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Shrinkage in Compacts of Iron Oxides and Ores

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Compacts have been pressed from (i) four, finely ground, iron ores and (ii) mixtures of sub-sieve ferric oxide with up to 40 wt % of either lime, alumina, silica, or water, and have been sintered in oxygen at temperatures in the range 1000 to 1400° C. Shrinkage, macro- and micro-appearance were recorded at each sintering stage.

The iron ores were classified into two groups: one was characterised by the red ferric oxide appearance and by significant shrinkage at 1000° C; the other was predominantly black and required a temperature of 1200° C to initiate shrinkage in 1 h. The shrinkages of the ores are discussed in terms of the presence of black ferric oxide, particle size, lime content, and dilution of the iron-bearing grains with inert oxides.

The mixtures were used to study the effect of inert oxides on the sintering of ferric oxide. The reduction in shrinkage in the case of alumina and silica is shown to be largely a consequence of dilution; the abnormally high shrinkage at 1000° C induced by 5 wt % of lime is probably due to the presence of low-melting-point ferrites.

1. Introduction

The pelletising of iron ore concentrates has become an important industrial process. It consists essentially in the balling-up of wet powders, which largely contain particles below sieve size, into spheres approximately 10 mm in diameter. Many investigations of a largely technological character [1] have been carried out to improve the room-temperature agglomeration. Much less attention has been paid to the mechanisms of strength development at the subsequent sintering stage. In the present work, a "powder-metallurgy" type of approach has been used to simplify the design of experiments; for example, dry pressing is used, and chemical-grade materials have been employed in many instances. Consequently, the problem becomes generalised, and workers in other fields may find the data to be of interest.

The work, which is based on isochronal heatings to successively higher temperatures, is described in the following order. A general survey of the variation of shrinkage with temperature is given. A question raised by such experiments was the extent to which reduction in shrinkage could be ascribed simply to adulteration of the plain oxide. To this end, common refractory oxides (i.e. CaO, Al_2O_3, and SiO_2) were added to ferric oxide, and the shrinkage with temperature was determined. Additionally, since industrial pelletising [2-4] uses wet mixtures, a Fe_2O_3/H_2O compact was prepared and treated. The description concludes with data on the shrinkage of oxidised and unoxidised magnetite.

Industrially, the criterion for acceptability as a blast-furnace feed is crushing strength; in the present paper, shrinkage, which is known [5, 6] to be directly related to strength, has been taken as a more convenient parameter. As a rough guide, linear shrinkage greater than 5% is acceptable.

2. Experimental

Wherever possible, powders were pressed dry at 8 ton/in.^{2} (1 ton/in.^{2} = 1.6 kg/mm^2) in a 12 mm diameter steel die with double-acting plungers. However, the ferric oxide that had been calcined at 1100° C, the Sierra Leone ore, and the Stripa ore could be compacted only by the use of a pressure of 30 ton/in.^{2} and with paraffin wax in trichlorethylene as a die-wall lubricant. For each batch of compacts, the procedure was as follows: measure the diameter in the green state, sinter at 1000° C, remeasure, reheat most of the samples to a higher temperature, and repeat the procedure. Sintering was carried out in cylinder oxygen in tube furnaces heated by silicon carbide elements. Heating and cooling were both carried out in the furnace; time at temperature was 1 h for temperatures up to and including 1200° C, and ½ h for temperatures above 1200° C.

The base for synthetic oxide mixtures was as-received, laboratory-reagent-grade (LG) ferric oxide (−350 mesh; already calcined, 1.42 wt % SiO_2, CaO nil). Silica was also of LG purity; alumina was Griffin and George grade 5/20; lime was analytical-grade carbonate, calcined in air at 800° C. These oxides, which were all −350 mesh BSS, were added singly to LG ferric oxide in the weight percentages 5, 10, 20, and 40. They were blended by hand, and pressed. Experiments involving 800° C-calcined carbonate were carried through continuously, to avoid hydration difficulties. The wet compact, which contained 23% H_2O (wet basis), was dried at 85° C for 16 h, then step-sintered in the standard manner.

