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THE APPLICATION OF THERMAL ANALYSIS IN FERROUS METALLURGY

PART I. THE STUDY OF THE VOLUME CHANGES OF IRON ORE PELLETS DURING REDUCTION

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ABSTRACT

The apparent volume increase of iron oxide pellets during reduction with $CO-N_2$ mixture was studied at 900 °C on porous hematite pellets which were prepared from four different magnetite concentrates.

A volume expansion dilatometer was developed and used for the continuous measurement of pellet volume changes (swelling) in course of reduction.

An anomalous swelling course was observed on some types of pellets.

An attempt was made to explain the anomalous swelling behaviour according to the lattice defect theory.

INTRODUCTION

The applied methods of thermal analyses have found wide interest in the iron-making industry[1–4].

Recently a new field of their application was introduced in connection with the swelling phenomena of iron oxide pellets during reduction in the blast furnace. Previously, only the static method[5] and the gas-pressure-drop method[6] had been employed.

Various authors have postulated different theories of iron ore pellet swelling in the individual reduction stages of hematite→magnetite→wustite→iron[5–9]. The majority agree that the most detrimental swelling occurs in wustite→ iron transformation[6,10–13].

In view of this work on the volumetric changes of iron ore pellets during reduction, it was of interest to investigate the anomalous swelling phenomena of some types of hematite pellets prepared from magnetite concentrates. The following work endeavors to contribute to the clarification of this phenomenon on the basis of the lattice defect theory[14–16].

CONCLUSIONS

The anomalous swelling of some types of hematite pellets which were prepared from magnetite concentrates has as an antecedent the magnetite hereditary structure which is the carrier of the original highly oriented lattice defect positions.

The orientation of lattice defects directs the distribution of iron nucleation points on certain crystallographic planes of iron oxide grains and, in consequence, causes the "irregular" reduction mode which was observed during the reduction of wustite to iron by carbon monoxide.

The rapid solid state diffusion of iron ions through straight-lined vacancy positions produces an unevenly distributed porous layer of metallic iron on individual wustite grains, which forces the oxide particles apart. As a result, the pellet volume enlarges, its internal structures weakens, and, in extreme cases, the pellet loses shape and disintegrates.

The methods of rearrangement of lattice defect positions and equalization of the distribution of iron nucleation sites were found effective for the treatment of "difficult" magnetite ores which possess highly oriented lattice structures or contain inherent impurities.

The high temperature treatment of oxidized magnetite pellets promoted intensive grain growth of hematite and eliminated the internal grain orientation.

The addition of selected compounds in sufficient quantity removed or inactivated the inherent crystal impurities and formed a fluid slag at the grain boundaries, initiating a spheroidal grain growth.

EXPERIMENTAL

Swelling method development

In 1967 the author developed a volume expansion dilatometer and has used this instrument for determination of the swelling course of most types of pellets produced in the world[17].

According to this method, four pellets (weighing approximately 10 g) are covered with sand (50 mesh, round silica sand) in a graphite crucible and preheated in the test furnace to 900°C under a N_2 atmosphere in 60 min. The reducing gas, consisting of a mixture of 40% CO–60% N_2 (600 cm^3/min), is then introduced. The change in pellet volume during reduction at 900°C alters the level of the packed sand layer, which is continuously measured with a linear differential transformer. The signal from the transducer is sent to an amplifier and recorded. Concurrently, the CO_2, the product of reduction, is absorbed in a flask with Lithasorb (Fisher Scientific Co.) which is suspended and continuously weighed on a balance.

The degree of swelling is calculated from the formula:

$$\% \text{ swelling} = \Delta V / V_0 \times 100$$

where $\Delta V = \Delta h \cdot K$; ΔV, volume change of pellets at a specific reduction degree (cm^3); Δh, dilatometric recording (cm); K, area of crucible (cm^2); and V_0, volume of pellets before reduction measured by mercury displacement method (cm^3).

The reduction degree is calculated from the total oxygen content in the original sample (determined by Fe_2O_3 and FeO analyses) and from the weight of absorbed CO_2, which is proportional to the quantity of oxygen removed.

The dilatometer is shown on Figs. 1 and 2.

