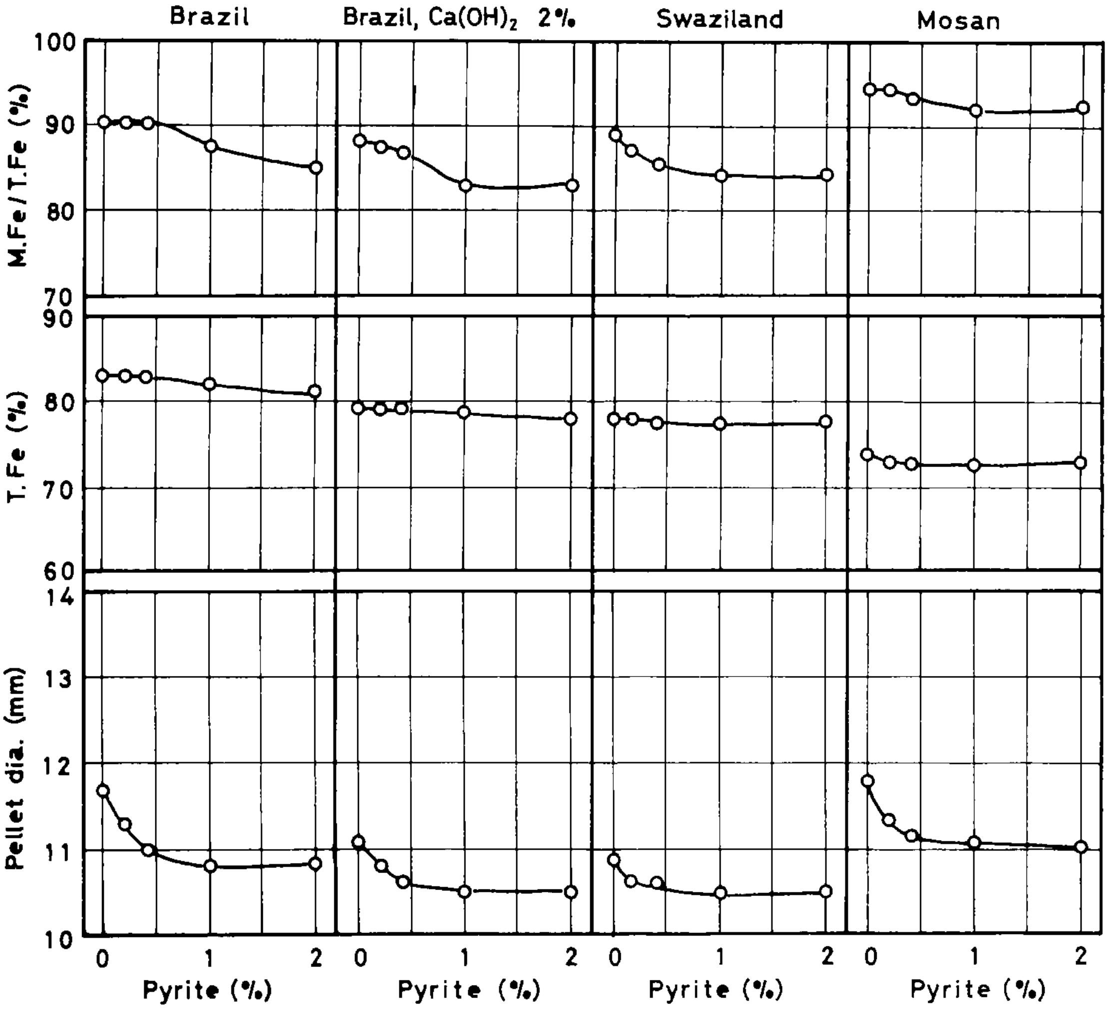


Fig. 4. Effects of pyrite addition on Fe content and diameter of pellets reduced at 1250°C for 30min

ore which had a high content of pyrite. Figure 4 gives the results of the reduction of pellets adding the pyrite of 0, 0.2, 0.4, 1.0 and 2.0wt% at 1250°C for 30 min.

According to the results, even when a small amount of pyrite such as 0.2wt% was added, a large effcct on the shrinkage of pellets was observed. However, with the increase in the addition of pyrite the formation of the liquid phase increased, while the shrinkage of the pellets increased, and the metallization ratio decreased. As clearly seen in the case of Brazil ore, the same addition of $Ca(OH)_2$ and pyrite showed the increase of the shrinkage of the pellets. The residual sulphur in the reduced pellets by the addition of pyrite is high, for example the residual sulphur content by the addition of 0.4wt% pyrite was about 0.2wt% (Table 3).

Table 3. Relation between the pyrite addition and pellet qualities ——pellet diameter and residual S.

Name of ore	Brazil		Swaziland	
Pyrite addition (wt%)	Diameter (mm)	Residual S (wt%)	Diameter (mm)	Residual S (wt%)
0	13.8	0.03	12.6	0.05
0.2	12.9	0.17	11.5	0.15
0.4	12.6	0.19	11.4	0.21
1.0	12.0	0.30	11.1	0.51
2.0	11.1	1.03	11.0	0.99

Reducing temp. : 1200°C
Reducing time : 20 min

IV. Conclusion

The effects of $Ca(OH)_2$, SiO_2 and pyrite addition to iron ore on the shrinkage and metallization of the prereduced pellets were studied. In the present work, green pellets contained 10wt% of coke were embeded in coke (−14 mesh) in crucible, and heated for the reduction. In this method, both reduction and sintering of the pellets would proceed simultaneously. It was clarified that the reaction products (silicate glass) during reduction is an important factor controlling the properties of the pellets. The formation mechanism and characteristics of the above substance remains much unknown and will require further study. However in the present paper, the following results were obtained about the relationship between the quality of the prereduced pellets and the addition of slag-forming materials.

(1) An addition of an appropriate amount of $Ca(OH)_2$ produces favorable results for the reduction of pellets from a point of view of the shrinkage and the metallization of the pellet.

The necessary amount of $Ca(OH)_2$ for the improvement of the shrinkage and metallization depends upon the origin of ores used and the reducing condidions.

(2) The higher the temperature is and the longer the time applies, the shrinkage of the pellets proceeds. This is due to the fact that the formation of the liquid phase is large, and sintering proceeds.

(3) When an optimum amount of $Ca(OH)_2$ is added, the formation of the liquid phase becomes maximum, and the shrinkage shows a good progress. In all ore samples containing the basic slag-forming materials of totally 2 to 3wt% the shrinkage proceeds exceedingly. Therefore, simple relationship can not be obtained between the basicity in the slag-forming materials and the optimum amount of CaO addition.

(4) When the addition of $Ca(OH)_2$ is large and the basic slag-forming materials was contained at the ratio of 5wt% or over, there is a retarding tendency of the shrinkage. This reason is that large amounts of fine reaction products with the high content of CaO are dispersed, and sintering of the liquid phase in the pellet is retarded by the high melting point of this substance.

(5) When the amount of the liquid phase increases, the passage of the reducing gas is hindered, and the reduction at the center of the pellets is retarded. Therefore, the pellets reduced for 30 min at 1200°C generally have a higher metallization ratio than those for 30 min at 1250°C.

(6) When the pellets are reduced at 1200°C, the formation of the liquid phase is comparatively low. The increase in the addition of $Ca(OH)_2$ gives the lower metallization ratio. With the increase of the CaO addition a large amounts of fine substance with a high CaO and considerable FeO content are formed, and the metallization ratio becomes lower.

(7) When the pellets are reduced at 1300°C the formation of the liquid phase becomes fast. With the increase in the addition of $Ca(OH)_2$ the metallization ratio increased. Because the addition of CaO inhibits the formation of fayalite which decreases the unreduced FeO in the pellets.

(8) In order to increase the density and the metallization of the prereduced pellets, the pellets should be reduced at a relatively low temperature to suppress the formation of the liquid phase as small as possible. This should be followed by a heating at a higher temperature in order to complete the reduction. However, it must be remembered that the formation of the liquid phase in this case is limited and sintering by the liquid phase does not proceed even at high temperature.

(9) The addition of SiO_2 is not favorable from a point of view of shrinkage and metallization of the pellets.

(10) The addition of pyrite has a favorable effect on the shrinkage of the pellets, however,

since considerable amounts of sulphur remain in the reduced pellets, the treatment of desulphurization must be carried out additionally.

(11) The chemical compositions, reducibility and fluidity of the reaction products appearing in the process of reduction are important factors governing the shintering and reduction of the pellets.

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Chapter 4

The effect of the addition of $Ca(OH)_2$, Al_2O_3 and MgO on the property of prereduced pellets

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and Sogo SAYAMA

Synopsis

In this study the effect of the addition of $Ca(OH)_2$ *on the shrinkage, metallization and fusibility of prereduced pellets was examined. It was found that an optimum amount of* $Ca(OH)_2$ *improved the strength and quality of the pellets, especially the fusibility of the pellets. The basicity in the range of 0.5–1.0 controlled by the addition of lime was favorable for the separation of the metallic iron from the silicate slag in the secondary fusion process. It was observed that the prereduced pellets with the addition of lime fused at a temperature 100°C lower than that of the prereduced pellets without lime. Further, it was found that the addition of about 1–2 wt%* Al_2O_3 *or MgO was also favorable for the shrinkage of prereduced pellets.*

I. Introduction

Grang-cold pellets are produced as cold-bound pellet by using Portland cement as a binder[1]. In the case of the prereduced pellet, the addition of CaO in the production process is considered to be effective in its secondary fusion process. In the previous report, the sintering process of ore particles in pellets by the addition of $Ca(OH)_2$, SiO_2 and pyrite was investigated[2]. As a result, it was found that a proper amount of CaO improved the shrinkage and the metallization ratio of pellets. In this report, the reduction process of the pellet produced with the addition of $Ca(OH)_2$ was investigated and it was proved that the addition of a CaO component was also effective in aiding fusibility. Further, the effect of the addition of Al_2O_3 and MgO on the shrinkage of the pellets was also investigated.

II. Experimental

In the experiment iron ores from Brazil and Swaziland were used. The chemical composition of the ores are shown in Table 1. Green compacts (14.0 mm in diameter, 5 mm in height, about 3 g in weight) which contained 10 wt% of coke as an internal carbon material were prepared. The reduction expriment was conducted as follows ; the green pellet contained coke after dehydration was embeded in a stainless steel crucible (40 mm in diameter, 70 mm in height) together with coke (−14 mesh). The crucible was placed in a

Table 1. Chemical compositions of ores tested. (wt%)

Ore	T.Fe	FeO	SiO_2	Al_2O_3	CaO	MgO	S	C.W.
Brazil	65.20	0.20	4.29	1.32	–	0.14	0.01	0.66
Swaziland	63.65	0.18	4.68	2.15	–	–	0.01	0.31

vertical tube furnace which was preheated at the reducing temperature of the pellets. After the reduction the crucible was cooled to room temperature. Hereinafter this method is called as the internal and external reductant combined method (illustlated in Fig. 1). The experimental procedure concerned with the fusibility of the reduced pellet will be described later.

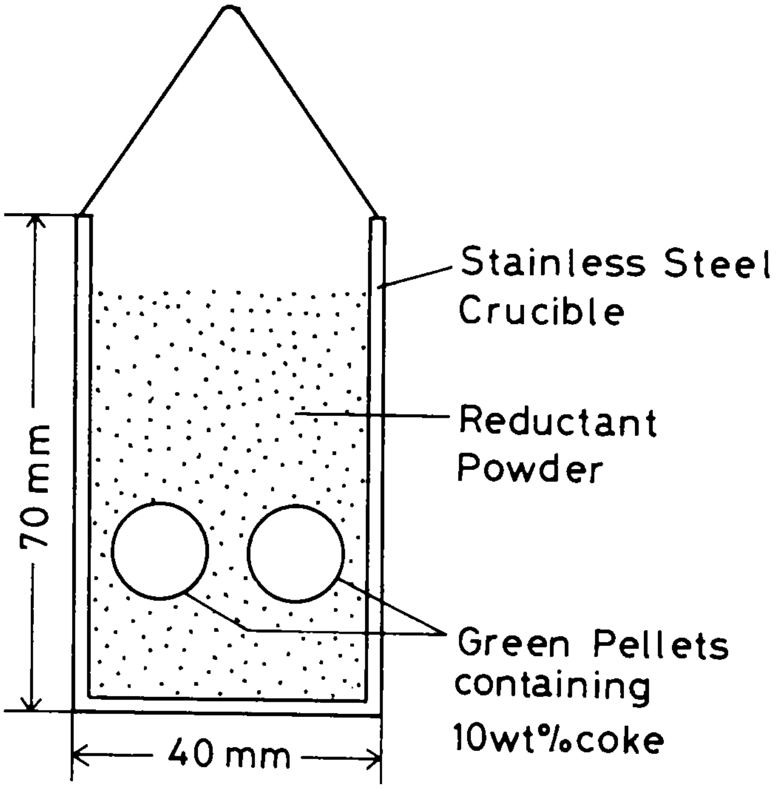


Fig. 1. Method of the metallized pellets production.

Ⅲ. *Results and Discussion*

1. The Process of Sintering

From the previous report in the case of the internal and external reductant combined method[2)], it is believed that the reduction product FeO, Al_2O_3, CaO and these compounds or possibly liquid phase components generally react simultaneously on the surface of SiO_2 (quartz) particles. In this way sintering is advanced by the generation of the liquid phase, and at the same time the metallic iron begins to separate out. The hematite ore particles are subdivided in contact by the liquid phase in the reducing process, and they are reduced with losing their own original shape.

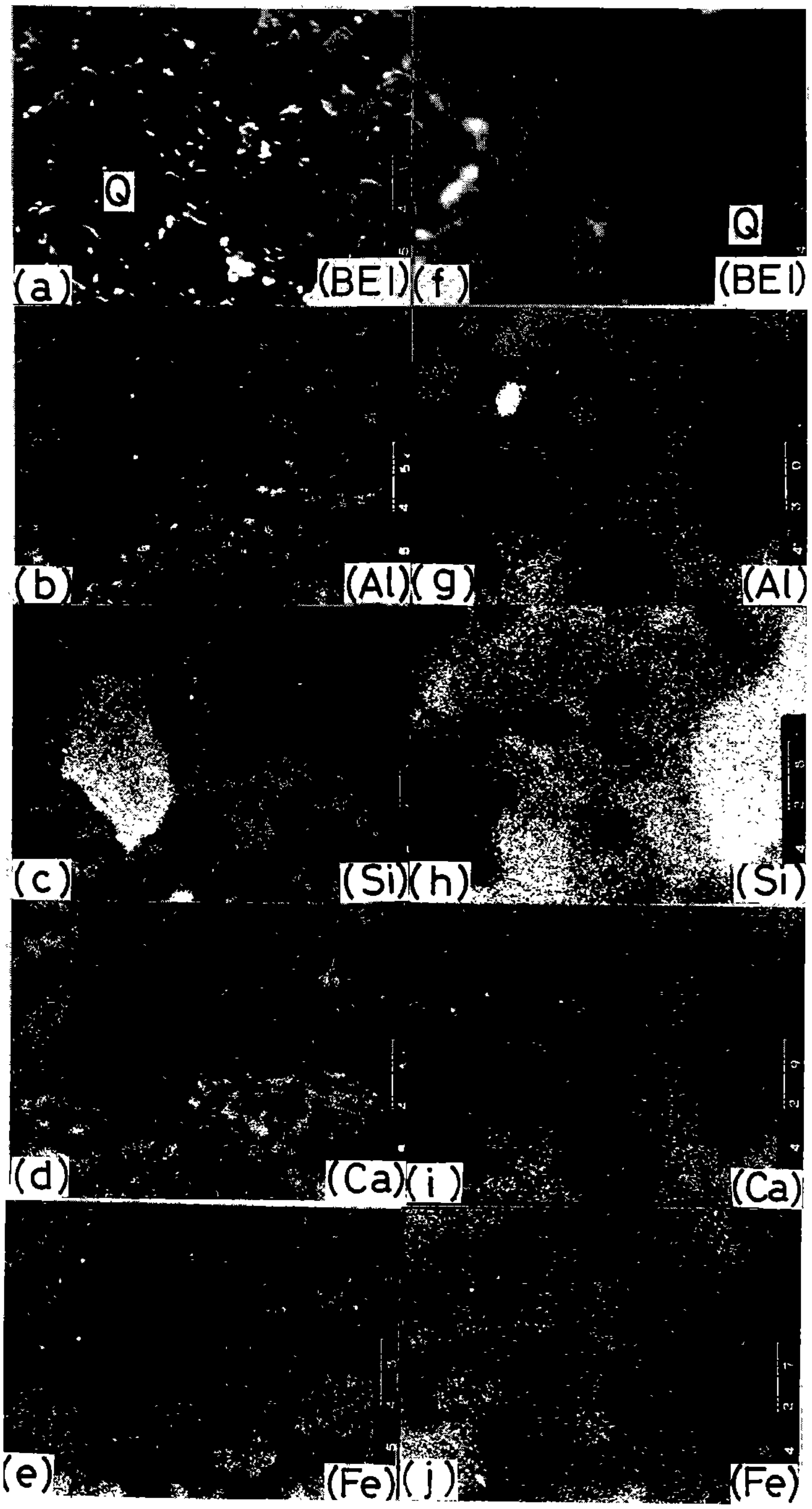
To accelerate the liquid phase generation, reduction experiments at temperatures higher than 1250°C were conducted. Photo. 1(a)-(e) show the structures of the green pellets of Brazil ores with 3 wt% $Ca(OH)_2$ reduced at 1300°C for 15 minutes. Photo. 1(f)-(j) show the enlarged photographs of the Brazil pellets reduced at 1250°C for 12 minutes. It was confirmed that the reaction mainly occured on the surface of SiO_2 and that a liquid phase composed of Al, Si, Ca and Fe oxides was generated. The slag composition was approximately as follows : 43 % SiO_2, 11 % Al_2O_3, 37 % CaO, 7 % FeO. In addition to quartz, corundum and metallic iron can be observed in this photograph.

As presented in the previous report[2], when 3 wt% $Ca(OH)_2$ was added, the liquid phase was generated relatively well and as a result, the sintering proceeded. By the addition of 7 wt% $Ca(OH)_2$ the reaction products containing a higher content of CaO (the approximate composition : 8 % FeO, 50 % SiO_2, 12 % Al_2O_3 and 28 % CaO) were produced. Due to the higher melting point, a tendency to hamper the generation of the liquid phase was seen. Further, the formation of calcium ferrite was not observed after reduction. In this report as shown in Photo. 2(a)-(e), when the reduction was further advanced, the surface of the metallic iron formed a smooth shape in the liquid phase and the liquid phase divided into two phases was also often observed (photo. 2(a)-(e)). From an analytical result by EPMA, the presence of the two phases was caused by the fact that fayalite is crystalized and separated from the liquid phase at a lower melting point. In Photo. 2(f)-(j) concerned in the Brazil ore reduction, smooth phaped wustite is observed. It is considered that this wustite was formed by the interaction between the wustite and the liquid phase. Because the passage of the reducing gas was hindered by the liquid phase during the progress of liquid sintering, the reduction of the central part of the pellet did not progress well, so that much wustite was observed. In the outer part of the pellet, however the metallic irons were finely distributed.

2. The Fusibility of the Reduced Pellet

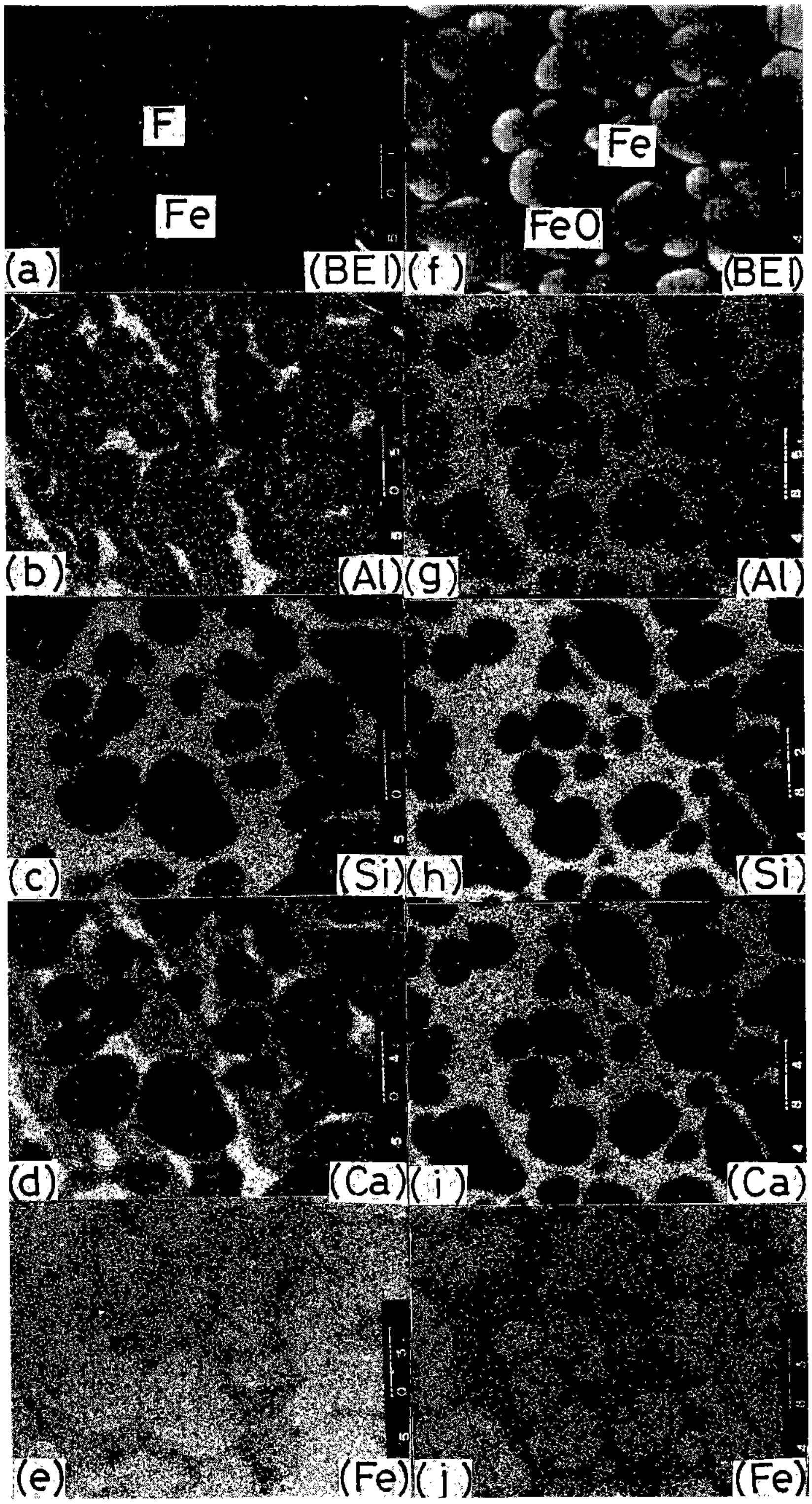
In order to obtain the basic data when pellets are smelted in the steel manufacturing process, the fusibility of the reduced (metallized) pellet containing $Ca(OH)_2$ was investigated. The pellets of the Brazil and Swaziland ores containing 0, 3 and 7 wt% $Ca(OH)_2$ were reduced at 1250°C for 30 minutes, and used as the experimental samples for the fusibility test.

After putting the reduced pellet with fine coke (−14 mesh) into a crucible made of graphite, the crucible was heated in a Tamman furnace (Fig. 2). The time required for



(a)-(e) Brazil, $Ca(OH)_2$ 3 wt%, 1300°C, 15 min, x500.
(f)-(g) Oeazil, $Ca(OH)_2$ 3 wt%, 1250°C, 12 min, x51500.

Photo. 1. Liquid phase formation at the early stage of prereducing of pellets observed by EPMA (central part).



Fe : metallic Fe. FeO : wustite. F : fayalite.
(a)-(e) Swaziland, $Ca(OH)_2$ 3 wt%, 1250°C, 30 min, x500.
(f)-(j) Brazil, $Ca(OH)_2$ 7 wt%, 1250°C, 30 min, x500.

Photo. 2. Formation of fayalite and wustite in liquid phase of prereduced pellets observed by EPMA (central part).

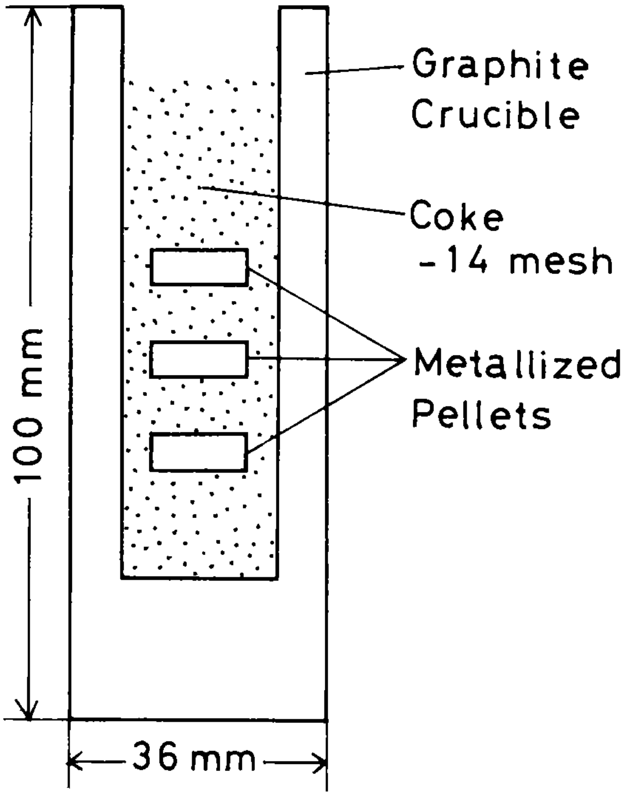


Fig. 2. Experimental method of the fusibility test.

increasing the temperature from room temperature to a fixed smelting temperature (1350–1480°C) was within 10 minutes. After the fixed temperature had been reached, it was kept for 7 minutes and then the smelting test of the reducing pellets was performed.

