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Sintering in Ferric and Chromic Oxides: Further Work

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Surfaces and fractures in variously-sintered ferric oxide and chromic oxide compacts have been scanned for metal content by electron microprobe analysis. Also, fractures in these oxides have been examined at temperatures up to 1000° C by the electrical conductivity probe, using an atmosphere of gettered argon. The microprobe analysis gave indications of high metal contents in sintered surfaces, and the conductivity probe showed no significant variation of resistivity with temperatures up to 800° C. It is inferred that a thin metal film exists on the surface of particles of "black" ferric and chromic oxides. A model is proposed to account for sintering phenomena in these oxides.

1. Introduction

Extensive work by the author on the sintering of ferric and chromic oxide [1-4] has shown the importance of the black film which may be present on the surface of the oxide particles. In reviewing the early work [1,4] on chromic oxide, it was tentatively concluded that the film consisted of the oxide Cr_3O_4; much of the evidence, however, suggested that the film was metallic. More recently, further work using microprobe analysis on ferric and chromic oxide sintered compacts gave support to the latter hypothesis. This microprobe work stimulated renewed interest in the diagnostic use, on fractures, of electrical conductivity/temperature traverses [1, 3, 4]. This paper describes results with the two techniques, and proposes a model for sintering of these oxides, which is shown to be compatible with a multiplicity of experimental observations.

2. Experimental and Results

Specimens were fabricated from laboratory reagent grade powders with particle size approximately 1 μm, by cold-pressing at 8 tsi (12.8 kg/mm^2), and sintering at temperatures up to 1400° C, generally in an oxygen atmosphere. Details of the fabrication of the pure oxide specimens and the oxide/carbon specimens have been previously reported [2, 3, 5].

2.1. Electron Probe Microanalysis

Fracture surfaces and the surfaces of sintered specimens were examined by electron probe microanalysis using a Cambridge "Geoscan". The beam penetration was reduced by operating throughout at an accelerating voltage of 15 kV (the minimum possible to ensure a reproducible and reasonably strong signal). The spot would be 0.5 to 1.0 μm in diameter. Some specimens were vacuum-coated with carbon to facilitate electron leakage. Particular care was taken to load ferric oxide and hematite fractures quickly into the instrument, so as to avoid possible oxidation.

The results (table I) give evidence for the existence of films rich in metal, but with one exception (C4) this applies only to compact surfaces, not fractures. All samples, coated or not, had sufficient electrical leakage to obviate instrument instability, and hence it was not possible to diagnose metal films by this means in runs D, E and F. No correction was made for density variations, since results obtained with a coarse probe beam are at best inconclusive. The data on metal standards do not appear to be consistent with oxide data; since the bulk geometry of the standards is completely different from that of the porous oxides, the results on the former have been ignored.

TABLE I Microprobe analysis.

Run	Sample and treatment	Analysed area	Colour of area	Average metal signal* (arbitrary units)
A	1. Fe_2O_3, 1000° C	SSCC	red	9.0
	2. Fe_2O_3, 1400° C	SSCC	black	9.85
B	1. Cr_2O_3, 800° C	SSCC	green	1.83
	2. Cr_2O_3, 1400° C	SSCC	black	3.90
	3. "Cr_2O_3/1 % graphite" reacted 1400° C	SSCC	metallic	3.87
C	1. Fe standard			3.9
	2. Fe_2O_3, 1000° C	SSCC	red	2.2
	3. Fe_2O_3, 1215° C	SSCC	black	2.6
	4. Fe_2O_3, 1215° C	FC	black	2.5
D	1. Cr standard			5.9
	2. Cr_2O_3, 1000° C	FU	green	4.0
	3. Cr_2O_3, 1400° C	FU	black	3.8
E	1. Cr standard			6.6
	2. Cr_2O_3, 1000° C	FU	green	3.95
	3. Cr_2O_3, 1400° C	FU	black	4.07
F	1. Fe standard			3.4
	2. Hematite, 1400° C	SU	black	2.2
	3. Hematite, 1400° C	FU	black	2.28

Notes (i) All treatments in oxygen, except that argon was used for B3. (ii) SSCC = sintered surface, carbon coated; FU = fracture, uncoated; etc.
*Run-to-run changes are not significant.