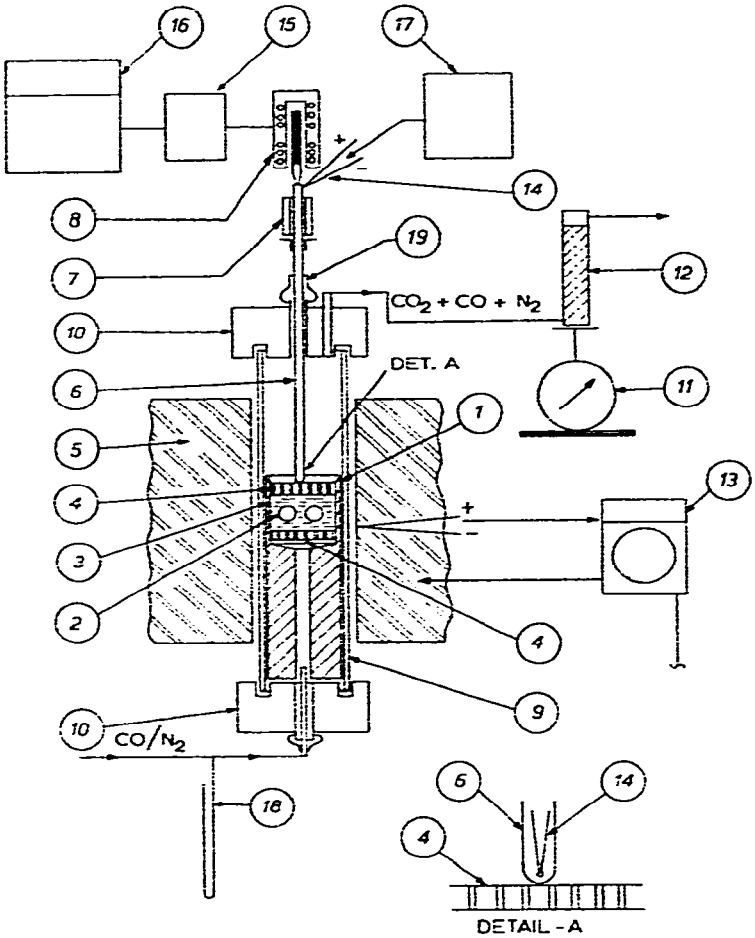


Fig. 1. Apparatus for determination of swelling course of iron ore pellets. *1*, graphite crucible (38 mm in diam. × 38 mm); *2*, 4 pellets; *3*, silica sand; *4*, perforated graphite disc; *5*, electric furnace; *6*, alumina tube with thermocouple; *7*, load (250 g); *8*, differential transformer; *9*, alumina tube; *10*, water-cooled brass block; *11*, balance; *12*, lithasorb flask; *13*, thermoregulator; *14*, Pt–PtRh13 thermocouple; *15*, amplifier; *16*, recorder; *17*, potentiometer; *18*, manometer; *19*, rubber boot.

The evaluation of two of the most typical swelling curves shown on Figs. 3 and 4 has been done by measuring the hot compression strength of partly reduced and, to-a-certain-degree, swollen pellets.

Reduced pellets were reheated to 900 °C in the furnace in an N_2 atmosphere and their strength was measured at this temperature on a universal tensile–compression testing machine.

Fig. 3 shows that the "normal" type of pellet exhibited the lowest strength at a maximum degree of swelling which occurred at 30–40% oxygen removal. Further reduction, accompanied by slow contraction of pellet volume, resulted in restoring of pellet strength. At 70% reduction pellets only deformed when tested. High metallic iron content contributed to their ductility at 900 °C.

Fig. 4 reveals the strength relationship to the swelling course of pellets which exhibited a high volume increase during metallization. This type of pellet, after