Fig. 3 illustrates the major slag composition, i. e., CaO, Al_2O_3 and SiO_2 of the reduced pellet which was manufactured by the addition of 3 and 7 wt% $Ca(OH)_2$ in a phase diagram. According to this diagram, the slag composition spreads over the range which Pseudo-wollastonite, gehlenite, anorthite are crystallized.

Photo. 3(a)-(h) show the state of separation of the slag from the metallic iron phase in the sample after cooling. From these results, it has been proven that the smelting temperature could be decreased by more than 100°C by the addition of $Ca(OH)_2$ to the reduced pellet.

Photo. 4(a)-(e) show the EPMA images of the pellet produced from the Swaziland ore without $Ca(OH)_2$ which did not fuse at 1350°C. Photo. 4(f)-(j) illustrate the slag which was separated from the Brazil ore by the addition of 7 wt% $Ca(OH)_2$ after smelting the reduced pellet at 1350°C. No iron is observed in the slag phase, but the crystallization of wollastonite which mainly consists of SiO_2 and CaO is observed.

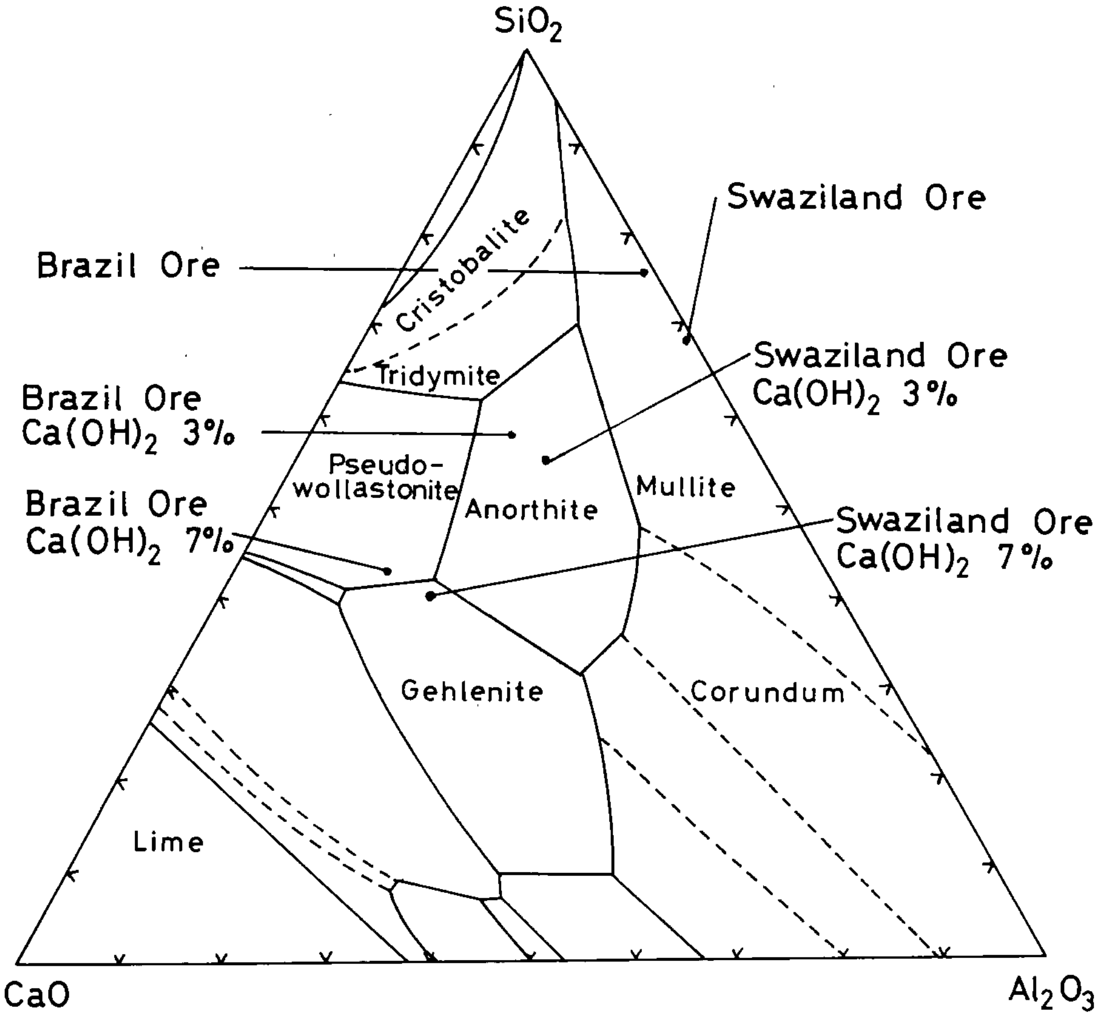
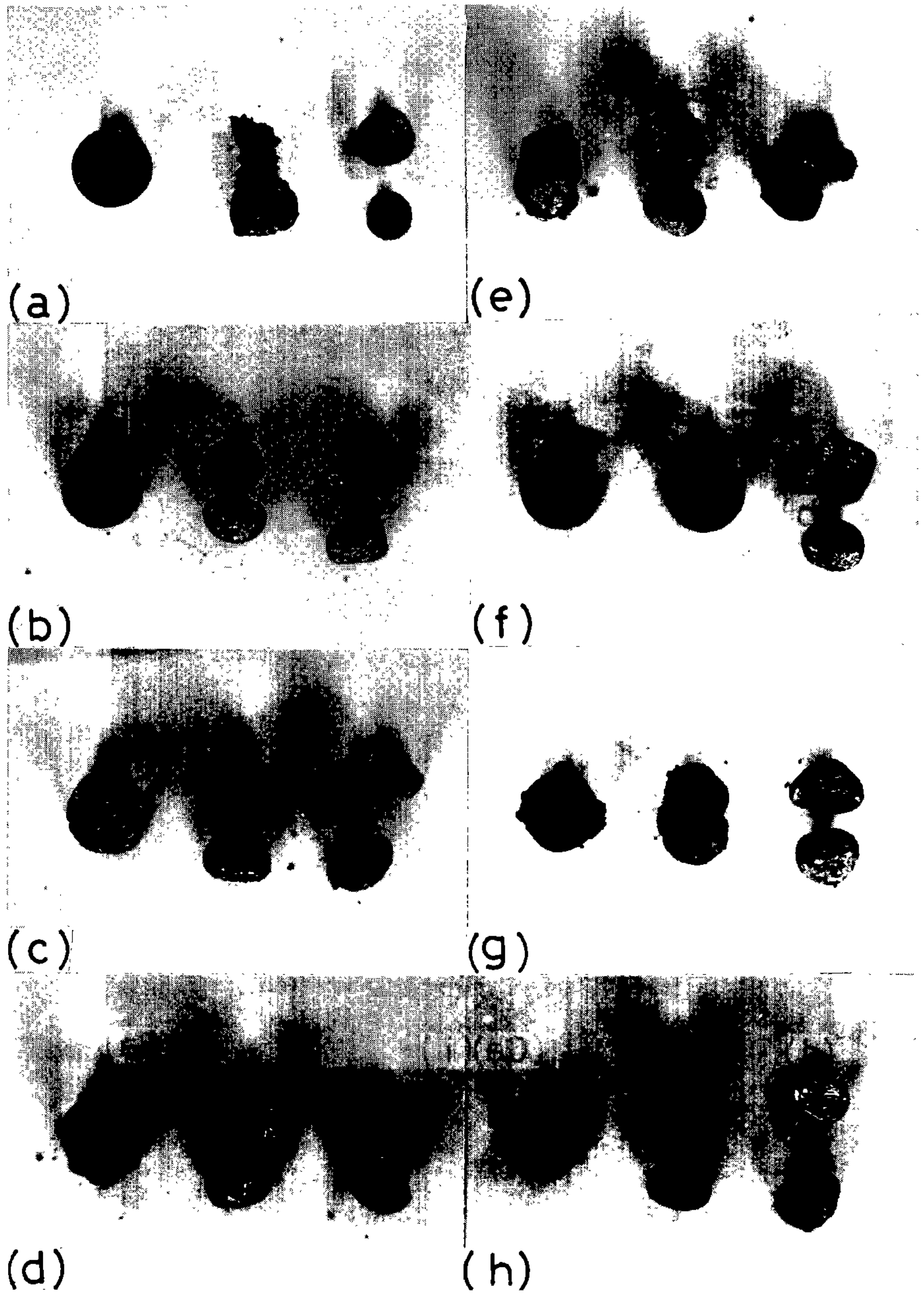


Fig. 3. The composition of slag-forming materials in metallized pellets shown in phase diagram of system CaO-Al_2O_3-SiO_2.

3. The Addition of Al_2O_3 and MgO

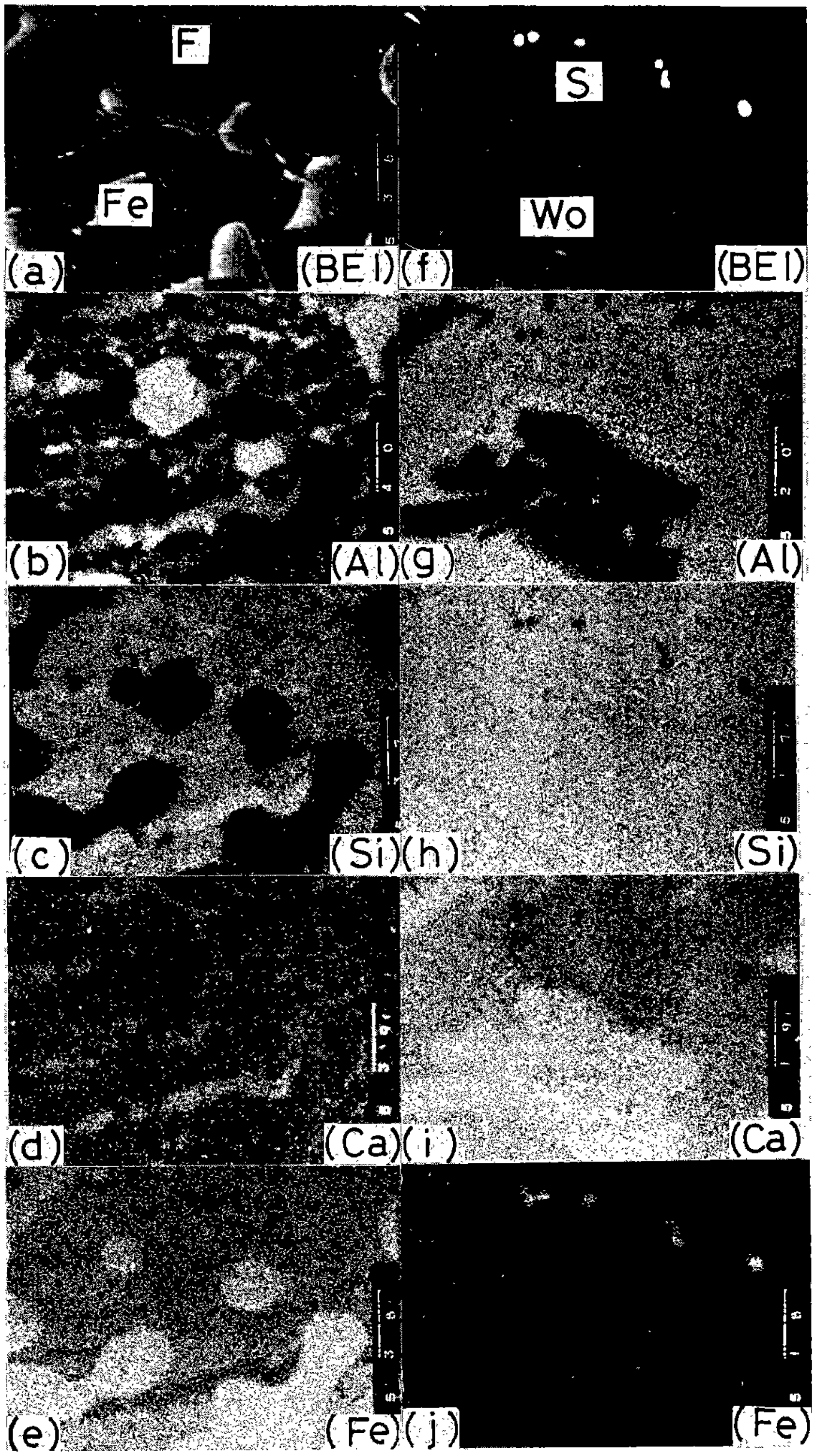
The influence of the addition of Al_2O_3 and MgO on shrinkage was investigated using the Brazil and Swaziland ores. It was observed that the Al_2O_3 component exists mainly in the Brazil ore as corundum, while it exists mainly in the Swaziland ore as Kaolinite. The Brazil pellets was reduced at 1200°C for 30 minutes without additives, but in this case, the liquid phase was generated in smaller quantity and the pellet was likely to crack.

Fig. 4 illustrates the Brazil and Swaziland ore to which 0–4 wt% Al_2O_3 or MgO were added and reduced. As a result, in the case of the Brazil ore, the addition of 1 wt% Al_2O_3 is evidently desirable for the shrinkage of the pellet. The addition of MgO, by contrast, has little effect on the shrinkage of the pellet. In the case of the Swaziland ore, 1–2 wt% of MgO is effective in shrinking the pellet, but the effects of the addition of Al_2O_3 are not clear.



upper : slag(porous). lower : iron.
left : $Ca(OH)_2$, 0 wt%. middle : 3 wt%. right : 7 wt%.
(a) Brazil, 1350°C. (b) 1380°C. (c) 1420°C. (d) 1440°C.
(e) 1480°C. (f) Swaziland, 1350°C. (g) 1390°C. (h) 1440°C.

Photo. 3. Effect of $Ca(OH)_2$ addition on the separation of slag and iron after fusibility tests. Reduced pellets were embeded in coke (—14 mesh) and were heated for 7 min at various temperatures.



Fe : metalic Fe. F : fayalite. Wo : wollastonite. S : slag.
(a)-(e) Swaziland (central part), $Ca(OH)_2$ 0 wt%, 1350°C, 7 min, x500.
(f)-(g) Brazil (separated slag), $Ca(OH)_2$ 7 wt%, 1350°C, 7 min, x500.

Photo. 4. Distribution of slag and metallic iron after fusibility tests observed by EPMA.

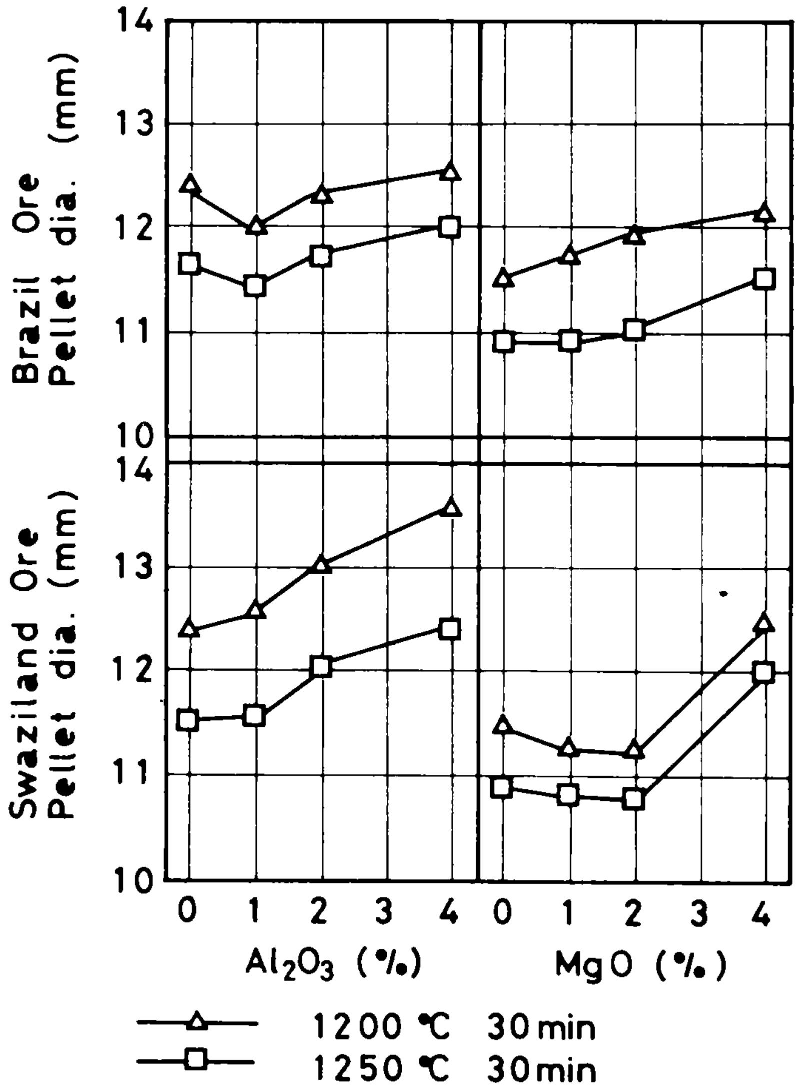
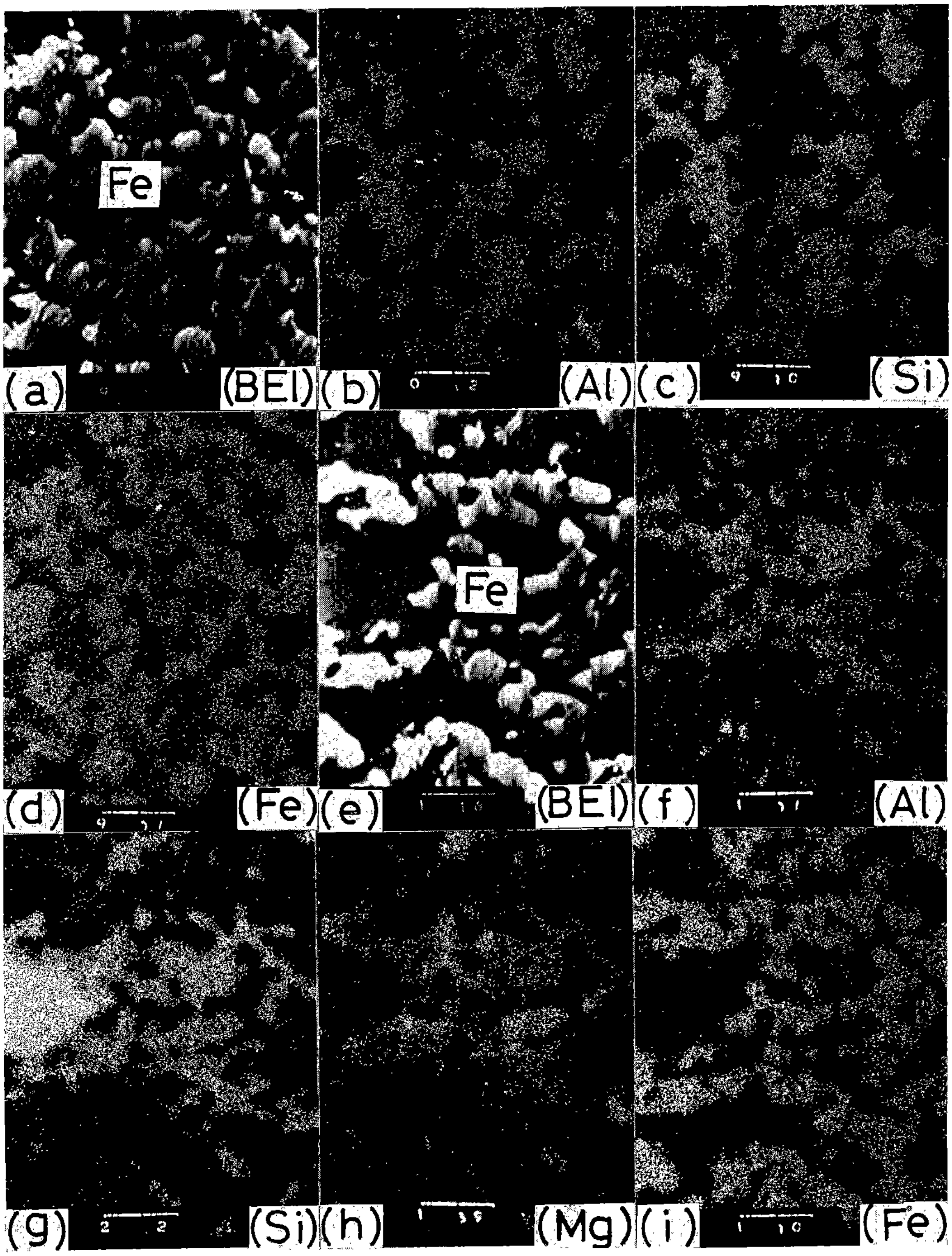


Fig. 4. Effects of Al_2O_3 and MgO addition on diameter of pellets reduced at 1200 and 1250°C.

The liquid phase generated in the reducing process of the pellet of the Brazil ore, was studied by EPMA. Photo. 5(a)-(d) show the structure of the pellet reduced at 1200°C for 30 minutes by the addition of 1 wt% Al_2O_3. In this case, the quantity of the liquid phase is large. Photo. 5(e)-(i) show the structure of the pellet reduced at 1250°C for 30 minutes by the addition of 2 wt% MgO. Because of the high temperature of 1250°C and the addition of basic component MgO, the generation of the liquid phase is large.

IV. *Conclutions*

The effects of the addition of $Ca(OH)_2$, Al_2O_3 and MgO to green pellets of iron ores on the shrinkage process and fusibility of the prereduced pellets were investigated. The pellets



Fe : metallic Fe.
(a)-(d) Brazil, Al_2O_3 1 wt%, 1200°C, 30 min, x500.
(e)-(i) Brazil, MgO, 2 wt%, 1250°C 30 min, x500.

Photo. 5. Microstructure of reduced pellets containing Al_2O_3 and MgO reagents observed by EPMA (central part).

were produced by the internal and external reductant combined method (shown in Fig. 1) and the fusion test was performed using a Tamman furnace (Shown in Fig. 2). The results obtained are as follows:

(1) The Addition of $Ca(OH)_2$

When the reduction was performed at 1200°C, the reaction product of high FeO and CaO content and of lower fluidity are formed by the $Ca(OH)_2$ addition. Consequently, by increasing the addition of $Ca(OH)_2$ a tendency to decrease the rate of metallization was observed. When the reduction was conducted at a relatively high temperature of 1300°C, increasing the generation of the liquid phase, the formation of fayalite was limited by the addition of about 7 wt% $Ca(OH)_2$ and a tendency to increase a metallization ratio was observed.

For the improvement of the fusibility of the pellet, a proper amount of $Ca(OH)_2$ was added so that the basicity of the slag components will be about 0.5–1.0. As a result, the smelting temperature could be decreased by more than 100°C in contrast to the experiment without the addition of $Ca(OH)_2$.

(2) The Addition of Al_2O_3 and MgO

The effect of the addition of Al_2O_3 on the shrinkage process was investigated by using Brazil and Swaziland ores. The Brazil ore has a smaller content of Al_2O_3 than Swaziland ore. In regard to the Brazil ore, the addition of about 1–2 wt% Al_2O_3 was desirable for shrinkage and produced a pellet with higher density. The addition of MgO was also investigated by using those two ores which are relatively free from MgO. The addition of 1–2 wt% MgO was favorable for the shrinkage of the Swaziland pellet. From the above results the addition of Al_2O_3 or MgO is desirable for shrinkage of the pellets, but the effects would seem to depend on the origin of the ore.

It is observed that the kind of additives and the composition of the slag-forming materials are important factors for the production of the prereduced pellets.

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Chapter 5

Mechanism of Abnormal Swelling in the Process of Prereduced Pellet Firing

Sogo SAYAMA and Yoshinobu UEDA

Spnopsis

An investigation has been made on the growth mechanism of metallic filaments formed at the reduction stage of FeO to Fe, in the process of prereduced pěllet firing. Six kinds of iron ore were tested in the respective reducing atmosphere of CO and H_2. *Using a scanning electron microscope, an observation was made on the phase of ore during reduction. In* H_2 *atmosphere, no abnormal swelling occurred. But, in CO atmosphere, abnormal swelling occurred in pellets due to the formation of metallic filaments.*

There is a big difference in microstructure between ore having swelling properties and ore having no such properties. The former usually shows a fine and orderly phase such as intergrowth, and the latter is usually of irregular mosaic structure. Prior to swelling, fine steps parallelled to (111) of FeO appear during the period of reduction to Fe. At an early stage of reduction of FeO to Fe in CO atmosphere, cracking takes place, and then ore particles break down. After further reduction, neeale-like FeO phase seems to change into fibrous iron. The microscopic observation revealed that there were considerable destorted and branched filaments but little straight whisker-like iron crystals. An electron diffraction pattern of filament shows the (111) plane of α *-Fe, which coincides with the plane of steps displayed on FeO. The carbon combined with metallic iron is contained in much higher percent in the metallic filament than in granular iron produced by topochemical reduction of FeO.*

(Issued in Proc. lst Int'l Conf. on Compaction and Consolidation of Particulate Matter, Powder Advisory Centre, London, (1972), 89.)

