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Electrical Conductivity and Sintering in Iron Oxides at High Temperatures

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Two raw materials were chiefly used, namely laboratory ferric oxide and a high grade hematite. All experiments were carried out in an oxygen atmosphere, in the range 600 to 1300° C.

The conductivity/temperature determinations described are of two kinds, *viz* those on loose powders and those across fractures in previously compacted and sintered material. In the former, indications were obtained of differences in electrical behaviour above 1100° C which could be correlated with the appearance (red or black) of the powder. In the latter, unstable electrical behaviour was noted above the Tammann temperature in the hematite, but not in the ferric oxide.

Additionally, isothermal sintering experiments were carried out, at 975 to 1200° C on red ferric oxide, and at 1350 to 1400° C on black ferric oxide. The temperature dependence was approximately the same for both materials and the results are compatible with the electrical data, on the assumption that conductivity in general reflected particle surface conditions, whereas shrinkage was dependent on internal lattice movements.

1. Introduction

Measurements of electrical conductivity on powders and fracture surfaces have been used by the author [1] for the investigation of the sintering behaviour of chromic oxide, and it appeared to be of interest to apply them to the case of ferric oxide. In the chromic oxide work, much useful information was obtained by making use of the Friederich/Meyer effect [2] at an operating temperature of 500° C. Such a temperature was suited to the conductivity of the oxide and the sensitivity of the available apparatus, and was conveniently low for meaningful diagnosis. However, with ferric oxide it was found that a temperature of not less than 800° C (i.e. more than 0.50 T_m) was necessary to provide an adequate electrical signal. Admittedly, useful indications were obtained, for example that the available oxides were n-type in the range 600 to 900° C, and that tests at higher temperatures (and also tests at 800° C after previous heating to over 1100° C in oxygen) resulted in a faintly n-type product. But in general it seemed that use of the Friederich/Meyer effect was less profitable than a direct investigation of the variation of conductivity with temperature in a constant atmosphere i.e. 100% oxygen. The conductivity/temperature relation for loose powders, then, forms the principal subject of the present paper (section 2.1); a brief programme of isothermal sinterings (section 2.3) provides parallel data on the temperature dependence of shrinkage; sections 2.1 and 2.3 are complementary in discussion. Section 2.2 describes experiments on conductivity/temperature across fractures in pre-sintered compacts.

The present results have considerable relevance to the matter of "black" (as distinct from red) hematite. At this point it suffices to say that "black" hematite consists of red particles coated with a black layer [3]. The layer is either magnetite or a transitional structure [4, 5]. Heating to high temperatures in oxygen converts red to "black" hematite.

2. Experimental Method and Results

2.1. Conductivity/Temperature; Powder Samples

The raw materials consisted of the following.

(i) Red ferric oxide of laboratory reagent grade. This contained 1.42 % SiO_2, CaO nil; the powder passed completely through a 350 mesh (45 μm) BS sieve, and was largely less than 5 μm in particle size.

(ii) Precipitated magnetic powder (laboratory reagent). The particle size was similar to that of the ferric oxide.

(iii) Hematite. This was a black coarse micaceous high-grade concentrate from Sierra Leone. It contained 98.95% Fe_2O_3, 0.30% SiO_2, 0.20% Al_2O_3, CaO nil. Sieve analysis showed 21 % over 100 mesh, 31 % 100 to 150 mesh, and 40 % 150 to 200 mesh (i.e. it was largely composed of particles larger than 75 μm). A portion was crushed to less than 350 mesh BSS in a small planetary mill.

For an electrical measurement, two platinum wires approximately 3 mm apart were laid parallel along the bottom of a sintered alumina boat and were connected directly to a DC resistance meter ("Avometer"). The sample of oxide powder was poured over the wires, and the boat assembly was then transferred to a tube furnace with atmosphere of cylinder oxygen. The furnace was raised from room temperature to approximately 1300° C over a period of 4 h, and the resistance was measured at intervals from 800° C upwards during this time. The instrument was in circuit only when readings were taken; reversal of polarity made no difference to the reading. The accuracy of reading was low beyond the range 1 to 10,000 Ω.