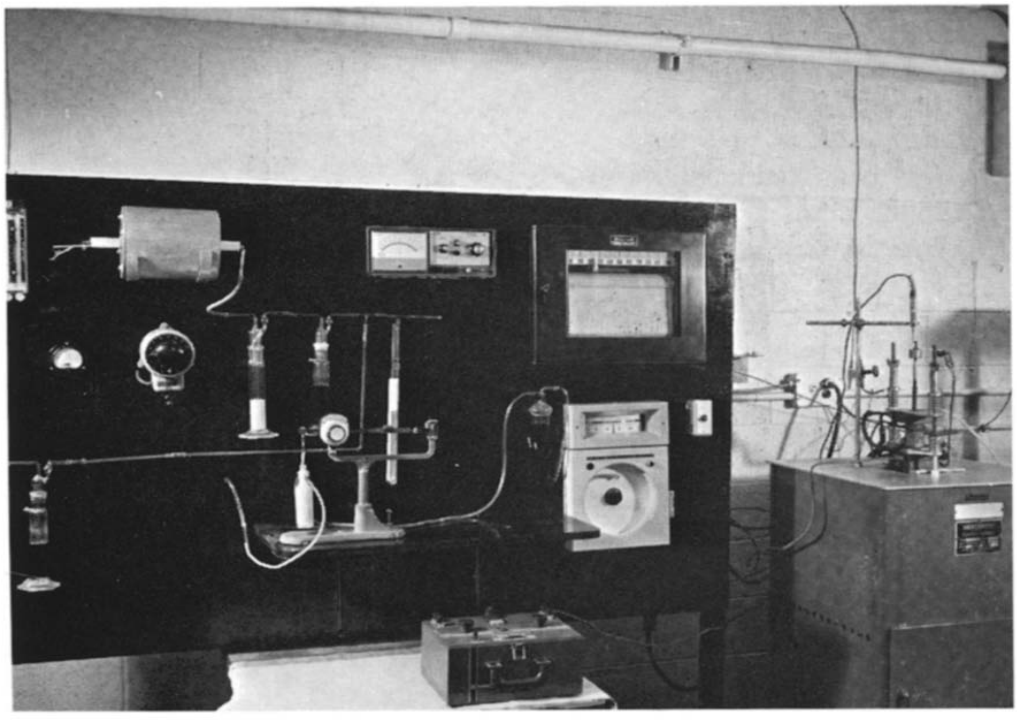


Fig. 2. The apparatus for the determination of the swelling course of iron ore p·llets.

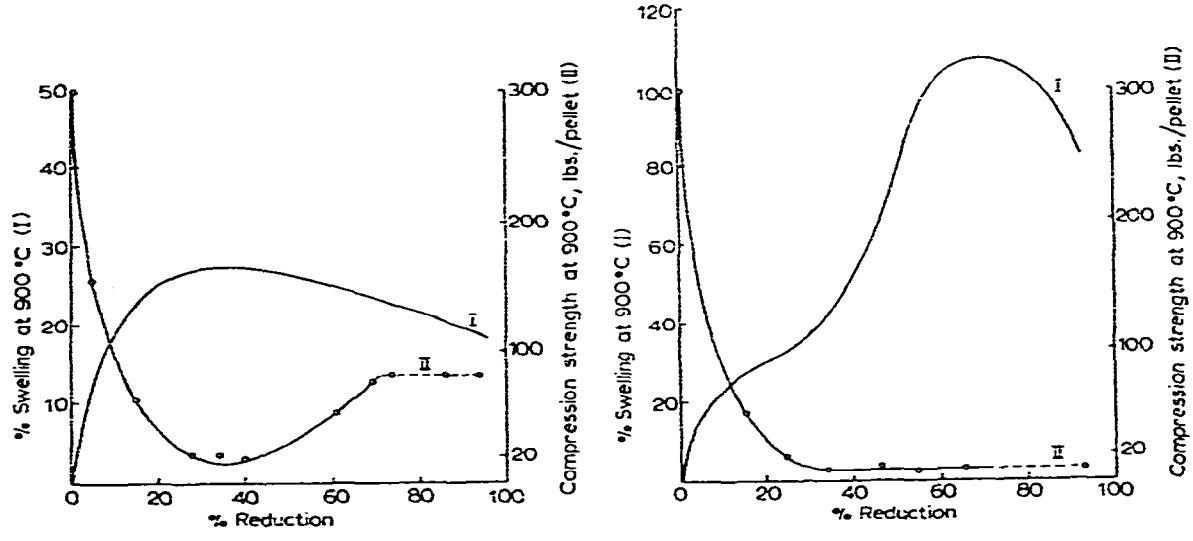


Fig. 3. The hot-strength relationship to the "normal" swelling course of iron oxide pellets during the reduction at 900 °C with $CO-N_2$ mixture. I, the swelling curve at 900 °C; II, the pellet strength measurements at 900 °C.

Fig. 4. The hot-strength relationship to the "anomalous" swelling course of iron oxide pellets during reduction at 900 °C with $CO-N_2$ mixture. I, the swelling curve at 900 °C; II, the pellet strength measurements at 900 °C.

reaching the lowest strength at 30–40% reduction, did not recover its strength during the following reduction to metal.

Preparation of iron oxide pellets

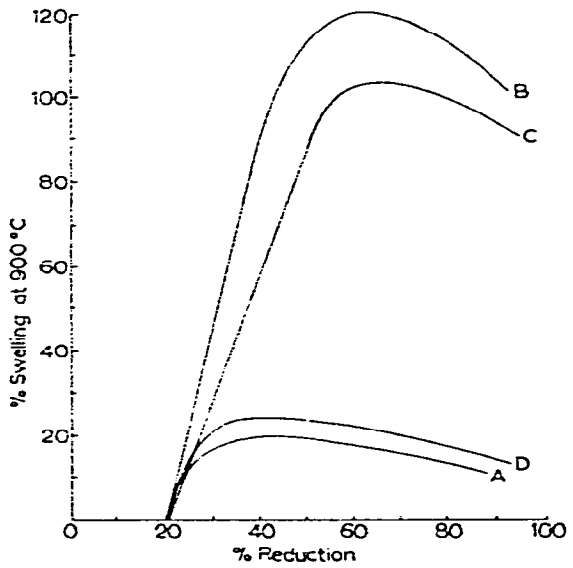
The volume changes of iron oxide pellets during the reduction with $CO–N_2$ mixture at 900 °C were studied on four types of magnetite concentrates (Table I).