2.2. Electrical Conductivity across Fractures

The variation with temperature of the electrical conductivity of fractures was measured. Two "cats-whisker" platinum wires in contact with the fracture were connected directly to a DC resistance meter ("Avometer"). To increase the likelihood of detection of films, three modifications were made to the earlier technique [3]. Firstly, measurements were taken at the lowest permissible temperatures, in order to avoid possible oxidation. Secondly, an argon atmosphere was used, since earlier results could have been the resultant from whole or part gettering with 100 % oxygen (argon would tend to decompose the oxides, but speed of dissociation would be slow at the essential temperatures). The argon was purified *in situ* by using chromium getters before and after the specimen with the three boats inside a ceramic inner guard tube. Thirdly, electrical sensitivity was increased by decreasing the distance between the cats-whisker contacts to about 1 mm; even so, accuracy was low with resistances greater than $10^7\ \Omega$.

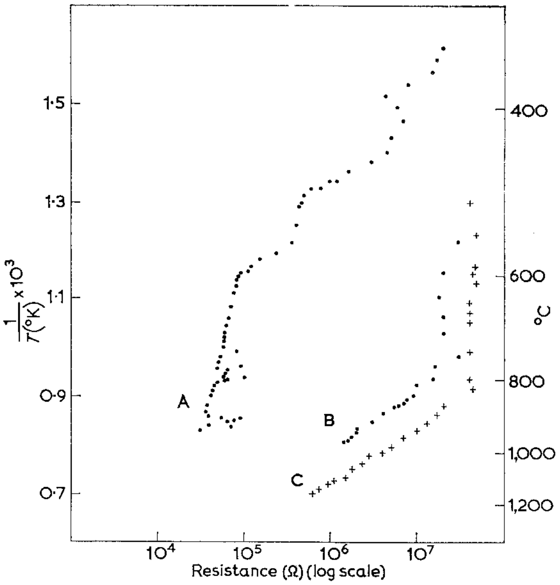

Figure 1 Electrical conductivity versus temperature: ferric and chromic oxide fractures. A Chromic oxide/1% graphite compact, reaction-sintered at 1410° C; tested ungettered. B Sintered compact as A; tested in gettered argon. C Hematite sintered at 1400° C in oxygen; tested in gettered argon. (The temperature-dependence of samples B and C above 800° C is approximately equivalent to 40 kcal/mole.)

Three fresh fractures were tested, two in Cr_2O_3/1 % graphite compacts reaction-sintered [5] in argon at 1410° C, one in hematite sintered in oxygen at 1400° C [6]. For the first of the chromic oxide samples the upstream getter was inadvertently omitted, but the run is included in the results (fig. 1). The conductivity traverse for the latter is generally similar to previous ungettered traverses [7]; it falls rapidly but unevenly as temperature rises. Momentary increases in resistance were observed at 700 to 900° C and may be ascribed, as previously, to changes in microcircuitry with sporadic film oxidation. In contrast, the curves on the properly gettered samples show essentially no change in conductivity up to 800° C.

3. Discussion

From previous data on chromic oxide [1, 7] it was inferred that the black film was not hyper- or hypostoichiometric oxide, but either Cr or Cr_3O_4. The film did not appear to dissolve in acid, but other evidence [4] indicated strong chromium enrichment in grey/black compact surfaces. Hot-compression tests on compacts [7] gave no evidence of plasticity, but a measure of toughness was apparent in ball-hardness test [5], and graphical analysis of as-sintered hardness versus sintering temperature [9] suggested that metallic bonding existing after optimum sintering was destroyed by over-sintering. Previous microprobe work using a Cambridge "Microscan" on metallographic sections was inconclusive; the high metal content on the outside of present compacts (A2, B2, and C3, table I) may be ascribed to the greater "dissociation" possible at free surfaces. The coloured compact surfaces (A1, B1 and C2) were all lower in metal. Significant correspondence of metal content may be noted in runs B and C. For example, fracture C4 agrees with the surface C3 of the same compact, not with a low-fired red surface C2; again, B2 had the dark green/black appearance of the film noted previously [1], whereas B3 had a metallic-looking coating [4], strongly suggesting that the former film was metallic. Conductivity probe results point to the same conclusion. Decrease of resistance with rise in temperature is at a minimum for assemblages of black particles [3]; compacts of red ferric oxide show much higher apparent activation energies for conduction. It appeared likely that a significant component of the conductivity is of negative coefficient (i.e. metallic), and this is clarified and confirmed (fig. 1) under conditions more conducive to the stability of metal films.