The results are illustrated graphically in figs. 1 and 2; fig. 1 relates to ferric oxide, fig. 2 to hematite. A conductivity/temperature line for magnetite in oxygen is included in fig. 1; fig. 2 contains a superimposed summary of the results of other workers on ferric oxide [2, 6].

2.2. Conductivity/Temperature across Fractures

The basic materials were ferric oxide and hematite as in 2.1, but in this instance they were consolidated as follows. Compacts were pressed from the ferric oxide at 8 tsi (12.6 kg/mm^2) in a steel die; one compact was sintered at 1200°, the other at 1400° C, both in oxygen for 2 h.

Two compacts were pressed from the hematite, one from a 200 to 240 mesh crushed fraction, the other from as-received powder (5% of ferric oxide was added to the latter as a binder to facilitate pressing). These were pressed at 30 tsi (48 kg/mm^2) using a solution of paraffin wax in trichlorethylene as a die wall lubricant, and sintered at 1400° C for 2 h. All compacts were then fractured and subjected to a conductivity/temperature test; the contacts were of the "catswhisker" type, otherwise the technique used was that described in section 2.1. The results are illustrated in fig. 3. The step in one of the ferric oxide curves was probably due to displacement of a whisker.

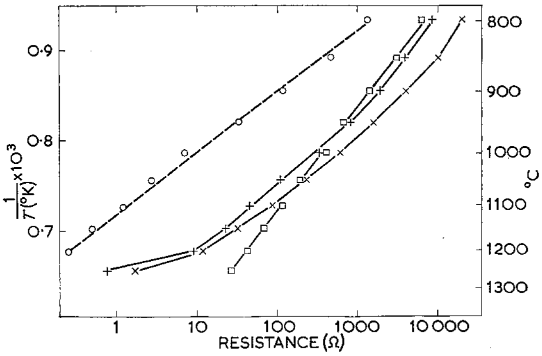


Figure 1 Electrical resistance versus temperature for ferric oxide and magnetite powders. × ferric oxide, experiment 1; + ferric oxide, experiment 2 (repeat of 1); □ ferric oxide, ex experiment 2, lightly crushed; ○ magnetite. Oxygen atmosphere throughout.

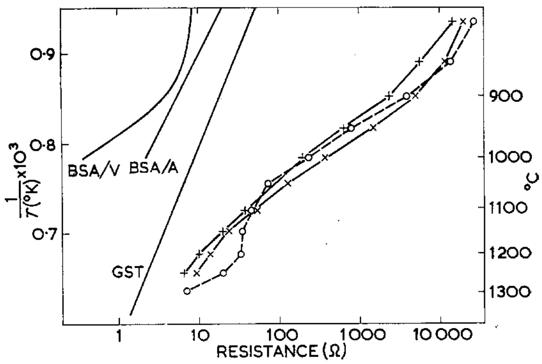


Figure 2 Electrical resistance versus temperature for hematite powders. × hematite as-received; + hematite, repeat of 1; ○ hematite, ground less than 350 mesh BSS. Above tests in oxygen. GST, BSA/A and BSA/V refer to tests on ferric oxide in consolidated form. GST [6]: prefired in air to 1250 to 1300° C, tested in air; BSA [2]: prefired in air to 1000 to 1050° C, tested in air (A) and vacuum (V) respectively. The position of these curves on the resistance scale is not significant.