TABLE I

Magnetite	*% Fe_2O_3*	*% FeO*
A	68.8	30.2
B	74.8	24.2
C	66.2	29.3
D	71.5	26.8

Magnetite "A" was a chemical grade magnetite (Fisher Scientific Co.), magnetites "B", "C", and "D" were natural magnetite concentrates. The impurities in "B" and "C" consisted of silica and alumina only. The magnetite "D" contained 0.32% of TiO_2 and 0.10% V_2O_5. Their grain size was 100%, −325 mesh. The concentrates were pelletized with water on a laboratory disc (40 cm in diam.), to the size of 8–10 mm.

First, the dried green pellets were tested according to the described swelling method. The results are shown on Fig. 5.



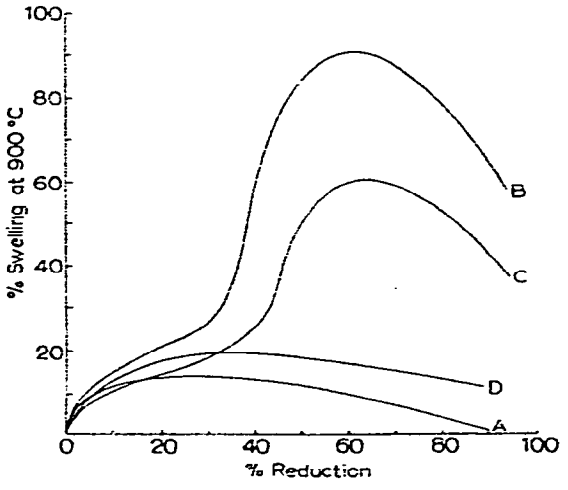


Fig. 5. The swelling courses of "green" magnetite pellets.

Fig. 6. The swelling courses of magnetite pellets oxidized at 950 °C.

The second series of swelling tests was performed with pellets which were oxidized at 950°C, 30 min in the air in a muffle furnace. The swelling curves of the oxidized pellets are shown on Fig. 6.

The third type of swelling test was conducted with pellets which were oxidized 30 min at 950°C and indurated 30 min at 1320°C in the air in a muffle furnace. In addition, the magnetite "D" mixture with 2% limestone was pelletized with water, oxidized, and indurated. The results of swelling tests of indurated pellets are shown on Fig. 7.

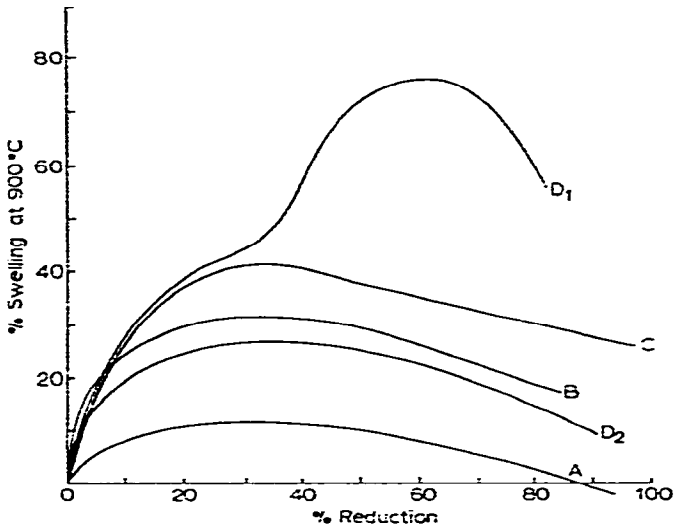


Fig. 7. The swelling courses of magnetite pellets oxidized at 950°C and indurated at 1320°C.

Discussion of results

It has been demonstrated on Fig. 3 that the "normal" swelling course of porous hematite pellets during the reduction with CO–N_2 mixture at 900°C exhibited the maximum volume increase of 10–40% at 30–40% oxygen removal as a consequence of the crystallographic rearrangement of the hematite hexagonal lattice into the cubic lattice of magnetite and wustite[9]. The subsequent reduction of wustite to iron took place without crystallographic change and was accompanied by pellet volume decrease. Figs. 8 and 9 are the micro-cross sections of partly metallized pellets which exhibited the "normal" swelling pattern. The individual dark gray wustite grains are covered with a white equally wide iron layer. This type of reduction mode has been called "topochemical"[18].