I. Introduction

Special attention has recently been focussed on the production of pre-reduced pellets as an important process of manufacturing iron. The pellets are produced by heating green compacts of ore powder under a reducing condition, but, in some cases, some kinds of ore showed abnormal sweelling, which made it impossible to manufacture pellets with sufficient strength. Abnormal swelling was frequently observed at the reaction temperature between 600°C and 1050°C in the atmosphere of CO. Under these conditions, the reduction of FeO did not proceed topochemically, but accelerated the formation of metallic filaments. . Other kinds of ore, however, showed no abnormal swelling even under the similar conditions. The purpose of our study is to clarify the mechanism of abnormal swelling and find the effective ways for the prevention of swelling.

Much research has been presented on a basis of the metallic filaments forming a principal cause for such abnormal swelling. Some report that the growth mechanism of filaments is probably due to the diffusion of supersaturated ferrous ions in FeO achieved toward a few iron nuclei with high mobility. The needle-like iron crystals grow in this way.

The phase changes of ores during reduction and the appearance of metallic filaments have not so far been made clear by the conventional optical microscope. The appearance of the scanning electron microscope has made it possible for us to observe the microstructure of ores stereographically.

Accordingly, interesting phenomena were observed with respect to the abnormal swelling. In the present paper, a discussion is made on the growth mechanism of metallic filaments in the process of the reduction.

Wenzel1) suggested three different causes of the abnormal swelling of iron ore pellets. One of them is the precipitation of carbon resulted from the Boudouard reaction. The second cause is a high gas pressure produced by the reaction $FeO + C = Fe + CO/CO_2$ in the interface between Fe and FeO. In this reaction, carbon diffuses through the iron lattice up to the interface in the region between the Boudouard curve and the FeO-Fe equilibrium curve. The third cause is the directional crystallization of metallic filaments.

Fuwa et al.2)suggested that the growth of filament is a common phenomenon observable when relatively pure iron oxide is reduced in the atmosphere of CO. Discussion has been presented on many factors forming the causes of swelling. These factors include (a) incomplete recrystallization of hematite3) (b) Na in iron oxide4) (c) Ca in iron oxide5) (d) intergrowth and twins6) (e) γ-hematite7) and so forth.

Ishimitsu et al.7) considered that the breaking down of grains is inevitable before swelling at the early stage of reduction. Hence, a discussion will have to be made from the view-points of the breaking down of grains and growth of fibrous iron.

The above works relate to the swelling caused during the reduction of oxidized pellets and massive ores. The present investigation was made on a process of producing prereduced pellets, which comprised reducing green compact of ore powder directly. In previous work8), the authors considered that the swelling may be attributable to the unstable ore phase during reduction. As for the raw materials with swelling properties, fine and orderly structure such as intergrowth was considered as one of the factors forming the unstable phase.

II. Ores Tested and Experimental Procedure

Six kind of iron ore were tested. The chemical composition and special features of ore structure are shown in our previous paper$^{9)}$.

Powdered ore damped with 10 wt% of water was pressed into compacts with a die under the pressure of 320kg/cm^2. A green compact weighing about 2.5g is 14.1mm in diameter and about 5mm in height : and it is about 35% in porosity. Prior to the reduction tests, the green compact was dried at 200°C. Dried compacts were reduced in a reaction tube of 30mm in inside diameter using a horizontal electric furnace. A compact on silica boat placed in the reaction tube was reduced by applying shock heat at a required temperature. After reduction, the reducing gas was purged by N_2 stream, and reaction tube was cooled at room temperature. One of four reducing gases : CO, H_2, CO : CO_2= 50 : 50, H_2 : N_2= 50 : 50, was used at the flow rate of 200cc/min.

The swelling index (S. I.) is given by the following expression.

$$\text{S. I.} = \frac{D_a - D_i}{D_i} \times 100\%$$

where D_i and D_a are the diameters of pellets before and after the reduction.

Carbon in reduced pellets were determined by the combustion method. Carbon insoluble in dil-HNO_3 was regarded as free carbon.

III. Results

1. Reduction in CO Atmoshere

Fig. 1(a-h) shows the expermental results (S. I., metallic Fe content, total carbon content and free carbon content) obtained by CO reduction at various temperatures. These reduction experiments and microscopic examinations revealed the process of reduction. The swelling observed in each ore was as follows ;

(1) Swaziland

At the reducing temperature between 600 and 650°C, the precipitation of carbon resulted from the Boudouard reaction was recognized remarkably in this ore. Photo. 1(a)(b) gives a pellet degraded by the precipitaion of carbon. The degradation is different from abnormal swelling caused by the metallic filaments grown in other ores. At a temperature above 750°C, the precipitation is negligible, and no swelling takes place, but iron formed on FeO topochemically is observed, as shown in Photo. 2(a).

(2) Brazil

The Brazil pellet swells and degrades at the temperature between 600 and 650°C. Swelling is caused not by carbon precipitation, but by metallic filaments. This is because the pellet contains a low percent of free carbon. Metallic filaments appear at a relatively low temperature of about 600°C. Photo. 2(b) shows the grown metallic filaments. In the process

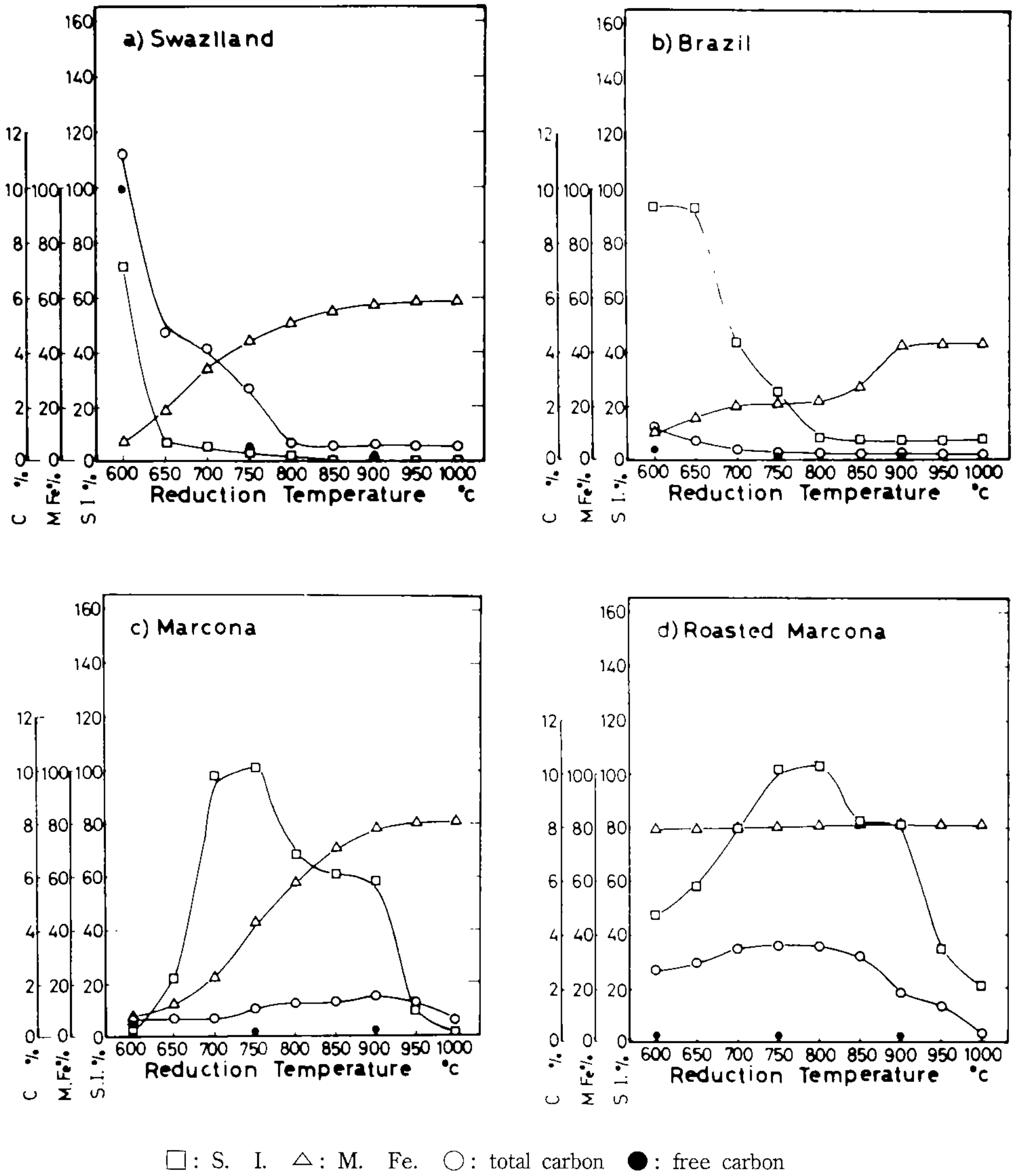
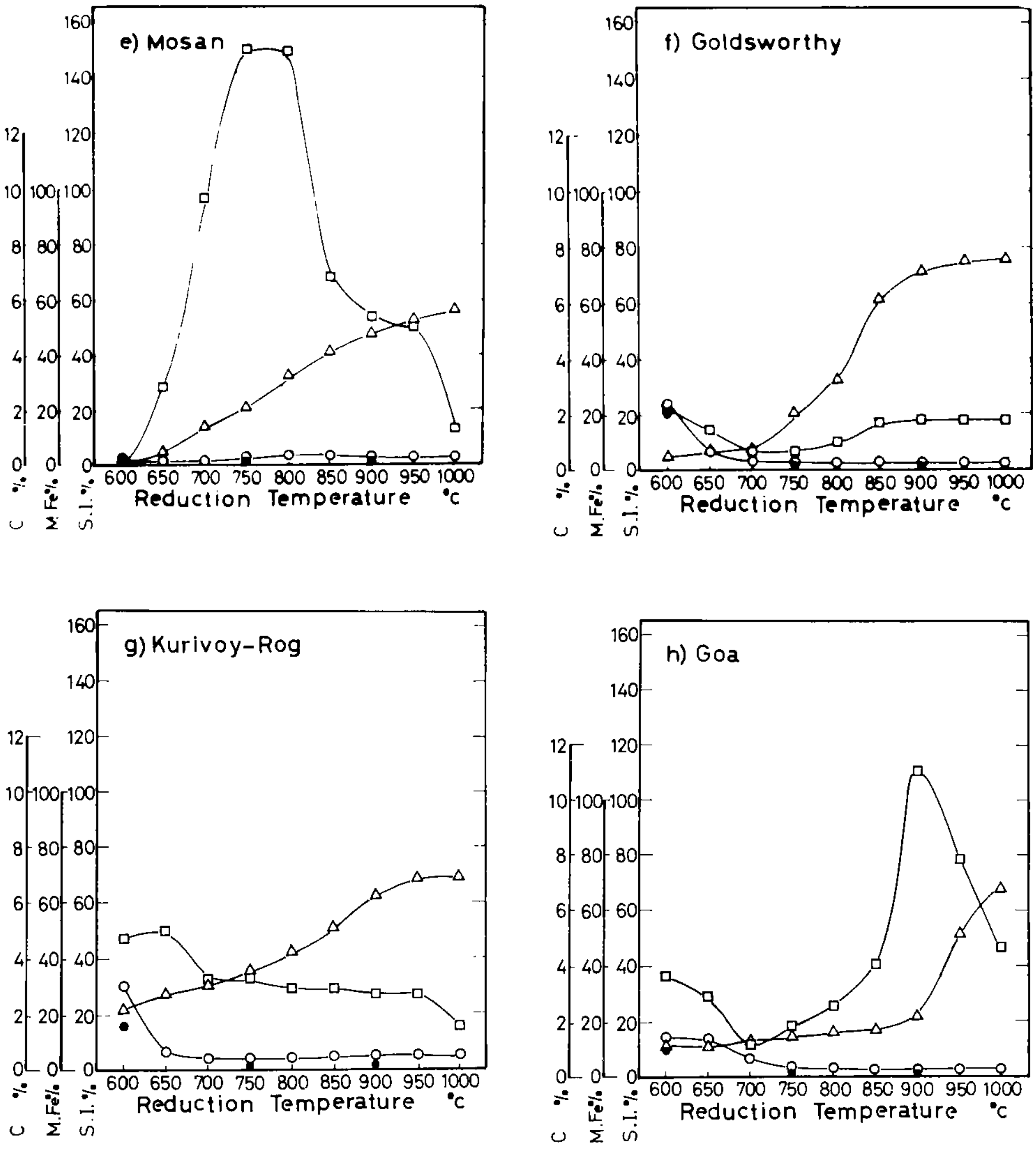


Fig. 1. Swelling index, metallic Fe contents, toal carbon contents and free carbon contents in pellets reduced in an atmosphere of CO at various temperatures for 60 min.



□: S. I. △: M. Fe. ○: total carbon ●: free carbon

Fig. 1. (cont.)

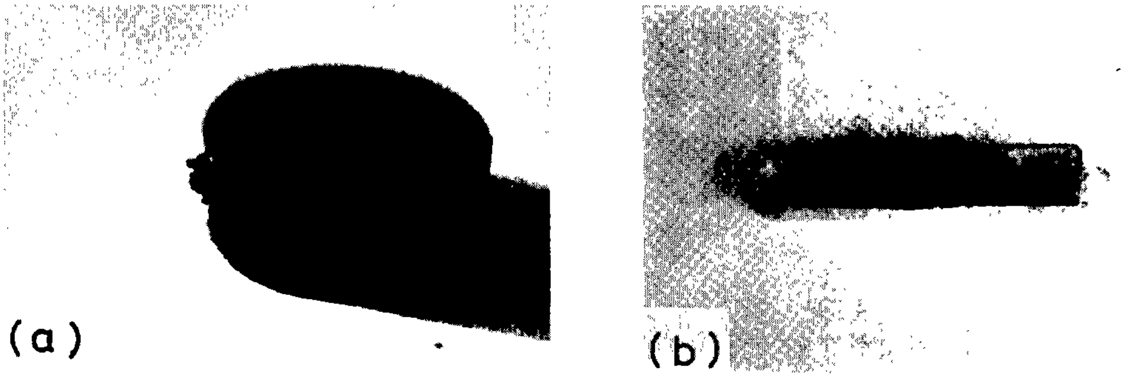


Photo. 1. Degradation of Swaziland pellet caused by the precipitation of carbon. (a) reduced at 600°C for 30 min. (b) reduced at 600°C for 120 min.

of reduction, a step-like micro structure is observed as in Photo. 2(c).
Photo. 2(d) shows the growth of metallic filament reduced at 750°C. The growth have a tendency to arrange in fixed direction of ore particle.

At a higher temperature than 850°C, the reduction of FeO proceeds topochemically, whereby a decreasing tendency of the swelling is shown, Photo. 2(e).

(3) Marcona

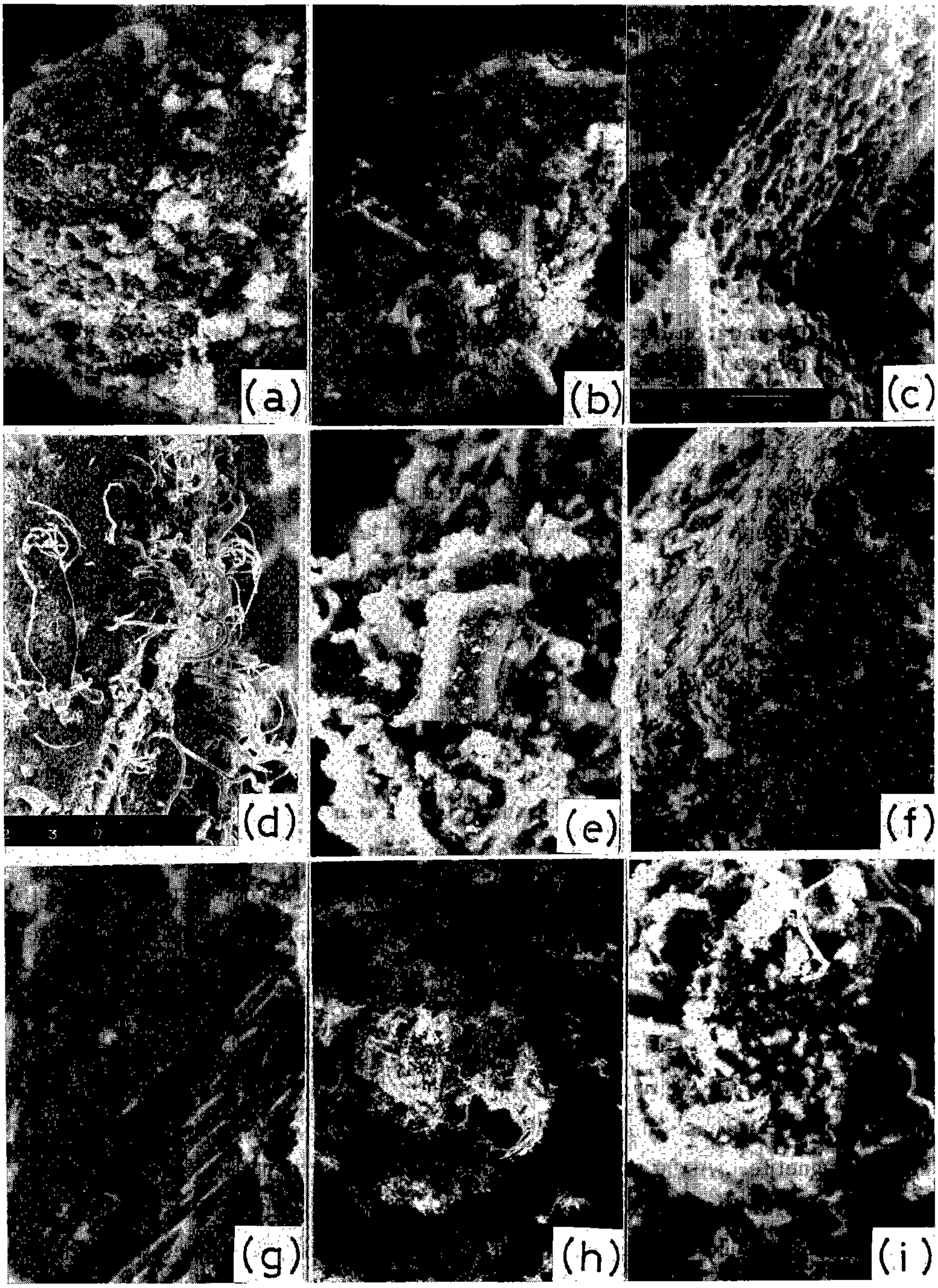
Orderly steps are clearly seen on FeO. Some steps are seen in two different directions, Photo. 2(f). Photo. 2(g) is an enlarged picture of Photo. 2(f). The plane of step is assumed to be (111) of FeO, because the plane edge forms an angle of about 120°. At 700°C wherein a pellet remarkably swells, it is observed that steps have cracked open in the form of tiny rod and that the cracked rods of FeO have changed into metallic filaments, Photo. 2(h) (i). Most of metallic filaments were observed to be in distorted and branched forms, Photo. 2(j) is a enlarged picture of the root of metallic filament. It is supposed that there is a relation between the appearance of steps and the direction of filament growth.

(4) Roasted Marcona

The recrystallization caused by the phase change from magnetite to hematite is insufficiently achieved when magnetite is roasted at 1000°C. The reduction of roasted ore proceeds rapidly, because the phase of this hematite is more unstable than that of original Marcona magnetite. As far as this ore was concerned, the reduction was almost completed even at a temperature as low as 600°C, producing fine bud-like iron, Photo. 2(k). At 700°C or thereabout, metallic filament grows. The amount of carbon combined with metal which was produced from roasted Marcona is very large (approx. 3%). The reason is probably that the cementation lasted for a long time due to the early formation of metallic filaments.

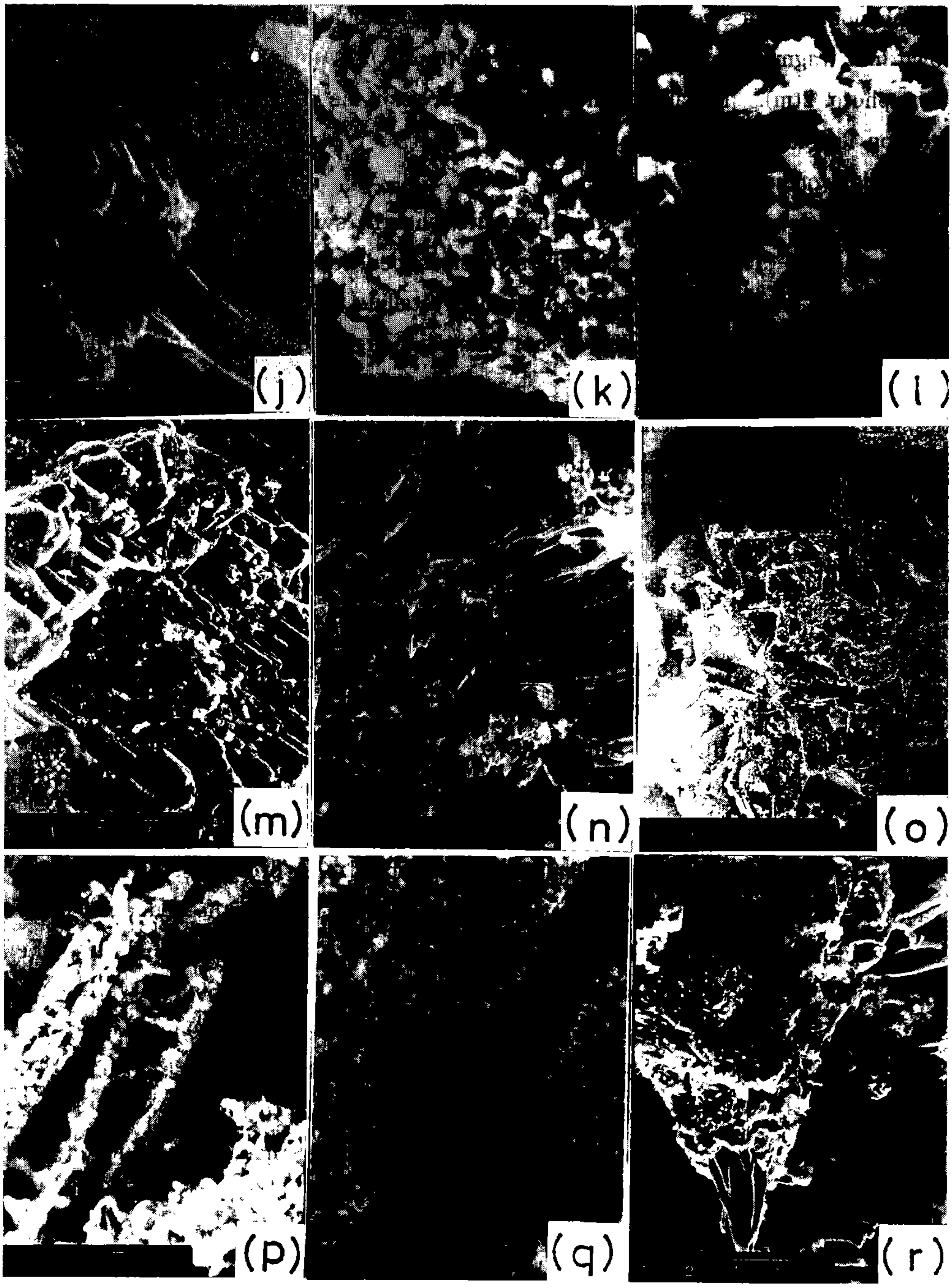
(5) Mosan

The swelling index of this magnetite gave the highest value among all the ores tested.



(a) Swaziland, 800°C, 30min, x1000. (b) Brazil, 600°C, 60min, x1000. (c) Brazil, 750°C, x1500. (d) Brazil, 750°C, 30min, x750. (e) Brazil, 950°C, 60min, x1000. (f) Marcona, 650°C, 60min, x1000. (g) enlarged picture of (f), x5000. (h) Marcona, 700°C, 60min, x250. (i) enlarged picture of (h), x1000.

Photo. 2. Surface structure of ore powder reduced in an atmosphere of CO.



(j) Marcona, 750°C, 30min, x5000. (k) Roasted Marcona, 600°C, 60min, x1000. (l) Mosan, 900°C, 15min, x1000. (m) Mosan, 750°C, 30min, x500. (n) Mosan, 750°C, 30min, x750. (o) Goldsworthy, 750°C, 20 min, x150. (p) enlarged picture of (o), x1500. (q) Kurivoy-Rog, 750°C, 30min, x1500. (r) Goa, 1000°C, 60min, x500.

Photo. 2. (cont.)

The phenomenon of swelling is similar to that or Marcona. Ore particles expand and break down into fragment during the reduction, Poto. 2(1). And a directional structure is also seen, photo. 2(m). Metallic filaments are not seen on the flat plane of particle, but generally seen on its side plane (Photo. 2(n)).

(6) Goldsworthy

At 850°C or thereabout, this hematite slightly swells, and metallic filaments are observed, too. This original ore gives piller-shaped hematite. It is considered that the filament was formed, keeping the original crystalline form of Fe_2O_3 (Poto. 2(o) (p)). Consequently, abnormal swelling is not caused though metallic filaments are grown.