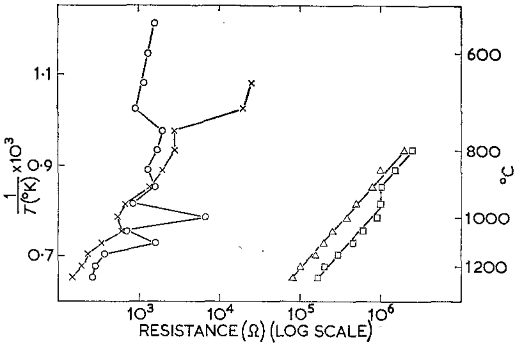


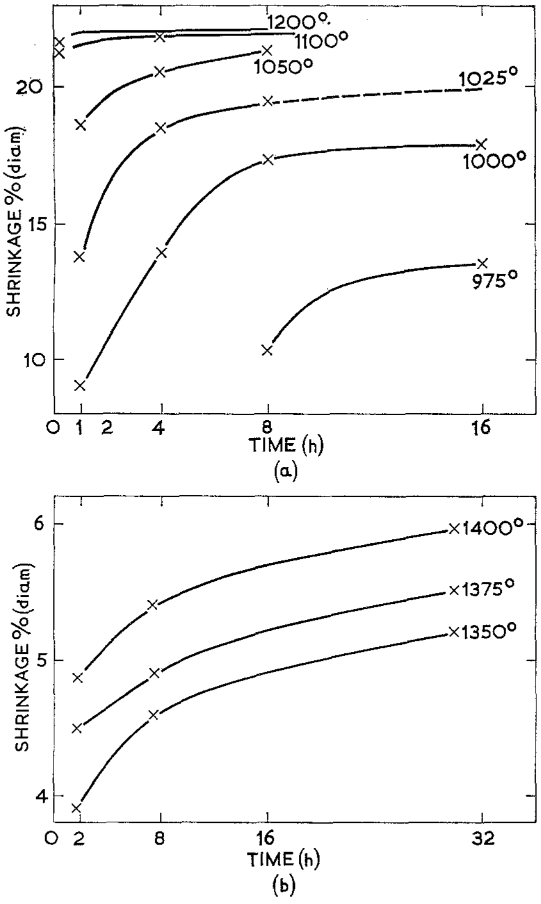
Figure 3 Electrical resistance versus temperature for ferric oxide and hematite fractures. Key to compact base: × as-received hematite (5% ferric oxide added, see text), sintered 1400° C; ○ crushed hematite (200 to 240 mesh fraction), sintered 1400° C; △ ferric oxide sintered 1200° C; □ ferric oxide sintered 1400° C. Oxygen atmosphere for sintering and testing.

2.3. Isothermal Sintering

Three materials were used initially. The first was ferric oxide as above (red oxide). The second was the same oxide after repeated calcinations (1 h) in oxygen to 1000, 1100, 1150, and 1200° C successively, with the object of converting the powder to "black" oxide. The technique of "calcination at 1000° → light grinding → 1100° → grinding repeat, etc" was chosen in order to minimise agglomeration [3]. A third material consisted of a hematite mix (50% 200 to 240 mesh; 50% less than 350 mesh [7]) conditioned as for the ferric oxide so as to ensure an all-black appearance. Isothermal sintering experiments were carried out in the range 1350 to 1400° C on this material, but the results were irrational and are not reported. The behaviour may be due to sintering at temperatures where densification reversal [8] operates, and may be connected with a feature of the behaviour of fractures of hematite reported in section 2.2.

Compacts, approximately of equal height to diameter, were pressed from the ferric oxides; red oxide at 8 tsi (0.5 in.* die), and black oxide at 30 tsi (0.375 in. die) using paraffin wax as a die wall lubricant. Non-standard compacts were discarded. One sample was used for each time/temperature condition. The temperature range 975 to 1200° C was used for the red oxide, and 1350 to 1400° C for the black oxide; these covered approximately the same range of density, i.e. on and about 4.5 g/cm^3 ($\simeq$14% porosity). The samples were placed on an alumina tray and care was taken that the furnace position and similar details remained constant. Temperatures at the sample position were checked between runs; nominal temperatures are quoted, since there was only a small, constant difference between nominal and true. The work tray was pushed in and out slowly by hand, the average time for transfer being 7 min. Times recorded are for "fully in" to "start of withdrawal". Cylinder oxygen remained flowing throughout.