The "anomalous" swelling during reduction was observed on some types of pellets[10,12]. Fig. 4 exhibits the two-stage swelling course which reaches the maximum volume expansion exceeding 100% at 60–70% oxygen removal. The increase of pellet volume during the reduction of wustite to metallic iron is accompanied by a further reduction in pellet strength and, in practice, in the blast furnace, has caused operating difficulties[6]. The "anomalous" swelling phenomenon has been attributed

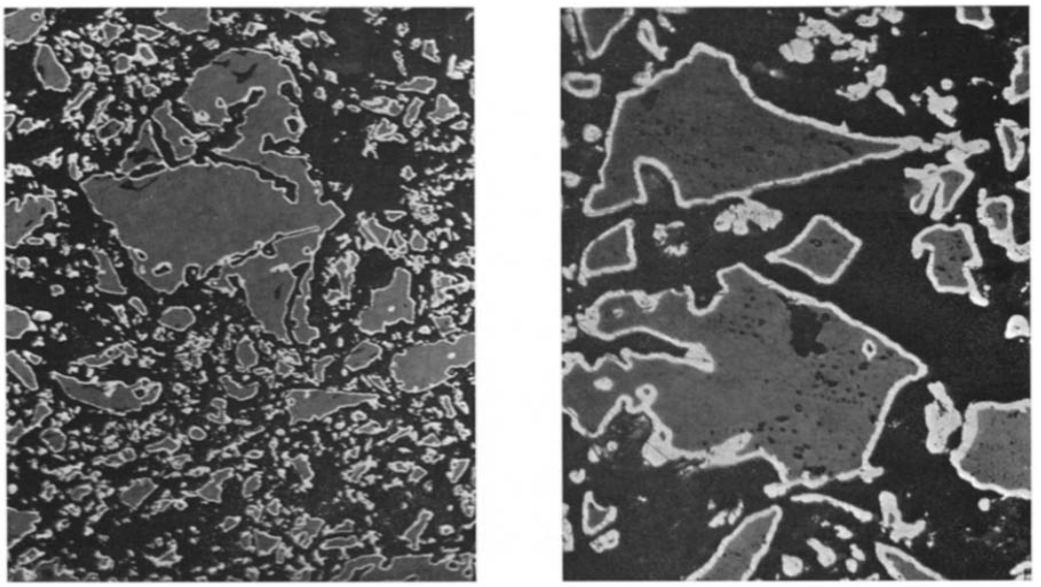


Fig. 8. The uniform iron layer formation on wustite grains by the reduction of a magnetite ore with $CO-N_2$ mixture at 900°C. 150 ×.

Fig. 9. The uniform iron layer formation on wustite grains by the reduction of an oxidized magnetite ore with $CO-N_2$ mixture at 900 C. 450 ×.

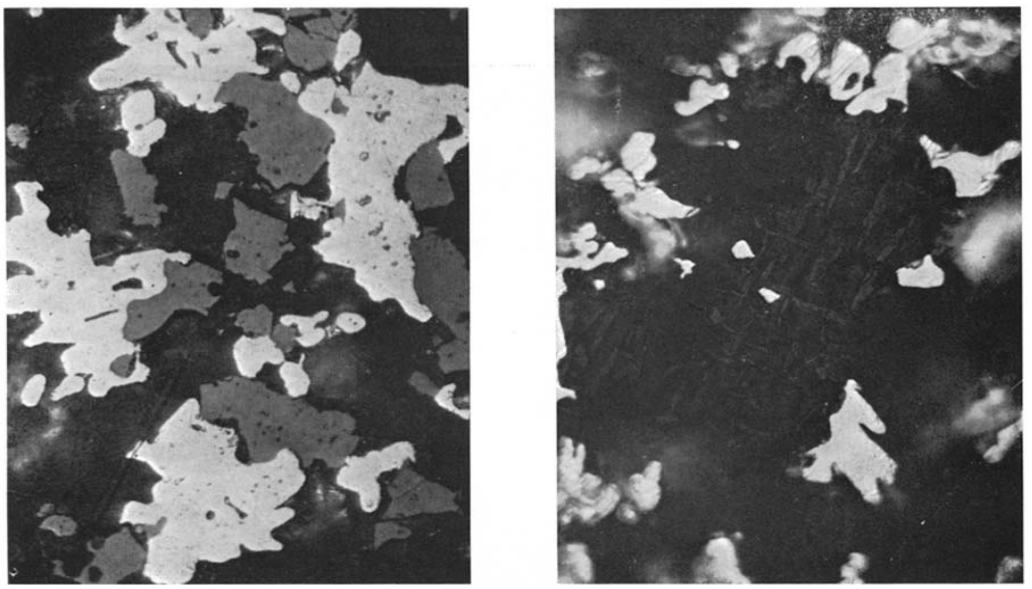


Fig. 10. The formation of an iron layer on certain plains of wustite grains by the reduction of a magnetite ore with $CO-N_2$ mixture at 900°C. 450 ×.