(7) Krivoy-Rog

The swelling index is relatively lowered to be nearly 30 %, while the temperature range of expansion widely canges from 600 to 950°C. In Photo. 2(q) is illustrated a state of growth of fibrous metallic iron developed in fissures of flat ore grains.

(8) Goa

This ore expands up to a maximum at about 900°C. While the expansion coefficient of other ores is lowered to about less than 20 % at 1000°C, this ore has a feature to highly expand up to about 45 %. It is observed that the fibrous metallic iron grows on the side of its flat surface in a bundle (refer to Photo. 2(r)).

2. Influence of Reduction Atmosphere

Mosan and roasted Marcona that swelled in CO atmosphere at about 750°C were reduced in H_2 atmosphere at 750°C. Under the H_2 atmosphere, the reduction of ore proceeded topochemically, and no metallic filament was observed. In order to study a difference in reaction process between the reduction by CO and that by H_2, the reduction tests were carried out by dividing the reduction into the following two stages : $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$ and $FeO \rightarrow Fe$. Two reducing gases : $CO : CO_2 = 50 : 50$ and $H_2 : N_2 = 50 : 50$ were used in the reduction stage of $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$. The swelling indexes of FeO produced from Fe_2O_3 or Fe_3O_4 are shown in TABLE 1. TABLE 1 shows that the reducing atmosphere does not affect swelling in the reduction stage from Fe_2O_3 or Fe_3O_4 to FeO, because no abnormal swelling was recognized. In the succeeding stage, FeO (that is a product of Test 1-in TABLE 1) was reduced in either atmosphere of CO or H_2. The swelling indexes of the products obtained from FeO are shown in TABLE 2. As is clear from this Table, abnormal swelling was recognized especially in the atmosphere of CO in the reduction stage of FeO to Fe. Metallic Fe content of the products reduced in CO atmosphere is higher than that reduced in H_2 atmosphere, as shown in TABLE 2. The reason is probably that the specific surface of pellet was enlarged by disintegration of FeO particles in the case of CO reduction.

Table 1. **S. I. and M. Fe contents of FeO produced from Fe_3O_4 and Fe_2O_3 in different atmospheres at 750°C**

Test NO.	Tested ores	Reducing condition Amosphere	Time (Hr)	S.I. (%)	M. Fe (%)
1	Mosan (Fe_3O_4)	CO : CO_2=50 : 50	2	1.4	0
2		H_2 : N_2 =50 : 50	0.5	1.4	0.79
3	Roasted Marcona (Fe_2O_3)	CO : CO_2=50 : 50	2	7.1	0
4		H_2 : N_2 =50 : 50	0.5	7.1	1.53

Table 2. **S. I. and M. Fe contents of the products from FeO reduced in the atmosphere of CO and H_2 for 1 hour. FeO are prereduced products shown in Table 1.**

Test NO:	Tested ores	Amosphere in prereducrion to FeO	Atmosphere in reduction of FeO to Fe	S.I.(%)	M·Fe(%)
5	Mosan	CO : CO_2=50 : 50	CO	64.0	36.7
6			H_2	0.7	24.9
7		H_2N_2 =50 : 50	CO	61.6	36.8
8			H_2	0.7	25.8
9	Roasted Marcona	CO : CO_2=50 : 50	CO	58.9	76.7
10			H_2	2.6	53.7
11		H_2 : N_2 =50 : 50	CO	65.2	78.7
12			H_2	2.6	56.8

3. Carbon Combined with Metal

Carbon in metallic iron is analyzed with EPMA. The procedure of correction calculation for quantitative measurement of light elements (Be-O) using EPMA has not been established, and a sample which contains such a fine inclusion as carbide usually gives the abnormal value of X ray intensity. Hence the intensity is shown without correction, in Fig. 2. The X ray intensities of pure iron and graphite are 23416 cps and 10667 cps, respectively. From these results, it is found that the amount of carbon contained in the metallic filaments was much larger than that in the granular iron produced topochemically. Since a filament is about 0.5–5 microns in diameter, the specific surface of filments is very large. That is why the cementation of metallic filaments seems to advance with ease. Even in a piece of filament the X ray intensity of carbon varies with analysing points. Accordingly, the metallic filament is thought to be not mere single crystal. The amount of carbon combined with metal in a swelled pellet, occasionally reaches about 3% as average. Therefore, it is assumed that

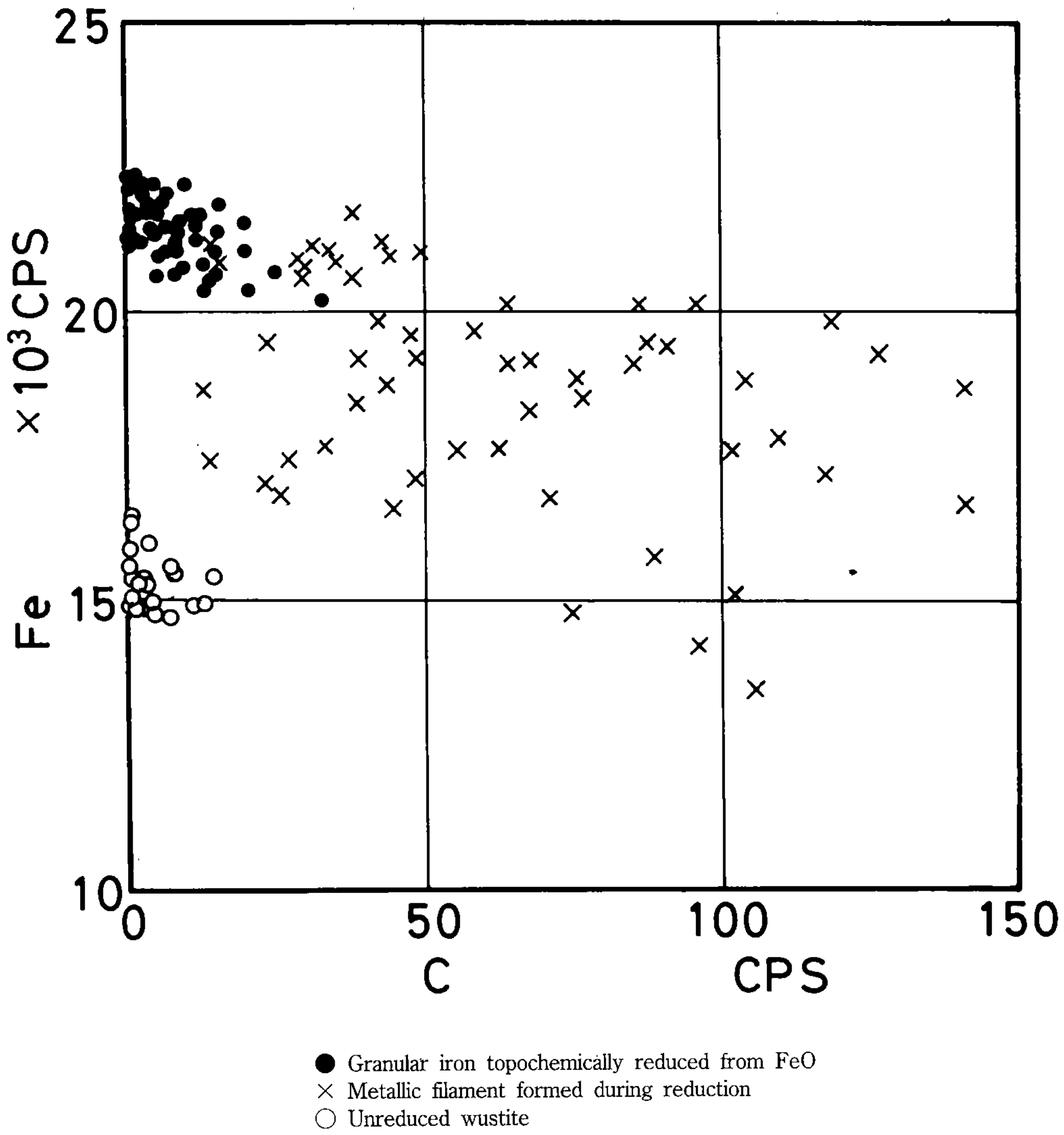


Fig. 2. X-ray intensities of Fe and C in reduced pellets by the microanalysis with EPMA

carbide may be present in metallic filaments.

4. Electron Diffraction of Metallic Filament

The electron diffraction pattern of metallic filaments produced from roasted Marcona is given in Photo. 3. The (111) trace of α-Fe generally appears on the pattern. This indicates that the filaments grow in the direction of $<110>$. In addition to the trace of (111) of α-Fe, the patterns of cementite were recognized in some parts of a filament, thus the presence of carbide was confirmed (Photo. 4).

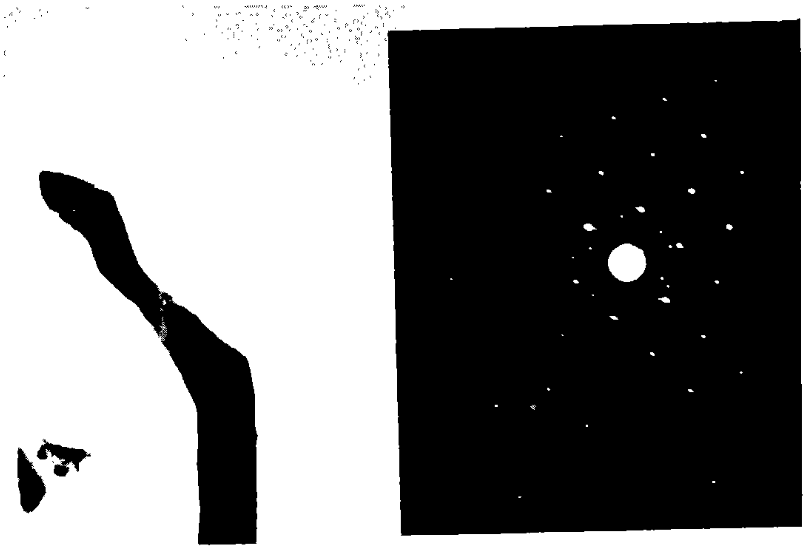


Photo. 3. Electron diffraction pattern of α-Fe (III) and tested fibrous iron. x10000

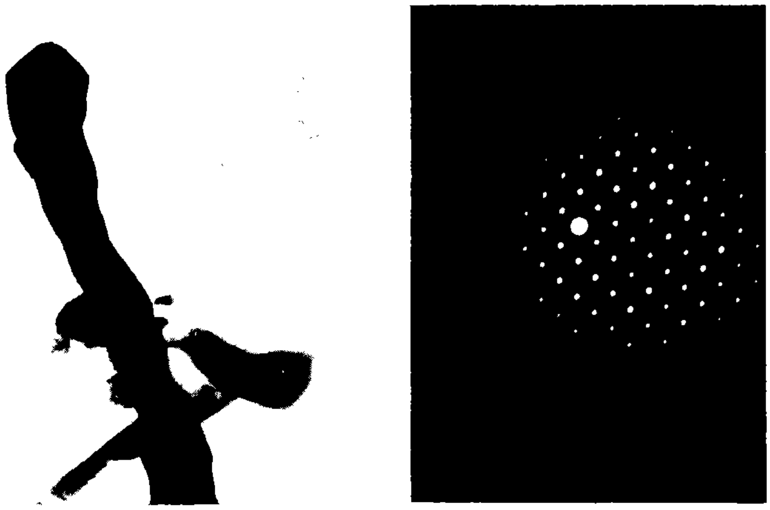


Photo. 4. Electron diffraction pattern of cementite and tested fibrous iron. x10000

5. Observation of fructure surface of reduced iron

According to Wenzel[2)], a direct reaction of carbon solid-dissolved in reduced iron and FeO on the reaction interface, can generate CO or CO_2 gas, and the pressure of which breaks down the grains of ores. For verifying this phenomenon an experiment was conducted. Adopting a plate Fe_2O_3 single crystal from shiretoko as a sample, the fracture surfaces perpendicular to the c face of the sample after reducing at 950°C for 30 min. in a stream of H_2 and CO, are illustrated in Photo. 5 and photo. 6. In any case, the fissures parallel to the c face of the samle are observed. However, in the case of reduction by H_2, the reduced iron is relatively compact, while in the CO-reduction the reduced iron is porous, and long and slender metal irons are observed. Further, a fracture phenomenon at the place considered to be reaction interface of M. Fe and FeO could not be observed.

There exists an Auger electron spectral method as one of the surface analysis method. This is a method where an electron beam applied to a sample excites atoms comprising the sample surface to emit Auger electrons, and fix the elements existed on the sample surface by detecting Auger electrons. For Auger electrons, only the electrons generated in the thin sample surface range of about 10 Å are detected, and an analysis of a range much smaller than EPMA is possible. Using a scanner type Auger electron microscope, a point analysis can be done while observing secondary electron beam images of high scale factor. Further, this electron microscope has an excellent function for local analysis of samples. Fig. 3 and Fig. 4 show Auger spectra of metallic iron reduced by H_2 and CO respectively. For the H_2–reduced metallic iron, carbon is not observed, but in the CO-reduced metallic iron, the existence of carbon is observed at the same degree at any point of analysis. Although spectrum of oxygen is also observed, it is considered to be caused by oxide film of metal iron.

Ⅳ. Conclusion

Observing the reduction process of fine iron ores and generating fibrous metal iron, the following results were obtained.

(1) For the ores of high expansibility, some regular steps appear in the reduction process. It is considered to be related to crystallization property of crude ores. Namely, it is estimated that the steps will appear parallel to the face of twin, intergrowth, etc. Which becomes a weak point in the reduction process. As main cleavage face of Fe_2O_3 is (0001) and that of Fe_3O_4 is (111), the steps are also considered to appear parallel to these cleavage faces. However, the details are still unknown.

(2) For fibrous metallic iron, it seems that these exists a regularity also in the direction of elongation. For many examples, fibrous metallic iron does not grow on the crystal face of iron oxide, while it grows in the direction parallel to the crystal face of iron oxide. Further,

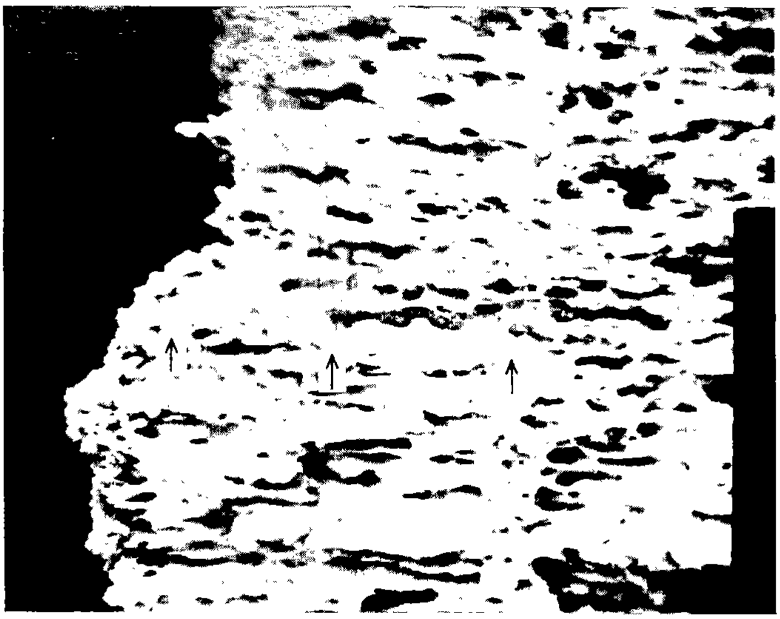


Photo. 5. Section of platelet Fe_2O_3 crystal reduced to metallic iron in H_2 at 950°C for 30min. x800
↑ marks correspond to the position for Auger analysis.

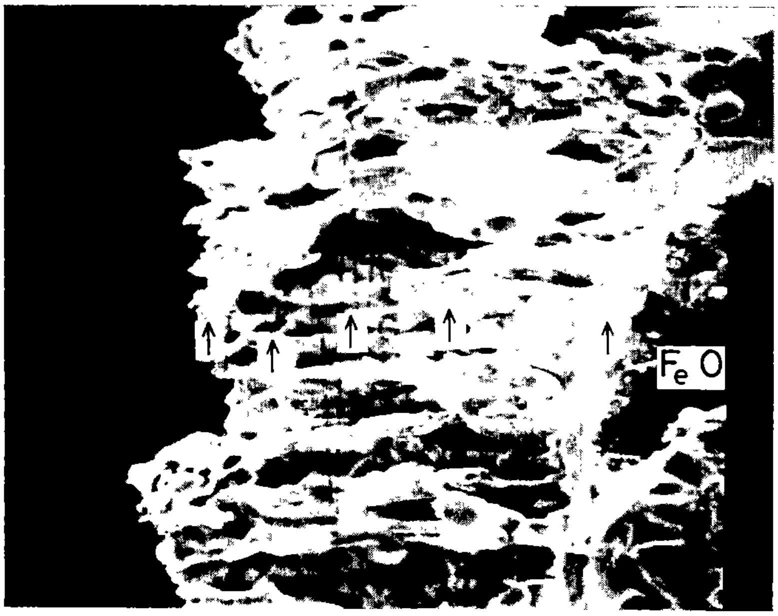


Photo. 6. Section of platelet Fe_2O_3 crystal reduced to metallic iron in CO at 950°C for 30min. x800
↑ marks correspond to the positfon for Auger analysis.

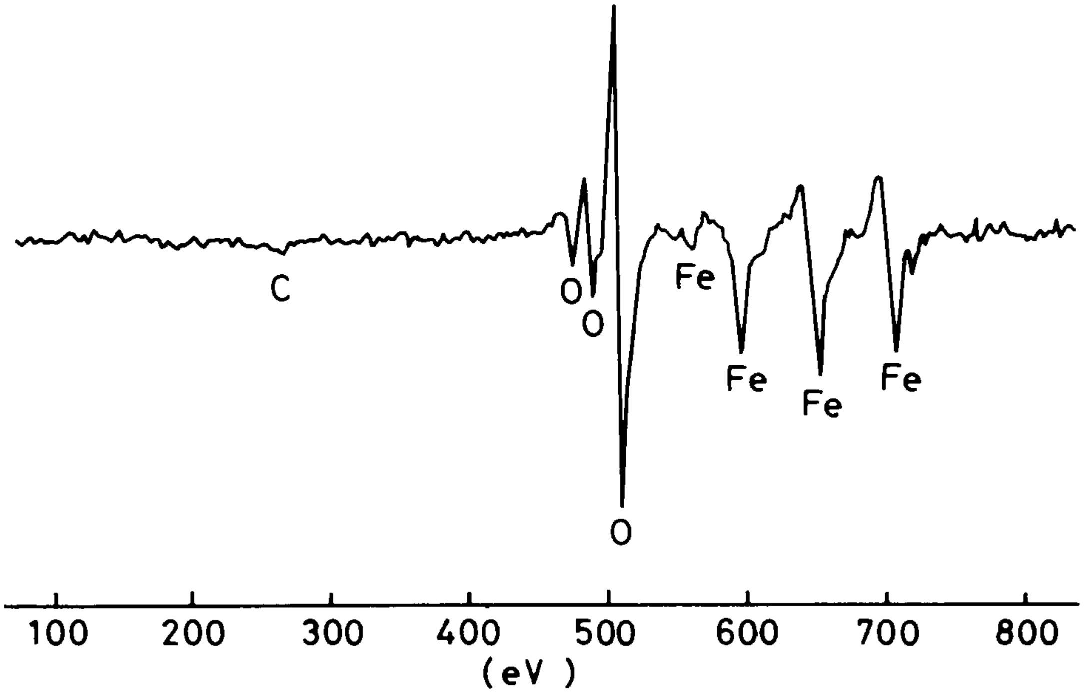


Fig. 3. Auger spectra of the sample showed in Photo. 5.

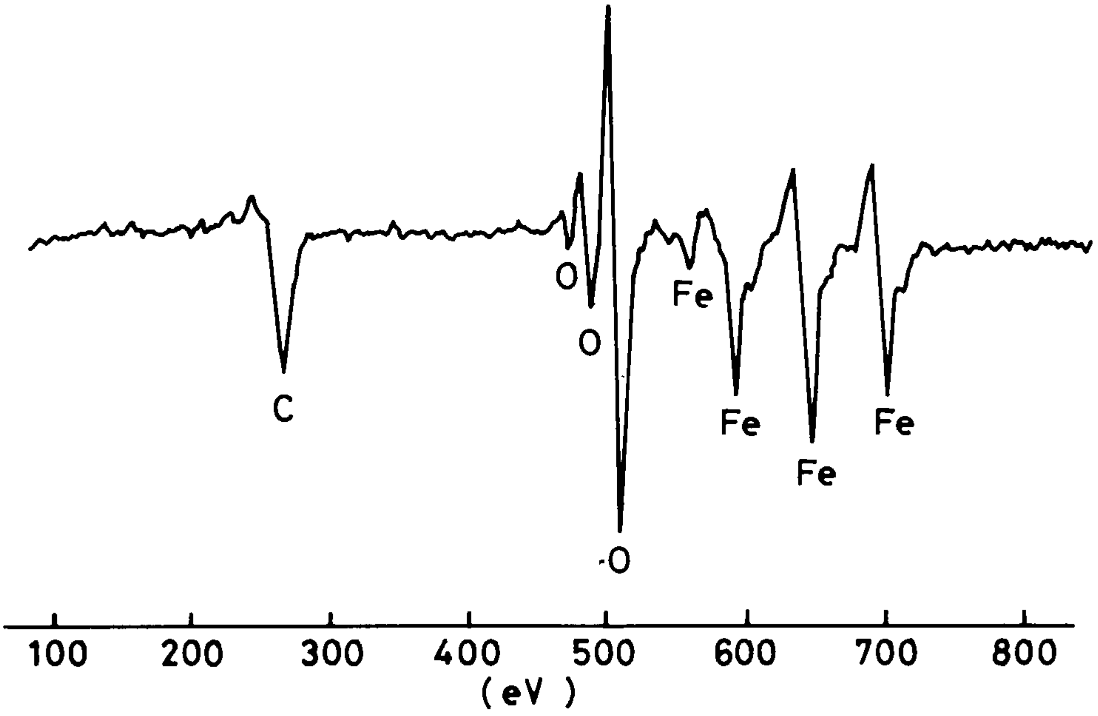


Fig. 4. Auger spectra of the sample showed in Photo. 6.

fibrous metallic iron often grows on the crystal face where the steps appear.

(3) On the electron diffraction figure, (111) pattern of α-Fe is observed and its direction of elongation is considered to be 〈110〉. Further, the existence of cementite was also identified.

(4) The quantity of carbon in fibrous metallic iron is usually higher than that in metallfc iron grown by the reduction of surfaces of iron oxide grains. It is considered to be attributed to the small thickness of 0.5–5 μ of fibrous metallic iron and the easiness of carburization based on a large specific surface area.

(5) For Swaziland ore, a particularly violent carbon precipitation reaction occurs and its pellet is readily expanded and pulverized.

(6) Ishimitsu et al.[7] indicate a trend of iron oxide grains to pulverize before an abnormal expansion. such a trend will be observed in Mosan ore (Photo. 2(1)). Further, Marcona ore (Photo. 2(h) (i)) gives a result where disintegrating is likely to occur.

(7) Wenzel et al.[2] estimate that one of the causes of abnormal swelling is disintegrating of ore by gas pressure caused by CO or CO_2 generated in the reaction interface. Depending on the results obtained by SEM observation and Auger electron spectral analysis method, as the existence of carbon is detected in metal iron and on the reaction interface in the case of CO-reduction, disintegrating of ore by generated gas is also regarded as one of the causes of abnormal swelling. However, it is evident that the most important cause of abnormal swelling is attributed to growth of fibrous metallic iron.

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Chapter 6

Fibrous Iron Growth during Reduction of Fe_2O_3 and Fe_3O_4 Single Crystal

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Synopsis

The change of crystal structure during reduction of iron oxide and the growth mechanism of fibrous iron were investigated.

In order to elucidate the crystallographic transition of Fe_2O_3 *during reduction, platelets of* Fe_2O_3 *single crystal with flat (0001) plane were used as the sample. Each of* Fe_3O_4*, FeO and Fe was prepared by reducing the* Fe_2O_3 *sample at 750°C with* CO-CO_2 *and* H_2-H_2O *gaseous mixtures of appropriate compositions. Further a reduction test of octahedral* Fe_3O_4 *single crystal was conducted. The structures of the products were analyzed by X-ray diffraction including the Laue method and scanning electron microscopy.*

The X-ray diffraction revealed that the (0001) plane of Fe_2O_3 *changed to the (111) plane of* Fe_3O_4 *and (111) plane of FeO by the epitaxial reaction. SEM revealed that as the reduction proceeded, steps parallel to the (0001) plane of* Fe_2O_3 *appeared remarkably, and fibrous iron grew from some nuclei on the steps. The fibrous iron was not seen on the (0001) plane of* Fe_2O_3*, and the direction of most active growth was* $[2\bar{1}\bar{1}0]$ *of* Fe_2O_3*. It became apparent that the growth of fibrous iron proceeds from the base.*

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I. Introduction

Regarding the reduction mechanism of iron oxide, for instance on the degradation and abnormal swelling of iron ore, many reports are available. In the previous report,[1)] the authors clarified the swelling mechanism in the reduction process using green pellets of natural ores of six origin. As a result of this study, it was ascertained that a definite relationship exists between the crystal structure of iron ore and its swelling properties. From the microscopic observation it was clearly proved that ore which has swelling properties shows good crystallization, although it has a little intracrystal defect such as intergrowth. In contrast to the former, the ore of no swelling properties forms an irregular mosaic structure. However, because the iron ore used was polycrystalline, the relationship between the crystal planes and the reduction characteristics was not sufficiently studied in the previous work.