The chemical and sieve analyses of the ores are given in tables I and II respectively. The Sierra Leone ore was much coarser than the others as-received; it was crushed and blended to give a mixture of equal parts of 200/240 mesh fraction and −350 mesh BSS, to be comparable with previous material used at the laboratory [7, 8]. However, additional work showed that the shrinkage of the −350 mesh powder on its own was of the same order as that of the mixture. The other materials were used in the mesh grading given in table II; calcination in air at 800 and 1100° C for 1 h made insignificant changes to the grading of the ores.

In an additional series of tests (tables VI and VII), LG magnetite was subjected to 1 h oxidation treatments [9-19] before compaction and sintering. Each of the oxidised magnetites was compacted using high pressure and was subsequently step-sintered (table VII).

The ground ores, powders, and compact surfaces were examined visually and by reflection under crossed nicols. Powder specimens were mounted on a glass slide using a solution of canada balsam in xylene. Crossed nicols, unlike ordinary illumination in the microscope, differentiates between red and black ferric oxide. This is not to be confused with the use of nearly crossed (80°) nicols, which produces grain contrast in microspecimens of sintered hematite [9, 20], though not in magnetite [20].

TABLE I Chemical analysis.

Constituent (wt %)	Oxfordshire	Kiruna	Conakry	Stripa	Sierra Leone
Fe_2O_3	31.38	59.74	74.80	63.80	98.95*
FeO	2.51	24.00	0.4	6.97	Not determined
CaO	19.50	4.6	Trace	1.9	Nil
MgO	3.00	1.6	0.7	1.7	Nil
Al_2O_3	6.1	1.2	10.4	0.8	0.20
SiO_2	8.84	3.87	1.48	20.24	0.30
Loss on ignition	25.70†	Slight gain	8.5	Slight gain	Not determined

*αFe_2O_3 by X-ray diffraction
†−16.2% CO_2

TABLE II Sieve analysis.

Mesh Size BSS	Conakry	Oxfordshire	Stripa	Kiruna
+150	0.8	0.4	0.8	Trace
−150 +200	18.5	17.3	23.6	7.2
−200 +240	5.3	5.6	6.3	5.1
−240 +300	12.7	15.9	15.1	14.1
−300 +350	5.1	4.6	5.9	6.5
−350	57.6	56.6	48.3	67.1

All figures in wt %; as-received condition.
LG Fe_2O_3 and LG Fe_3O_4 were both 100% less than 350 mesh.

3. Results

Results on ores and plain oxides, before and after calcination, are summarised in fig. 1 and tables III and IV, on synthetic oxide mixtures in fig. 2 and table V, and on LG magnetite in tables VI and VII.

The black appearance noted in tables III, IV, and V is probably due to a coating around red ferric oxide grains, because continued grinding of any black hematite ore effected a change in colour to maroon; under crossed nicols, such a change could be followed as an increase in the number of fine red particles. Black ore grains were, prior to grinding, often "peppered" with red spots, denoting gaps in the coating (fig. 3). The silica content in the Stripa ore could be seen as discrete particles side by side with the iron-bearing grains. Ore and gangue particles could not be resolved in the case of Oxfordshire and Conakry; but some differentiation into dark and light particles was noted in Oxfordshire ore calcined to 800° C.

4. Discussion

The black coating observed in the present work is probably the film of transitional structure between α-Fe_2O_3 and Fe_3O_4, whose constitution is discussed in conflicting investigations [21, 22] on the heating of hematite crystals.

Important factors that affect shrinkage are: (i) lime content; (ii) dilution of the ferric oxide base with inert oxides; (iii) presence or otherwise of "black hematite" film on the particles; and (iv) particle size. It can be shown, from consideration of relative volumes, that the effect of silica and alumina on the high shrinkage of the LG ferric oxide may be explained simply on the basis of dilution, given the premise that shrinkage is proportional to the number of Fe_2O_3/Fe_2O_3 contacts [25]. The behaviour of silica- and alumina-containing compacts is in contrast with that of lime-containing compacts. The fact that 5 wt % of lime has such a large effect may suggest that chemical interaction has taken place, and that the defect structure of ferric oxide has been modified [26]. However, in analogous experiments [20], Fe_2O_3/MgO mixtures behaved similarly to Fe_2O_3/Al_2O_3; this indicates that the lime effect is more likely to be due to the low melting points attainable in the Fe_2O_3/CaO system [27] (i.e. to liquid-phase sintering rather than impurity of lower valency). The "wet" LG ferric oxide shows particularly high shrinkage, and a form of activated sintering may be taking place [28].