Fig. 11. The formation of an iron layer on certain plains of wustite grains by the reduction of an oxidized magnetite ore with $CO-N_2$ mixture at 900°C. 1200 ×, etched.

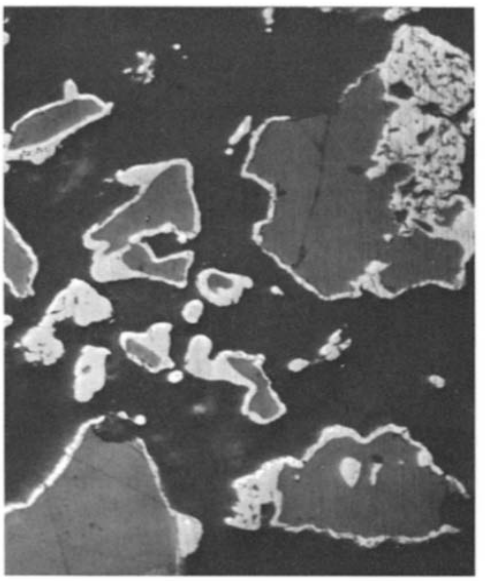
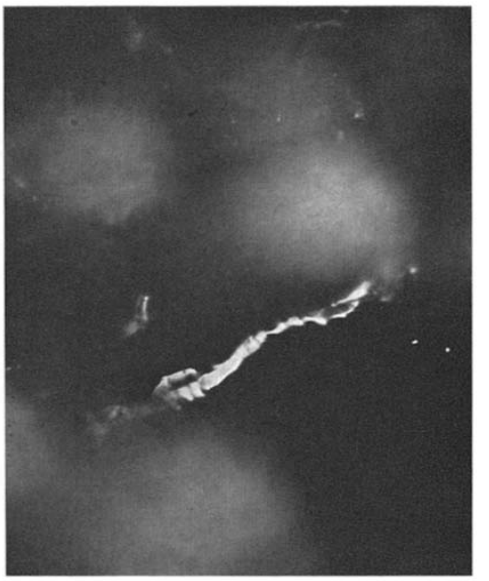


Fig. 12. The formation of an un-uniform iron layer on wustite grains by the reduction of a magnetite ore with $CO-N_2$ mixture at 900 °C. 450 ×.

Fig. 13. The formation of an un-uniform iron layer on wustite grains and the iron filament growth from wustite surface by the reduction of an oxidized magnetite ore with $CO-N_2$ mixture at 900 °C. 1200 ×.



Figs. 14 and 15. The iron filaments formation during the reduction of a magnetite and oxidized magnetite ore with $CO-N_2$ mixture at 900 °C. 1200 ×.

by various authors to Fe-whiskers growth[10] and the formation of this type of iron has been ascribed to the presence of CaO[11] or alkalies[6] at the wustite–Fe interface.

The present examination of the cross sections of partly metallized pellets which exhibited "anomalous" swelling, revealed:

(*a*) the wustite grains reduced to iron only on certain plains (Figs. 10 and 11); or

(*b*) an uneven thickness of iron layer which covered entirely the wustite grains (Figs. 12 and 13), and

(*c*) the formation of iron filaments in the form of wires and strips growing from the wustite surface (Fig. 14 and 15) which accompanied both types of described irregular reduction pattern.

The pellets prepared from magnetite "A", green, oxidized or oxidized and indurated exhibited on Figs. 5, 6, and 7 similar types of swelling curves with a maximum of volume increase of 10–20% at 30–40% reduction.

The reduction of green pellets of magnetite "A" took place without a volume change in the magnetite→wustite reduction step. This phenomenon is common to all types of magnetite pellets. The magnetite pellet volume increase starts when the wustite lattice is transformed into the lattice of FeO with a minimum of vacancies and when the superficial Fe-ions, diffusing to the iron nucleation points at the wustite surface, begin to form a metallic film.

The green pellets of magnetite "A" (Fig. 5) exhibited the maximum volume expansion of 20% at 30–40% reduction.

The oxidized and oxidized-indurated pellets of magnetite "A" increased in volume immediately when the reduction of hematite started. The maximum volume increase of 12 and 8%, respectively, took place at 30–40% reduction followed by a pellet volume decrease (Figs. 6 and 7).