In the present work, Fe_2O_3 and Fe_3O_4 single crystals were used as the test samples and the changes of crystalline orientation in the reduction course of $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$ was studied by means of X-ray diffraction methods including Laue method. In addition the growth mechanisms of fibrous iron which makes a cause of swelling was discussed by using a scanning electron microscope (SEM).

II. Experiments

1. Test Samples

In the present work, the following single crystals were used as the test samples : natural platelet Fe_2O_3, natural octahedral Fe_3O_4, artificial Fe_2O_3 and artificial Fe_3O_4. The natural Fe_2O_3 single crystal was quarried from Shiretoko peninsula, Hokkaido, Japan. It is a platelet crystal develpod along the direction of (0001) plane. The flat (0001) plane is 5 to 10 mm wide and about 0.5 mm thick. The parting plane is (0001) and $(10\bar{1}1)$ as shown in Photo. 1 (a).

The natural Fe_3O_4 single crystal was quarried from Kayaki, Kyushu, Japan. It is an octahedron surrounded by the planes of (111). The size of the particle is approximately 3 mm diameter (Photo. 1 (b)).

Artificial Fe_3O_4 single crystal was prepared by the hydrothermal method.[2)] As shown in Photo. 1 (c), the crystal is octahedron of about 0.5 mm diameter.

Artifical Fe_2O_3 single crystal was prepared by the flux method.[3)] The structure of the platelet crystal was shown in Photos. 1(d) to (f).

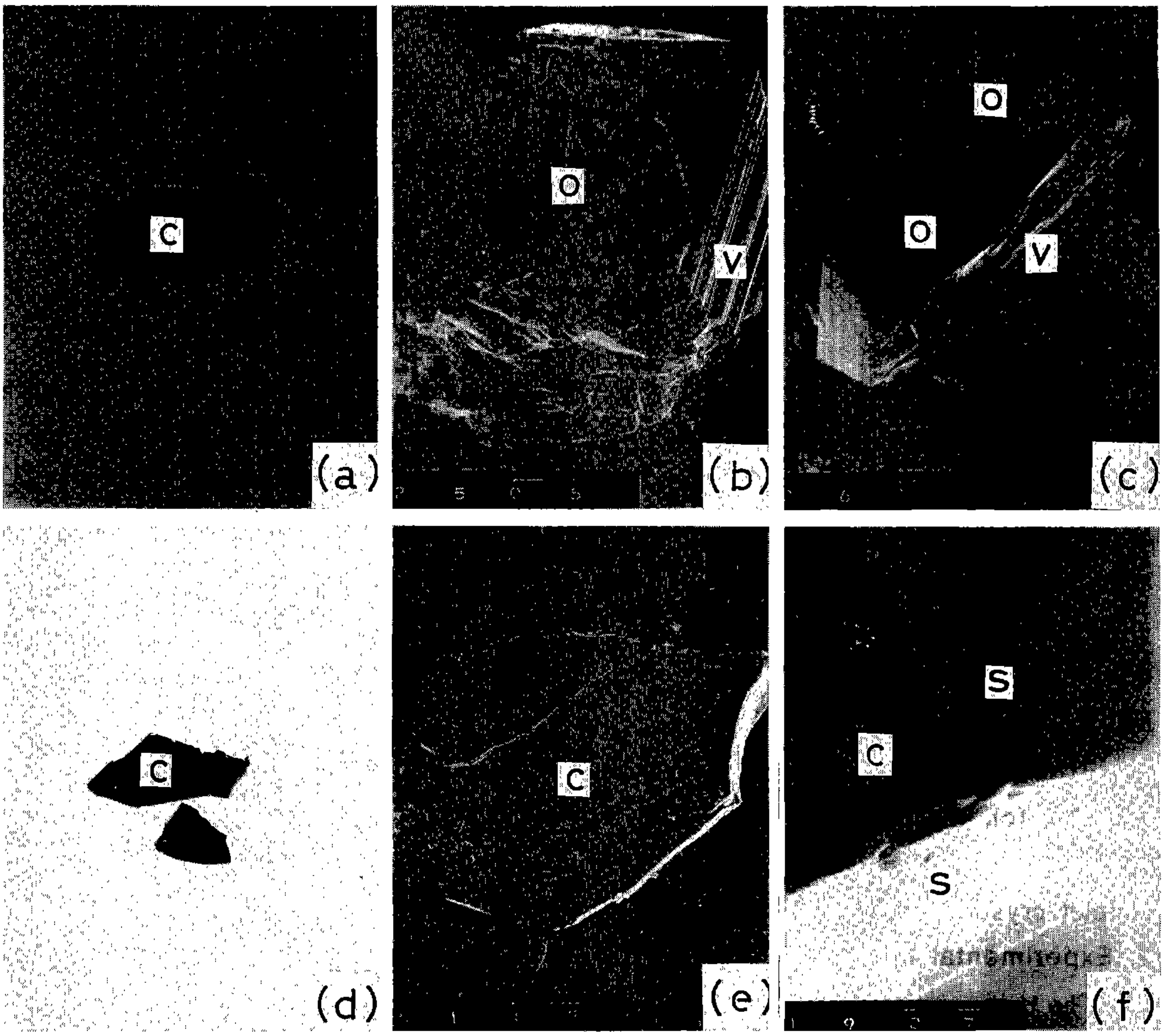
2. Experimental Method

The test samples (1~5 mm diameter) were placed on a sample holder made of iron (10 mm diameter and 5 mm high) to make SEM observation. Subsequently the holder was placed on a quartz boat. Using a horizontal tube furnace (32 mm inner diameter), the test sample was reduced.

Since the highest degree of swelling in the reduction of green pellets was obtained at approximately 750°C in the previous work, the reduction experiment was conducted at 750°C. The reducing gas was the gaseous mixtures of $CO\text{-}CO_2$, $H_2\text{-}H_2O$ and $H_2\text{-}N_2$, and the flow rate was 200 cc/min.

The test sample after reduction was cooled by moving the furnace to the gas outlet side. After cooling, the reduction gas in the reaction tube was replaced by N_2 and the test sample was removed. The surface of test sample placed on a sample holder after reduction was observed by SEM. The products at various oxidation stages were prepared by changing the composition of gaseous mixture at 750°C.

In addition to SEM observation of platelet Fe_2O_3 single crystal, X-ray diffraction was applied to the analysis of the crystal structure. After reduction of Fe_2O_3 single crystal, the



(a) Shiretoko Fe_2O_3 single crystal (×1.5)
(b) Kayaki Fe_3O_4 single crystal (×25)
(c) Artificial Fe_3O_4 single crystal (×75)
(d) Artificial Fe_2O_3 single crystal (×1.5)
(e) The same to sample (d) (×25)
(f) The same to sample (d) (×1500)
c : (0001) of Fe_2O_3
O : (111) of Fe_3O_4
v : Vertical section of octahedral Fe_3O_4
s : Section plane of Fe_2O_3 platelet

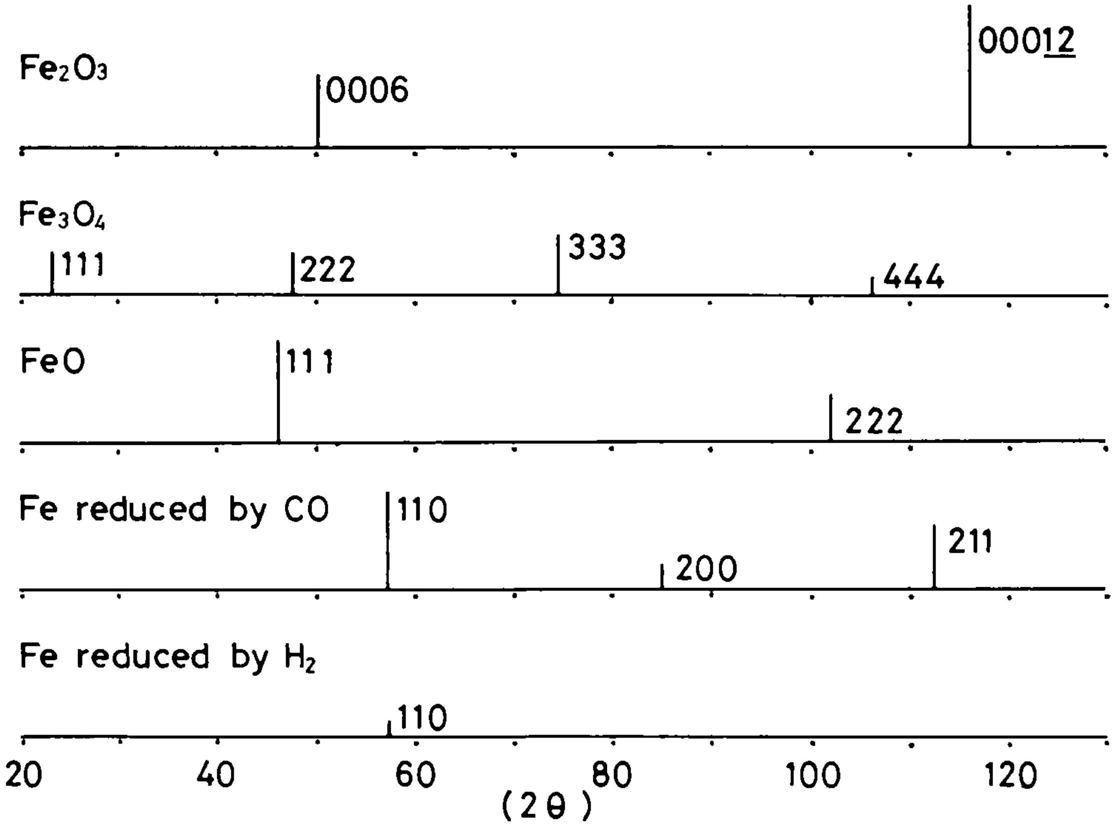
Photo. 1. Iron oxide samples

crystal was mounted onto the sample holder of the powder X-ray diffraction apparatus and X-ray diffraction was conducted. Further, this sample was subjected to the crystallographic analysis by the transition Laue method. In this case, a W-target was used and the distance between the sample and film was set at 40 mm.

Ⅲ. Experimental Results

1. X-ray Diffraction with Diffractometer

Figure 1 gives the results of X-ray diffraction for natural platelet Fe_2O_3 single crystals



Fe_3O_4, FeO and Fe were prepared in a gas stream of CO : CO_2=15 : 85 or H_2 : H_2O=20 : 80, CO : CO_2=50 : 50 or H_2: H_2O=50 : 50 and CO or H_2, respectively at 750°C

Fig. 1. X-ray diffraction lines of reduced products from platelet Fe_2O_3 single crystal (Fe-target was used as a X-ray source.)

reduced to various oxidation stages under the flow of CO-CO_2 and H_2-H_2O gaseous mixtures. When a Fe-target is used, the diffraction lines for the (0006) and (000$\underline{12}$) planes of Fe_2O_3 which are related to the (0001) plane were observed.

Fe_2O_3 crystals were partially reduced under the flow of CO-CO_2 or H_2-H_2O gaseous mixture. With regard to Fe_3O_4, the diffraction lines of the (111), (222), (333) and (444) planes which is related to the (111) plane were observed. In the case of FeO, the diffraction lines of the (111) and (222) planes were observed.

From the above results, it can be seen that the (0001) plane of Fe_2O_3 changes to the (111) plane of Fe_3O_4 and then to the (111) plane of FeO by the epitaxial reaction.

However, the diffraction lines of metallic Fe obtained by CO and H_2 reduction were quite different. When CO was used as the reducing gas, strong diffraction lines of the (110), (200) and (211) plane were seen. But in the case of H_2 reduction, only a very weak diffraction line of the (110) plane was seen. Even when reduction advances to Fe, it can be expected from the diffraction line that the (111) plane of Fe formed by H_2 reduction coincides with the (0001) plane of Fe_2O_3. Although X-ray diffraction was conducted with a Mo-target, the diffraction line of the (222) plane of Fe was not observed because of weak intensity.

2. Diffraction by Laue Method

Successively the diffraction by the Laue method was conducted. Laue patterns of the platelet sample reduced from Fe_2O_3 to metallic iron with CO-CO_2 and H_2-H_2O gaseous mixtures were observed.

Laue patterns of the platelet Fe_2O_3 (Photo. 2(a)) before reduction are shown in Photo. 2(b). A three-fold symmetry is seen when X-ray incident beam is normal to the (0001) plane. Laue patterns of the reduction product Fe_3O_4 (Photo. 2(c)) show a six-fold symmetry which is related to the three-fold symmetry of Fe_3O_4 single crystal prospected normal to the (111) plane (Photo. 2 (d)). Laue patterns of FeO also show six-fold symmetry (Photo. 2 (e)). There was no difference between the patterns of partially reduced oxides prepared in a gaseous mixture of CO-CO_2 or H_2-H_2O.

It can be seen from Photo. 2 (f) that Fe reduced by H_2 retains its six-fold symmetry, that the orientation of the (111) plane of Fe in an average manner coincides with the (0001) plane of Fe_2O_3.

In contrast, Fe reduced by CO shows no symmetric orientation of crystal (Photo. 2 (g)) indicating that polycrystalline iron was produced.

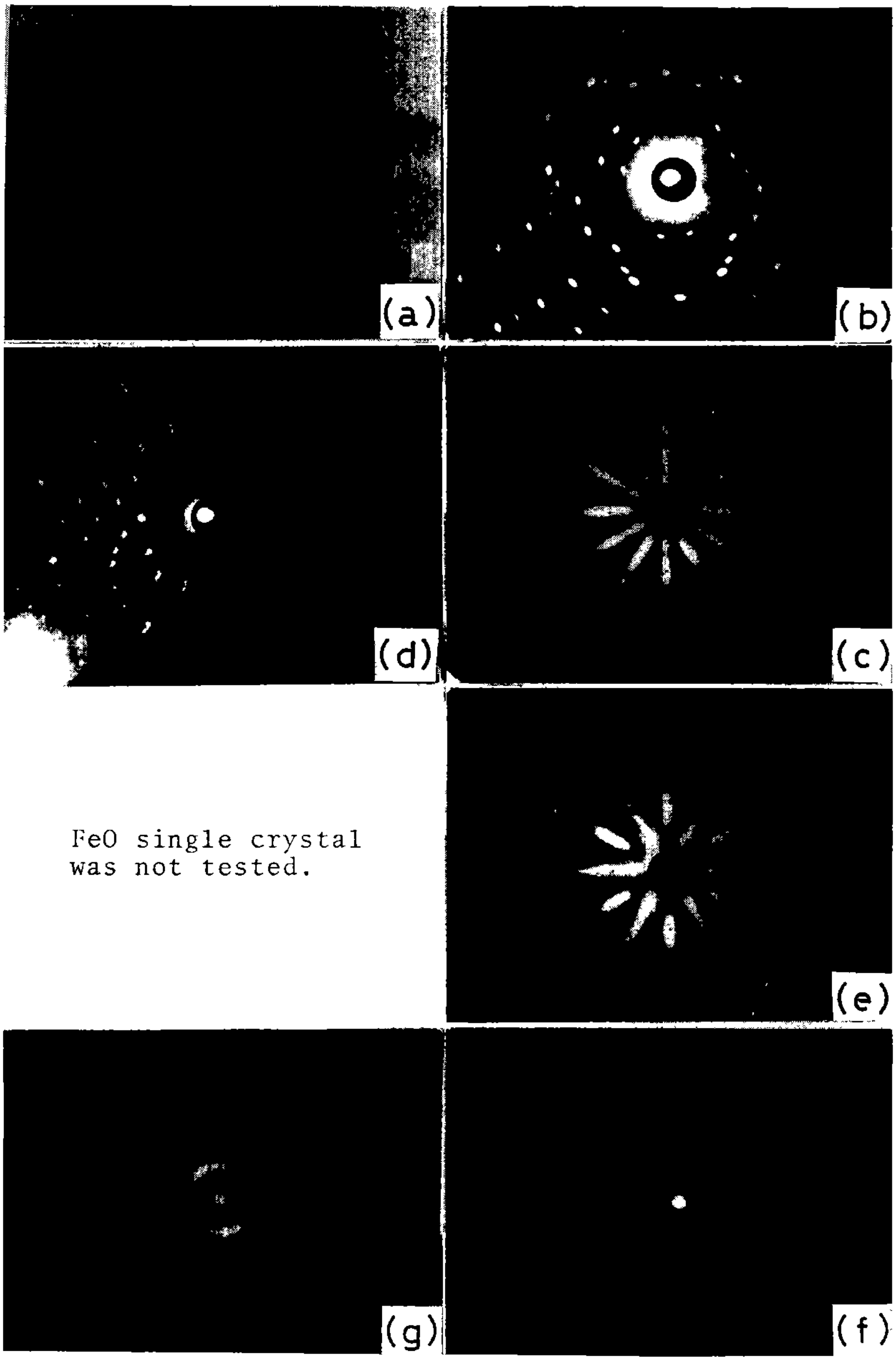
It is not clear why the patterns for the reduction products of Fe_3O_4, FeO and Fe (except Fe reduced by CO) show a six-fold instead of the three-fold symmetry. Nevertheless from the above results it may by expected that those reduction products have somewhat regular structure keeping crystal axes (namely [111] for Fe_3O_4, [111] for FeO and [111] for Fe) towards the same direction normal to the (0001) plane of Fe_2O_3.

3. Microscopic Observation

(1). Reduction of Platelet Fe_2O_3 Single Crystal by CO-CO_2 Gaseous Mixture

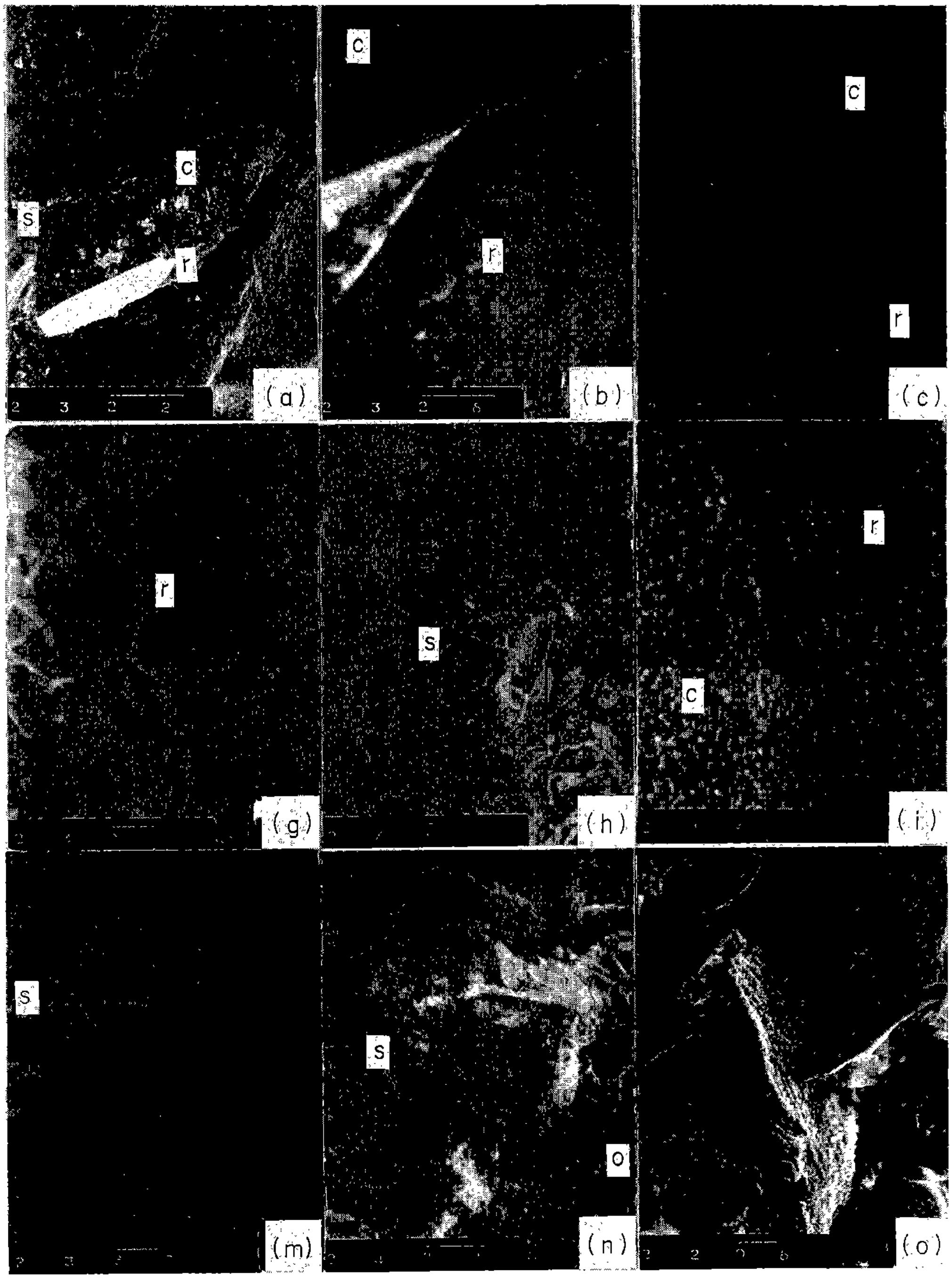
The surface structures of the crystals prior to reduction are shown in Photos. 3 (a) and (b). In an enlarged picture the mark c indicates the (0001) plane and the mark r the $(10\bar{1}1)$ plane. The other plane marked s is the section plane of the (0001) plane having $[2\bar{1}\bar{1}0]$ of Fe_2O_3. In Photo. 3 (c) the surface structure of the sample reduced to Fe_3O_4 by CO-CO_2 gaseous mixture is shown. In the (111) plane of Fe_3O_4 fine irregular cracks are seen and on the section plane a regular step formation can be recognized. In the reduction stage of FeO it is seen large cracks developing in parallel with the (111) plane of FeO (Photo. 3 (d)).

In Photo. 3 (e) the surface structure of Fe reduced from Fe_2O_3 single crystal by CO is shown. As can be seen from this photograph, the outward appearance is almost completely intact and the size changes are negligible small. As can be seen in Photo. 3 (f), there is absolutely no growth of fibrous iron on the (0001) plane of Fe_2O_3 while a remarkable



(a) The original crystal of Fe_2O_3 (×1.5)
(b) Fe_2O_3 before reduction, X-rav incident beam was normal to (0001).
(c) Reduced Fe_3O_4
(d) Fe_3O_4 octahedral single crystal, X-ray incident beam was normal to (111).
(e) Reduced FeO
(f) Fe reduced by H_2
(g) Fe reduced by CO

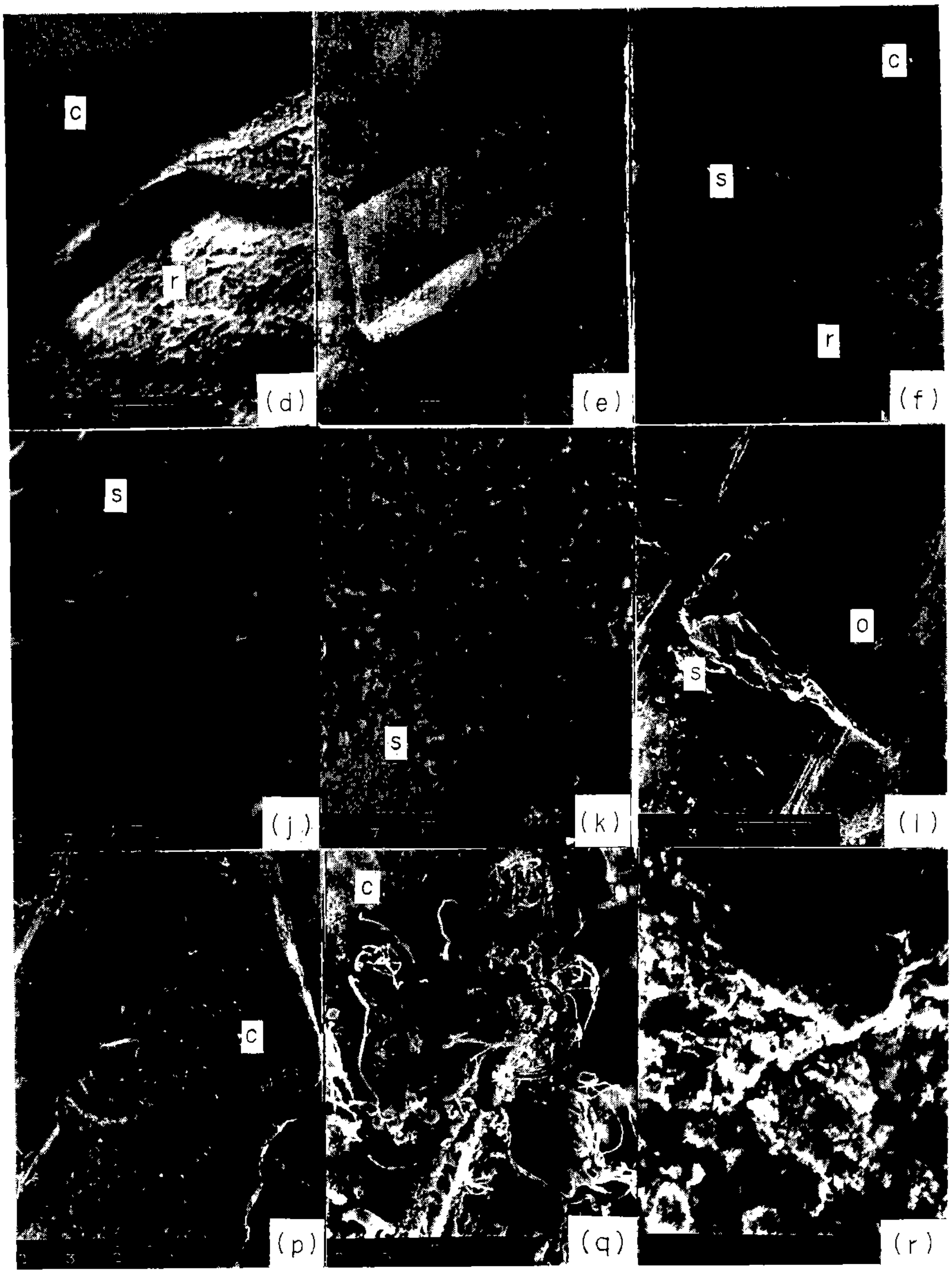
Photo. 2. Laue patterns of iron oxide samples reduced from platelet of Fe_2O_3 single crystal.



c : (0001) of Fe_2O_3
r : $(10\bar{1}1)$ of Fe_2O_3
s : Section plane having $[2\bar{1}\bar{1}0]$ of Fe_2O_3
o : (111) of Fe_3O_4

(a) Fe_2O_3 before reduction (×25)
(b) Enlarged picture of (a) (×750)
(c) Fe_2O_3, CO : CO_2=15 : 85 (×2500)
(d) Fe_2O_3, CO : CO_2=50 : 50 (×2500)
(e) Fe_2O_3, CO, (×25)
(f) Enlarged picture of (e) (×250)
(g) Enlaged picture of (e) (×2500)
(h) Enlarged picture of (e) (×750)

Photo. 3. Surface structure of iron oxides reduced at 750°C for 30 min in an atmosphere of CO-CO_2 and H_2-N_2.