In the work on ores and plain laboratory oxides, the highest shrinkage is given by LG ferric oxide, and this may be taken as a standard

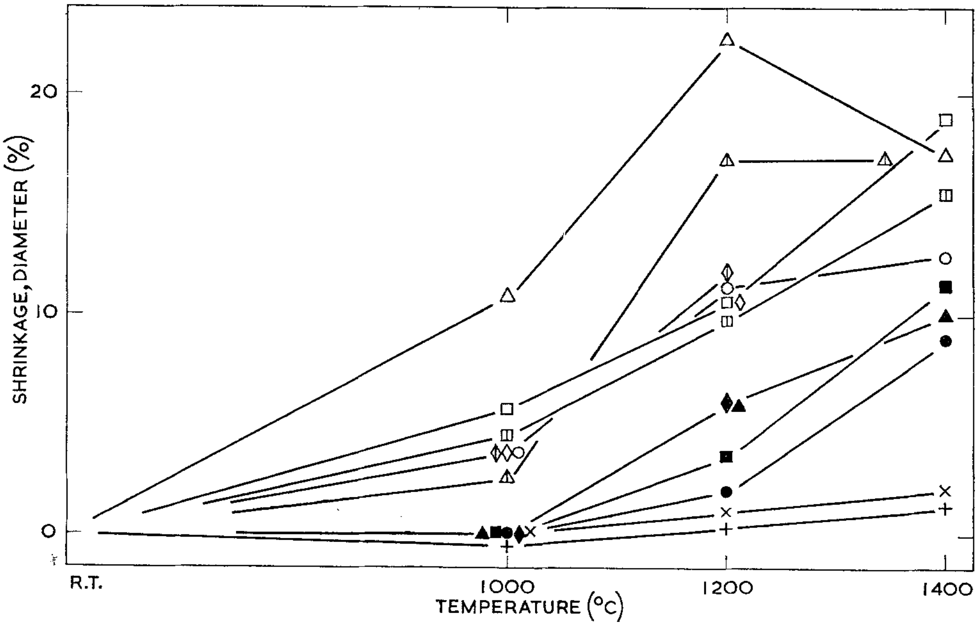

Figure 1 Shrinkage of ore and iron oxide compacts versus sintering temperature: □ Conakry→ ◫ calcined 800° C→ ■ calcined 1100° C; ◇ Oxford→ ⟠ calcined 800° C→ ◆ calcined 1100° C; + Stripa; × Sierra Leone; △ LG Fe_2O_3→ ◬ calcined 1000° C→ ▲ calcined 1100° C; ○ LG Fe_3O_4; ● Kiruna.