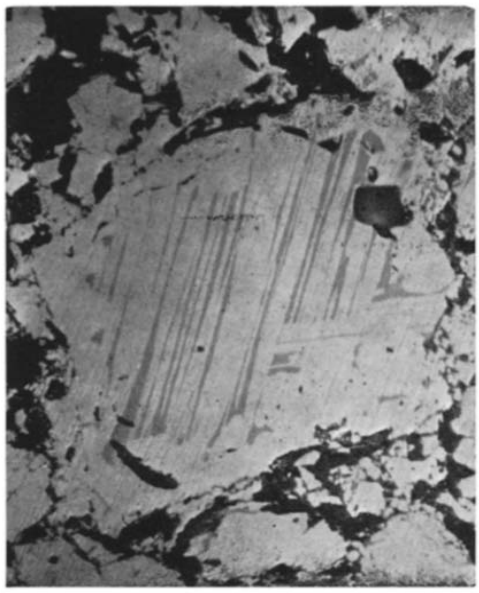
The micro-cross sections of partly metallized green, oxidized, and oxidized-indurated pellets of magnetite "A" revealed the formation of a uniform dense iron layer covering entirely the individual wustite grains (Figs. 8 and 9).

The green pellets of magnetites "B" and "C" began to swell at 20–25% reduction, and they reached the maximum volume expansions of 80 and 100%, respectively, at 60% reduction (Fig. 5).

The oxidized magnetite pellets "B" and "C" after reaching a plateau on the swelling curve at 30% reduction continued to swell and reached the maximum volume expansions of 60 and 80%, respectively, at 60% reduction (Fig. 6).

The oxidized-and-indurated pellets of magnetites "B" and "C" exhibited the "normal" type of swelling curve with maximum volume expansions of 30 and 40%, respectively, at a reduction degree of 30–40% (Fig. 7).

The microscopic examination of partly metallized and highly swollen green and oxidized magnetite pellets "B" exhibited on Figs. 10 and 11 dark gray wustite grains with a white porous iron layer formation only on certain planes of the wustite crystals. The long filaments of iron were visible at a focus beyond the surface of the sample (Fig. 14).



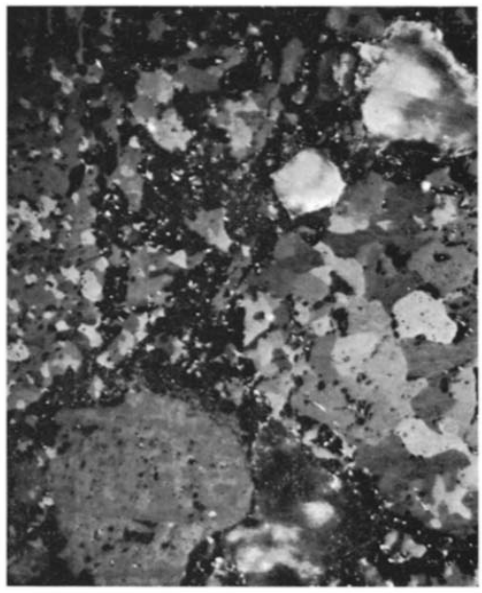
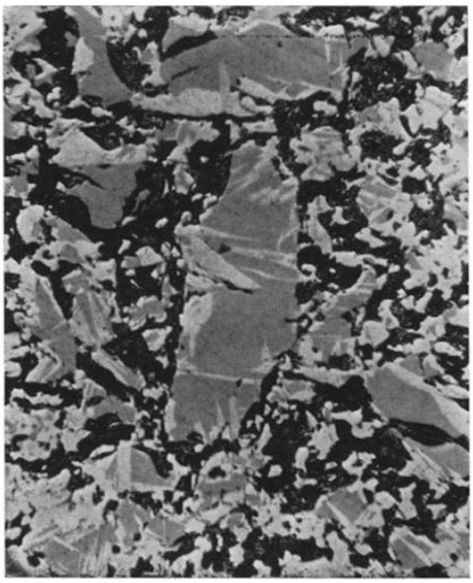


Fig. 16. The hematite grain showing parallel lamellae of primary magnetite. The oxidation of magnetite ore pellet at 950°C. 450 ×.

Fig. 17. The anisotropic hematite polycrystals in the process of growth. The induration of oxidized magnetite pellet at 1320°C. 450 ×, polarized light.