(i) Fe_2O_3, H_2 (×750)
(j) Enlarged picture of (i) (×2500)
(k) Another part of (i) (×2500)
(l) Fe_2O_3, H_2 : N_2=20 : 80 (×750)
(m) Fe_3O_4 before reduction (×25)

(n) Fe_3O_4, CO : CO_2=50 : 50 (×2500)
(o) Fe_3O_4, CO (×750)
(p) Artificial Fe_2O_3, CO : CO_2=50 : 50 (×1500)
(q) Artificial Fe_2O_3, CO (×1500)
(r) Artificial Fe_3O_4, CO (×1500)

Photo. 3. continued.

appearance of fibrous iron is seen on the section plane of (0001). On the plane of $(10\bar{1}1)$ small protuberances were also observed (Photo. 3 (g)). Especially, the highest growth of fibrous iron is seen in the direction of $[2\bar{1}\bar{1}0]$, and it coincides with the direction made by the intersection of the two parting planes of Fe_2O_3 which are (0001) and $(10\bar{1}1)$, respectively (Photo. 3 (h)).

(2). Reduction of Platelet Fe_2O_3 Single Crystal by H_2-H_2O Gaseous Mixture

The surface structure of Fe reduced by H_2 is shown in Photo. 3 (i). Different from the case of CO-CO_2 reduction, the appearance of steps and cracks in parallel with the (111) plane of FeO is not seen. Photrgraphs 3 (j) and (k) give the c and s planes of Fe reduced by H_2 respectively. At the stage wherein metallic iron is produced, the reduction characteristics of the single crystal were shown to be clearly different from the case of CO or H_2 reduction. Namely, in the case of H_2 reduction the growth of fibrous iron was not observed. In order to know whether it is possible to grow fibrous iron by H_2 reduction or not, a reduction test was conducted with a diluted H_2 gas (H_2 : N_2=20 : 80).

The results obtained are shown in Photo. 3 (1). From Photo. 3 (1), it can be seen that there is a tendency of fibrous iron growth when reduction is conducted under the flow of H_2-N_2 gaseous mixture of low H_2 concentranion. However, as compared with the case of CO reduction, the growth of fibeous iron is indeed mild.

(3). Reduction of Octahedral Fe_3O_4 Single Crystal by CO

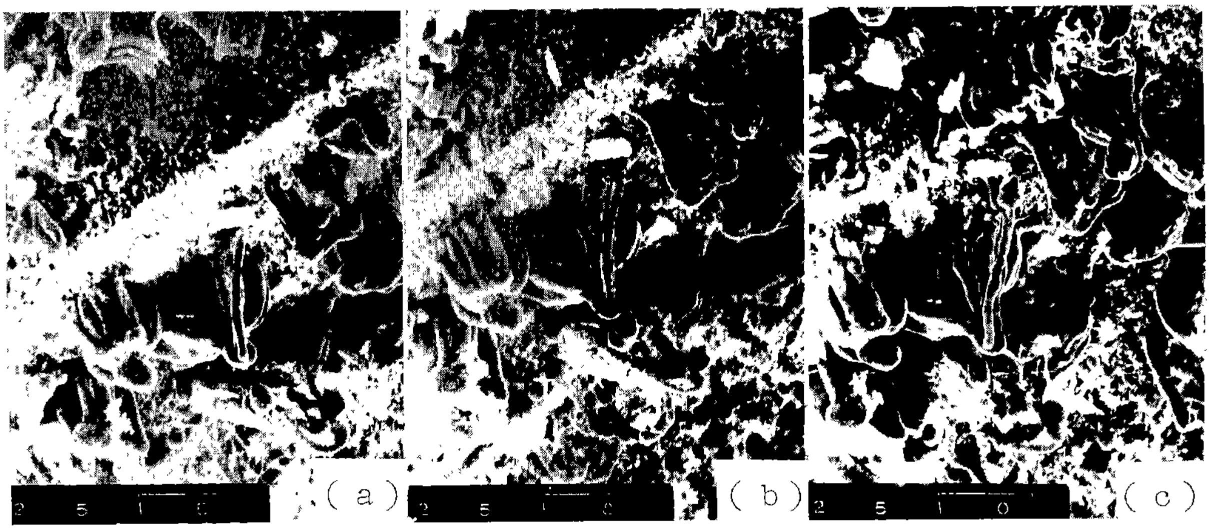
Photograph 3(m) give the (111) plane and the vertical section of Fe_3O_4 single crystal prior to reduction. Photographs 3 (n) and (o) show the surface structures of FeO and Fe reduced from Fe_3O_4 single crystal, respectively. As can be seen, no growth of fibrous iron was seen on the (111) plane of Fe_3O_4, while on the vertical section a remarkable growth of fibrous iron was seen.

(4). Reduction of Artificial Iron Oxide by CO-CO_2 Gaseous Mixture

The suface structure of FeO reduced by CO-CO_2 gaseous mixture from artificial Fe_2O_3 is shown in Photo. 3 (p). Steps, parallel to the c-plane of FeO, are seen on the r-plane. It is obvious from Photo. 3 (q), that fibrous iron does not grow on the (0001) plane of Fe_2O_3, but on the section plane. The surface structure of the reduction product of artificial Fe_3O_4 by CO is shown in Photo. 3 (r). The photograph shows that steps are formed and fibrous iron grows on the vertical section of Fe_3O_4.

(5). Growth of Fibrous Iron

Photographs 4 (a) to (c) give the surface structures of platelet Fe_2O_3 single crystal reduced by CO for 30 min, 45 (30+15) min and 90 (30+15+45) min, respectively. Observations were made in the course of fibrous iron growth especially at the same site. It is apparent that the growth of fibrous iron proceeds from the base in the course of reduction.



Reduction time : (a) 30min, (b) 45min, (c) 90min

Photo. 4. Continuous observation of fibrous iron growth by a reduction test of Fe_2O_3 single crystal at 750°C in CO atmosphere (×1500).

IV. Discussion

As a result of the above experiments, it was ascertained that in the cause of reduction ($Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$), steps made their appearance in parallel with the (0001) plane of Fe_2O_3 and the (111) plane of Fe_3O_4. These steps made a regular appearance with a spacing of approximately $1 \sim 2\mu$. The formation of these steps, as reported by Bleifuss,[4] may be considered as follows. Namely, in the transition of $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$ a relaxation of the crystal occurs because of the stress arising from the rearrangement of oxygen and iron ions. Further, the cracks appeared on the (0001) plane of Fe_2O_3 may be considered to be formed by the contraction of the crystal accompanied by the transition.

As can be seen from the results of X-ray diffraction, the (0001) plane of Fe_2O_3 and the (111) plane of Fe_3O_4 are extremely stable. This is probably due to the fact that a stable layer of close packed oxygen atom exists with a stabilized form in the crystal. Because of this, the (111) plane of FeO coincides with those of Fe_2O_3 (0001) and Fe_3O_4 (111). Because steps appear on the section of these planes, it may be surmised that the direction of the crystal axes does not change in the course of crystallographic transition of $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$, and that the crystal is formed by the layers accumulated each other. Each of these layers is loosely bonded and the presence of grain boundaries and interstices may be anticipated. From the observations of the course of fibrous iron growth, it was clearly shown that the fibrous iron grows from the base.

A higher diffusion rate of Fe^{2+} ion in the grain broundary may be readily surmised.

Further, it was also considered that the presence of grain boundary in paralleled with the $(10\bar{1}1)$ plane may be possible. Thus it was considered that in the direction of $[2\bar{1}\bar{1}0]$ made by the two parting planes of (0001) and $(10\bar{1}1)$, the diffusion of Fe^{2+} ion is facilitated. Because of this, growth of fibrous iron would be most intense in $[2\bar{1}\bar{1}0]$. Further, in the course of reduction the growth of fibrous iron would be negligble on the (0001) plane because there is a minimum possibility of forming such a grain boundary on the stable (0001) plane.

Regarding the growth mechanism of fibrous iron, Fuwa and Banya$^{5)}$ and Gränse$^{6)}$ explained as follows on the basis of Wagner's work.$^{7,8)}$ According to them, it is highly probable that the growth of fibrous iron is caused by the supersaturated Fe^{2+} ions in FeO crystal. The supersaturated Fe^{2+} ion in FeO migrates to iron nuclei with a high mobility.

Based on their experimental results, the authors considered that the growth of fibrous iron proceeds by a similar mechanism, but the nucleation site of metallic iron on the specific location of FeO is most imoportant. Namely the growth of fibrous iron is only seen in a two dimensional direction, parallel to the (0001) plane of Fe_2O_3 and the (111) plane of Fe_3O_4. Thus the diffusion of Fe^{2+} ion seems to occur rapidly and intensely in this direction, since the growth of fibrous iron appears remakably in the same direction. In the case of CO reduction the growth of fibrous iron is remarkable while in the case of H_2 reduction no growth is seen, whereas the growth of fibrous iron is very little at a slow reduction rate with a low concentration of H_2. Thus the discussion was made on the cause of the growth of fibrous iron.

In the case of CO reduction iron nuclei are favourably formed on the section plane of (0001) of Fe_2O_3. As a result, Fe^{2+}ion diffuses mainly to the nuclei through the grain boundary developed parallel to the (0001) plane of Fe_2O_3, and at nucleation site the following reaction occurs, *i. e.*, $Fe^{2+} + 2e^{-} = Fe$. When the number of nuclei is small, it is surmised that the growth of fibrous iron is brought about by the diffusion of Fe^{2+} ion to the nuclei and by successive iron formation. Thus reduction proceeds non-topochemically, and results in the production of polycrystalline iron as confirmed by the X-ray analysis.

In the case of H_2 reduction, H_2 reacts with FeO and forms a thin layer of metallic iron over the surface.$^{1)}$ Therefore, it is considered that reduction of Fe_2O_3 proceeds topochemically.

When a diluted H_2 is used as the reduction gas, reduction proceeds at a slow rate on the surface of the crystal, and nucleation is fairly limited on the section plane of (0001) plane since the concentration of hydrogen is low. It is surmised that the diffusion rate of Fe^{2+} ion to the nuclei formed on the section plane is relatively high as compared with the surface reaction. Due to this reason, when the concentration of H_2 is low, the growth of fibrous iron is seen. However unlike the case of CO gas reduction, a mild surface reaction proceeds simultaneously, so that the crystal is gradually covered with a Fe layer. Consequently the growth of fibrous iron becomes discontinuous and a long fibrous iron is harbly formed as observed in the case of CO gas reduction.

Reduction of Fe_3O_4 single crystal proceeds by the mechanism almost similar to that for reduction of Fe_2O_3. Namely, in the grain boundary developed in parallel with the (111) plane, the diffusion of Fe^{2+} ion occurs readily. Because of this reason no growth of fibrous iron is seen on the (111) plane of the original Fe_3O_4 crystal. And as result of this experimental work, it was clarified that fibrous iron is grown on its vertical section.

Reduction of natural iron ore will be dealt with here.[1,10] From the results of reduction of Swaziland Fe_2O_3 ore (of poor crystallization), when ore with irregular crystal grain structure is subjected to reduction, the diffusion of Fe^{2+} ion becomes difficult since a regular grain boundary cannot be obtained. Bcause of this fact, no growth of fibrous iron is seen. In the case of Brazil Fe_2O_3 ore, since this ore has a laminated structure parallel to the (0001) plane and the grain boundary readily appear in the course of reduction, a growth of fibrous iron is seen in the direction parallel to the (0001) plane. Likewise in the case of Mosan Fe_3O_4 ore, the regular steps of the same direction appears evidently and fibrous iron was seen.

In comparison of single crystal with natural ore, it was noted that an intense growth of fibrous iron was seen in the natural ore. This would be due to the fact that natural ore is subjected to dynamic metamorphism and recrystallization which results in an increase in defects of the crystal. It is surmised that the formation of such a grain boundary arises readily from the above morphology banded structure, for instance in Brazil and Mosan ores.[11] Watanabe and Yoshinaga[12] pointed out that one of the causes for the formation of fibrous iron may be attributed to the presence of microtwin (in the case of Yampi ore) and intergrowth (for underfired Marcona pellets). Ende *et al.*[13] observed fine hematite intergrowth in lime added pellets which showed abnormal swelling. Recently, Lu[14] payed attention to the intergrowth as one of the causes of swelling. From our experimental results, it was considered that intracrystal defects such as twin and intergrowth may well be one of the factors which enhance swelling.

Investigations on the influence of additives (alkaline metal oxide and slag forming materials) and metallographic examinations (such as pore structure in natural ore as well as pellets) are of further interest.

V. Conclusion

Using iron oxide single crystal as the test sample, the change of crystal structure during reduction and the growth mechanism of fibrous iron were investigated. The results obtained are summarized as follows :

(1) The (0001) plane of Fe_2O_3 changed to the (111) plane of Fe_3O_4 and the (111) plane of

FeO by the epitaxial reaction during reduction. As reduction proceeded, steps parallel to the (0001) plane of Fe_2O_3 appeared on the section plane normal to the (0001) plane.

(2) It is considered that the samples reduced to FeO are composed of the stacking of thin FeO crystallines ($1\sim2\mu$), and that the axis of each crystalline orient towards the same direction of [111].

(3) As the reduction reaction proceeded further, iron nuclei were formed preferentially on the section plane of the (111) plane of FeO. Supersaturated Fe^{2+} ions migrate readily to iron nuclei through the grain boundary developed parallel to the (111) plane of FeO. It is surmised that metallic iron was formed at nucleation site and fibrous iron was grown by the base growth mechanism.

(4) Fibrous iron was not seen on the (111) plane of FeO, but on the section plane of (111). Because nucleation of metallic iron hardly occurs on the (111) plane of FeO and the grain boundary in which Fe^{2+} ions migrate readily is scarcely formed, the growth of fibrous iron on the (111) plane is negligible.

(5) It is considered that the existence of intracrystal defect such as a loosely bonded grain boundary is necessary in the case that the diffusion of Fe^{2+} ion is relatively higher as compared with the growth rate of nucleus.

(6) The growth of fibrous iron is observed remarkably in the case of CO reduction, while no flbrous iron is observed for H_2–reduction. The above experimental facts may well be explained by the following mechanism.

Since the rate of the surface reaction by H_2 is higher than that by CO, the surface of FeO crystal is covered completely with Fe layer in a short reduction time. In this case the diffusion of Fe^{2+} ion towards the specific iron nuclei will not take place, therefore reduction proceeds with a topochemical reaction. When H_2 diluted with inert gas is used as the reduction gas, the location of nucleation of Fe is fairly limited on the section plane of FeO (111). If the diffusion rate of Fe^{2+} ion towards the nuclei is higher than the rate of the surface reaction, the fibrous iron grows. However, since the surface reaction proceeds simultaneously, FeO crystal is covered with Fe layer gradually. Consequently, the growth of the fibrous iron is discontinued.

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Chapter 7

Reduction of Platelet Fe_2O_3 Single Crystal Reacted with Na_2O, K_2O, CaO and Silicate Slag at the Surface of Fe_2O_3 c Plane

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Synopsis

The effect of K_2O, Na_2O and CaO on the reduction behavior of Fe_2O_3 was investigated. Platelets of Fe_2O_3 single crystals were prepared by the flux method. The size of the crystals was approx. 3mm in width and 0.3mm in thickness. For the reaction of Fe_2O_3 with K_2O, Na_2O, and CaO, small amounts of each carbonate powder were placed on the flat plane (0001) of Fe_2O_3 and heated at 1100～1300°C in the air. It was confirmed by EPMA that the reaction products with those substances were formed on some parts of the Fe_2O_3 crystal. The crystals were reduced at 750°C in CO and H_2 streams, and the surface structures were observed by SEM.

The results obtained were as follows. When alkaline metals (as Na_2O, K_2O) were present in Fe_2O_3, the abnormal swelling took place during the reduction. It was considered that the swelling was caused by (1) the cracking of the crystal at the early stage of the reduction, (2) the fibrous iron formation and (3) the carbon deposition on the reduced iron. The fibrous iron formation was also observed in the grain boundary of calcium ferrite. The reduction with a glassy slag (SiO_2-Al_2O_3-CaO) was also investigated and no swelling phenomenon was shown.

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I. Introduction

It is known that impurities contained in hematite especially alkali and alkaline earth metal elements have remarkable effects on its reduction behavior. Khalaffalla and Weston, Jr.[1] conducted an investigation on the impurities which enhance the reduction of wustite, and reported that the minute addition of alkali and alkaline earth metals enhances the reduction. They recognized that the larger ion radius resulted in the more enhancing effect. This is surmised as follows. The relatively large cations penetrate into the wustite lattice. The penetration causes increases in the disturbance of the lattice and also in the surface reaction rate. In other words, this may be attributed to the Vol'kenshtein effect which is seen when alkaline metals are added to iron catalysts. Regarding this point, Ende *et al.*[2] measured the lattice constant in the oxidized pellets with addition of several percent of $NaKCO_3$, which underwent the reduction to Fe_3O_4 and FeO. They recognized that the lattice constant increased with the addition of alkali elements. They also reported that an abnormal swelling was seen in the reduction step from wustite to metallic iron. They have explained that the lattice constant of wustite increases by the addition of an alkali component, on accounts of the large influence in the solid state diffusion and the surface reaction. The stepwise reduction behavior from wustite to iron, thus, remarkably changed. Ende *et al.* surmised that the reason why the pellets swell in sponge structures is due to the anisotropical growth of the metallic iron from the wustite phase, but could not make a clear statement on the growth of the fibrous metallic iron. Nakazawa *et al.*3) conducted an investigation on the reduction of the pellets pretreated in sea water, and reported that the Na portion in the interstices of the hematite phase had the distinct relation with the extent of the abnormal swelling, and surmised that the growth of the fibrous metallic iron was the cause of the abnormal swelling. Further, Lu4) reported that the abnormal swelling was seen in the reduction of the pellets when Na_2CO_3 was added. He also recognized that the degree of the swelling was reduced by carrying out a prereduction treatment. These reports2–4) came to the conclusion that the abnormal swelling was caused by the addition of an alkali component.

On the other hand, Bleifuss5) reported that Ca, one of alkaline earth metals, also enhanced the grouth of the fibrous iron and caused the abnormal swelling. On the basis of the experimental results of synthetic calciferrous magnetite as the sample, he discussed on the growth mechanism of the fibrous iron. With advance in the reduction, a phase with the high concentration of CaO forms on the surface of calciferrous magnetite and supresses the growth of the iron nuclei. As a result the iron nuclei from only on the limited site. When the reduction advances and the iron nuclei generate, the diffusion of ferrous ion to these iron nuclei occur and the metallic iron formed pushes up the iron phase. According to this root growth mechanism the fibrous metallic iron grows. Khalaffalla and Weston, Jr.1) reported on the reduction rate, but did not on the swelling of hematite. Regarding the cause of the enhancement of the reduction, they stated that by the addition of impurities the wustite crystal lattice was disturbed and the numbers of the active sites increased. This is based on the lattice disturbance mechanism. The abnormal swelling discussions were based on the increasing lattice disturbance of wustite which arised with the impurities.2,3,5) Therefore, if there is the lattice disturbance due to the addition of impurities in hematite, it may be considered that the increasing reduction rate and the swelling volume appears.

In the former reports, the influence of impurities on the reduction behavior were mainly examined by measuring the reduction rate, the swelling index and the gas flow resistance of the reduction gas, *etc.* It may be noted that few hematite granules are microscopically observed in the course of the reduction and supplementary experiments is insufficient to support their respective reduction mechanism theories. The authors in the present report, mainly using an electron scanning microscope, conducted the microscopical observation of the impurities which are said to have an influence on the reduction behavior and the effect on hematite reduction. The samples used was of artificial single crystal platelet hematite which was reacted with Na_2O, K_2O, CaO and silicate slag at high temperatures. The basic investigations were microscopically carried out on the above mentioned reduction reaction.

Ⅱ. Preparation of Samples and the Experimental Method

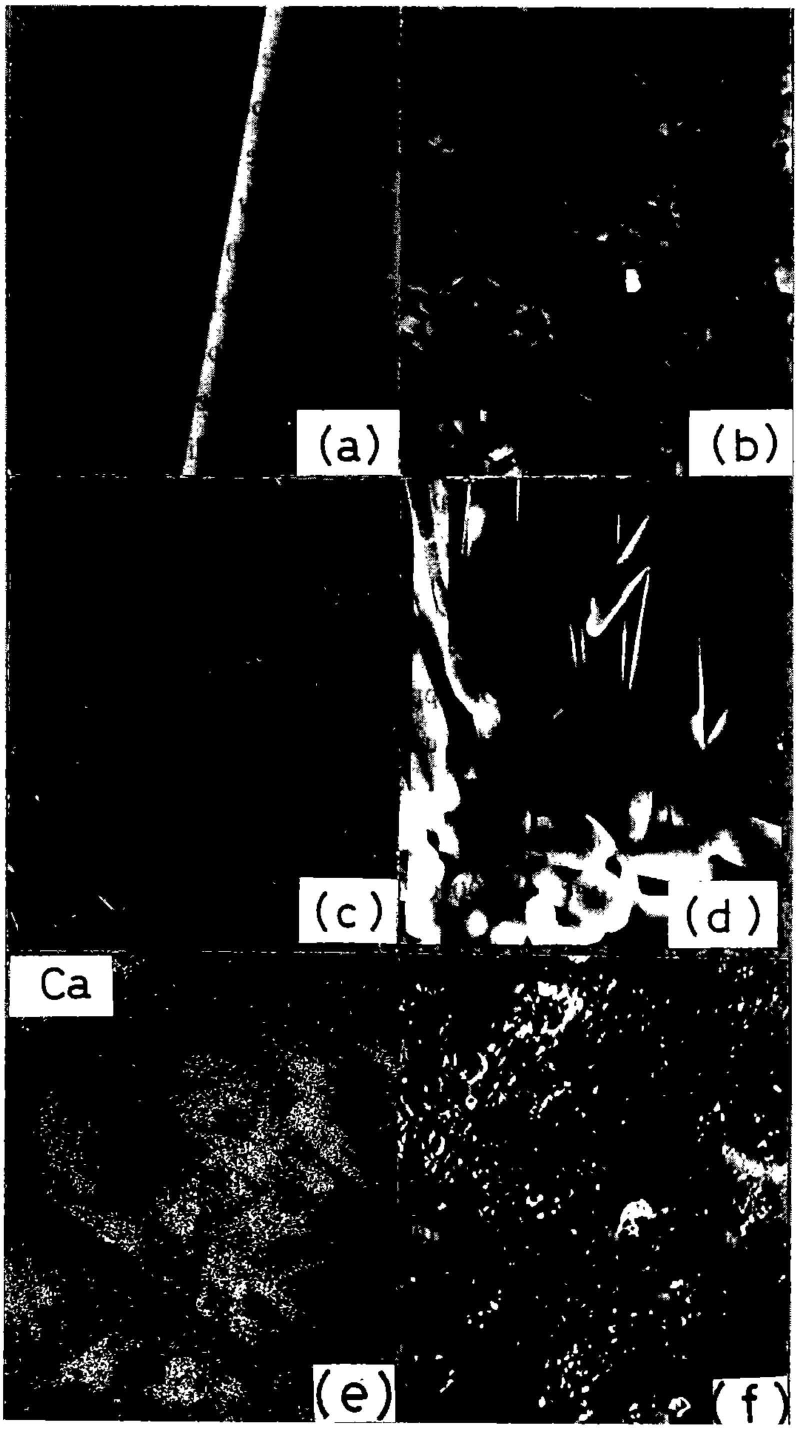
1. Growth of Fe_2O_3 Single Crystal

It is convenient to use homogeneous hematite as the sample for the reduction experiments. The advantage is that the artificial homogeneous Fe_2O_3 single crystals have a flat plane (c plane) with few cracks or voids and the reaction sites where the reaction with the impurities occur may be readily observed. The growth of Fe_2O_3 single crystal was carried out by the flux method. The Fe_2O_3 reagent contained Al_2O_3 of 0.04, MgO of 0.10, MnO of 1.20 and TiO_2 of 2.00 %. As the flux, borax glass powder ($Na_2B_4O_7$) was used. The raw material used was of a powder mixture, the mixing ratio of which was Fe_2O_3 reagent 3 to the borax glass 7.[6,7] The material weighing 20 g was placed in a 30 cc platinum crucible. The temperature of the material was raised to 1200°C at a rate of 100°C/h in an electric furnace and kept for 10 h. Then the furnace was cooled at a rate of 3.3 °C/h to 800°C. Then the crucible was removed from the furnace and allowed to cool down at room temperature. The Fe_2O_3 crystals grown in the crucible were separated by dissolving the flux in a warm 10% HNO_3 solution.