Changes in radial shrinkage were selected as the most consistent parameter for illustration and discussion. Fig. 4 shows the isothermal sintering curves obtained; fig. 5 is derived from fig. 4 by the method of Jordan and Duwez [9]. Additionally, plots of log shrinkage versus log time (not illustrated) have slopes of approximately 1/3 for red oxide at the lower end of the temperature range; at higher temperatures, and with black oxide, the slope decreases markedly,



(a)

(b)

Figure 4 Shrinkage versus time for red and black ferric oxide; (a) red oxide; (b) black oxide.

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*1.0 in. = 2.5 cm

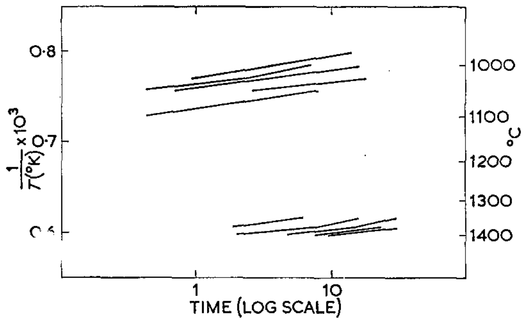

Figure 5 Time intercepts versus temperature of sintering; materials as in fig. 4.

i.e. sintering is largely completed and the derivation is not meaningful.

3. Discussion

In the fracture tests (fig. 3), the hematite was electrically unstable above the Tammann temperature (about 750° C), in contrast with the ferric oxide; possibly this is connected with their different behaviour during sintering. The uncrushed ore was more stable, consistent with the likelihood [1, 10] that compact fracture has avoided fresh, transgranular, paths.

In isothermal sintering (fig. 5), the same temperature dependence is operative for red and black ferric oxide, indicating a similar shrinkage mechanism. The high apparent activation energy in both (table I) suggests that lattice diffusion is operative [2, 11, 12].

A somewhat speculative explanation for the variations in powder conductivity (figs. 1 and 2) may be offered as follows. The hematite is composed of red particles largely covered by a black surface layer [3-5], and the overall conductivity is likely to be that resulting from a series-parallel arrangement of red and black surface patches [13]; this state is probably reached also by oxidation of magnetite (fig. 1), and by heating ferric oxide to high temperatures [14]. The typical 800 to 1150° C behaviour may be synthesised from two elements, that is, conduction through a red network, represented by the conductivity of ferric oxide above 1150° C, and "black" conduction as in pre-heated and crushed ferric oxide (fig. 1). Alternatively, transparticle conduction, or continuing formation of magnetite [2], may occur above 1150° C in as-received ferric oxide. But in general, the sintering and conduction results are compatible, given that the latter reflects particle surface conditions [13], whereas shrinkage is dependent on internal lattice movements.

TABLE I Apparent activation energies

Material, conditions, and source	Q (kcal/mole)
Conductivity	
Hematite and ferric oxide powders below 1100° C (best figure from figs. 1 and 2)	61
Magnetite powder, fig. 1	69
Ferric oxide powder above 1150° C (×, + in fig. 1)	230
Ferric oxide powder, blackened (□ in fig. 1)	41
Ferric oxide compacts [6] (GST in fig. 2)	21
Ferric oxide compacts [2] (BSA/A in fig. 2)	26
Hematite fracture below 700° C, fig. 3	10
Hematite fracture above 700° C, fig. 3	15
Ferric oxide fracture (i.e. above 700° C), fig. 3	22
Sintering	
"Black" ferric oxide (1350 to 1400° C), fig. 5	200
Red ferric oxide (975 to 1200° C), fig. 5	200
Diffusion (from [11])	
For Fe in $FeO_{1.087}$ temp. range 690 to 1010° C	30
For Fe in Fe_3O_4 temp. range 750 to 1000° C	55
For Fe in Fe_2O_3 temp. range 930 to 1270° C	112
For O in Fe_2O_3 temp. range 1150 to 1250° C	146

Correspondence of apparent activation energies with previous data is only partial (table I). But agreement exists between the average activation energy for conduction in as-received powders and that for magnetite during oxidation; also it is clear that the average surface valency in black oxide is low, and it may be significant that the activation energy across fractures is even lower.

Acknowledgements

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