It remains to consider what model of sintering is appropriate. In doing so, it must be remembered [2, 3] that compacts of black-coated particles of ferric oxide shrink more slowly than red; compacts of red oxide are characterised by oxide-oxide particle contacts (A, fig. 2) whereas black oxide compacts have contacts of sandwich construction (C). There are two significant temperatures; the temperature at which the onset of shrinkage occurs, and the temperature of formation of black film. In ferric oxide the former temperature is the lower and shrinkage begins at about 800° C as a result of sintering by ion diffusion (model A). In chromic oxide, black film is visible after heating to 1000° C in oxygen (films appear to form inside compacts), and shrinkage is negligible up to not less than 1600° C. When shrinkage is activated by reducing conditions [5], the passivating mechanism, which operates through loss of trioxide and film formation [1, 4, 8], is rendered inoperative and shrinkage begins at 1200° C and continues rapidly. In activation-sintered chromic oxide it appears likely that the end product has the morphology indicated in B (fig. 2), but that in ferric oxide the progression A → B is followed at optimum sintering temperatures (about 1200° C) by a tendency to type C (i.e. by incipient dissociation; 1200° is equivalent to 0.85 T_m).

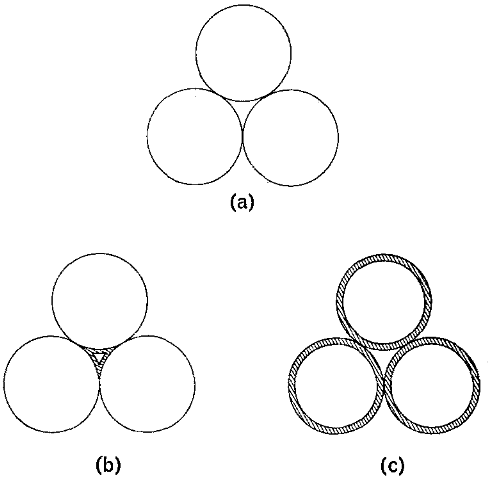
(a)
(b) (c)

Figure 2 Sintering of ferric and chromic oxide particles (schematic). Shaded areas represent thin metal films.

The present hypothesis is able to account qualitatively for several phenomena which had previously been considered to require separate explanations. For example, the tendency for blackening of powders to be accompanied by a change to apparent p/n neutrality [1, 3] is consistent with a high metallic contribution to conduction. Sintering studies [3] in red and black ferric oxide may be explained on the basis that grain-boundaries in black oxide compacts (i.e. of type C) undergo solution of the black film at sufficiently high temperatures out of contact with oxygen-containing atmospheres; thereafter ionic diffusion as in red/red contacts will occur across the boundary, giving the same temperature dependence but with a higher threshold temperature. The erratic behaviour of black hematite shrinkage [3] could be due to film formation and solution occurring alternately. The densification reversal or bloating found when sintering ferric oxide and activated chromic oxide at temperatures above the optimum for shrinkage [2, 9] can probably be explained by reoxidation, the accompanying large volume change providing the driving force. The same force may explain reduction cracking in sintered iron ore compacts [10], given that mildly reducing conditions will not only inhibit film stability, but will be oxidising to metal film.

With this hypothesis, it is unnecessary to make inferences regarding the innate semiconductor character of the oxide [8], although the notion of a self-adjusting nil diffusion (SAND) layer of stoichiometric oxide between chromium film and substrate remains compatible. Such a layer, and the neutral p/n layer of $(Cr,Fe)_2O_3$ of Footner *et al* [11] could well be important in the technology of alloy scales. However, the view that film in itself is beneficial [4] is not consistent, though it may be that coating of porosity surface in chromic oxide (as in B, fig. 2) by reduction and vapour transport will tend to buffer against passivity.

A hysteresis cycle apparently of the type found by the author in chromic oxide [8], and the consequent inference of a (two-dimensional?) metal film will be noted in Anderson's work on zinc oxide [12, 13]. The occurrence of film formation on oxides of such different crystallographic and defect structures suggests that the phenomenon is fairly general. Mineralogists, of course, customarily distinguish between appearance and streak. In conclusion, one may note that metal films on oxide particles, like oxide films on metal, increase sintering temperatures.

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