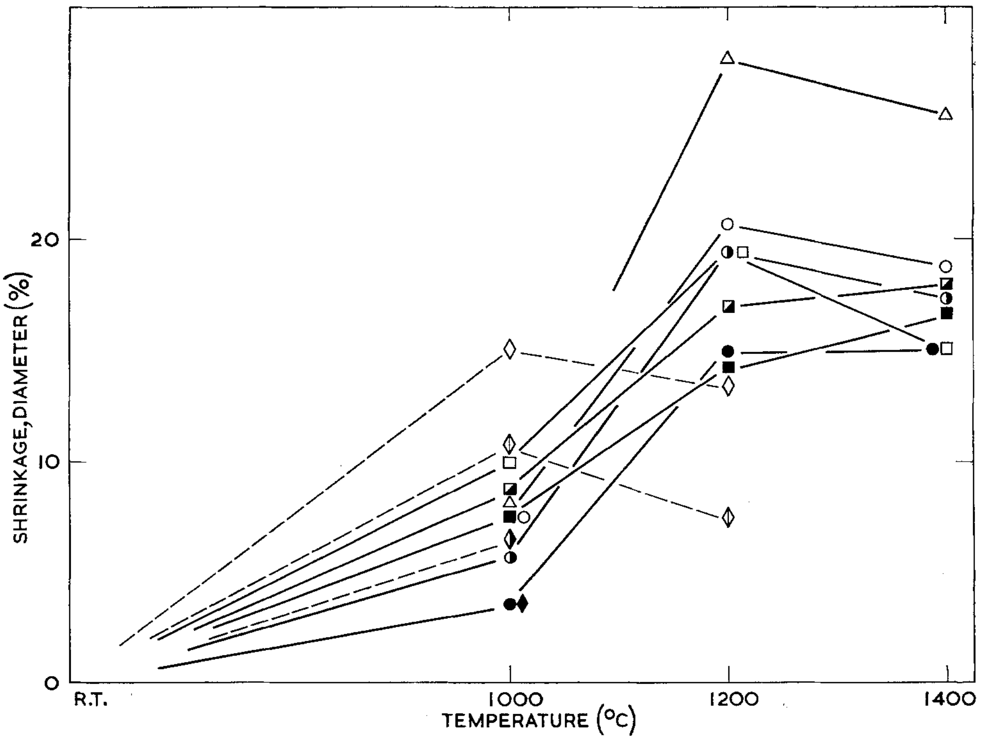

Figure 2 Shrinkage of ferric-oxide-base compacts versus sintering temperature.

	5%	10%	20%	40%
Silica-containing		□	◪	■
Alumina-containing		○	◑	●
Lime-containing	◇	◇	⬖	◆
Water-containing			△	

TABLE III Appearance of red oxide* compacts.

	Visual observation	Under crossed nicols
Green state	Red†	Red†
Sintered 1000° C	No change in colour, small cracks appear	Red + little black
Sintered 1200° C	Dark grey, cracks healed	$\frac{3}{4}$ black, $\frac{1}{4}$ red
Sintered 1400° C	Black, cracks along different paths	Black, few red spots

*Refers to compacts of: (i) LG Fe_2O_3, as-received and calcined 1000° C; (ii) Conakry, as-received and calcined 800° C; (iii) Oxfordshire, as-received and calcined 800 and 1100° C.

†For Conakry and Oxfordshire ore read red/brown and brown/yellow respectively.

TABLE IV Appearance of black oxide* compacts.

	Visual observation	Under crossed nicols
Green state	Dark grey	Black, few red spots
Sintered 1000° C	Dark grey to black	,, ,, ,, ,,
Sintered 1200° C	Black	,, ,, ,, ,,
Sintered 1400° C	Black	Black, trace red spots

*Refers to compacts of: (i) LG Fe_2O_3, calcined 1100° C; (ii) Conakry ore, calcined 1100° C; (iii) Kiruna, Stripa, and Sierra Leone ores.

TABLE V Appearance of synthetic oxide compacts.

Alumina series	Appearance of iron-bearing particles as for LG Fe_2O_3.
Silica series	Generally as for LG Fe_2O_3; tendency for less black at 1200 and 1400° C; also tendency for bloating and then glazing to occur as the content increases to 40 wt %.
Lime series	As compared with LG Fe_2O_3, a strong tendency for the amount of black to increase for a given temperature. A phase which appeared bright yellow under crossed nicols (possibly a calcium ferrite) became visible at 20 wt % CaO.
Wet compact	As for LG Fe_2O_3.

TABLE VI Oxidation of magnetite powder.

Temperature of oxygen treatment (°C)	Magnetism	Visual inspection	Inspection under crossed nicols
20	Strong	Black	Black
300	Strong	Black, slightly red	¼ red, ¾ black
400	Strong	Red-black, loose	½ red, ½ black
500	Strong	Red-black, loose	¾ red, ¼ black
600	Fair	Red-black, loose	¾ red, ¼ black
700	None	Red-black, loose	¾ red, ¼ black
800	None	Red-black, caked	½ red, ½ black
900	None	Black, caked	¼ red, ¾ black
1000	Slight	Black, caked	Black, few red spots, fine-grained