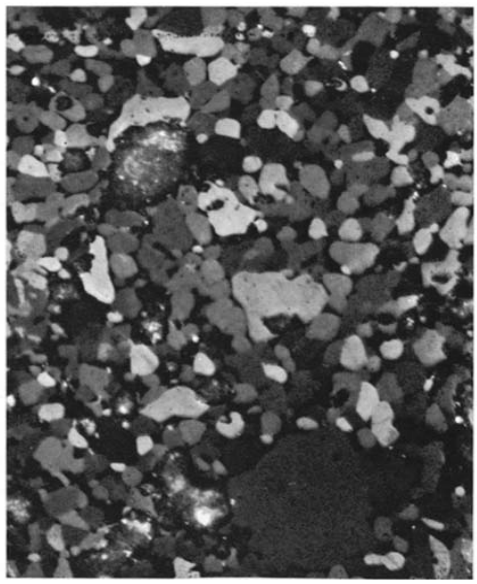


Fig. 18. The precipitation of secondary magnetite in hematite grains. The hematite decomposition at 1320°C. 450 ×.

Fig. 19. The hematite graingrowth in presence of liquid phase. The induration of oxidized magnetite pellet containing 2% limestone at 1320°C. 300 ×, polarized.

The metallized green and oxidized pellets "C" likewise revealed the "irregular" reduction mode of wustite (Figs. 12 and 13). The white iron layer surrounding the wustite particles varies in thickness, becoming highly porous on certain wustite planes. Fe^{2+} ion surface diffusion phenomena generated the growth of iron filaments out from the wustite surface (Fig. 13).

A remarkable change of reduction pattern was observed in the microstructure of partly metallized normally swollen pellets "B" and "C" which were oxidized at 950°C and indurated at 1320°C. The wustite grains were reduced topochemically, showing uniform iron layer formation covering entire grain surface.

The behaviour of green and oxidized pellets "D" during reduction manifested similarity to the normal reduction conduct of pellets which were prepared from magnetite "A". However, the high temperature induration at 1320°C of oxidized magnetite pellet "D" induced severe swelling during reduction (Fig. 7). Microscopic examination revealed the "irregular" reduction mode of individual wustite grains, resembling a type shown on Figs. 12–15.

After addition of 2% limestone to the magnetite "D" prior to pelletization and oxidation at 950°C and induration at 1320°C, these pellets during the reduction again exhibited a "normal" swelling curve (Fig. 7) with a maximum of 25% at 30–40% reduction and the topochemical reduction pattern of the wustite grains.

It was demonstrated that the "normal" swelling course of porous iron oxide pellets during reduction with CO–N_2 mixture at 900°C ensues from the "topochemical" reduction pattern of wustite. On the contrary, the anomalous swelling course of iron oxide pellets is a consequence of the "irregular" reduction pattern of wustite.

It is evident that there is a definite association between the type of reduction pattern of the original magnetite ore and of the hematite which is generated by oxidation of this ore at medium temperatures. The oxidation of magnetite ores did not alter the orignal type of reduction pattern.

Fig. 16 shows a microsection of the unreduced magnetite pellet "B" which was oxidized at 950°C. The white hematite grains expose the highly oriented dark lines of primary magnetite. The sharp edges of hematite grains and poor bridging among small hematite grains indicate that the temperature was too low to promote the solid state reactions of graingrowth and crystal lattice rearrangements.

Fig. 17 exhibits the microstructure of the same magnetite "B" which was oxidized and then indurated at 1320°C. The large polycrystalline hematite crystals are in process of graingrowth, with no evidence of any internal grain orientation.

The reduction of indurated pellet "B" followed the "normal" swelling pattern and consequently exhibited the topochemical reduction mode of wustite.

The magnetite "C" behaved identically. The irregular reduction mode changed into the topochemical after exposure of oxidized pellets to the high temperature treatment.

The magnetite "D", which could be compared with magnetite "A" in respect to the topochemical type of reduction and normal swelling behaviour of the original

ore and oxidized ore, did, however, exhibit after high temperature heating, high volume expansion and formation of cracks in pellets.

Fig. 18 shows the microstructure of an unreduced pellet "D" which was oxidized and heated at 1320 °C. The white hematite grains reveal the precipitation of secondary magnetite. The residual hematite forms the oriented lamellae inside the grains. The thermodecomposition of hematite at this temperature and 0.21 atm O_2 possibly was caused by the presence of impurities such as V_2O_5 and TiO_2 which lowered the hematite decomposition temperature. The hematite–magnetite reversion was accompanied with a rearrangement of the hexagonal hematite lattice into the cubic lattice of magnetite with side effects, resulting in formation of cracks in grains and re-orientation of lattice defects.

The microstructure of unreduced pellet "D" which was indurated with addition of limestone reveals on Fig. 19 a well-developed network of round hematite grains. The round shape of grains is an indication of the type of graingrowth which takes place in the presence of a liquid phase. The basic additive reacted with acid-type impurities, V_2O_5 and TiO_2, and formed low temperature slags at the hematite grain boundaries.

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