The obtained crystals were of platelets with the well developed c plane, and the sizes were a diameter of 3~5 mm and a thickness of 0.2~0.3 mm. The platelet crystal was apparently flat, but under the magnification in many cases thin terrace and twin like formations were seen. These formations appear in the course of the growth of the crystal. Photograph 1(a) shows the c plane (right) and the side view (left) of the grown Fe_2O_3 crystal. Since there was a possibility that the Fe_2O_3 crystal was doped by the Na portion of the flux, the atomic absorption analysis of Na in the crystal was conducted and the doped amount was found to be 0.008%. But the analysis of B was not conducted because of the very weak sensitivity of the spectrum. The other impurities in the grown crystal were 0.01% Mg, 0.47% Mn and 0.46% Ti.

2. The Reaction of Fe_2O_3 with the Added Impurities in the Air

For the experimental investigation of the influence of Na, K and Ca on the reduction of Fe_2O_3, it is necessary to make solid solutions of metal oxides and Fe_2O_3 crystals or the chemical compounds.



(a) (0001) plane of Fe_2O_3 (right) and the side plane (×1500)
(b) the one reacted with Na_2CO_3 at 1100°C in air (×1500)
(c) the one reacted with K_2CO_3 at 1100°C (×1500)
(d) the one reacted with $CaCO_3$ at 1300°C (×1500)
(e) the reduced picture (Ca image) of (d) (×150)
(f) the one reacted with silicate slag (×150)

Photo. 1. Surface textures of Fe_2O_3 crystals.

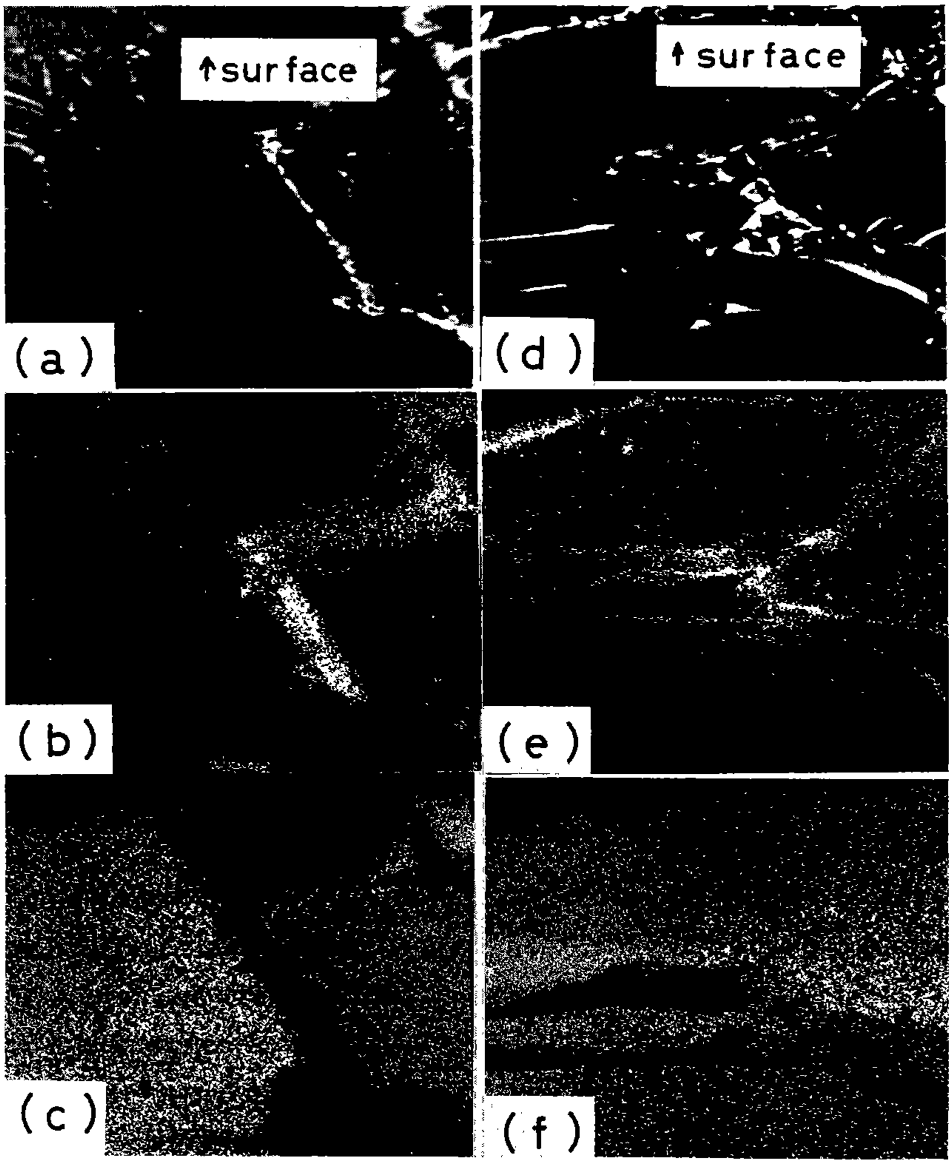
NaCl and Na_2CO_3 were used for the additive of Na. However, in the case of NaCl (the melting point of approximately 800 °C), it was observed by a high temperature optical microscope that above 800°C the gradual evaporation began and at 1000°C even the traces disappeared to result in no reaction with Fe_2O_3. In the case of Na_2CO_3, above the melting point of 850°C the partial decomposition was observed by a microscope (the generated vapor condenced on a window of the microscope), and at 1000°C a phase which seemed sodium ferrite was formed. When it was continuously heated over 1300°C, the phase suggestive of sodium ferrite melted and the compound decomposed. Photograph 1(b) shows the surface of the sample heated at 1100°C. The adhesion structure of the fine reaction products of $1\sim2\ \mu$ m, and the cracking between the crystals are seen. The distribution of the Na component inward the crystal was observed on the c plane of the Fe_2O_3 crystal fractured by EPMA. As shown in Photos. 2(a) to (c) which are the images of the back scattering electron, Na X-ray and Fe X-ray (the surface facing upwards) respectively, the Na component penetrates clearly into the crystal through the cracks and the grain boundaries.

K_2CO_3 has the melting point of approximately 890°C. Above 890°C, the partial evaporation is seen and a phase of potassium ferrite perhaps forms. When the temperature is continuously increased, the gradual evaporation of the K component occurs, but the decomposition does not complete even at 1300°C unlike the cases of Na_2CO_3. In Photo. 1(c) the surface of the sample heated to 1100°C is shown. Fine needle like crystals are seen on the surface. The distribution of the K component in the crystal was observed on the fractured crystal by the EPMA. The results are shown in Photos. 2(d) to(f). From these results, it may be also seen that the K component are distributed along the cracks and the grain boundaries.

While $CaCO_3$ decomposes into CaO by approximately 900°C, the reaction with Fe_2O_3 does not proceed so much, but at 1280°C a phase of probable calcium ferrite begins to from.
In Photos. 1(d) and (e) which show the surfaces of the samples heated to 1300°C, a compound of $CaO\text{-}Fe_2O_3$ system is seen to grow by the solid reaction in a radiating fashion. Photograph 1(f) shows the Fe_2O_3 surface reacted with the slag (SiO_2 62%, Al_2O_3 14%, CaO 24%) at 1350°C.

3. Identification of the Reaction Products between Fe_2O_3 and Various Carbonates

In order to identify the phases of ferrites which were formed on the c plane of Fe_2O_3, the plate like Fe_2O_3 samples were pulverized and analyzed by the powder X-ray method. However, since the layer of the reaction products was exceedingly thin and the amounts of the products were very little, no other diffraction lines except Fe_2O_3 were seen. Thus, in order to increase the volume of the reaction products, pulverized Fe_2O_3 crystals were mixed with the additives concerned at a rate of approximately 2 : 1 and then in the cases of Na_2CO_3 and



(a) back electron image (BEI) of the side plane, reacted with Na_2CO_3 at 1100°C
(b) NaKα image of (a)
(c) FeKα image of (a)
(d) BEI of the side plane reacted with K_2CO_3
(e) KKα image of (d)
(f) FeKα image of (d)

Photo. 2. Textures of the section plane of Fe_2O_3 platelet and its X-ray images. (×150)

K_2CO_3 the mixture was heated at 1100°C, and in in the case of $CaCO_3$ the mixture was heated at 1300°C. These samples were analyzed by the X-ray diffraction method. The X-ray diffraction showed β-$NaFeO_2$ as a compound of Na_2O and Fe_2O_3, and $KFeO_2$ as a compound of K_2O. However the latter diffraction lines disappeared in a very short time in air.

Besides these $KFeO_2$ diffraction lines, there were several other ones which could not be identified. In this case a remarkable decrement of the Fe_2O_3 diffraction lines was seen. Of three types of the binary calcium ferrite in the CaO-Fe_2O_3 system, namely $CaO \cdot Fe_2O_3$, $2CaO \cdot Fe_2O_3$ and $CaO \cdot 2Fe_2O_3$, in the present case, the production of $CaO \cdot 2Fe_2O_3$ alone was recognized.

4. Experimental

With the Fe_2O_3 crystals reacted with Na_2CO_3 or K_2CO_3 at 1100°C and $CaCO_3$ at 1300°C, the reduction experiments were carried out in the same manner as reported in our previous publication.[8)] Namely, the Fe_2O_3 crystals were placed on an SEM sample holder made of iron. The holder was placed on a quartz boat and inserted in a horizontal tube furnace for the reduction experiments. Reduction gases used were a CO gas and a gas mixture ($CO : CO_2 = 50 : 50$).

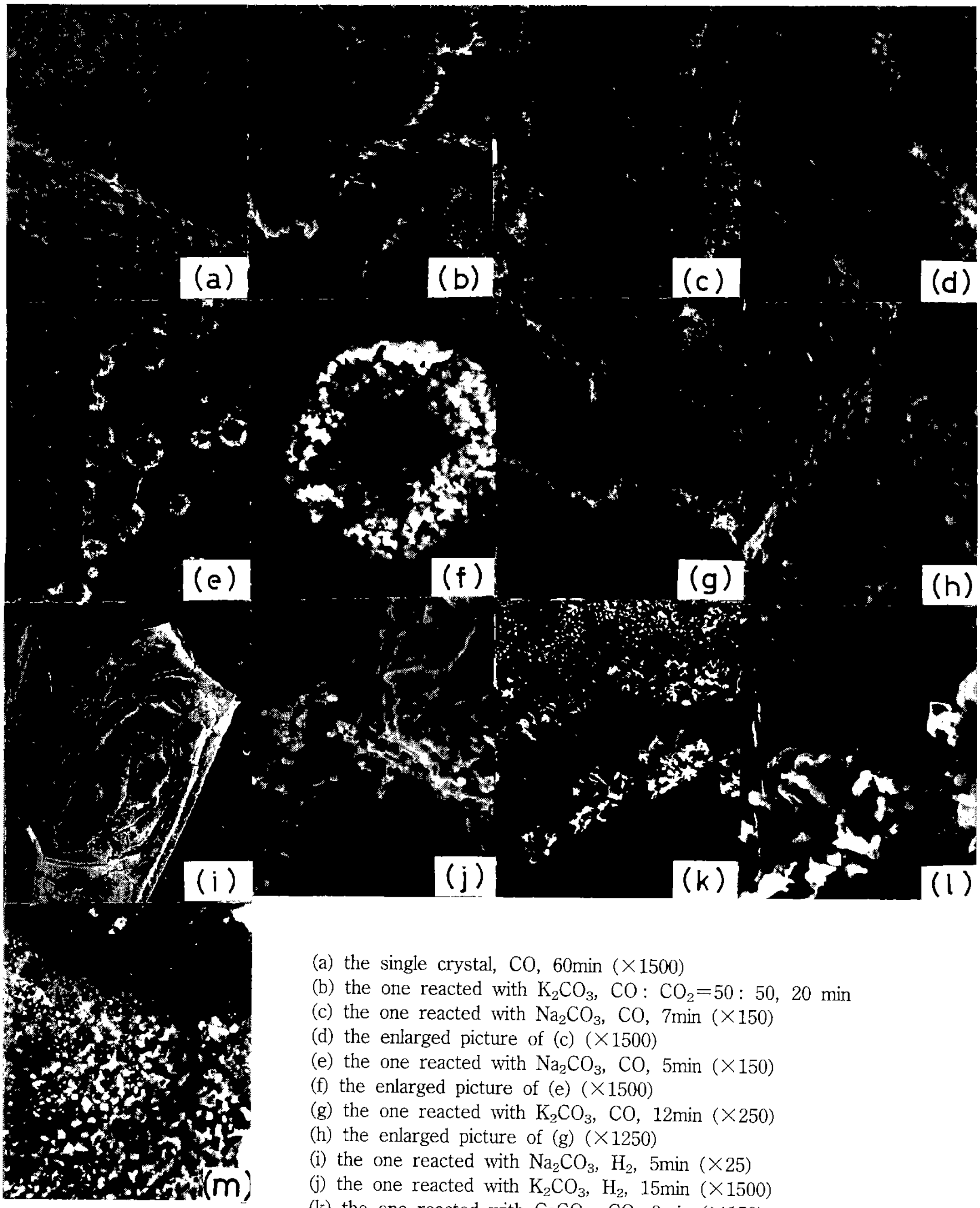
The reduction temperature was set at 750°C. The samples after the reduction were cooled in the reaction tube by shifting the electric furnace in the direction to the gas outlet. After the exchange of the atmosphere to N_2 gas, the cooled samples were removed together with the SEM sample holder. The surface of the sample were observed with a SEM.

Ⅲ. Experimental Results

1. Reduction of Fe_2O_3 Crystals Reacted with Additives at High Temperatures

Photograph 3(a) shows the surface of the synthetic Fe_2O_3 crystals reduced in CO of a 200 cc/min gas flow at 750°C for 60 min. The growth of the metallic iron protuberances is seen on the side face of the c plane of the Fe_2O_3 crystals ; however the extent is about a tenth as small as that of the natural Fe_2O_3 single crystals reported in our previous paper.[8)] This suggests that the lattice defects arising from the impurities in the crystal, are much more for the natural crystal.

Photograph 3(b) shows the results when the samples produced through the approxmately uniform reaction with K_2O on the c plane of Fe_2O_3 are reduced to FeO in $CO : CO_2 = 50 : 50$ gas flow of 200 cc/min. As may be seen, by the time the reduction to FeO is completed, a large crack appears to penetrate inwards from the c plane of the Fe_2O_3 crystal. Photographs 3(c) and (d) show the results when the reaction product samples produced through an approximately uniform reaction of Na_2O on the c plane of Fe_2O_3 are reduced for 7 min in a CO gas flow of 200 cc/min. The development of the large cracks are seen, and the enlarged Photo. 3(d) shows the fine structure within the cracks. These seem metallic iron protuberances or deposited carbon particles. This will be discussed later on the carbon deposition phenomenon. When the sample in which the reaction with a minute amount of Na_2CO_3 powder partially proceeds on the c plane of Fe_2O_3 is reduced for 5 min in a CO gas



(a) the single crystal, CO, 60min (×1500)
(b) the one reacted with K_2CO_3, CO : CO_2=50 : 50, 20 min
(c) the one reacted with Na_2CO_3, CO, 7min (×150)
(d) the enlarged picture of (c) (×1500)
(e) the one reacted with Na_2CO_3, CO, 5min (×150)
(f) the enlarged picture of (e) (×1500)
(g) the one reacted with K_2CO_3, CO, 12min (×250)
(h) the enlarged picture of (g) (×1250)
(i) the one reacted with Na_2CO_3, H_2, 5min (×25)
(j) the one reacted with K_2CO_3, H_2, 15min (×1500)
(k) the one reacted with $CaCO_3$, CO, 9min (×150)
(l) the enlarged picture of (k) (×1500)
(m) the one reduced with silicate slag, CO, 30min (×1500)

Photo. 3. Surface textures of Fe_2O_3 reduced at 750°C in CO and H_2 atmosphere.

flow, the spot like reactions proceed and the onset of the cracks linking the holes together are seen. The enlarged Photos. 3(e) and (f) show the protuberance in the holes.

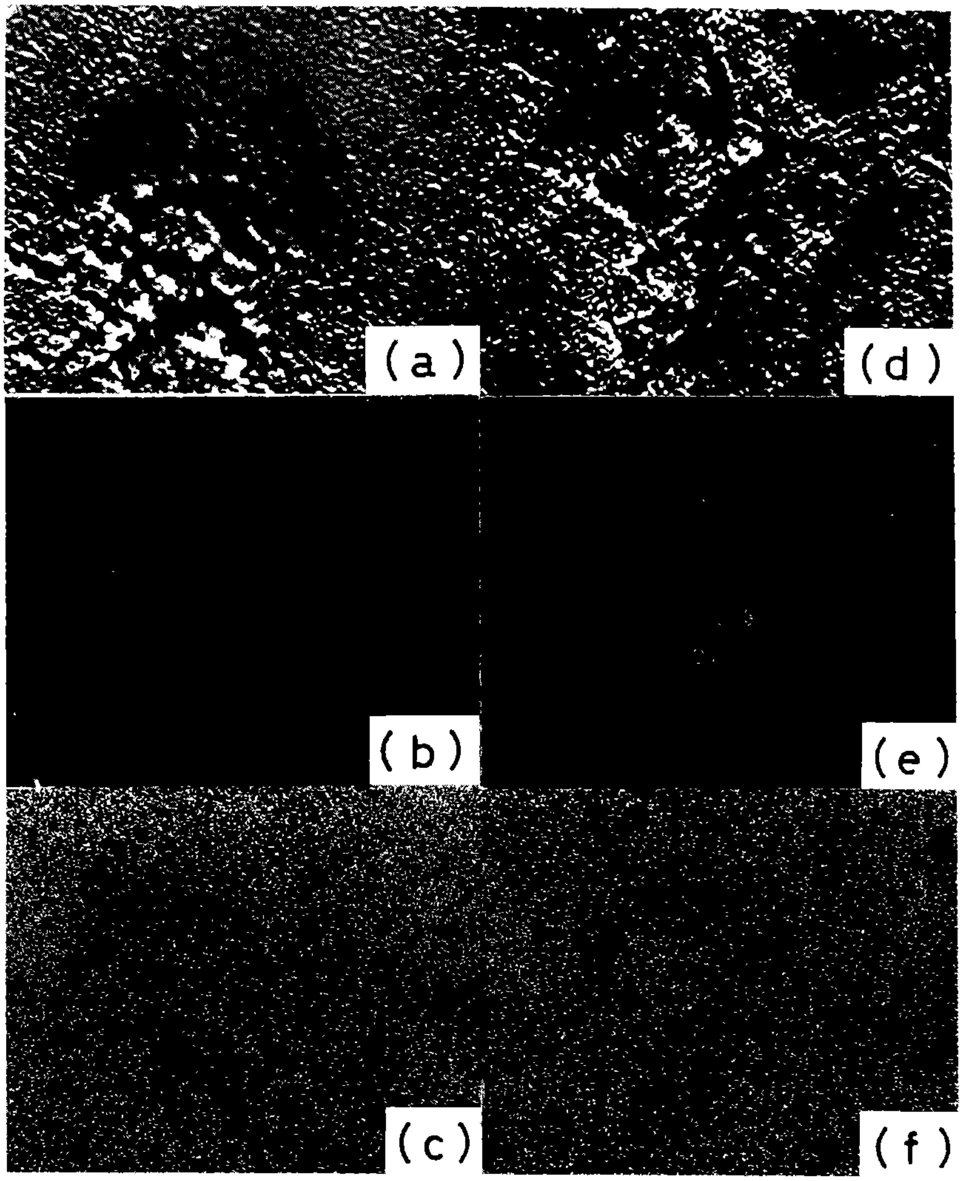
When K_2O is reacted approximately uniformly with Fe_2O_3 for 12 min, the development of the cracks was same as seen in the case of reaction with Na_2O and the growth of the fibrous iron was also seen in the cracks (Photos. 3(g) and (h)). In the reduction with H_2, the cracks appear in the initial stage. Photograph 3(i) shows the surface of Fe_2O_3 reacted with Na_2O in an H_2 flow of 200 cc/min for 5 min, and Photo. 3(j) the one with K_2O for 15 min in which the protuberances of metallic iron are seen in the cracks.

The samples of Fe_2O_3 on which calcium ferrite was grown were prepared by reacting CaO with the c plane of Fe_2O_3. When the samples were reduced for 9 min in a CO gas flow, the reduced surface was shown in Photos. 3(k) and (l). In the grain boundaries between calcium ferrite and unreacted Fe_2O_3, and in the cracks eveloped in the calcium ferrite, the fibrous iron grown can be observed in the progress of the reduction. The structure after the CO reduction of the Fe_2O_3 platelet reacted with the slag (SiO_2-Al_2O_3-CaO) is shown in photo. 3(m). Small protuberance was hardly seen at the boundary of the slag and Fe_2O_3.

2. Reduction of the Plate of Fe_2O_3 with Na_2CO_3 or K_2CO_3 Powder Places on the c Plane of the Crystal

In the reaction of $Fe_2O_3+M_2CO_3=M_2O \cdot Fe_2O_3+CO_2$(where M = Na, K), an investigation was conducted to determine whether or not the mixture of the carbonates decomposed at a lower temperature than the individual decomposition temperatures. The samples were prepared by mixing the powders of Na_2CO_3 or K_2CO_3 and Fe_2O_3 at a rate of 2 : 5. With a thermobalance the decomposition temperature in air was measured and the reaction products were identified by X-ray diffraction. In both the cases of Na_2CO_3 and K_2CO_3, the decomposition of the carbonates commences at approximately 580°C, considerably lower than the individual decomposition temperatures (melting point), and Fe_2O_3 compounds namely $NaFeO_2$, $KFeO_2$, *etc.*, are produced. Further in the case of $CaCO_3$ the decomposition commences at around 600°C, and CaO is produced. Even in the presence of Fe_2O_3, no compounds were produced until approximately 800°C.

Based on the above results, in order to determine the influence of the presence of Na_2O or K_2O powder on the reduction of Fe_2O_3, the reduction experiments were carried out by placing a small amount of Na_2CO_3 or K_2CO_3 powder on the plate-like Fe_2O_3 crystals, in contrast to the experiments described in *Section III. 1* where the reduction followed the high temperature formation of the compounds. Photographs 4(a) to (c) are the results of the surface observations by EPMA (back scattering electron, Na X-ray and Fe X-ray images) when Na_2CO_3 is placed on the c plane of Fe_2O_3 and the reduction is carried out in a CO gas flow at 750°C for 15 min. Also Photos. 4(d) to (f) are the results of the ones when K_2CO_3 was

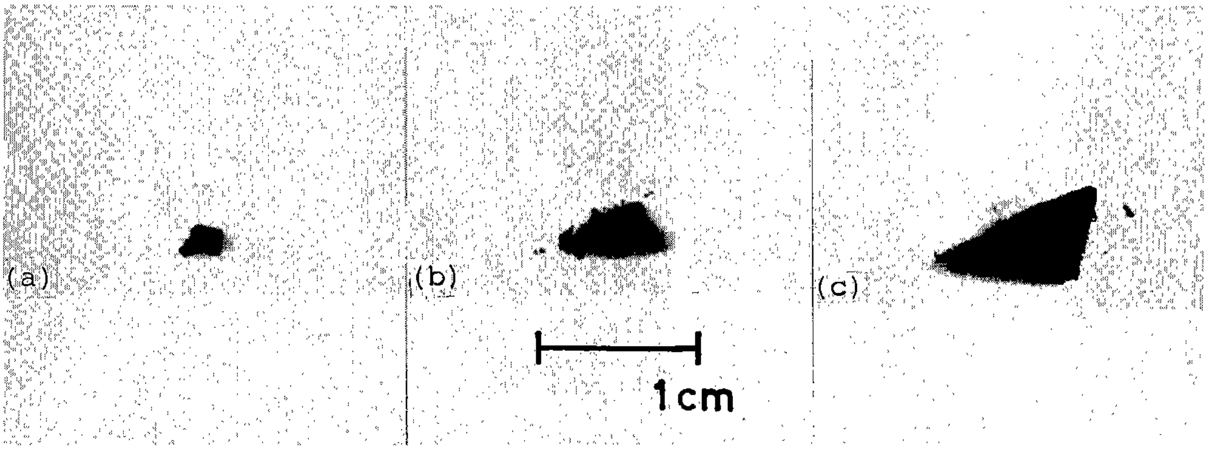


(a) BEI of the surface reduced with Na_2CO_3
(b) NaKα image of (a)
(c) FeKα image of (a)
(d) BEI of the surface reduced with K_2CO_3
(e) KKα image of (d)
(f) FeKα image of (d)

Photo. 4. Surface textures of Fe_2O_3 reduced with Na_2CO_3 or K_2CO_3 powder on its (0001) plane at 750°C for 15 min in CO atmosphere and its X-ray images. (×150) used under the same conditions. In the experiments described in *Section III. 1*, however, cracks appeared. For the purpose of detecting the behavior of these carbonates during the reduction, the observation was further made by EPMA. The X-ray images of Photos. 4(b) and (e) show that on the surface of the sample after the reduction Na and K remain very scarcely, which seems to suggest that Na and K ions have migrated into the cracks. Such results are also seen in the similar experiments of *Section III. 1*, for instance when Na_2O or K_2O is placed on the c plane of Fe_2O_3 and reduction is conducted, the evidence of Na or K on the surface was hardly observed.