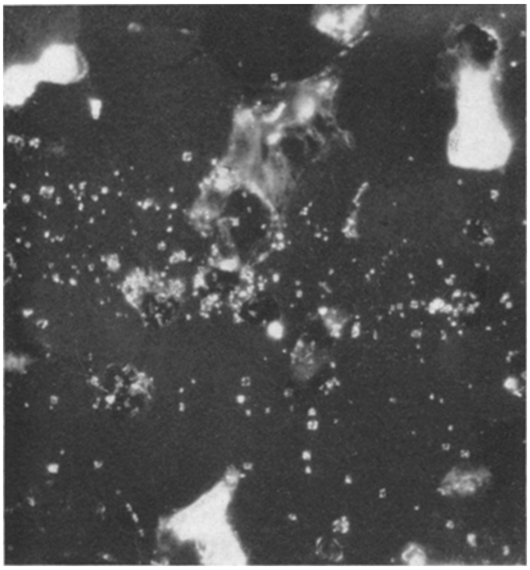

Figure 3 Sintered hematite, partly polished, showing a black surface with red spots (large, light areas are pores), under crossed nicols (×50).

TABLE VII Shrinkage in compacts of oxidised magnetite.

Temperature of oxygen pretreatment (°C)	Shrinkage % in O_2 at 1000° C	Shrinkage % in O_2 at 1200° C
20	4.0	11.3
300	5.2	12.5
400	5.8	11.8
500	6.9	13.7
600	5.3	11.1
700	5.3	12.3
800	5.7	12.5
900	4.4	11.2
1000	2.9	9.2

Notes All sintered compacts were black to the eye and under crossed nicols; they were very weakly, if at all, magnetic. Shrinkages at 1400° C were unreliable because of distortion.

(fig. 1). The lower shrinkage of the as-received Conakry ore is probably due solely to the dilution effect. Oxfordshire ore shrinkage at 1000° C is appreciable and is consistent with a dilution effect; the lime content is high and beyond the range (fig. 2) where it would accelerate shrinkage. The silica reduces contacts between the iron oxide grains in the Stripa ore, and this may explain this ore's inferiority to the Sierra Leone ore.

Table III refers to (i) cracking at or below 1000° C and (ii) cracking accompanied by shrinkage reversion at 1400° C. The cause of the former is not known, but it is thought to have its origin in slight thermal or mechanical shock in the pre-shrunk state; such cracks tend to heal up at 1200° C as part of the normal densification process. Cracking and/or bloating at 1400° C is probably of different origin, and is possibly connected with the presence of small amounts of liquid phase or gas at a late stage in the consolidation process [23, 24].

On the basis of shrinkage and appearance, the four hematite ores and oxides may, in a general way, be subdivided into two types. Sierra Leone ore, Stripa ore, and high-temperature-calcined ferric oxide exemplify a structure based on black, comparatively coarse, −350 mesh, iron-bearing particles; in contrast, Conakry ore, Oxfordshire ore, and as-received ferric oxide are red and fine-grained. The red oxides show a small, perceptible shrinkage at 1000° C, whereas the black oxides do not shrink at this temperature in 1 h. Red oxides are preferably pressed at low pressure, and agglomerate easily; black oxides are more difficult to compact. Although the red powders tend to be finer in the sub-sieve range, this may be largely fortuitous, since fine grinding is necessary to break up black particles, where such exist. Rigorous experiments to analyse the relative effects of particle size and presence of black surface would probably be difficult to arrange, since film formation by heating necessarily increases the particle size. However, some relevant information was obtained in the magnetite oxidation experiments (tables VI and VII). The products of preoxidation of magnetite may be classified into three types: (i) magnetite coated with hematite (300 to 500° C); (ii) hematite particles (600 and 700° C); and (iii) hematite coated with black film (900 and 1000° C). Subsequent shrinkage of types (i) and (ii) is similar (table VII), presumably because (i) will quickly be converted to (ii) in the heating up to sintering temperature. Type (iii) is inferior to the others and, whilst the result is not without ambiguity, it does appear that the lower shrinkage is due to black film *per se*, since particle agglomeration was not serious at 900 to 1000° C.

5. Conclusion

The sintering behaviour of impure oxide mixtures has been analysed in terms of solid-state sintering as modified by various factors. This information is useful for determining how to blend feed materials, so as to increase the shrinkage and hence increase the strength of the sintered compact.

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