3. On Carbon Deposition

When Fe_2O_3 crystals (about 3 mm in diameter) reacted with Na_2CO_3 or K_2CO_3 are reduced in a CO gas flow at 750°C for 60 min, the development of carbon deposition is shown in Photos. 5(a) to (c) for the cases of no, Na_2CO_3 and K_2CO_3 additives, respectively. The carbon deposition reaction occurred fiercely on the Fe_2O_3 crystal reacted with Na_2CO_3 or K_2CO_3. From these results it may be seen that in the presence of alkali metals Na and K accelerates the carbon deposition reaction.



(a) Fe_2O_3 without alkaline compound
(b) reacted with Na_2CO_3
(c) reacted with K_2CO_3

Photo. 5. View of carbon deposition after reduction at 750°C for 60min in CO atmosphere.

IV. Discussion

Khalaffalla and Weston, Jr.[1] explained (1) that the enhancement of the reduction by the addition of the impurity was based on the Vol'kenshtein effect; (2) that while the changes in the physical properties such as porosity accompanied by the presence of the additives had the influence on the reduction ; but (3) that it was not too much important. In the present report the authors did not investigate the reduction rate, but discussed on the effect of additives on the reduction behavior of Fe_2O_3. Our discussions were mainly based on the microscopical observation on the abnormal swelling observed by SEM. The abnormal swelling phenomenon is the volume expansion of more than 20% during the reduction of iron ore.[10) Wenzel *et al.*[11) suggested three causes of the abnormal swelling. One of them is the carbon deposition. The second cause is the cracking of the ore induced by the stress at the reaction interface. The third cause is the formation of fibrous iron. However, it is now clear that the most important cause is the growth of fibrous iron.

From our experimental results, the effect of the additives (Na, K, Ca) on the abnormal swelling of Fe_2O_3 may be roughly divided into the following three categories ; namely, the degradation due to the onset of cracks which appear in the initial stages of the reduction, the growth of fibrous iron, and the carbon deposition reaction. The discussions will be continued on these items as follows.

1. Onset of Cracking

Na_2CO_3 or K_2CO_3 powder was placed on the c plane of plate like Fe_2O_3 single crystals at 1100°C in an electric furnace. When the surface of Fe_2O_3 on which the above-mentioned compounds are produced are subjected to the reduction, numerous cracks generate from the surface of the samples in the inward direction. These cracks obviously much more developed, compared with those of the reduced Fe_2O_3 single crystal (Photo. 3(a)). The cracks appear in the initial stages of the reduction to FeO. As for the formation of these cracks, Na_2O or K_2O compounds are produced on the surface of the Fe_2O_3 crystals, and Na_2O or K_2O migrates *via* the fine cracks of the grain boundaries of the cracking. The induced stress becomes one of the causes (*cf.* Photo. (2)).

The other mechanisms may be considered as follows. Through the surface and the cracks of the sample, the compounds formed between Fe_2O_3 and Na_2O or K_2O within the crystal commence to decompose in the progress of the reduction. As a result on the surface and the inside of the sample FeO cracks are produced. Since Na_2O and K_2O can neither exist singly nor form compounds with FeO, the Na and K ions pass through the grain boundaries and diffuse into the Fe_2O_3 crystal. Because the solid solution of Fe_2O_3 and the alkali elements with the large ion radius has the disturbed crystal lattice, the reduction rate increases. In this manner alkali metal ions diffuse through the weak bonded surfaces (cleavage surface) of the cracks within Fe_2O_3 and with the increasing rate of the reduction, the cracks grow from the surface to the inside. And another possibility for the crack is due to the alkali metal (such as Na, K) carbonate which is formed by the reaction of alkali metal oxide with CO_2 during the reduction $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$.[9) Therefore, in the case of CaO the formation of cracks does not seem remarkable, because the above reaction hardly occurs.

2. Growth of Fibrous Iron

Fibrous iron grows in abundance in the cracks on the surface of the plate like Fe_2O_3 single crystals. It is well Known that when Na or K are present in hematite the growth of fibrous iron is enhanced. As for the cause, it has been reported that Na or K ions give lattice defects to hematite crystals. Some have the opinion that this results in the abnormal reduction.[2,3] The results of the present experiments supports the above concepts.

When the samples produced by the reaction of the plate like Fe_2O_3 single crystal with CaO at 1300°C are subjected to the CO reduction, in the grain boundaries of calcium ferrite and Fe_2O_3 and the cracks of calcium ferrite phase, the growth of fibrous iron is seen. Apart from the Bleifuss' mechanism[5] which is described in detail in the introduction of the present paper and the previous report,[8] we suggest the necessary conditions (the presence of grain boundaries *etc.*) for the growth of fibrous iron, in which the ferrous ion diffuses to the iron nucleus. When an Fe_2O_3 single crystal is reduced to FeO, the step-like structure parallel to the (0001) plane of Fe_2O_3 appears on the section normal to the (0001) plane. The (0001) plane of Fe_2O_3 changed to the (111) plane of FeO by the epitaxial reaction during reduction. The fibrous iron grew on the section of the (111) plane of FeO, but the growth of fibrous iron on the (111) plane was negligible. In the present experiments, since the formation of the iron nuclei and the diffusion of the iron ion were easier in the crystal grain boundaries, the fibrous iron substantially grew according to the root growth mechanism.[8] The increase in the reduction rate may be elucidated by the formation of cracks. In the sample reacted with the silicate slag, the metallic iron protuberance along the grain boundaries was hardly seen after the reduction. In this case, because the grain boundaries which allow the easy diffusion of ferrous ion are not formed, no fibrous iron is seen as surmised.

3. Carbon Deposition Reaction

When the samples prepared from the plate like Fe_2O_3 single crystals and Na_2O or K_2O by the solid reaction method are subjected to the CO reduction, in the late period of the reduction carbon deposits and the reduced iron acts as a catalyst of the carbon deposition reaction. When Na or K is present, the reaction is abnormally enhanced. The enhancement was also recognized in Hirao's investigation[12] on the effect of carbon deposition reaction when NaCl or Na_2CO_3 is used as the additive. Suzuki and Tsutsumi[13] found in their research of carbon deposition in a blast furnace that the more the alkali volume was, the larger the volume of carbon deposition. In the present results it is clear that alkaline component promote the carbon deposition reaction. However, as for the mechanism, we cannot establish a theory available for the explanation of the mechanism thereof.

V. Conclusion

On the synthetic Fe_2O_3 single crystals as the samples, the abnormal swelling and the effect of the additives Na_2O, K_2O and CaO were mainly observed by a SEM. The Fe_2O_3 samples reacted with Na_2O, K_2O and CaO were prepared by the solid reaction of the platelet Fe_2O_3 and the carbonates concrened. With the surface observations and the related investigations a discussion was made. As for the abnormal swelling when alkali metals Na or K are used as the additives, the addition have the following three effects.

(1) When Na_2O and K_2O are used as the additives, in the initial stage of the reduction fine cracks appear in the crystal. It is considered that the cause of the crack generation is the stress induced by the migration of Na_2O or K_2O inwards the crystal and the formation of the alkali metal carbonates during the reduction.

(2) The remarkable growth of fibrous iron is seen inside the crack generated. It is considered that the growth is enhanced due to the lattice defects which comes from the presence of alkali metal ions in hematite crystal.

(3) When the samples are subjected to the reduction in a CO gas flow, the intense carbon deposition reaction occurs and the crystals disintegrate.

When an alkaline earth metal CaO is used as an additive, the growth of fibrous iron is seen in the grain boundaries of the developed calcium ferrite. It is suggested that the presence of CaO may be one of the causes of the abnormal swelling. Further glassy slag phase (SiO_2-Al_2O_3-CaO) additives which has no definite grain boundary hardly affect on the swelling. It is surmised that the formation of grain boundaries which allow the easy diffusion of ferrous ions to iron nucleus is necessary for the root growth mechanism of fibrous iron.

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Chapter 8

Reduction Test of Artificial MIO (Micaceous Iron Oxide Fe_2O_3) Doped with Na_2O and K_2O and Natural MIO

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Synopsis

In order to examine the effect of alkali component on iron ore reduction, reduction tests were made using artificial MIO (Fe_2O_3 single crystals). MIO was grown in conc. NaOH or KOH solution by hydrothermal method and contained Na 0.12wt% or K 0.20wt%, respectively. It is considered that Na_2O and K_2O form solid solution in Fe_2O_3 crystal. In this experiment CO was generally used as reduction gas. After reduction the surface of the specimen was observed with SEM. In marked contrast to the reduction of artificial Fe_2O_3 grown by flux method (Na, K trace) and natural MIO (Na trace, K 0.01wt%), in this case fibrous iron grew intensely and the growth postition had no dependence on crystal plane index of Fe_2O_3. It is surmised that lattice defects coused by the solution of alkali element would enhance swelling phenomena during reduction.

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I. Introduction

It is well known that alkaline metal-components cause abnormal swelling in the reduction process of iron ore ; using pellets indurated after the addition of Na_2CO_3 and those prepared from ores treated by sea water, Ende *et al.*[1] and Nakazawa *et al.*[2] have respectively carried out reduction tests, both of which have revealed that an abnormal swelling occurs. However, in these experiments, microstructures of iron oxide grains in the course of reduction were not observed. The authors considered that the use of Fe_2O_3 single crystals uniformly doped with alkaline metals was ideal for studying the effect of alkaline metal components (Na, K) on the reduction behavior of Fe_2O_3. Fe_2O_3 single crystals grown by the flux method in which $Na_2B_4O_7$ was used as flux, described in a previous report,[3] were not practically subjected to doping (Na 0.008%). In Fe_2O_3 grown by $Na_2B_4O_7$-K_2CO_3 mix flux method potassium was scarcely doped, either (K, trace). In the previous work,[3] therefore,

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※ The Government Industrial Research Institute, Osaka to test the effect of the addition of sodium and potassium on the reduction behavior, powders of Na_2CO_3 and K_2CO_3 were put on the c plane of the Fc_2O_3 single crystals grown by the flux method and heated in air, and the crystals reacted with these alkaline metal oxides were used as samples. In the work, it was observed that alkaline metal components enhanced the growth of fibrous iron. But the crystal plane of Fe_2O_3 which showed intense fibrous iron growth was not clear. Therefore it is necessary to investigate using Fe_2O_3 single crystals uniformly doped with those alkaline components.

The authors observed that thin sheet-shaped Fe_2O_3 single crystals grown by hydrothermal synthesis method contained some amount of alkaline components. In this work, these Fe_2O_3 single crystals called micaceous iron oxide (MIO) were used as samples and the reduction tests were done ; the investigated results of the growth of fibrous metallic iron will be described below.

II. Samples and Experimental Procedure

1. Growth of MIO

When an aqueous solution of iron sulfate (III) is reacted with sodium hydroxide and neutralized, precipitate of iron hydroxide (III) is generated. Further, when this precipitate is hydrothermally treated, hexagonal sheet-shaped Fe_2O_3 single crystals are educed and sodium hydroxide-sodium sulfate mixed solution is produced as a mother liquor.[4] The growing conditions of MIO and characteristics of the MIO obtained are as follows :

By the addition of 100, 200, 300, or 350 g of NaOH to 200 cc aqueous solution of $Fe_2(SO_4)_3$ at a concentration of 0.5g/cc, the precipitate is produced, and water is added to each solution until its total amount becomes 300 cc. The precipitate together with the mother liquor is poured into a flask made of silver, which is put in an autoclave. After keeping the autoclave at a temperature of 200°C (pressure : about 17kg/cm^2) for 2 hr, it is allowed to cool to room temperature. As a result of hydrothermal reaction, Fe_2O_3 single crystals (MIO) are grown in the flask. These crystals are washed with water to remove the mother liquor.

With increasing the amount of NaOH from 100 to 300 g, the diameter of MIO increases from about 5 to 50 μm. When the amount of NaOH is more than the above-mentioned values, say 350g, sodium ferrite is generated so that large MIO's are not obtained. Also in the case of using KOH as alkali component of the mother liquor, MIO is grown under nearly the same conditions. It was confirmed that the crystals used in the experiments were 30~50 μm in diameter.[5] Concentration of sodium component in MIO grown in the mother liquor containing NaOH was 0.12%, while that of potassium component in the crystal grown in the mother liquor containing KOH was 0.20%. These values are larger than 0.03%–the concentration of alkaline metals contained in iron oxide which is considered to begin influencing an abnormal swelling.[2] Table 1 shows the lattice constants of various Fe_2O_3. As a result, it can be said that the lattice constants of these MIO are not so much different from those of high grade reagent Fe_2O_3 (99.9%) and of Fe_2O_3 produced by oxidation of electrolytic iron.

Table 1. Lattice constants of micaceous iron oxide (MIO).

	a_o (A)	c_o (A)
High grade Fe_2O_3 reagent (Cerac)	5.0355	13.741
Fe_2O_3 produced by oxidation of electrolytic iron at 1000℃	5.0354	13.747
Fe_2O_3 (MIO) grown in NaOH solution	5.0364	13.751
Fe_2O_3 (MIO) grown in KOH solution	5.0360	13.750

2. Reduction Method

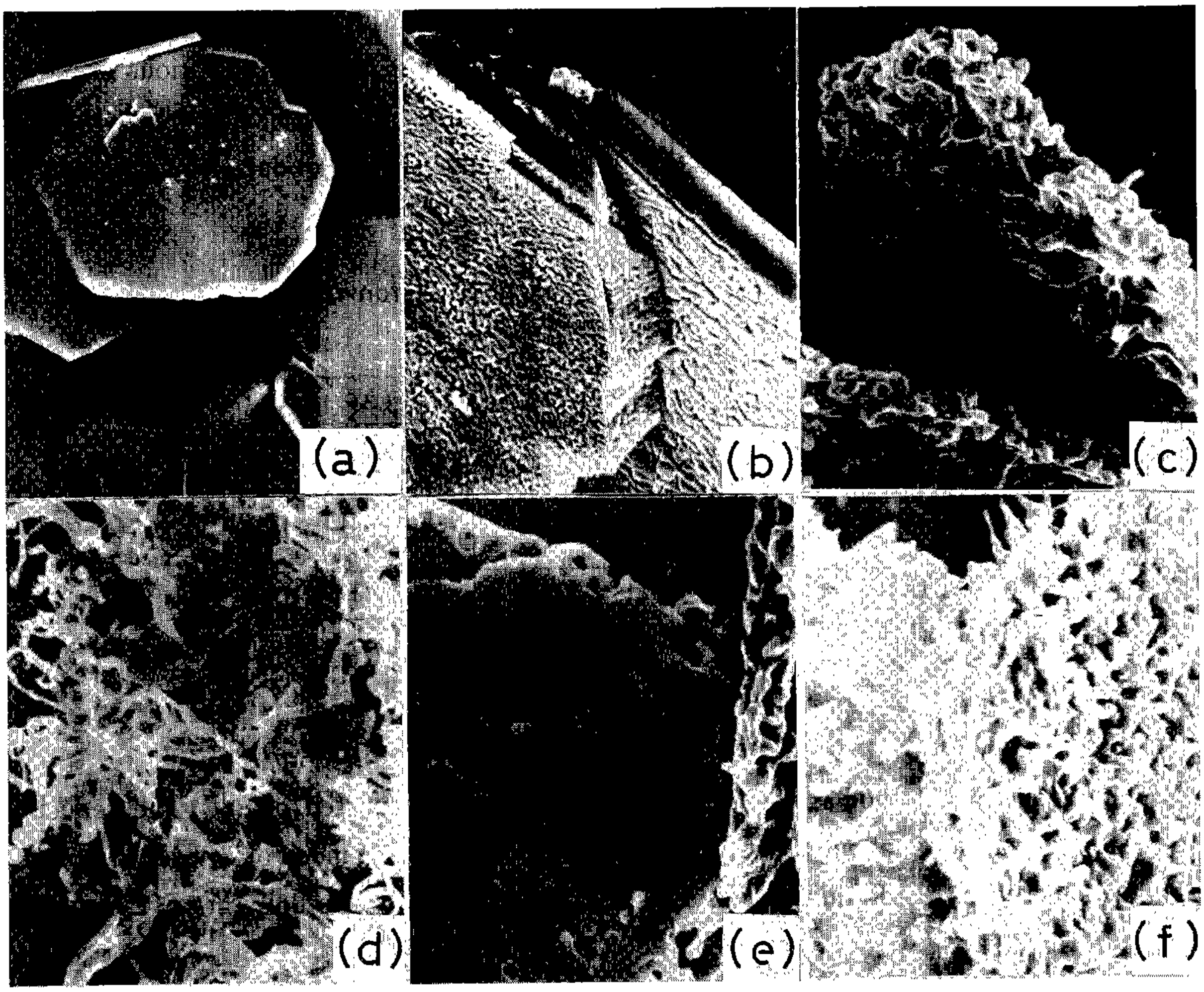
The reduction method is the same as the previously reported one.[3] The reduction temperature was set at about 750°C where the reduction swelling index of powder compact of iron ores increases.[6] Reduction gases used were CO and H_2 at a flow rate of 200cc/min.

Ⅲ. Results of Artificial MIO Reduction

The scanning electron micrograph of MIO grown in the mother liquor containing NaOH is shown in Photo. 1(a). Both the crystals grown in the mother liquors containing NaOH and KOH have the similar hexagonal-forms, and their surfaces are smooth. These flat surfaces are c plane of Fe_2O_3[5] which is the same as in cases of Shiretoko platelet Fe_2O_3 single crystals used in previously reported experiments[7] and Fe_2O_3 single crystals grown by flux method and without alkaline reaction.[3] However, MIO used in the present experiments are 30~50 μm in diameter and 1~3 μm in thickness and remarkably smaller than the single crystals used in the previous experiments[3,7]: 1~10 mm in diameter and 0.2~1 mm thick.

Photograph 1(b) shows the sample surface of MIO reduced to Fe_3O_4 in an atmosphere of 15% CO and 85% CO_2, where MIO is grown in the mother liquor containing NaOH. Fine cracks are observed on the surface. Such structures are held even in the case of MIO reduced to FeO.

MIO which is grown in the mother liquor containing NaOH and reduced at 750°C in a CO stream for 15 min is shown in Photo. 1(c), where even on the c plane of the micaceous Fe_2O_3 crystal the growth of metallic iron protuberances is observed. This is a phenomenon which is



(a) MIO grown in NaOH solution, before reduction. (×500)
(b) Reduced product from sample (a), CO : CO_2=15 : 85, 750°C, 30min. (×1500)
(c) CO, 750°C, 15min. (×1500)
(d) CO, 700°C, 30min, (×1500)
(c) H_2, 700°C, 15min. (×1500)
(f) MIO grown in KOH solution, reduced by CO, 750°C, 10min. (×1500)

Photo. 1. Surface structure of artificial micaceous-iron-oxide (MIO) reduced under various reduction conditions.

considerably different from the results of CO reduction of Shiretoko natural Fe_2O_3 single crystals[7)] or artificial ones grown by flux method and without alkaline reaction[3)] ; the growth of fibrous metallic iron or protuberances was not observed on the c plane of those crystals.

The result of reduction by CO at 700°C for 30 min is shown in Photo. 1(d), where the hexagonal form before the reduction disappears and fibrous iron becomes predominant in number. When the reduction proceeds further and the reduction time exceeds about 40 min, carbon begins to deposit on the reduced iron. Between the cases of reduction temperatures of 700°C and 750°C, no diffrence of the growth degree of protuberances was observed.

Next, the reduction test was done in an H_2 stream. photograph 1(e) shows the result of hydrogen reduction at 700°C for 15 min. In this instance, the surface of the crystal is smooth and the growth of the protuberances of metallic iron is very slight. In the previous report7) using bigger Fe_2O_3 crystals, fibrous iron was hardly observed for H_2 reduction, either. And reduction reaction mechanisms of CO and H_2 were discussed in the same report. Photograph 1(f) shows the result of CO reduction of MIO grown in the mother liquor containing KOH at 750°C for 10 min. On the c plane of the crystal, still the protuberances of metallic iron grow up. According to the above-mentioned results, MIO doped with Na_2O or K_2O shows a behavior of growth of fibrous iron or protuberances of metallic iron even on the c plane of the crystal in the course of reduction.

The mechanism of this phenomenon is considered as follows : Alkaline metal ions cause the defects in lattice of Fe_2O_3, and as a result the diffusion of Fe^{2+} ions to the iron nuclei produced on the c plane of Fe_2O_3 crystal in the course of reduction of Fe_2O_3 to metallic iron becomes easy and accelerates the growth of fibrous iron or protuberances.

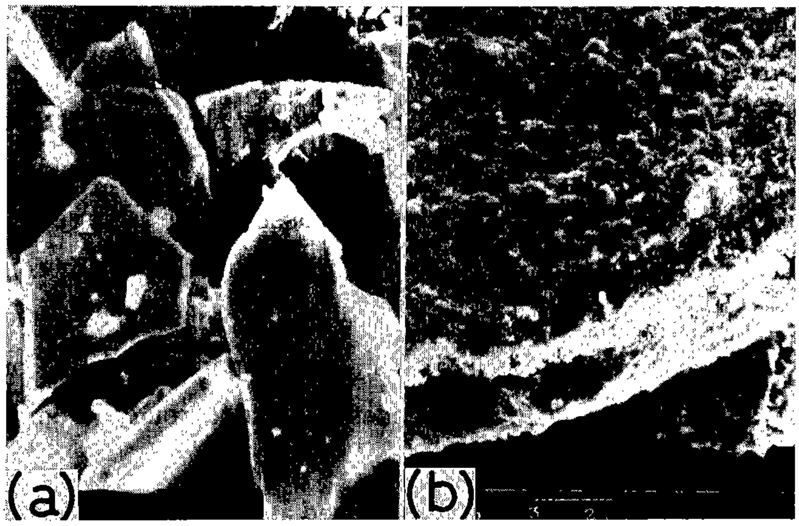
Ⅳ. *Results of Natural MIO Reduction*

The grain size of MIO doped with alkaline metals is remarkably smaller than that of Fe_2O_3 single crystals used in the previous work.2) It is also considered that not only the lattice defects but the crystal grain size will influence the relationship between the surface reaction and diffusion of Fe^{2+} ion. Reduction tests of MIO having much the same grain size and without doping were, therefore, carried out to compare the results with those of the alkalin doped MIO. The sample used was Austrian MIO and was composed of Fe_2O_3 and the following impurities : SiO_2 1.37, Al_2O_3 1.67, MgO 1.21, CaO 0.38, TiO_2 0.12, K_2O 0.01 wt% and Na_2O trace.

In Photo. 2(a) the surface structure of the natural MIO is shown. It can be seen that the sample size is almost the same as that of the artificial MIO. Photograph 2(b) shows the surface of the natural MIO reduced in CO stream at 750°C for 15 min. In this case the growth of fibrous iron was not observed on the c plane of the MIO. In the previous work3) using bigger artificial Fe_2O_3 single crystals without alkaline doping, the growth of fibrous iron from the c plane of Fe_2O_3 was not observed, either. From the result, it is confirmed that the sample size hardly affect the reduction behavior, and on the other hand the alkaline metal concentration was one of the most important factors influencing the swelling phenomena.

Ⅴ. *Conclusion*

In order to investigate the influence of alkaline metals on the abnormal swelling of iron oxide, reduction experiments by CO were done by using micaceous Fe_2O_3 single crystals



(a) MIO before reduction. (×500)
(b) Reduced by CO, 750°C, 15min. (×1500)

Photo. 2. Surface structure of natural micaceous-iron-oxide (MIO).

(MIO) doped with sodium or potassium as samples.

As result, it was found that when MIO's doped with alkaline metals were reduced, fibrous iron or protuberances grew even from the c plane of the crystals. For Fe_2O_3 single crystals contained no alkali, the growth of fibrous iron was not observed on the c plane. Consequently, from the fact that when Fe_2O_3 single crystals doped with alkali components are reduced, fibrous iron grows from allover the surfaces of crystal grains, alkali components are considered to be one of the causes which enhance abnormal swelling.

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